FOAMED EVA-BITUMEN BLENDS AND COMPOSITES

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FOAMED EVA-BITUMEN BLENDS AND COMPOSITES

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ABSTRACT

FOAMED EVA-BITUMEN BLENDS AND COMPOSITES

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The thermal conductivities of foamed polymer based materials are much lower thermal conductivity values than unfoamed polymeric materials. Especially, thermal conductivity values of foamed polymers with closed-cell structure decreases to 0.03 W/m.K. The reinforcement of foamed polymeric materials by mixing with bitumen lowers the raw material cost.

The main objective of this study is to make a new thermal insulation material with low thermal conductance. In this study, the effects of concentration of calcium carbonate as inorganic filler and the effects of cross-linking on the properties foamed and unfoamed ethylene-vinyl acetate (EVA) copolymer based bituminous blends and composites were investigated. Applications such as thermal, mechanical characteristics of foamed and unfoamed EVA based bituminous composites were investigated.

Foamed EVA based bituminous composites were prepared by using Brabender Plastic Coder, PLV 151. Mixing was made at 120 ºC at 60 rpm for 15 minutes. The prepared blends were molded by a technique called Hand Lay-up Self-expanding Batch Molding (HLUSEBM) which was firstly applied by our group. The molding temperature was 170 ºC at which chemical blowing agent and cross-linking agent decomposes.

According to test results, at moderate chemical blowing agent and EVA content, the best closed-cell structure with high porosity and low thermal conductivity values were obtained. The compressive properties of foamed polymer based bituminous composites (FPBBCs) increase with increasing CBA and EVA content.

With increasing calcium carbonate and EVA concentration, the porosity of FPBBCs increases but thermal conductivity of them decreases. On the other hand, with increasing filler content but with decreasing EVA concentration elastic modulus of FPBBCs increases but elastic recovery decreases.

Keywords : Foamed polymer based bituminous composites, ethylene-vinyl acetate, EVA, cross-linking, thermal conductivity, compression test

ÖZ

KÖPÜRTÜLMÜŞ EVA İÇEREN BİTÜMLÜ KARIŞIMLAR VE KOMPOZİT MALZEMELER

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Köpürtülmüş polimerik malzemelerin ise ısıl iletkenlik değerleri köpük formda olmayanlarınkine göre daha da düşüktür. Özellikle kapalı hücre yapılı polimerik köpüklerin ısıl iletkenlik katsayıları 0,03 W/m.K'ne kadar düşmektedir. Köpürtülmüş polimerik malzemelerin bitüm ile karıştırılarak desteklenmesi ise hammadde maliyetini düşürmektedir.

Bu çalışmanın ana amacı, düşük ısıl iletkenliğe haiz yeni bir ısı yalıtım malzemesi yapmaktır. Bu çalışmada, anorganik dolgu maddesi olarak kalsiyum karbonat konsantrasyonunun, çapraz bağların, köpürtülmüş ve köpürtülmemiş etilen vinil asetat (EVA) kopolimeri içeren bitümlü karışımların ve kompozitlerin özellikleri üzerindeki etkileri incelenmiştir. Köpürtülmüş ve köpürtülmemiş EVA içeren bitümlü kompozitlerin ısıl, mekanik karakteristikleri gibi uygulamaları araştırılmıştır.

Köpürtülmüş EVA içeren bitümlü kompozitler Brabender Plastic Coder, PLV 151 kullanılarak hazırlanmıştır. Karıştırma işlemi 120 ºC, 60 tur/dakika'da 15 dakika boyunca yapılmıştır. Hazırlanmış olan karışımlar, ilk defa grubumuz tarafından uygulanmış olan El Yordamı ile Yaymalı Kendiliğinden Köpüren Kesikli Kalıplama tekniği ile kalıplanmıştır. Kalıplama sıcaklığı 170 ºC olup, kimyasal köpürtme maddesi ve çapraz bağlama maddesi bu sıcaklıkta bozunmaktadır.

Test sonuçlarına göre, ortalama kimyasal köpürtme maddesi (KKM) ve EVA içeriğinde, yüksek gözeneklilik ile en iyi kapalı hücre yapısı ve düşük ısıl iletkenlik değerleri elde edilmiştir. Köpürtülmüş polimer içeren bitümlü kompozitlerin sıkıştırma özellikleri artan KKM ve EVA konsantrasyonu ile artmaktadır.

Artan kalsiyum karbonat ve EVA konsantrasyonu ile, köpürtülmüş polimer içeren bitümlü kompozitlerin gözeneklilik değerleri artarken, ısıl iletkenlik değerleri düşmektedir. Diğer taraftan, artan dolgu maddesi içeriği fakat azalan EVA kompozisyonu ile köpürtülmüş polimer içeren bitümlü kompozitlerin elastik modülü değerleri artarken, elastik geri kazanım değerleri düşmektedir.

Anahtar Kelimeler : Köpürtülmüş polimer içeren bitümlü kompozitler, etilen vinil asetat, EVA, çapraz bağlama, ısıl iletkenlik, sıkıştırma testi

To my Brother,

Ahmet Murat Çankaya who is in our memory…

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And finally, I dedicate this dissertation to each and every member of my family, to my altruistic mum and hardworking dad and especially to my brother Ahmet Murat Çankaya who was my best friend and pioneer in my life till August 17th, 1999… He is in our memory and will be forever…

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NOMENCLATURE

A	Interfacial area (cm^2)
a	Weight of specimen in air (gr)
b	Weight of specimen and wire in water (gr)
C_p	Heat capacity (J/gr.K)
C_t	Compression set expressed as a percentage of the original thickness of test specimen
$f(\theta)$	Heterogeneity factor
ΔG_v	Difference between the gas and polymer phases of the standard Gibbs free energy per unit volume (J)
ΔG^*_{hetero}	Gibbs free energy of heterogeneous bubble nucleation (J)
ΔG^*_{homo}	Gibbs free energy of homogenous bubble nucleation (J)
k	Thermal conductivity constant of the material (W/m.K)
k_c	Contribution to thermal conductivity due to thermal convection in gas (W/m.K)
k_g	Contribution to thermal conductivity due to thermal conduction through gas (W/m.K)
k_r	Contribution to thermal conductivity due to thermal conduction through radiation (W/m.K)
k_s	Contribution to thermal conductivity due to thermal conduction through solid (W/m.K)
moh.	Unit of mineral hardness
P_o	Initial pressure of nucleation process (atm)
P_s	Final pressure or surrounding atmosphere pressure (atm)
r^*	Critical bubble radius (µm)
t_o	Original thickness of test specimen (m)
t_f	Final thickness of test specimen (m)
Q	Time rate of one-dimensional heat flow through the metering area of the test apparatus (W)
T_o	Initial temperature of nucleation process (K)
T_1	Temperature of hot surface (ºC)
T_2	Temperature of cold surface (ºC)
V_b	Volume of the bubble nucleus (m^3)
vol. %	Volume Percentage
w	Weight of totally immersed sinker and partially immersed wire (gr)
W	Watt
wt. %	Weight Percentage
x	Distance the heat must flow (m)

Greek Letters

σ	Interfacial tensions of a polymer–gas bubble
θ	Wetting angle
α	Thermal diffusivity (m^2/s)
ρ	Density (gr/cm^3)
Ω	Electrical resistance (ohm)
λ	Thermal conductance (W/m.K)

Abbreviations

ABFA	Azobisformamide
ABS	Acrylonitrile-butadiene-styrene polymer
ASTM	American Society for Testing and Materials
CA	Cellulose acetate polymer
CBA	Chemical Blowing Agent
DC	Direct current
EBA	Ethylene-butyl acrylate copolymer
EVA	Ethylene-vinyl acetate copolymer
EP	Ethylene-propylene polymer
EPDM	Ethylene-propylene diene monomer
FA	Foamed asphalt
HDPE	High density polyethylene
HLUSEBM	Hand Lay-up Self-expanding Batch Molding
ITS	Indirect tensile strength
PBA	Physical Blowing Agent
FPBBC	Foamed Polymer Based Bituminous Composite
LDPE	Low Density Polyethylene
M10	Metric 10
MFI	Melt flow index
OBSH	4,4’Oxybis(benzenesulphonohydrazide)
PE	Polyethylene
PET	Polyethylene terephthalate
PF	Polfluorene polymer
PP	Polypropylene
PPO	Polyphenylene oxide
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVC	Polyvinyl chloride

RA	Release Agent
RAP	Reclaimed asphalt pavement
Rpm	Pound per meter
SBR	Styrene-Butadiene Rubber
SBS	Styrene-Butadiene-Styrene Copolymer
SEBS	Styrene-ethylene-butylene-styrene polymer
SEM	Scanning Electron Microscopy
TP	Thermoplastic
TS	Thermoset
UF	Urea-formaldehyde polymer
UV	Ultra violet light
X-PE	Cross-linked polyethylene

CHAPTER 1

INTRODUCTION

Bitumen, which is also called as asphalt, is gathered from the residue at the bottom of the vacuum distillation of crude oil. Bitumen is a complex mixture of organic and inorganic compounds which can be grouped into two classes as asphaltenes and maltenes. Asphaltenes are defined as the black-colored fraction of bitumen that is insoluble in n-heptane. Maltenes, which are composed of saturated compounds, aromatic compounds and resins, are soluble in n-heptane [1].

Since bitumen is highly waterproof, very adhesive and durable as a binder, it is accepted as a very valuable engineering material. Its uses range from waterproofing membrane in roofing and structural applications to the construction of pavements of roads with an aggregate.

As a binder, bitumen is a thermoplastic liquid which behaves as an elastic solid at low service temperatures or during rapid loading. However; at high temperatures or during slow loading, it behaves as a viscous liquid. This classical dichotomy creates a need to improve the performance of an asphalt binder to minimize the stress cracking that occurs at low temperatures and plastic deformation at high temperatures [2].

Several additives are being used to increase the performance of asphalt binders. Polymers are most widely used as additives in asphalt modification. Various types of polymers are used to change asphalt binders to achieve wider performance range. Many polymer modified asphalt binders tend to behave more as a polymer rather than bitumen [2].

In this study, foamed polymer based bituminous composites (FPBBCs), to be used as thermal isolation materials, were prepared from bitumen, filler ($CaCO_3$), polymer, magnesium stearate and a chemical blowing agent which was used to foam conventional polymer based bituminous blends. Ethylene vinyl acetate (EVA) copolymer was used as polymer. Thermal and mechanical properties, density and porosity values and morphologies of FPBBCs were examined.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Bitumen

As a term, bitumen is used by European and Eastern countries; however the term asphalt is used by Americans. The sources of bitumen can be classified into two categories. First bitumen is derivated from petroleum crude oil; second category includes the natural asphalt deposits [3].

Bitumen is a viscoelastic substance which behaves as an elastic solid at low temperatures or during rapid loading. At high temperatures or slow loading, it behaves as a viscous liquid. This classical dichotomy creates a need to improve the performance of bitumen to minimize the stress cracking that occurs at low temperatures and plastic deformation at high temperatures [2].

2.1.1 Definition of Bitumen

Bitumen and asphalt are both generic terms. In USA, the word asphalt is used as synonymous with bitumen- the refinery product which has now largely replaced the natural asphalts that occur in Trinidad, Venezuela, Cuba etc. Outside USA however, the word asphalt is generally taken to mean a mixture of refinery bitumen with a substantial proportion of solid mineral matter [4].

The American Society for Testing and Materials (ASTM) defines bitumen as a generic class of amorphous, dark colored, cementitous substances, natural or manufactured, composed principally of high molecular mass hydrocarbons, soluble in carbon disulfide

[5]. In literature bitumen is used as a generic term referring to flammable, brown or black mixtures of tar like hydrocarbons, derived naturally or by distillation from petroleum. It can be in the form of viscous oil to a brittle solid, including asphalt, tars, and natural mineral waxes. Substances containing bitumen are called bituminous, e.g., bituminous coal, tar, or pitch [6].

Bitumen is a semi-solid material which can be produced from certain crude oils by distillation. It can also be found in nature as “natural asphalt”. It is a mixture of four main components–aromatics, paraffins, asphaltenes and resins [7]. The term bitumen consists of a wide variety of reddish brown to black materials of semisolid, viscous to brittle character that can exist in nature with no mineral impurity or with mineral matter contents that exceed 50% by weight [8].

At room temperature bitumen is a flexible material with a density of 1 g/cm^3, but at low temperatures it becomes brittle and at high temperatures it flows like a viscous liquid. The physical, mechanical and rheological properties of the bitumen depend basically on its colloidal structure, linked to the chemical composition, in particular to the proportion of asphaltenes and maltenes [7].

2.1.2 Chemical Composition of Bitumen

Knowledge of bitumen chemistry has progressed rapidly as more sophisticated methods of analysis have been developed. There are a lot of techniques such as solvent fractionation, thermal diffusion, sulfuric acid precipitation, adsorption and elution or by a combination of these procedures used for determining the composition of bitumen. The study of these fractions has been made by most available methods including infrared and ultraviolet spectrometry, x-ray analysis and electron-microscope techniques [9].

Bitumen is made up of polar and non-polar compounds in complex association. The interaction of polar compounds determines bitumen structure and mechanical properties [10].

Bitumen is a mixture of hydrocarbons and compounds of a predominantly hydrocarbon character, varying both chemically and molecular size. These hydrocarbon components change from the nonpolar aliphatic wax compounds to highly polar condensed aromatics. Carbon and hydrogen compose approximately 90-95% of bitumen. The rest of the bitumen consists of heteroatoms such as nitrogen, oxygen and sulfur [9].

The knowledge of bitumen chemistry is largely based on separation by means of organic solvents into groups of similar properties. [11]. Asphalts are colloidal dispersions of very high molecular weight hydrocarbons called asphaltenes (dispersed phase) in a dispersion medium called maltenes. Asphaltenes are obtained after freeing asphaltic bitumens from carbenes and carboids by precipitation with light petroleum naphtha of 86-88°C. They are highly aromatic and contain condensed rings. [11]. Asphaltenes are also agglomerates of the most polar molecules in the bitumen and this polarity is derived from the hetero-atoms namely sulfur, oxygen and nitrogen. Maltenes are the dispersion oil medium of lesser aromaticity and consist of two fractions namely oils and resins [12]. Asphaltic resins are amorphous solids of reddish to dark brown color and are soluble in light petroleum naphtha as well as in the solvents for asphaltenes [11]. Resins are transition chemical compounds between oils and asphaltenes, and they are chemically very similar to asphaltenes but with lesser polar characteristics [12]. Oily constituents represent the remainder of asphaltic bitumens [11]. They appear as fluorescent oils, and their viscosity varies not only with the source of the asphaltic bitumen but also with the method of processing [11]. They contain various types of hydrocarbons and can be further separated into aromatic, cycloparaffinic, and aliphatic fractions [11]. The concentration of asphaltenes, their particle size and the nature of dispersed phase and dispersion medium are the key aspects, which determines asphalt properties and behavior [12].

On review of the basic aspects of bitumen chemistry, it is precise to conclude that bitumen is made up of polar and non-polar compounds in a complex association [12]. Hence, the bitumen chemistry depends on two main aspects namely crude source and the manufacturing process [12].

By properly choosing the feedstocks and processing conditions, it is possible to produce high performance bitumen with correct balance in chemical composition, molecular weight distribution and physical characteristics [12].

Bitumen quality varies with the variation in crude oil source and the processing scheme, causing considerable difficulty in improving its performance characteristics. Rheological properties of bitumen depend largely on asphaltene content [12].

At constant temperature, the viscosity of the bitumen increases as the concentration of asphaltenes dispersed in maltenes is increased. However with asphaltene content and saturate/resin ratio remaining constant, the increased aromatic content does not have any effect on the rheology of bitumen other than marginal reduction in shear susceptibility [12].

Elemental analysis is an averaging; it gives little information on molecular arrangements and so sheds little light on physical properties. Bitumen does contain trace amounts of metals, mainly vanadium and nickel. Table 2.1 shows several asphalts that give an indication of the range observed in elemental analysis [11].

Table 2.1 Elemental analysis of bitumen regarding with its sources.

Element (wt %)	Mexican	Arkansas	Boscan	Calif
Carbon	83.77	85.78	82.90	86.77
Hydrogen	9.91	10.19	10.45	10.94
Nitrogen	0.28	0.26	0.78	1.10
Sulphur	5.25	3.41	5.43	0.99
Oxygen	0.77	0.36	0.29	0.20
Vanadium	180 ppm	7 ppm	1380 ppm	4 ppm
Nickel	22 ppm	0.4 ppm	109 ppm	6 ppm

Although all asphalts are predominantly carbon and hydrogen most of the molecules contain at least one heteroatom (S, N, and O). The heteroatoms are often present in sufficient amounts such that on average every molecule has one. These may be in the rings, in non ring components or as functional groups attached to compounds. These together with polarisable aromatic rings contribute polarity [11].

It is the arrangement of different elements/atoms, into molecules that determines the interactions of these molecules and hence the physical properties. Because the heteroatoms often impart functionality and polarity they have a disproportionate effect on the properties. This includes effects such as aging, the more reactive the hetero atoms age faster (e.g. sulfur) [13].

2.1.3 Microstructure of Bitumen

Asphalt is a highly complex residue of crude oil which most technologists consider to be a natural colloid composed of two phases, dispersed and continuous. The dispersed phase asphaltenes can be described as high molecular weight, semi-polymeric, aliphatic/aromatic complexes which are present in asphalt as either discrete, uniformly dispersed particles, or flocculated or agglomerated electrostatically-bound clusters, or mixtures of both the discrete and flocculated forms. The continuous phase, alternately referred to as the petrolene, malthene or oils and resins phase, have been the subject of some effort to analytically separate and characterize individual components [14].

The microstructure of bitumen is generally understood as multi phase colloidal system. Bitumen classified into two categories sol-type bitumen and gel-type bitumen according to microstructure. In practice most bitumens are somewhere between these two states. A schematic representation of these two states is shown in Figure 2.1 [15].

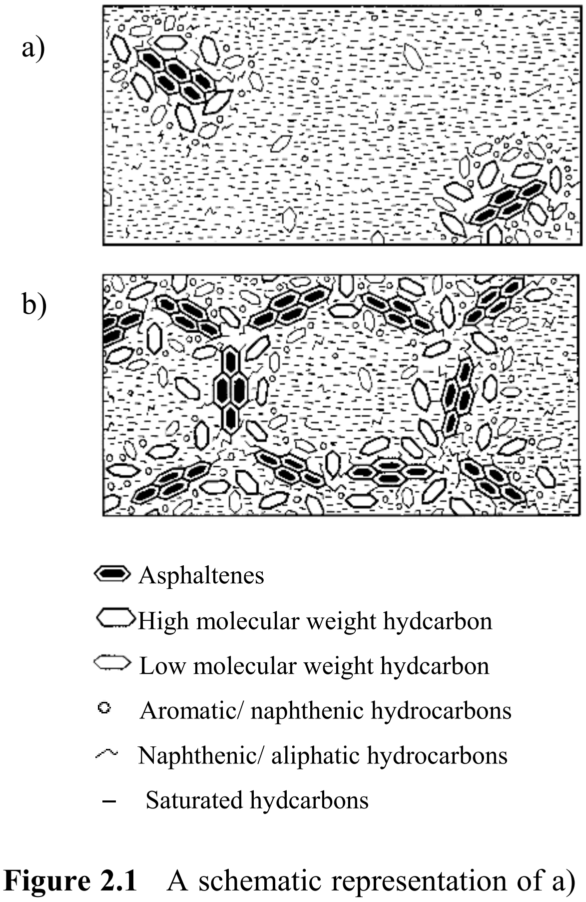


Figure 2.1 A schematic representation of a) sol-type bitumen, b) gel-type of bitumen [15].

In sol-type bitumens, asphaltene bitumens well dispersed within maltene continuum. In gel-type bitumen, the asphaltene micelles are not well dispersed and form large agglomerations. The degree of dispersion asphaltenes is controlled by the relative amounts of resins, aromatics and saturated oils. As the ratio of aromatics increases, the dispersion of asphaltenes increases because the aromatics form stabilizing layer around the asphaltene micelles. The saturate oils have little solvent power in relation to the asphaltenes, so that as the saturate fraction increases, there is a great tendency for the asphaltenes to aggregate to form gel structure. However a high ratio of saturates tends to reduce viscosity because of their low molecular weight [15].

2.1.4 Uses of Bitumen

Bitumen, which has thermoplastic nature, water resistance and adhesion towards most other substances, is a primary engineering material [3]. Nowadays, most of the bitumen used is produced as a by-product of crude oil refinery although natural bitumen is still used for special applications. There are over one hundred different industrial applications or products in which bitumen is used. Almost every home, building or traffic area uses bitumen in different form. Bitumen has uses that range from the construction of the pavements of roads with an aggregate to waterproofing membrane in roofing and structural applications. Consumption has grown to 75 million tonnes a year with road construction grabbing the lion's share (80 %) [16]. Bitumen serves primarily as a binder in asphalt compacted mixtures which in turn are widely used in many types of road, street, runway and parking area applications. The other uses of bitumen are paints and coatings, paper, rubber products, electrical cables and other products of electrical industry [3].

For many years well over 80 % of world consumption of bitumen, which is estimated at 100 million tonnes, has been used for paving applications, the construction and maintenance of roads. The rest is used for various purposes. The use of bitumen in road maintenance can be up to four times its use in road construction. The use of bitumen in industry accounts for less, than 20% of world bitumen production [11].

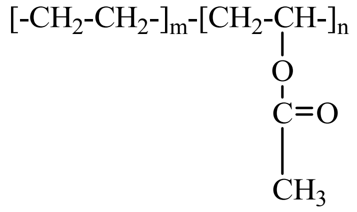
It is nevertheless important to those manufacturers and engineers who rely on its particular properties as an economical binder and protector. In many parts of the world it is used extensively to waterproof the roofs of houses, often in the form of shingles which are strips of felt first impregnated with bitumen and then covered on both sides with harder bitumen and a coating of mineral granules. A similar construction technique involves sheets of bitumen-saturated felt laid onto a flat roof with layers of bitumen below, between and above them. In more complex roofing projects, bitumen is to be found holding in place a protective coating of chippings on the cantilevered roof of a sports stadium. By contrast, bitumen is also used in dampproofing and floor composition tiles [11].

Other materials, particularly felts and papers, are impregnated with bitumen to improve their performance as regards insulation. Packaging papers, printing inks, linoleum, sound deadening felts hidden inside car bodies and the undersealing compounds beneath them, electrical insulating compounds and battery boxes are some of the hundreds of industrial and domestic products likely to contain bitumen [11].

2.2 Polymer

2.2.1 Properties of Ethylene-vinyl Acetate (EVA) Copolymer Resin

Ethylene-vinyl acetate (EVA) copolymers are the products of low density polyethylene (LDPE) technology and normally sold in pelletized form, approximately spherical in shape and about 1/8 in. in diameter [17]. The chemical structure of EVA resins is represented in Figure 2.2.



$$[-CH_2-CH_2-]_m-[CH_2-CH(-O-C(=O)-CH_3)-]_n$$

Figure 2.2 Structure of ethylene-vinyl acetate (EVA) copolymer

Incorporation of vinyl acetate in the ethylene polymerization process produces a copolymer with lower crystallinity than conventional ethylene homopolymer. EVA copolymers are thermoplastic materials consisting of ethylene chain incorporating 5 to 50 % vinyl acetate (VA), in general. Their properties are governed by the percentage content of VA and the melt index. The VA content controls the resin crystallinity and flexibility. Lower crystallinity resins have lower melting points and heat seal temperatures, along with reduced stiffness, tensile strength and hardness [17].

EVA copolymers are used in a variety of molding, compounding, and extrusion applications. Some typical end uses include flexible hose and tubing, footwear components, toys and athletic goods, extruded gaskets, molded automotive parts [17]. At 15 mole percent vinyl acetate, a copolymer with very similar mechanical properties to plasticized PVC is formed. There are many advantages to an inherently flexible polymer for which there is no risk of plasticizer migration, and PVC-alternatives are the area of largest growth opportunity. These copolymers have higher moduli than standard elastomers and are preferable in that they are more easily processed without concern for the need to vulcanize [18]. EVA copolymers with a low VA content are used in film; the presence of 2-7 % VA enhances such desirable film properties as toughness and optical clarity. Higher comonomer content resins (18-40 %) are used as wax-coating tougheners and in hot melt adhesives [17].

2.2.2 The Aim of Using Polymers with Bitumen

Many types of polymers are typically used in bitumen modification in different forms such as plastics, elastomers and reclaimed rubbers. Elastomers such as styrene-butadiene-styrene copolymer (SBS), styrene-butadiene rubber (SBR) and natural rubber can be used with bitumen. A plastic such as polyethylene (PE), polypropylene (PP), polystyrene and ethylene-vinyl acetate (EVA) are also used with bitumen. EVA and low density polyethylene (LDPE) are used as thermoplastics [2]. EVA is used as a thermoplastic in this study.

Mixing polymers into bitumen has important consequences on the engineering properties of bituminous materials. The extent of modification and the improvements in the performance characteristics depend on bitumen nature, polymer chemical nature, its dosage and chemical compatibility, molecular weight, particle size, as well as blending process conditions such as type of mixing/dispersing device, time and temperature play important role in determining the modified asphalt properties [19].

Bitumen modification by polymers improves its mechanical properties, increases the viscosity, allows an expansion of temperature range of service and improves the deformational stability and durability of bitumen [1].

Recently, the case of blends of bitumen with recycled polymers has been considered, with the advantage of disposing troublesome waste plastics [7]. Elastomer modification of bituminous materials is manifest in the following ways; softening temperature is increased, cold flow is reduced, change in penetration with temperature is reduced, brittleness temperature is lowered, elastic recovery is imparted, resistance to deformation under stress is increased markedly, ductility is increased, particularly at low temperatures [12].

2.2.3 Interaction between Bitumen and Polymer

The morphology of polymer modified bitumen is the result of the mutual effect of polymer and bitumen, consequently is influenced by bitumen composition, polymer nature and ratio [20].

Most polymers are insoluble to some degree, in the bitumen matrix, resulting eventually in gross separation of both phases. These phases may become a continuous phase or a dispersed one depending on polymer nature, concentration and its ability to swell with maltene molecules [19]. Bitumen phase is artificially enriched in asphaltenes by a physical distillation of the lighter species from the original bitumen because polymer is swelled by the maltenes. This is the case of many elastomers and thermoplastics such as EVA [1].

In general at low polymer content, the small polymer spheres swollen by bitumen compatible fractions are spread homogeneously in a continuous bitumen phase. By increasing polymer content, a continuous polymer phase may be obtained. The minimum percentage of polymer to ensure the formation of its continuous phase depends to a great extent on the base bitumen, the polymer itself and its ability to swell with maltene molecules [1]. Polymer stabilization can be achieved by mechanical dispersion of the modifier, swollen by compatible components in the maltene fraction. It is well known that the polymer may dissolve and/or disperse into maltenic medium enhancing the mechanical properties of mixtures [20].

Polyolefins are produced from olefinic monomers; the resulting homopolymers have nonpolar, nonaromatic nature. The typical range for their solubility parameter is 15.6-17.4 $\mathrm{MPa}^{1/2}$. This low solubility parameter reflects its incompatibility with an asphalt dispersion medium which is polar and aromatic. Polyolefins can also be copolymerized as either block or random copolymers such as EVA. The solubility parameter can be modified by the addition of a more polar comonomer yielding a more compatible system [2]. High molecular weight polymers have profound effects on the properties of bitumen. As the molecular weight of polymers increases, their compatibility with bitumen sharply decreases [21].

EVA is used as polymeric modifier in bituminous materials. Vinyl acetate content of EVA affects the modification of bitumen. At low polymer content, small polymer droplets swollen by bitumen light fractions appear in a continuous bitumen phase. By increasing the polymer concentration, continuous polymer phase appears [1].

2.3 Fillers

The term filler is usually applied to solid additives incorporated into the polymer to modify its physical (usually mechanical) properties. Air and other gases which could be considered as fillers in cellular polymers are dealt with separately [22].

A mineral filler is an inorganic additive which, when mixed with a bitumen, retains its original size and shape, does not react with the bitumen and does not assume colloidal properties in the filler-bitumen mixture [11]. The scientific evaluation of pulverized minerals involves first a consideration of their primary properties, such as particle size, size distribution, particle shape and surface configuration or texture and then the relation of these to the secondary properties of the powder, namely surface area, packing of the particles and void content and average void size in the compacted powder [23].

Many types of fillers have been used in bitumen composites such as silica, limestone, basalt, green stone, granite, fly ash, mica, oyster shells and asbestos. Almost every available pulverized stone has been used in bituminous composites because fillers are usually obtained from the nearest local source. It is apparent that most of the readily available mineral fillers and fibers may be used in one or more types of bituminous compositions [11].

2.3.1 Properties of Fillers

Fillers must be inert. They should not react with bitumen and must not decompose when mixed with them. Fillers must be physically sound and they should not crack or crumble during mixing or in service. Filler must be insoluble in water. Filler must be nonhygroscopic. Extensive use of bitumen as water proofing dictates that fillers should not absorb water into waterproofing material. Filler must be opaque. This requirement applies only to fillers used in products exposed to weather [11].

2.3.2 Effects of Fillers to Bituminous Materials

When mineral powders are used as fillers for asphalt the chemical nature of the mineral should be considered. Asphalts which by nature are slightly acidic show better adherence to alkaline than to acidic surfaces. Also, the age and history (weathering) of the mineral surface has considerable effect on its reaction towards asphalt. Any filler with some chemical affinity for asphalt tends to disperse in hot asphalt or cutbacks. Mineral powders which are not readily wetted by asphalt tend to agglomerate and are difficult to disperse in the liquid. The use of additives to improve dispersion may be effective but frequently is not economical. Surface texture (roughness) aids in the adherence of asphalt to a solid but this effect should not be confused with the bonding which is dependent on chemical forces [23].

For most practical uses, asphalts are blended with some kind of pulverized mineral to increase consistency of the binder. In an asphalt road the material in the aggregate, which is less than 74 microns in diameter, may be considered the binder for the larger pieces of aggregate comprising the paving mixture. In reality, the chief function of the fine powder present in a bituminous mixture is to increase the viscosity of the asphalt. The same result could be obtained by using a harder asphalt, but this would result in the sacrifice of longer serviceability to be expected from the softer asphalt used with the filler [23].

Fillers have a bonus value; those most commonly used are less expensive than the bitumen to which they added. Fillers increase impact resistance, shear, and compressive strength; reduce brittleness, impede or control deformation and sag; increase viscosity and alter flow properties. The softening point of bituminous compositions is increased by addition of filler. The relationship between softening point and filler content is linear up to about 40-50 weight % concentration for conventional fillers. Fillers decrease bitumen penetration (the penetration decrease-filler content relationship is similar to that of the softening point increase for fine fillers). Many types of fillers improve the weathering durability of bitumen. The resistance of bituminous compositions to deformation may be improved and regulated by addition of fillers. Fillers increase viscosity and lower the viscosity temperature sensitivity of bitumen. The rheological nature of bitumen is not changed by small concentrations of fillers. The viscosity increase is related to filler content up to about 40-50 % weight concentration of filler. Impact resistance is improved by fillers. Fillers of flat particle shape are far more effective than conventional powdered minerals [11].

2.3.3 Interaction Among Filler, Bitumen and Polymer

The interaction among filler, bitumen and polymer depends on composition of bitumen, type of filler & polymer, and their ratios in composite. The maltene fraction of the bitumen swells the polymer. Large polymer particles could have a negative effect on the adhesion of bitumen and aggregates. Small polymer particles can remain in between the film of bitumen and reinforce the composite [21]. A schematic representation of the polymer, bitumen, and aggregates in an asphalt concrete mix can be represented as in Figure 2.3 [24].

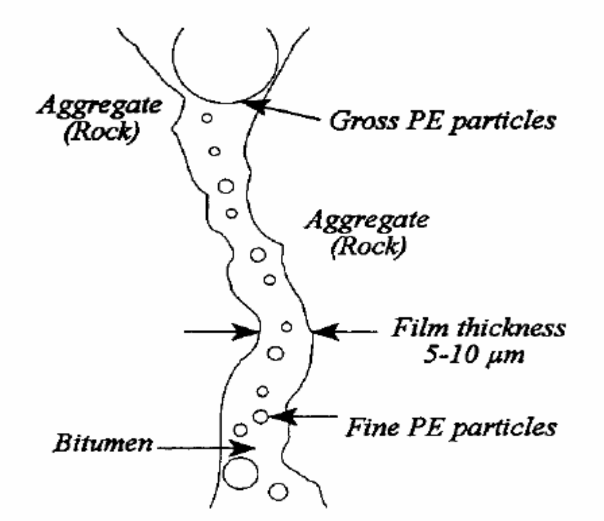


Figure 2.3 A schematic representation of the polymer, bitumen and aggregates in a bitumen concrete mix [24].

Calcium carbonate ($CaCO_3$) is used as filler in this study. The polarity of the polymer affects the interaction between $CaCO_3$ and polymer. EVA seems to have an affinity to $CaCO_3$. The phenomena with the EVA film around or close to the surface of the aggregates can be explained by the polarity of the different components in the asphalt mixture. The EVA phase will surround the aggregates. EVA film is seen a few millimeters from the aggregate; it is a possibility that a part of the polar asphaltenes surrounds the aggregate [25].

2.3.4 Calcium Carbonate ($CaCO_3$)

Calcium Carbonate ($CaCO_3$) is the most common deposit formed in sedimentary rocks. Natural $CaCO_3$, used as filler in plastics, is produced from chalk, limestone or marble found in the upper layers of the Earth's crust. $CaCO_3$ is abundant, largely inert, low cost, white filler. The primary function of calcium carbonate as a filler is to lower costs, while having moderate effects on mechanical properties [26].

Calcium carbonate occurs naturally in two crystalline forms, calcite and aragonite, the former being the more stable and abundant form. Calcite is rhombohedral, has a specific gravity of 2.71 and a hardness of 3.0 moh. Aragonite is the orthorhombic form and occurs naturally as needle-shaped prisms or spherulites in thermal springs. It has a specific gravity of 2.93 and a hardness of 3.5 moh. When heated, aragonite is transformed into calcite [27].

The production of calcium carbonate minerals is by open quarrying of the massive rock into pieces small enough to be crushed, followed by mechanical crushing and grading of the broken stone. The final stage is fine grinding by roll and ball milling, jet milling or micronising [27].

2.3.5 Magnesium Stearate ($C_{36}H_{70}MgO_4$)

Magnesium stearate, also called octadecanoic acid, magnesium salt, is a white substance which is solid at room temperature. It has the chemical formula $C_{36}H_{70}MgO_4$. Molecular structure of magnesium stearate is shown in Figure 2.4. It is a salt containing two equivalents of stearate (the anion of stearic acid) and one magnesium cation (Mg^{2+}). Magnesium stearate melts at about 88 °C, is not soluble in water, and is generally considered safe for human consumption. At polymer industry, magnesium stearate is used as mold releasing agent and lubricant. In this study, it is used for its lubricating and processing aid features. Its uses also include as a flattening agent for paints, varnishes and lacquers. Because it is widely regarded as harmless, it is often used as a filling agent in the manufacture of medical tablets and capsules. In this regard, the substance is also useful because it has lubricating properties, preventing ingredients from sticking to manufacturing equipment during the compression of chemical powders into solid tablets. It is used to bind sugar in hard candies. It is also a common ingredient in baby powders. In pure powder form, the substance can be a dust explosion hazard, although this issue is effectively insignificant beyond the manufacturing plants using it [28].

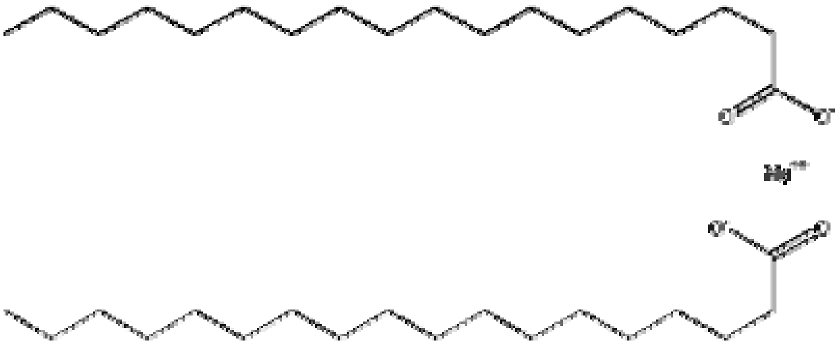


Figure 2.4 Molecular structure of magnesium stearate ($C_{36}H_{70}MgO_4$) [29].

2.4 Release Agents

Release agents (RAs) are substances that control or eliminate the adhesion between two surfaces. They are known by a variety of terms indicative of their function: adherents, antiblocking agents, antistick agents, external or surface lubricants, parting agents, and slip aids. Processors use RA in a wide variety of general handling operations, such as calendering, casting, molding, packaging and labeling, and protection of equipment. Processors can be confronted with parts adhering to mold or die surfaces. Plastics most frequently needing RAs include polyurethanes, polyesters (TPs and TSs), polyolefins, polycarbonates and epoxies [30]. RAs come in a wide variety of forms and modes of application. Both neat liquids and solvent solutions, as well as solids such as powders and flakes, compounded mixtures and pastes, emulsions, dispersions, prefomed films, in situ film formers, and integral migratory additives are available. Many formulated products serve more than one processing function and contain other additives, such as antioxidants. Combined lubricant-stabilizer packages are often used with polyvinyl chloride. The external treatment types can be applied by any of the standard coating methods, including brushing, dipping, dusting, spraying, electrostatic coating, and plasma arc coating [30].

Despite the diversity of products, RAs have some features in common, notably inertness to at least one of the surfaces in question at the temperature of the release process and low surface tension. Low surface tension is important in obtaining good wetting of a mold. It is also a reflection of the low intermolecular forces desirable in effective release compositions. Not surprisingly, inertness and weak cohesion are the opposite of good adhesive properties [30].

The release agent should be chosen with subsequent events in mind, as well as for ease of release and stability. In addition to ease of release, other selection criteria include prevention of buildup; mold cleanability; compatibility with secondary operations such as painting, plating, and ultrasonic welding; mold compatibility; type and time available for application; health and safety requirements and cost. As an example, when using silicone as an RA, it becomes difficult or impossible to paint on it or to attach it adhesively [30]. In this study, soft soap is used as release agent.

2.4.1 Soft Soap

Soft soap, which is also known as potassium stearate soap, is a salt-containing soap formed from vegetable oils reacting with potassium hydroxide. Its molecular formula is $CH_3\ (CH_2)_{16}COOK$. Molecular structure of soft soap is given in Figure 2.4. Potassium stearate soap is a soft, easily spreadable soap with colloid-granular structure, yellowish to dark and with odour specific for vegetable oils. It dissolves easily in water, producing rich foam [31].

At polymer industry, soft soap is used as mold release agent especially in rubber industry. In this study, soft soap is used for its dusting agent property in order to get rid of tackiness while ejecting the bituminous polymeric foam from the mold.

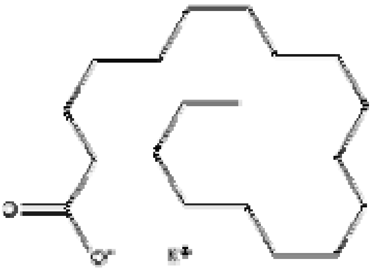


Figure 2.5 Molecular structure of soft soap (CH_3 $(CH_2)_{16}COOK$) [32].

2.5 Polymeric Foams

Foamed plastics are resins with a spongelike, cellular structure. Foamed plastics may be flexible or rigid, the cells closed or interconnected, and the density anything from that of the solid parent resin down to, in some cases, 0.016 gr/cm^3. Compressive strength of rigid foams is fair, making them useful as core materials for sandwich structures, especially where weight reduction is necessary. Both rigid and flexible types have good thermal and acoustical insulation properties. Other names for foamed plastics are cellular, expanded, and sponged plastics. There are several types of foamed plastics including syntactic foam, closed-cell foam, and open-cell foam [33].

Foam is a material, and foaming is a phenomenon. Both involve the presence of a gas phase encapsulated by a spherical shell dense phase. Foam contains porous structures perceived as gaseous voids surrounded by a dense phase or as a gas–solid composite. Since the beginning of the twentieth century, synthetic polymers have become increasingly important materials in industry. As plastication technology advanced and allowed for more sophisticated operations, the addition of a blowing agent became a natural extension of polymer processing. Combining chemistry and engineering principles, foaming methodology continued to expand in Europe and North America during and after World War II. Japan joined the developmental list in the 1960s. Presently, foam extrusion, injection molding, molded bead, x-linked foam, reactive foaming, and gelation are well-known methods of making polymeric foams, and polymeric foams have become a well-developed branch in the polymer industry [34].

Polymers, especially thermoplastic polymers, are characterized by their viscoelastic nature, which possesses processing and material uniqueness. When fit into processing and foaming criteria, their expanded cellular structure shows interesting properties. However, not every polymer is a good candidate for foam. Considering compatibility with gas, processing window, capability to hold dynamic foaming, and stability during gas replacement by air, few polymers are left on the list. Surprisingly, these polymeric foams developed solid and strong applications due to their unique properties [34].

The gaseous voids dispersed in the polymeric matrix evidently alter the polymer's structure, morphology, and properties. Its lighter density has lent itself to commercial flotation since the 1940s. Also, its cellular structure is a natural fit in insulation, which is currently a substantial business. That's why annual U.S. consumption of polymeric foams is forecast to rise to 7.8 billion lb in 2005, an amount valued at $17.6 billion. When a cell wall possesses enough elasticity, it can be used repeatedly in the athletic and furniture industries. Other industries, such as automotive, medical, and packaging are also enhanced by the usage of polymeric foams. The growth in diversity of applications and intensity of usage continue. In essence, it is performance oriented. A simplified performance dependency summary chart is presented in Figure 2.6. Materials and mechanisms are the primary variables that directly affect structure formation. When they are combined with residual gas, mechanical and thermal characteristics are determined [34].

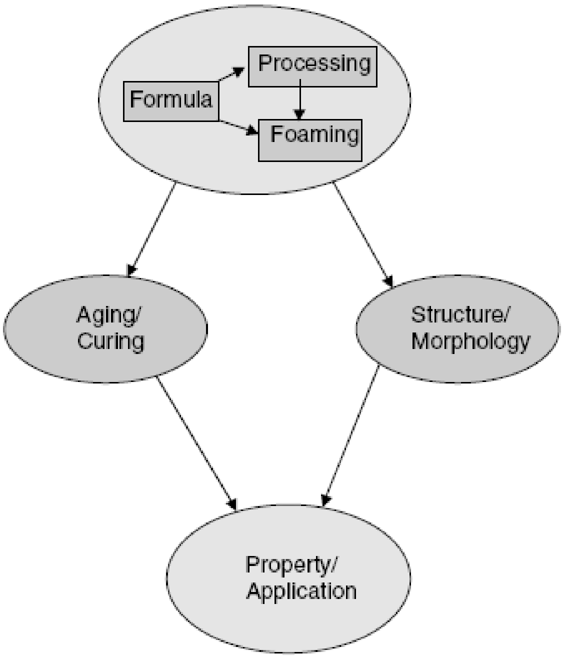


Figure 2.6 Polymeric foam performance dependency summary chart [34].

Polymeric foam can be viewed from different practical perspectives, such as products, technology, and components. Products can be categorized by dimension, density, cell size, cell density, morphology, and property; for instance, block versus film, high density versus low density, microcellular versus cellular, open cell versus closed cell, and rigid versus soft. As for technology, it is basically classified as soluble foaming and reactive foaming, or physical foaming and chemical foaming. Foam can also be classified in accordance with polymer materials such as thermoplastic and thermoset foam. Table 2.2 summarizes foaming perspectives and the terminology relevant to foaming [34].

Table 2.2 Foaming perspectives and terminology relevant to foaming [34].

Perspective	**Terminology**
Material	Thermoplastic (TP) and thermoset (TS)
Mechanism	Soluble foaming and reactive foaming
Nature	Flexible and rigid
Structure	Closed cell and open cell
Cell size	Microcellular and cellular
Density	High density and low density
Dimension	Board and thin sheet

For about a century foamed plastics, whether TP or TS, have been a large and special category within the plastics industry. They are known by different names such as cellular plastics, expanded plastic foams, structural plastic foams, and plastic foams. A plastic foam material is a plastic whose apparent density is decreased by the presence of numerous cells throughout its mass. It is a two-phase gas-solid system in which the solid is continuous and composed of plastic material [30].

Interest in cellular plastics is growing for a number of reasons. The principal reason has to do with the favorable economics of manufacturing innovative products at a lower weight. The banning of chlorofluorocarbons (CFCs) in the early 1980s, along with strong health, safety, and environmental considerations in the foam industry, have increased interest in developing better methods of controlling foaming operations. In order to control the foaming process effectively, two key events must be controlled: bubble nucleation and bubble growth during foam expansion. The use of nucleating systems to produce light density foams also has a potential impact on the disposable household, electronics packaging, and recreational sports markets [34].

Foams are available with open-celled construction, closed or interconnecting construction, or in combination. Their densities range from 1.6 kg/m^3 to over 960 kg/m^3 (0.1 Ib/ft^3 to over 60 Ib/ft^3). They can be rigid, semirigid, or flexible, colored or plain, and the foam can be virtually any TP or TS. They offer an extensive range of insulating properties, rigidity, compressive strength, cushioning and loading, structural characteristics, and others properties. Their performance depends to a great extent on the type of base plastic, the type of blowing system, and the method of processing. Each plastic can include fillers or reinforcements to provide certain desirable properties [30].

2.5.1 Foaming Mechanism

Production of foamed polymers includes four stages within the polymer:

1. Dissolution of foaming agent
2. Bubble nucleation
3. Bubble growth
4. Stabilization of the polymer.

Different mechanisms and parameters occur and sometimes overlap in different stages. When surrounding conditions change, competing mechanisms appear to make the kinetic process more complex. Sizable research and development efforts have been devoted to exploring the mechanisms, their individual roles, and their combined effects. Selected processing parameters and their effects are included in Table 2.3 [34].

Table 2.3 Processing parameters and their effects at different stages [34].

	Implementation	**Expansion**	**Stabilization**
Temperature	Solubility ↑ Viscosity ↓ Reactivity ↑ Diffusivity ↑ Interaction parameter ↓	Volatility ↑ Surface tension ↓ Viscosity ↓	Solidification ↓ Permeability ↑
Pressure	Solubility ↑ Viscosity − Homogenization ↑	Shear heat ↑ Surface tension − Nucleation ↑	Solidification −
Shear	Solubility − Dissolution ↑ Dispersion ↑	Nucleation ↑ Growth ↑ Cell distribution ↑	Solidification ↓

Almost all fabrication processes are used to produce foamed products. There are various combinations of plastics and blowing agents. The blowing agent expands the plastic, initiating cells that grow to produce the final foam. As gas is produced, equilibrium is established between material in the gas phase and the material dissolved in the solid state. The gas dissolved in the solid state migrates from the solution into the gas phase. The cells formed are initially under higher than ambient pressure because they must counteract the effects of surface tension. The pressure due to surface tension depends on the reciprocal of the cell radius, so the pressure within the cell is reduced as the cell grows. Small cells tend to disappear and large cells tend to get larger. This is because the gas migrates through the substrate (plastic) or the cell walls break. After forming cells, the foam has to be stable; the gas must not diffuse out of the cell too quickly, thereby causing collapse or excessive shrinkage. The stability of the foam depends on the solubility and diffusivity of the gas in the matrix. The many processes make for many methods of cell initiation, cell growth, and cell stabilization. And these methods lead to a convenient process classification [30].

The growth of the cell depends on the pressure difference across the cell membrane: between the inside of the cell and the surrounding medium. Such pressure differences may be generated by lowering the external pressure (decompression) or by increasing the internal pressure in the cells (pressure generation). Other methods of generating the cellular structure are by dispersing gas (or solid) in the fluid state and stabilizing this foamed state, or by sintering plastic particles together in a structure that contains a gas phase. Foamable compositions in which the pressure is increased within the cells with respect to the surroundings have generally been called expandable types. Both physical blowing agents (PBAs) and chemical blowing agents (CBAs) are used. There is no single name for the group produced by the decomposition processes; the principal processes are extrusion, injection molding, and compression molding. Both PBAs, and CBAs are also used at these processes [30].

Thermoplastic polymeric foams are made with nucleating agents to aid in cell formation. The use of nucleating systems to produce various density foams also has a potential impact on the packaging and nonpackaging markets. Packaging foams are used everyday for protecting furniture and other objects during transportation. Polyurethane foams are used in packaging, carpet backing, sports, leisure, automobiles, and home applications such as seat cushions, sound, and thermal insulation. Foams are used everywhere from household items to industrial cushions. Thermosetting foams such as polyurethane foams are made by generating bubbles within a liquid through a simple chemical reaction. Foam nucleation is different for different systems. Foaming mechanisms are quite complex, since it is difficult to monitor cell formation in polymers and liquids at its birth. The size of potential nuclei is very small, on the order of nanometers or angstroms in scale. Nucleation occurs in a fraction of a second, and therefore it is difficult for foam scientists to capture in real life [34].

2.5.2 Bubble Nucleation Studies

The birth of tiny bubbles in a polymer system is called nucleation of bubbles and is part of the process used to make polymeric foams. If the bubbles are generated from a single homogeneous phase containing no impurity or dirt, then the process is called homogeneous nucleation. This process is rare, since most resins are made with additives for various reasons. If tiny particles are present in the liquid, and if they assist in the formation of cells, then the process is called heterogeneous nucleation, since the nucleation took place at a solid and liquid interface [34].

It is interesting to note that the physics of various nucleation mechanisms depend on energy levels involved in the systems. In other words, the birth of bubbles in a liquid or solid requires an increase in the free energy of the system. That increase is used to create new surfaces through the formation of tiny bubbles. The birth of a gas bubble in a polymer through a reversible thermodynamic process has an excess free energy associated with it. Mathematically, that can be expressed as [34] :

$$\Delta G = -V_b \, \Delta G_v + A\sigma$$

where V_b is the volume of the bubble nucleus; ΔG_v is the difference between the gas and polymer phases of the standard Gibbs free energy per unit volume; σ is the surface tension of the liquid or polymer; A is the interfacial area; V is the volume of the bubble and subscript b stands for bubble.

Thus, lowering the surface tension by using surfactants will assist in the formation of bubbles. Nucleating agents such as talc, diatomaceous earth, and silica are more effective because they offer voids at the interface. Several investigations involving the theoretical and experimental analyses of bubble nucleation in fluids and polymers have been available in the literature since 1900 [34]. Calcium carbonate ($CaCO_3$) was used as nucleating agent in this study.

2.5.3 Nucleation Models and Experiments

2.5.3.1 Classical Nucleation Principles

Classical nucleation theory is based on the following three basic principles outlined by Kumar:

- The probability of nucleation is directly proportional to an exponential function, exp (–W*/k.T), where W* is the minimum work required to make the system unstable and to generate a large number of bubbles in a continuous phase. Einstein first proposed this relationship in 1930.
- Fluctuations that create a stable nucleus form and decay by the same path.
- In 1931, Onsagar developed an idea that applies macroscopic laws to microscopic entities such as bubble embryos containing clusters of gas molecules [34].

2.5.3.2 Homogeneous Foam Nucleation

Homogeneous nucleation represents the formation of a second phase (e.g., a gas bubble) in the primary phase (e.g., molten polymer). Homogeneous nucleation occurs when a sufficient number of dissolved gas molecules form clusters for a long enough time to make a critical bubble radius to cross over the resistance path, as shown in Figure 2.7 [34].

Figure 2.8 shows a single phase containing molten polymer saturated with gas at a certain pressure. Figure 2.8 shows the formation of a second gas phase when the pressure is reduced from P_o to P_s.

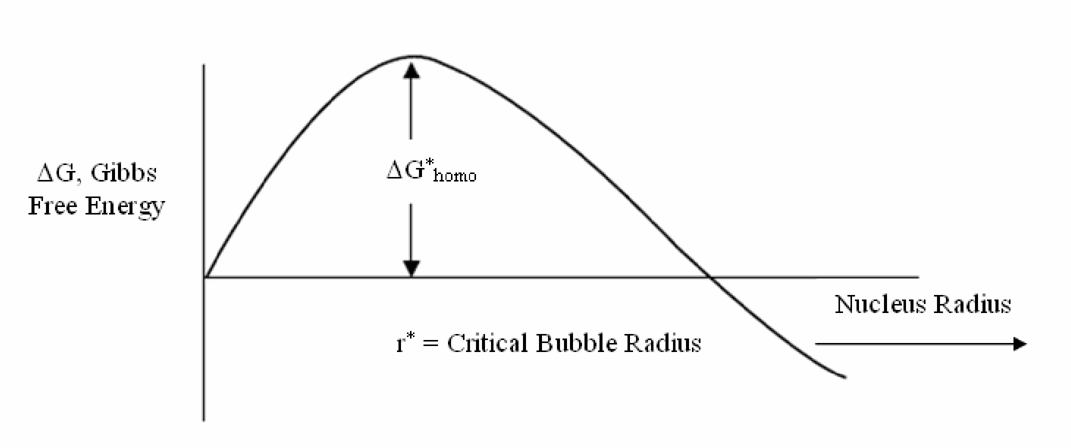


Figure 2.7 Homogeneous bubble nucleation [34].

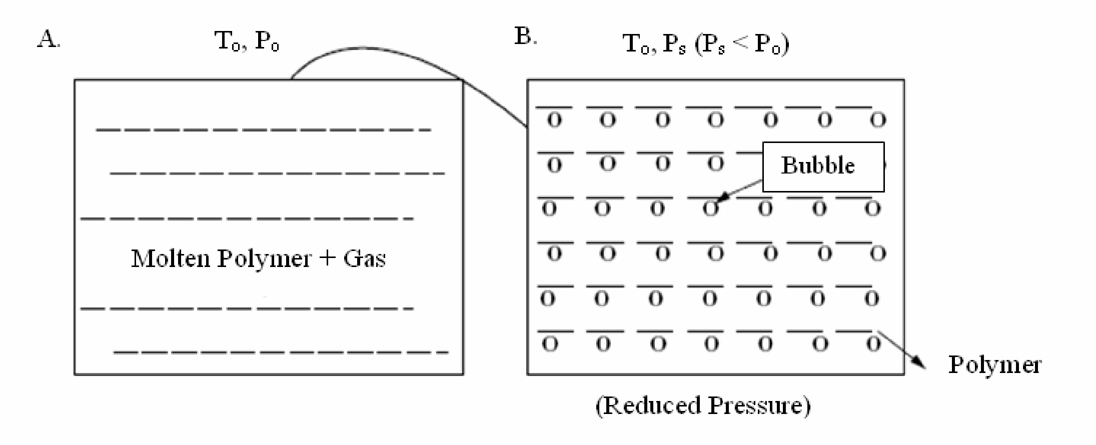


Figure 2.8 Typical nucleation process. T_o = temperature; P_o = initial pressure (higher than surrounding pressure); P_s = final pressure or surrounding atmosphere pressure [34].

The spherical shape of the nucleus is assumed to represent minimum resistance for nucleation for a given volume. In general, such an assumption is reasonable. But in polymeric systems nonspherical geometries might be encountered [34].

It should be cautioned that gaseous foaming agents often soften the polymer, and therefore surface tension of the polymer may decrease or increase based on the foaming agent dissolved in it. Hence, such effects must be taken into account when predicting real-life examples [34].

2.5.3.3 Heterogeneous Foam Nucleation

This is the most common type of nucleation found in polymer systems containing additives. The efficiency of producing bubbles depends on several factors, such as the type and shape of nucleating particles and interfacial tensions of solid and solid–gas interface. Blander and Katz proposed a simple heterogeneous nucleation model for liquids in 1975. The primary benefit comes from the interface, which acts like a catalyst for nucleation. The presence of tiny particles and cavities reduces the activation energy required to achieve a stable nucleus. Figure 2.9 shows the reduction of Gibbs free energy associated with the heterogeneous nucleation process [34].

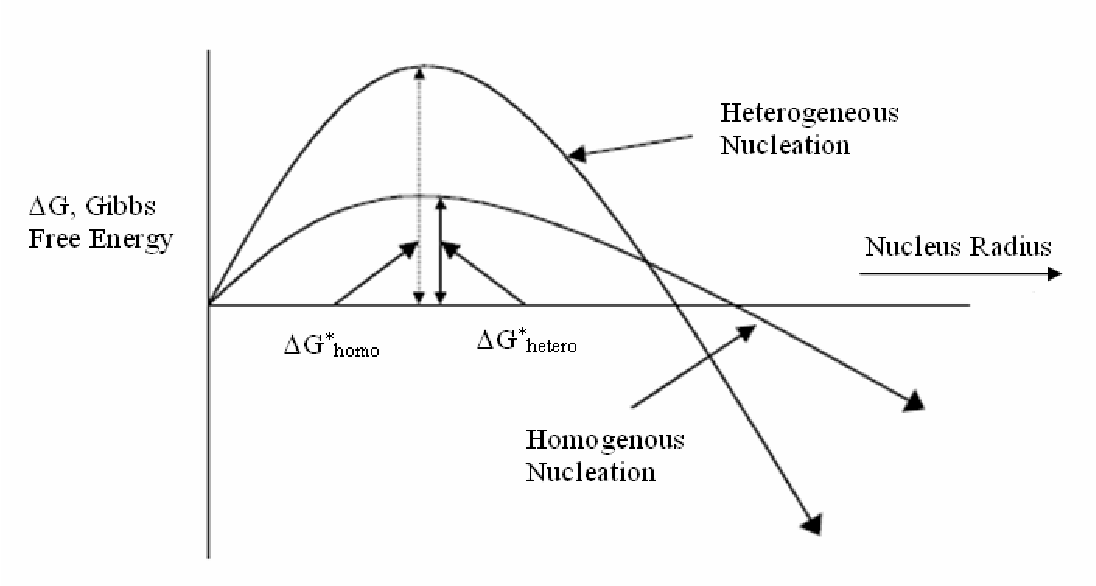


Figure 2.9 Heterogeneous bubble nucleation. $\Delta G^*_{hetero} < \Delta G^*_{homo}$ [34].

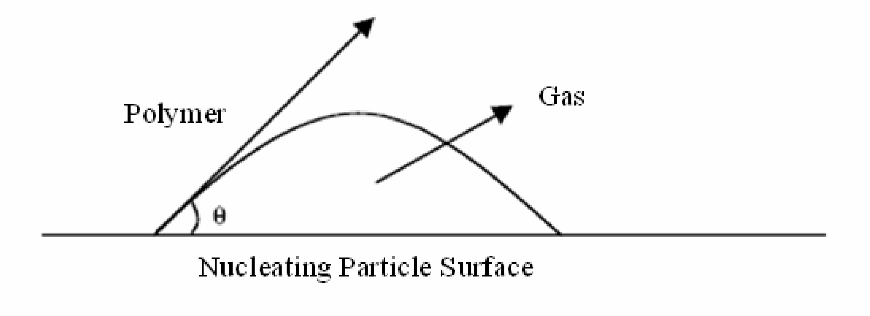


Figure 2.10 Schematic of nucleating particle interaction with gas and polymer [34].

The thermodynamics of heterogeneous nucleation and its mathematical analysis are given in Uhlmann and Chalmers. The heterogeneity factor can be used to correct the activation energy term derived for homogenous nucleation, as shown in the following [34]:

$$\Delta G^*_{hetero}=\Delta G^*_{homo}\,f(\theta)$$

For the configuration shown in Figure 2.10, Uhlman and Chalmers derived an expression for $f(\theta)$ as [34] ;

$$f(\theta)=\frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

$$\Delta G^*_{hetero}=\frac{16\pi\sigma^3}{3\Delta P^2}f(\theta)$$

where θ is the wetting angle, $f(\theta)$ is the heterogeneity factor, and σ represents the interfacial tensions of a polymer–gas bubble.

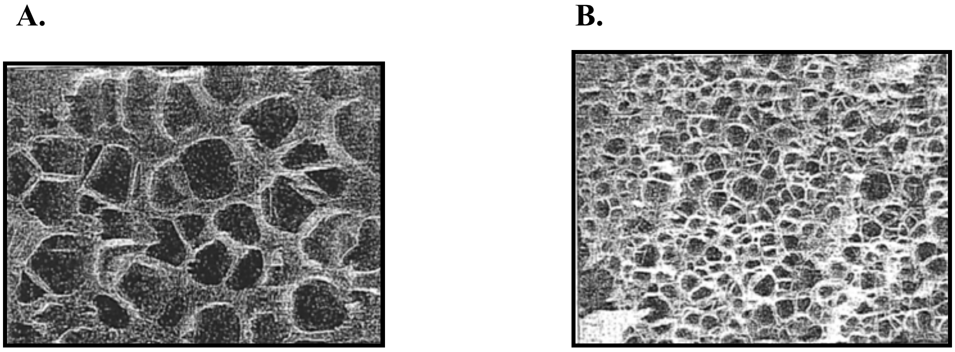


Figure 2.11 Heterogeneous nucleation assisted by rubber particles. (A) Polystyrene (PS) with rubber particles. (B) Polystyrene (PS) with no rubber particles [35].

According to Colton and Suh, for a typical wetting angle of 20º, $f(\theta)$ is on the order of 10^{-3}, which means it is easy to produce several orders of magnitude of more bubbles using nucleating sites. This explains why polystyrene produces more bubbles when rubber particles are added, as shown in Figure 2.11 (A) and Figure 2.11 (B). These examples show nucleation of bubbles when the polymer is not sheared. There are several useful chemical nucleating agents available commercially. They are as follows:

- Citric acid/sodium bicarbonate (endothermic)
- Azodicarbonate (exothermic)
- p-Toluene sulfonyl hydrazide (exothermic)
- Sodium borohydride (endothermic)

These agents are often added to nucleate cells [34].

2.5.3.4 Microvoid Nucleation

The classical nucleation models in the literature predict a negligible nucleation rate up to a gas saturation pressure of about 34.475 MPa. Kumar has concluded that the cell nucleation phenomenon in thermoplastics is not well described by the classical homogeneous nucleation theory. This is a new model for nucleation based on the heterogeneity of rubber particles introduced into the polymer where stress-induced microvoids on the rubber provide the nucleation sites [34].

The schematic diagram of microvoid nucleation model is shown in Figure 2.12. This diagram shows the presence of a single microvoid surrounded by a finite amount of polymer. The pressure inside the microvoid tends to grow into a cell while the opposing surface and elastic forces tend to collapse the microvoid. The scanning electron microscope (SEM) picture of microcellular foams obtained by foaming the nucleated polystyrene (PS) at 388 K is also shown in Figure 2.13. This micrograph indicates that both particles and cells vary in their diameters significantly over the cross section of the micrograph [34].

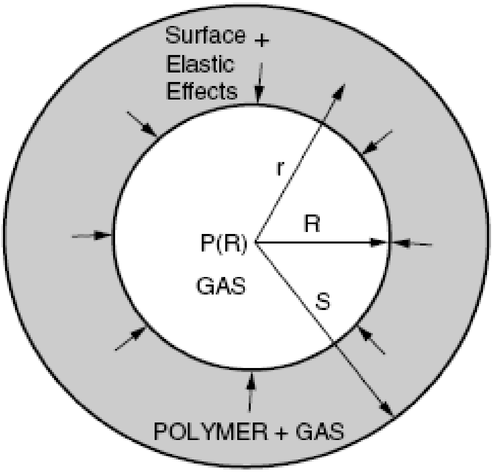
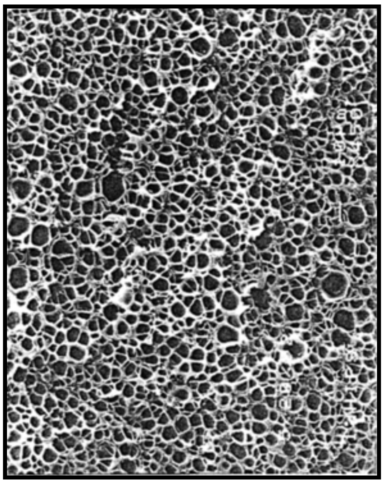


Figure 2.12 Schematic diagram of a single microvoid surrounded by a finite amount of polymer [34].



Saturation Pressure = 13.8 MPa (2000 psig)
Foaming Temperature = 388 K
Gas: Nitrogen
Heating Medium: Ethylene Glycol Bath

Figure 2.13 Microcellular foams produced from nucleated PS [34].

Particle size distribution plays a role in dictating the slope of cell size distribution data. It appears that there is a strong correlation between particle size and cell size prior to nucleation. This clearly indicates the ability of the rubber particles to control cell size during nucleation. In general, there is good agreement between theoretical predictions and the experimental data [34].

2.5.4 Foam Growth in Polymers

After cell nucleation, the bubbles grow due to the diffusion of excess gas in the polymer. The viscosity of the polymer, the gas concentration, the foaming temperature, and the amount of nucleating agent and its nature are some of the variables that control the foam growth process. The expansion dynamic of polymeric foam is very complicated. It has been increasingly scrutinized by investigators for the past 90 years [34].

2.5.4.1 Bubble Growth Models

Several investigations addressing the theoretical and experimental analysis of bubble growth and collapse in fluids and polymers have been available in the literature since 1917. Most of the models can be classified into three groups:

(1) The single bubble growth model; (2) the cell model (a swarm of bubbles growing without interaction); and (3) the combined nucleation and bubble growth model [34].

2.5.4.1.1 Single Bubble Growth Models (1917–1984)

Between 1917 and 1984, the published models focused on the growth or collapse of a single bubble surrounded by an infinite sea of fluid with an infinite amount of gas available for growth. Although these models gave several insights into bubble growth phenomena, their practical application in industry was severely limited because the foaming process involves the growth of numerous bubbles expanding in close proximity to one another with a limited supply of gas. This led to the development of a new model called the “cell model” [34].

2.5.4.1.2 Cell Model (1984–1998)

The cell model has been widely used to describe devolatilization, batch microcellular, and foam extrusion processes. Gross motion, no bubble motion, and motion without shear have different implications in the cell model.

The concept of a cell model was first introduced by Amon and Denson in 1984. Their study involved the growth of a group of gas bubbles separated by a thin film of polymer and dissolved gas during the injection molding process. The foam was divided into spherical microscopic unit cells of equal and constant mass, each consisting of a liquid envelope surrounding a single bubble; the gas available for growth was thus limited. Because it relied on a more realistic assumption of gas availability, the cell model yielded a final radius while single bubble growth models showed the growth of bubble radius was infinite. This fundamental improvement caused more interest in this area of research, and several studies have emerged since then. However, the Newtonian viscosity equation was used to describe the rheology of the polymer due to the complexity of the problem. Later it was modified to account for the non-Newtonian viscoelastic effects to make it more suitable for polymeric systems [34].

2.5.5 Types of Polymeric Foams by Cell Structure

A cell is a small particle or completely enclosed cavity within a plastic part. A cell is generally a gaseous void. A plastic material made up of numerous cells is referred to as a cellular plastic or foamed plastic [33]. There are three types of polymeric foams by cell structure. They are open-cell foams, closed-cell foams and syntactic foams.

2.5.5.1 Open-cell Foam

An open cell is a cell not totally enclosed by its walls and hence interconnecting with other cells. Open-cell or interconnecting-cell foam is foam in which the greatest proportion of cells is connected by open passageways to other cells. Such foam will absorb water when placed under water. An open cell structure of polymeric foam is represented in Figure 2.14 [33].

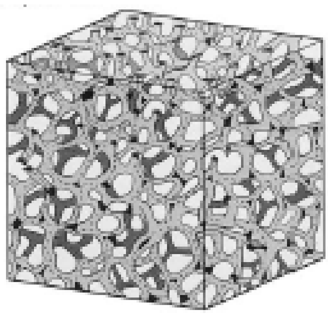


Figure 2.14 Representation of an open cell structure of a polymeric foam [36].

2.5.5.2 Closed-cell Foam

A closed cell is one that is totally closed by its walls and hence not interconnecting with other cells. Closed-cell, or unicellular, foams are those in which the greatest proportion of cells are not connected together by open passageways. Such a material only absorbs water or other liquid on the outermost surface cells. Closed-cell foams do make effective sound-absorbing materials. Furthermore, closed-cell foams are used for flotation devices and similar items. A closed cell structure of polymeric foam is represented in Figure 2.15 [33].

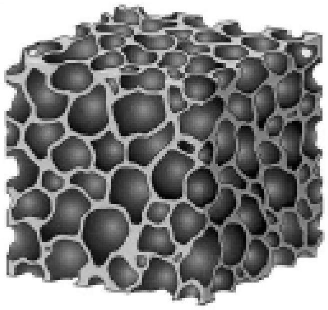


Figure 2.15 Representation of a closed-cell structure of a polymeric foam [36].

2.5.5.3 Syntactic Foam

Syntactic foam is a special type of plastic foam in which the cellular structure is formed by the use of small, hollow spheres made of resin, glass, or other hollow particles. The spheres are dispersed throughout a matrix of resin, usually thermosetting, which when cured resembles a conventional foam plastic. Once mixed, syntactic foam may be cast or formed in place by a pouring or trowling action [33].

2.5.6 Polymeric Foam Processing Techniques

The method for making foam is straightforward: generating bubbles and stabilizing them within a polymeric matrix. Bubble formation, in general, is a consequence of unstable phenomena or a way to dissipate a “disturbance” to resume a stable state. Boiling is a good example that is often described as a transient phenomenon. When a system is excited into an unstable foaming state, a stabilization mechanism must be established in time to transform the foaming into a stable foamed product. Again, the fundamental concept sounds very simple, but there are a great variety of methods for making useful polymeric foams [34].

There are two major foaming methodologies in the polymeric foam industry: soluble foaming and reactive foaming, or in other words physical foaming and chemical foaming The former involves physical variation in polymer states, and the latter is solely dependent on chemical reaction. The two methodologies can also be described as follows: blowing an agent into the polymer by mixing within a chamber to take advantage of the vaporization of gas while reducing pressure; or blending reactants to reactive conditions for gas evolution within a dense medium. In both methods, the same three steps - gas implementation, gas expansion, and foam stabilization - are involved.

Reactive foaming generates foaming through chemical reaction. Gas can evolve out of simple reactions between reactants, or simply by thermally induced decomposition. Polyurethane, polyisocyanurate, and phenolics are good examples of foams made by reactive foaming. Basically, the amount of gas is governed by reactant quantity and ratio, reaction rate by catalyst and thermal condition, and foam stability by additives. Thermoset polymerization amid a gas reaction makes it very unique. The exothermic reaction enhances foaming by enthalpy. Also, changing formula and reaction conditions creates a great product spectrum for reactive foaming. Slightly over half of the foam market is designated for reactive foaming products [34].

Another common practice is physical or soluble foaming which is done by preblending chemicals, which is to decompose into gaseous components under a certain temperature with the thermoplastic to cause decomposition inside the processor for foaming. Normally, this type of reaction generates volatile gases, which makes stabilization of the polymer very critical. It is very popular for low expansion products. To increase expansion, polymer strength has to be improved. A good practice is to generate x-links among the polymer backbone prior to gas generation. Great success in polyolefin foam has been established [34].

Besides physical and chemical foaming methodologies, there are many ways of their applications. Plastic foams are principally made by one of seven different processes:

(1) A foam may be made by incorporating a chemical blowing agent into the polymer to form a gas by decomposition at a given elevated temperature. Usually the blowing agents are in the form of fine powders, which can be either evenly dispersed in a liquid resin or mixed with molding pellets. The usual gas is nitrogen liberated from organic materials known as azo compounds. A typical blowing agent is azobisformamide (ABFA), also called azodicarbonamide. Blowing agents are available that decompose at temperatures from 110°C to as high as 280°C [33].

(2) Another method of producing foamed plastic is to inject a gas, usually nitrogen, into a molten or partially cured resin. The gas may be injected into the resin either in the barrel of an extruder or injection press or into a large mass in an autoclave [33].

(3) Some polyurethane foam is made by combining a bifunctional material such as a diisocyanate with polyester or other liquid polymer. During the polymerization process the isocyanate reacts to liberate a gas, which forms the cells [33].

(4) Foams may also be produced by the volatilization of a low-boiling liquid either by the heat liberated by an exothermic reaction or by externally applied heat. Commonly used in these foams are liquid fluorocarbons (e.g. Freon from Du Pont). This is the usual technique in production of polyurethane foams [33].

(5) A nonchemical, gas-liberating agent, such as finely divided carbon with gas adsorbed onto its surface, may also be used in a resin matrix. On heating the gas is released to produce the foamed cells [33].

(6) Foam may be made by whipping air into a colloidal resin suspension and then gelling the porous mass. Foamed latex rubber is made in this way [33].

(7) Finally, foam may be produced by the expansion of small beads of a thermoplastic resin by heating an internally contained blowing agent. This technique is employed for expansion of polystyrene beads used to make cups, packaging, display boards, etc. [33]

In addition to foaming methodologies, there are many ways in which foams can be processed and used: slabs, blocks, boards, sheets, molded shapes, sprayed coatings, extruded profiles, and foamed-in-place within an existing cavity, where the liquid material is poured and allowed to foam. Conventional equipment can be used: extruders, injection molding machines [30].

It is reasonable to view foaming from the perspective of material strength. Many interesting techniques have been developed around each methodology in the last half century. A summary on general technologies used to make polymeric foams is given in Table 2.4 [34].

Table 2.4 General technologies used to make polymeric foams [34].

Technology	**Polymers**	**Applications**
Reactive foaming	PU, Phenolics	Construction, automotive, sports, toy, furniture, packaging
Extrusion	PS, PVC, PE, PP, PET	Food, construction, decoration, packaging, medical
Injection Molding	PS, PP, PE	Automotive
Mold Bead	PS, PP, X-PE	Food, packaging, thermoforming
X-PE	PE	Sports, thermoforming

Plasticators, such as screw extrusion and injection molding, are very popular in making processing foamed polymers, owing to their capabilities in energy transfer to change the state of thermoplastic polymers to accommodate blowing agents in order to form a melting solution for subsequent bubbling while adequate reduction of pressure occurs. Temperature reduction is necessary to facilitate the stabilization process. Another common method is to saturate thermoplastic pellets with a blowing agent. When pressure reduction and temperature increase are applied for enough supersaturation, controlled foaming makes foamed products [34].

Based on production output, the most important processes are (1) extrusion (using PU, PS, PE, PVC, CA, etc.), (2) expandable (PS, PE, PVC, PU, phenolic, epoxy, PF, EP, SI, etc.), (3) spray (PU, EP, UP, etc.), (4) froth (PU, PVC, UF, EP, etc.), (5) injection molding (PE, PP, PS, PVC, etc.), (6) compression (PE, PVC, UP, etc.), (7) sintering (PS, PE, PTFE), and (8) leaching (PE, PVC, CA). The processes are identified by different names, with some overlap. They include bead molding, calender foaming, expandable plastic foam, expandable PS, expandable sheet stock, expandable PVC, extruded foam, injection-molded foam (low-, high-, and counterpressure types), mechanical foaming, reaction injection molding, reticulated foam, spray foam, steam foam molding, structural foam, syntatic foam, and the following, all starting with the word foamed (e.g., foamed blow molding): blow molding, casting, extruded film, frothing, gas counterpressure, injection molding, liquid, reservoir molding, rubber, PE, PS, PU, PVC, preform, sandwich structure, sheet stock, silicone, spray, steam molding, in-place, pouring, short-shot molding, and mechanical [30].

2.5.6.1 Blowing Agents

For the production of foamed or cellular plastics, depending on the basic material and process, different blowing agents (also called foaming agents) are used to produce gas and thus to generate cells or gas pockets in the plastics. They can produce rigid or flexible types and may be divided into two broad groups: physical blowing agents (PBAs) and chemical blowing agents (CBAs). Mostly, PBAs are compressed gases and volatile liquids. The compressed gases most often used are nitrogen and carbon dioxide. These gases are injected into a plastic melt under pressure (higher than the melt pressure) and form a cellular structure when the melt is released to atmospheric pressure or low pressure, as in a mold cavity with a short shot. The volatile liquids are usually aliphatic hydrocarbons, which may be halogenated, and include materials such as carbon dioxide, pentane, hexane, methylene chloride, etc. Chlorofluorocarbons were formerly used but they have now been phased out. The liquids act as a gas source by vaporizing during the process. Regardless of their physical form, they rely solely on pressure for controlling gas development in a foaming process [30].

CBAs, generally solid materials, are of two types: inorganic and organic. Inorganics include sodium bicarbonate, by far the most popular, and carbonates such as zinc or sodium. These materials have low gas yields and, compared with organic CBAs, the cell structure they create is not as uniform. Organics are mainly solid materials designed to evolve gas within a defined temperature range, usually called the decomposition temperature range. This is their most important characteristic and allows control over gas development through both pressure and temperature. This increased control produces a finer and more uniform cell structure as well as better surface quality in the foamed plastic. There are over a dozen different types available that decompose at temperatures from 104 °C (220 °F) to 371 °C (700 °F), possibly higher. Many of these CBAs can be made to decompose below their decomposition temperature through the use of activators [30].

Besides selecting the proper CBA to meet temperature requirements, other factors to be considered relate to the plastic and the process. They include the types of gases evolved, the solid decomposition residues, the degree of self-nucleation, any discoloring or staining characteristics, and regulatory approval. CBAs could affect certain plastics going through certain processes; they could become yellow, and their lifespan could be shortened. CBAs should possess the following desirable qualities: (1) long-term storage stability; (2) gas release over a controlled time and temperature range; (3) low toxicity, odor, and color of the blowing agent and its decomposition products; (4) no deleterious effects on the stability and processing characteristics of the plastic; (5) the cells they produce have uniform size; (6) the foams they produce are stable; gas is not lost from the cell, causing it to collapse; and (7) acceptable cost-performance relation and availability [30].

Examples of blowing agents for certain plastics are (1) physical blowing agents that evaporate at the processing temperature; (2) hydrocarbons such as pentane for the production of expandable polystyrene; (3) chemical blowing agents which split off, e.g., nitrogen at the temperature of processing; these are used in the foaming of PE and

PVC; and (4) blowing agents which, through the reaction of the raw material components, release gas (usually carbon dioxide); PU soft foam is produced in this manner [30].

2.5.6.1.1 Mixing of CBAs into Resins

Direct injection of nitrogen requires special equipment which will allow it to be injected into a hot melt, such as an extruder or injection barrel, whereas a CBA does not require this type of equipment. The most common means of using CBAs is by drum tumbling with the resin. A wetting agent such as white mineral oil is commonly used to ensure good adhesion to the resin pellets; this is particularly important if the mix is to be airconveyed to the hopper. Another mixing method is to use one of the many hopper metering and blending units available, which eliminates the labor required in drum tumbling and avoid a potentially poor mix. A third popular method uses a liquid dispersion of CBA compatible with the resin being foamed. An especially popular approach involves putting the CBA in a resin concentrate. A variety of resins is used and provides excellent dispersion of the CBA [30].

There are many types of blowing agents used commercially. Such as azocarbonamide, dinitrosopentamethylenetetramine, benzenesulphonohydrazide, azoisobutyronitrile, 4,4’Oxybis(benzenesulphonohydrazide),N,N’-dimethyl-N,N’-dinitrosoterephthalamide, sodium bicarbonate, terephthalazide and trihydrazinotriazine. In this study, 4,4’ Oxybis(benzenesulphonohydrazide) (OBSH) was used. Trade names include Celogen-OT and Nitropore-OBSH(USA), and Genitron OB(England).

2.5.6.1.2 Requirements to be Considered for Using CBAs

In addition to the requirements common to all additives, there are some special requirements to be considered while using CBAs. These include:

(1) The need for gases to be evolved within a narrow but clearly defined temperature range and in a controlled and reproducible manner.

(2) The decomposition temperature should be suitable for the polymer. For example, a decomposition temperature for a blowing agent system for PVC should not be above the maximum possible processing temperature that can be used if significant degradation is not to occur.

(3) Gases evolved should not corrode processing equipment. Whilst many hundreds of materials have been investigated as blowing agents the number in actual use is very small [30].

2.5.6.1.3 Celogen – OT ® [4,4'-Oxybis(benzenesulphonohydrazide)]

In this study, Celogen-OT ® was used. OBSH is a white crystalline compound [37]. Molecular structure of OBSH is given in Figure 2.16 . This blowing agent is in the class of hydrazide and its volatiles produced are N_2 and H_2O. Its decomposition temperature is around 150 ºC and its gas yield is 120-180 g/cm^3. Its decomposition rate is faster than azodicarbonamide but it has lower blowing power limits [22].

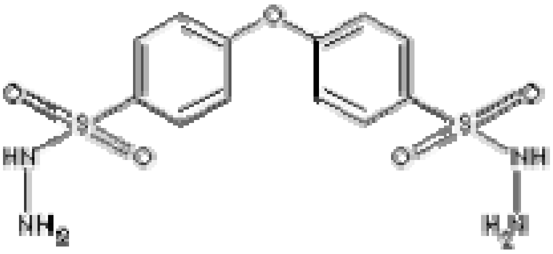


Figure 2.16 Molecular structure of Celogen-OT ® [38].

OBSH is one of the best blowing agents of the sulfonylhydrazide class. Since it is a difunctional sulfonylhydrazide, it imparts no smell to plastics or rubbers, because its decomposition gives nonvolatile and nontoxic oligomers. The main disadvantage of this blowing agent is that it disperses poorly in foam formulations. However, this can be partially alleviated by introducing small amounts of surfactants. This blowing agent is stable up to 100 ºC, is nontoxic, and does not impart color to the articles. The absence (up to 140 ºC) of stepwise changes in the kinetics of gas liberation at different temperatures of OBSH decomposition makes it possible to obtain foams with small, uniform cells [37].

OBSH is used for foaming poly(vinyl chloride), polyolefins, polysulfides, microporous rubber, or foamed materials based on mixtures of polymers and oligomers with rubbers. In the last case, OBSH acts not only as the blowing agent but also as a cross-linking agent. In this study OBSH is used with EVA [37].

2.5.6.2 Cross-linking (Curing) Agents

Cross-linking (curing) agent is a substance that promotes or regulates intermolecular covalent bonding between polymer chains, linking them together to create a more rigid structure [39]. The use of curing agents began with the serendipitous discovery of vulcanization of hevea rubber with sulfur by Charles Goodyear in 1838. The conversion of an A- or B-stage phenolic novolac resin with hexamethylenetetramine in the early 1900s was another relatively early example of the use of a curing (cross-linking) agent [40]. There are some methods for making cross-links between polymer chains, such as UV cross-linking.

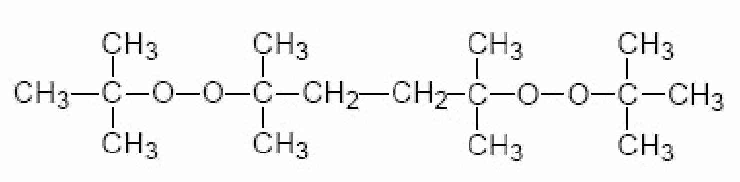
These additives create reactive (unstable) systems, so they are usually added by the processor just before final plastic processing. In most cases, the chemistry of these systems is very precise and sophisticated, so these additives are best specified by the polymer producer, not casually chosen and used by the average compounder/processor.

They are best described according to the polymer system in which they are used [41]. In this study, Luperox® 101G45 (2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane) was used as a cross-linking agent.

2.5.6.2.1 Luperox ® 101G45 (2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane)

Dicumly peroxide and 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane are organic peroxides that are most commonly used as curing agents for cross-linking polyolefins and elastomers. In this study, Luperox ® 101G45 which is a trade name of 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane was used as cross-linking agent. Molecular structure of Luperox ® 101G45 is shown in Figure 2.17.

Organic peroxides are often added to produce cross-linking in a system. Peroxides can be selected to decompose at a particular temperature for the application. Peroxides can be used to cross-link saturated polymers. Thermoplastics are most often cross-linked by peroxides, choosing the peroxide according to the processing temperature. Peroxide forms free radicals, which abstract less stable hydrogen atoms from the polymer, leaving polymer radicals. When two polymer radicals join, this forms a cross-link. The degree of cross-linking is low - not enough to cause rigidity, but enough to improve strength, creep-resistance, hot strength, and insolubility. Thus, polyethylene is cross-linked by 2 to 10 percent of peroxide during reactive extrusion to form piping and wire and cable insulation. Conversely, polypropylene radicals tend to cleave rather than cross-link, so peroxide is used to decrease melt viscosity for easier processability [41].



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3}$$

Figure 2.17 Molecular structure of Luperox ® 101G45 [42].

2.5.7 Bituminous Foams

Bituminous foams are not classifiable as plastics materials, but as thermoplastic organic, it conforms to many of the foaming operations. Asphalt is a very cheap mineral which, properly developed and commercialized, could have an extremely large potential [43].

The usual method of making bituminous foam is releasing gases under pressure in a thermoplastic material which has been disclosed. Another method utilizes sodium bicarbonate as the blowing agent, and an aluminum stearate surfactant in the softened asphalt. The temperature of the asphalt is controlled so that the gas release is obtained at a uniform rate, and the gas is effectively entrapped [43].

An apparatus designed to heat high melting asphalt and to inject gas or a blowing agent is needed where bituminous foam is aimed to be made. Cold-flow retarding agents (asbestos fillers, gallants, high melting resins) may be required to obtain acceptable properties. A variety of formulations are conceivable which would allow the hot melt to expand upon release of pressure and cool rapidly to obtain stable foam. On-site foaming for insulation beneath concrete slabs, and for direct application to basement walls, is one application which could use a substantial volume of asphalt. The inherent water and decay resistance of the asphalt and its low cost would readily offset the additional thickness required for adequate insulation [43].

2.5.8 Bituminous Polymeric Foams

There are many patented methods of making bituminous polymeric foams; however there is no completed study announced at academic literature. One of the most common methods mentioned is that asphalt combined with from 5-50 % EVA may be mixed with and alkali metal hydride at 205-371 °C, and hydrated calcium sulfate added as an activator. Intensive agitation causes the mixture to foam. Such processing would seem to be adaptable to standard urethane foaming equipment with accommodations for the high melt temperature of the asphalt blend [43].

2.6 Mixing

There are a number of different mixing operations that occur in polymer processing [44]. Mixing involves dispersion of stabilizers, pigments and other additives into polymer, exclusion of air and volatiles, transformation of solid polymer feed stock into melt and achieving a fluid state which is uniform in composition, temperature and deformation history [45].

When the materials to be mixed are solids, the mixing typically involves particulate solids. This type of mixing is referred to as solid-solid mixing. When a polymer has to be mixed with a particulate solid and both the polymer(s) and the filler(s) are in powder form, substantial mixing can take place with the use of solid-solid mixing. The remainder of the mixing then is accomplished by melting the polymer/filler mix to achieve complete wetting of the filler by the polymer. The mixing of the molten polymer with the solid filler is referred to as solid liquid mixing [44].

More typically, the filler is mixed in with the polymer when the polymer is melted. In this case, most of the mixing is solid-liquid mixing. This is the primary mixing action that occurs in plasticating screw extruders. Solid material is fed to plasticating screw extruders and is melted as it is conveyed forward by the rotating screw to the end of the screw [44].

There are two basic stages in mixing: dispersing additives in the polymer and achieving a uniform and shapeable state. The final degree of mixing may be achieved in one operation but more commonly there are two or more separate operations. There are two common types of mixers used such as the intensive mixer and the two-roll mill [45]. A schematic representation of dispersive mixing is shown in Figure 2.18 [44].

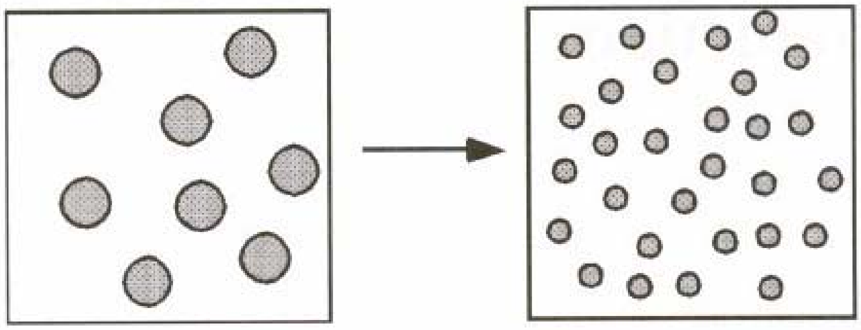


Figure 2.18 Schematic representations of dispersive mixing [44]

Distributive mixing is mixing in the absence of a cohesive resistance and is also referred to as extensive, simple, or nondispersive mixing. An example of distributive mixing is the mixing of two miscible polymer melts, e.g., polystyrene (PS) and polyphenylene oxide (PPO). Distributive mixing can occur in solids as well as in fluids. When a particulate solid is blended into a liquid without reducing the particle size, this is distributive solid-liquid mixing. A schematic representation of distributive mixing is shown in Figure 2.19 [44].

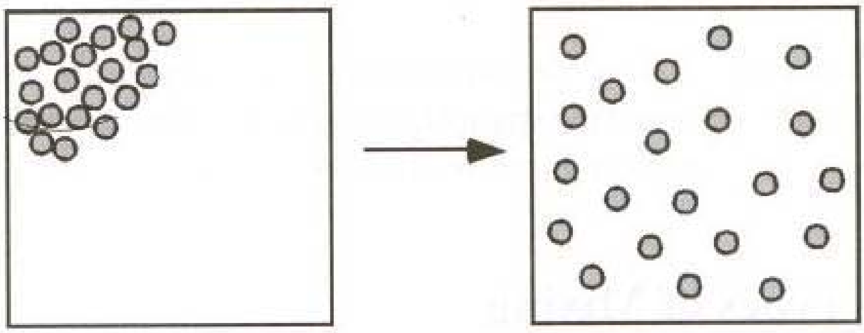


Figure 2.19 Schematic representations of distributive mixing [44].

Mixing can be defined as a process to reduce composition nonuniformity. The basic process involved in mixing is to induce relative motion between the ingredients of the mixture. There are three types of motion that can occur:

1. Diffusion, limited to low molecular weight materials;
2. Turbulent motion, limited to low-viscosity fluid; and
3. Convective motion, prevalent in high-viscosity fluids [44].

2.6.1 Internal Mixers

The original internal mixer was developed by Thomas Hancock around 1830. The Hancock masticator used only a single rotor to mix the material. Twin rotor mixers were introduced around 1880 by Werner and Pfleiderer GmbH; the mixing chamber in this machine was not fully enclosed. About forty years later, Banbury introduced an internal mixer equipped with a ram to force the material into the mixing chamber and to provide sealing. The rotors in the Banbury mixer are nonintermeshing and counterrotating. Intermeshing counter-rotating internal mixers were introduced by Cooke of Francis Shaw and Company and by Lasch and Stromer of Werner and Pfleiderer. Most internal mixers use counter-rotating rotors, but Brennan from

Teledyne-Readco developed a co-rotating internal mixer. Figure 2.20 illustrates a commercially available torque rheometer [44].

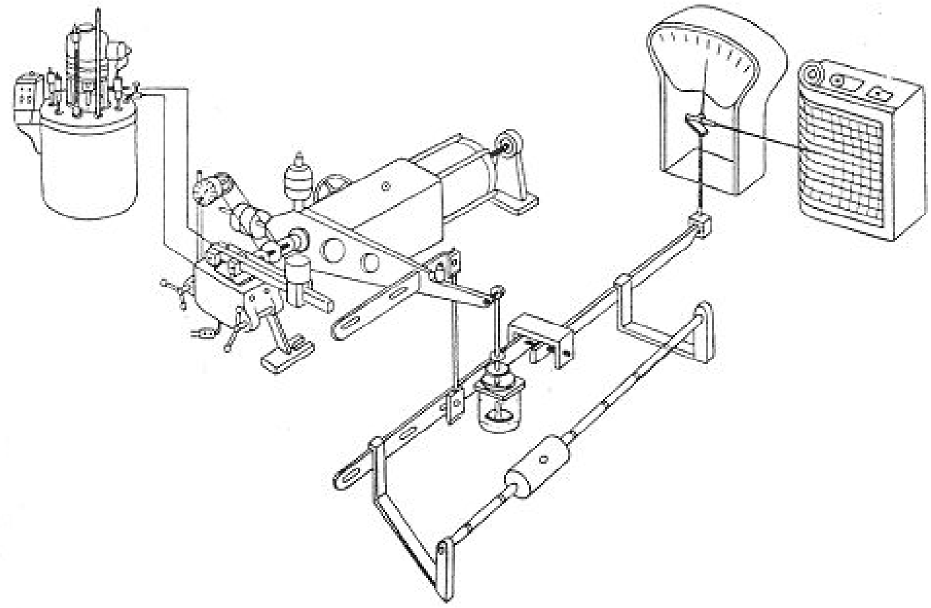


Figure 2.20 Schematic representation of brabender (Courtesy C. W. Brabender Instruments, Inc.) [44]

The main components of a batch internal mixer are the rotors, the mixer housing, the ram, the ramair cylinder, the feed hopper, and the door for discharge (Figure 2.21).

The advantages of the batch internal mixer are:

1. It accepts feed stock in various forms,
2. It has intensive mixing action,
3. It has a well-defined residence time,
4. Quick material changes can made, and
5. A wide range of mixing procedures can be used [44].

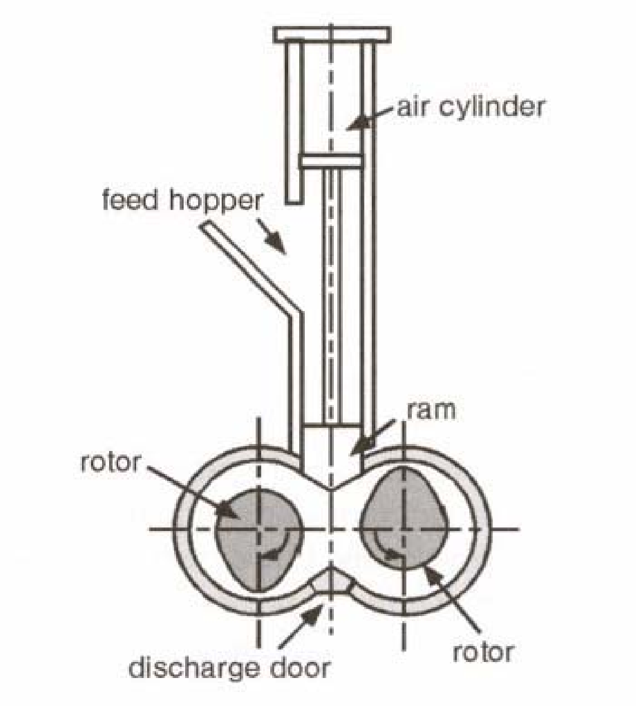


Figure 2.21 Schematic representation of a batch internal mixer [44].

The mixing action of the internal mixer is concentrated in the narrow gaps between the rotor and the housing. In these regions, high rates of shear and elongation occur, resulting in intensive mixing action. Because the mixer is usually equipped with high horse power drives, the mixer can handle high-viscosity materials quite well. Some disadvantages of the batch internal mixer are:

1. It is not a self-wiping mixing device,
2. Batch-to-batch variations can affect product quality,
3. It is difficult to achieve fine process control, and
4. It cannot handle high-temperature engineering plastics [44].

2.6.1.1 Order of Addition of Ingredients

The sequence of the addition of the ingredients is a key element to good mixing in internal mixers. Generally, the objective is to arrange the sequence to maintain adequate stiffness in the mixture until the most difficult step in the dispersion is achieved. A normal sequence of mixing of a filled polymer is as follows:

Step 1. Load polymer and one-half of the filler and mix until the material softens.
Step 2. Add remaining filler and mix until fully incorporated.
Step 3. Add plasticizers and/or softeners and complete mixing [44].

In some cases, a batch may soften too quickly before a good dispersion is obtained. In this case, an alternate technique may be used, referred to as "upside down mixing". In this technique, all ingredients are added at once, maximum ram pressure is applied, and maximum rotor speed is used. The main process variables in the batch mixing process are batch weight (fill factor), material feed temperature, mixer temperature, rotor speed, ram pressure, and sequence and timing of the feeding of the ingredients [44].

2.6.1.2 Degree of Fill and Rotor Speed

The mixing efficiency in the batch internal mixer is strongly influenced by both the degree of fill of the mixer and the rotor speed. Both these variables were studied by Ries, and the results are represented in Figure 2.22. The quality of the mix is plotted along the vertical axis, with the degree of fill along the horizontal axis. The mix quality of 6 is poor and 0 is the best; these rankings are based on the dispersion of the carbon black in the mixture [44].

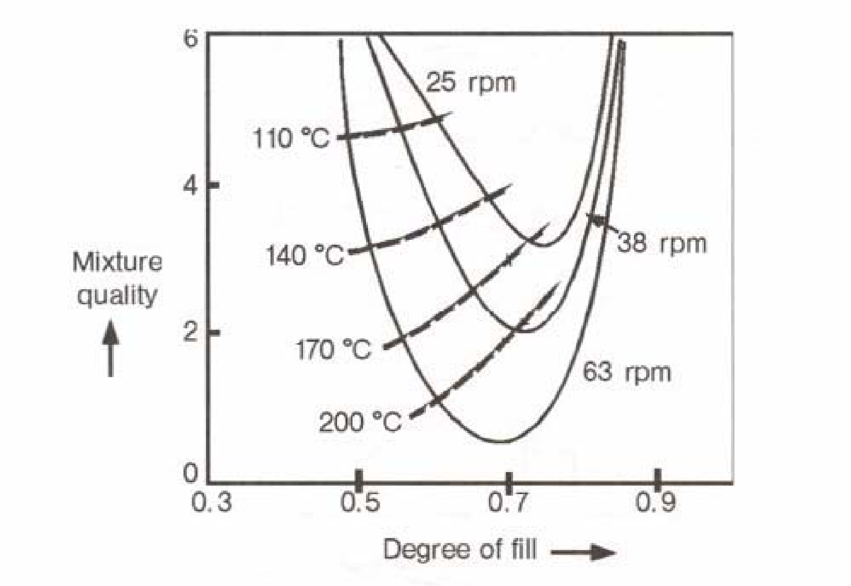


Figure 2.22 Mixture quality vs. degree of fill at three rotor speeds [44].

Figure 2.22 shows that the optimum degree of fill is in the range of 70 to 80 %. At low rotor speed, the optimum degree of fill is ~80 %, but the best mix quality achieved is marginal, around three. At high rotor speed, the optimum degree of fill is ~70 %; however, at this level of fill the quality of the mix is much better than at lower rotor speed. It is clear that the wrong degree of fill can be quite detrimental to the mix quality [44].

The discharge melt temperature is also indicated in Figure 2.22. As the rotor speed and the dispersion quality increases, the stock temperature increases as well. In some cases, the discharge melt temperature will limit the rotor speed that can be used. This can be the case when the material has limited thermal stability at elevated temperatures or when the material may cross-link at high temperatures. If high rotor speed is desired, the geometry of the rotor can be adapted to run at higher than normal speed [44].

2.7 Foam Molding

2.7.1 Structural Foam Molding

Structural Foam is a term commonly used to describe thermoplastic injection molding components made by the injection molding process which have a cellular core [46]. The part produced by structural foam molding is not homogeneous like the part produced by thermoforming or injection molding. Within the outer skin, there is a cellular structure with the cell size increasing toward the center. The part must have a wall thickness of 0.0187 in. for any significant amount of foaming to take place. Thus the structural foam part may actually require more resin than the equivalent part made by either thermoforming or injection molding if the wall thickness must be increased to accommodate the foaming processes. In addition, the molding process for structural foam molding is much longer than that of injection molding because of the time required for gas expansion. For these reasons, the piece part cost will be greater for a part produced by structural foam molding than for a similar part made by injection molding [33].

Parts made by the structural foam molding process have a swirled surface. Gas counterpressure structural foam molding and coinjection molding are variations of the process, which can produce a solid, nonswirled surface. Depending on the application, the additional mold cost for the gas counterpressure feature reduces the tooling savings over the injection molding alternative. Coinjection molding permits a solid material to be used for the outer skin and a foamed material for the inner structure, which can also be a less expensive material. This process requires sophisticated equipment [33].

Parts made by structural foam molding, gas counterpressure structural foam molding, or coinjection molding use closed molds and low pressures. The low pressure keeps the tool cost significantly lower than traditional injection molding, although the rate of molding is slower. These foam molding processes often allow the design of a component in one section (e.g. a steering wheel or a vacuum cleaner handle). The foam molding processes eliminate the need for assembly and the cost of fasteners. This results in a lower product cost even though the injection molding process has faster cycle times [33].

In this study, Hand Lay-up Self-expanding Batch Molding (HLUSEBM) Technique which is a new method firstly applied by our group. This technique is similar to structural foam molding technique except foaming is performed in self-expansion manner. There are some doubts that whether this technique can be used at plant production scale. However, it is a useful and economically feasible method that can be applied at laboratory scale. Details about Hand Lay-up Self-expanding Batch Molding (HLUSEBM) Technique are given in experimental chapter.

2.8 Characterization

2.8.1 Mechanical Properties

The mechanical properties, among all the properties of plastic materials, are often the most important properties because virtually all service conditions and the majority of end-use applications involve some degree of mechanical loading. The material selection for variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength [47].

There is a variety of methods which are useful in predicting mechanical properties of polymers. However, it is essential that there should be some consistency in the manner in which tests are conducted, and in the interpretation of their results. This consistency is accomplished by using standardized testing techniques. Establishment and publication of these standards are often coordinated by professional societies. In the United States the most active organization is the American Society for Testing and Materials (ASTM). Its annual book of ASTM standards comprises numerous volumes, which are issued and updated yearly; a large number of these standards relate to mechanical testing techniques [47].

2.8.1.1 Compression Test

Compressive properties describe the behavior of a material when it is subjected to a compressive load at a relatively low and uniform rate of loading. In spite of numerous applications of plastic products that are subjected to compressive loads, the compressive strength of plastics has limited design value. In practical applications, the compressive loads are not are not always applied instantaneously. Therefore, the standard test results that fail to take into account the dependence of rigidity and strength of plastics on time cannot be used as a basis for designing a part. The results of impact, creep, and fatigue tests must be considered while designing such a part. Compression tests provide a standard method of obtaining data for research and development, quality control, acceptance or rejection under specifications, and special purposes. Compressive properties include modulus of elasticity, yield stress, deformation beyond yield point, compressive strength, compressive strain, and slenderness ratio. However, compressive strength and compressive modulus are the only two values most widely specified in design guides [48].

In the case of a polymer that fails in compression by a shattering fracture, the compressive strength has definite value. For those polymers that do not fail by a shattering fracture, the compressive strength is an arbitrary one depending upon the degree of distortion that is regarded as indicating complete failure of material. Some material suppliers report compressive stress at 1 or 10 percent deformation of its original height. Some polymers may also continue to deform in compression until flat disk is produced. The compressive strength stress continues to rise without any well-defined fracture occurring. Compressive strength has not real meaning in such cases [48].

The universal testing machine used for tensile and flexural testing can also be used for testing compressive strength of various materials. For compression tests, the tensile testing machine of a constant-rate-of-crosshead movement is used. It has a fixed or essentially stationary member carrying one grip, and a movable member carrying a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and the movable member prevent alignment problems. A controlled-velocity drive mechanism is used. Some of the commercially available machines use a closed-loop servo-controlled drive mechanism to provide a high degree of speed accuracy. A load-indicating mechanism capable of indicating total compressive load with an accuracy of 1 percent of the indicated value or better is used. Lately, the inclination is toward using digital-type load indicators which are easier to read than the analog-type indicator so, an compression indicator, commonly known as the deflectometer or compressometer, is used to measure any change in distance between two fixed points on the test specimen at any time during the test. The advent of new microprocessor technology has virtually eliminated time consuming manual calculations. Compressive stress, compressive strain, compressive modulus, and statistical calculations are performed automatically and presented on a visual display or hard copy printout at the end of the test [48].

Recommended test specimens for this test are either rectangular blocks measuring ½ x ½ x 1 in. or cylinders ½ in. in diameter and 1 in. long. Specimens may be prepared by machining or molding. The test specimens are conditioned in accordance with procedure A of ASTM methods D618 [48].

The specimen is placed between the surfaces of the compression tool, making sure that the ends of the specimen are parallel with the surface of the compression tool. The test is commenced by lowering the movable crosshead at a specified speed over the specimen. The maximum load carried by the specimen during the test is recorded. The stress-strain data are also recorded either by recording load at corresponding compressive strain or by plotting a complete load-deformation curve with an automatic recording device. Compressive strength is calculated by dividing the maximum compressive load carried by the specimen during the test by the original minimum cross-sectional area of the specimen. The result is expressed in lb/in.^{2} Modulus of elasticity or compressive modulus, like tensile and flexural modulus, is also represented by the slope of the initial straight-line portion of the stress-strain curve and is calculated by dividing the change in stress by the corresponding change in strain [48].

2.8.1.1.1 Constant Deflection Compression Set Test (ASTM 3574 Test D)

In this study, Constant Deflection Compression Set Test (ASTM 3574 Test D) is performed on bituminous polymeric foam samples. This test method consists of deflecting the foam specimen to a specified deflection, exposing it to specified conditions of time and temperature and measuring the change in the thickness of the specimen after a specified recovery period. As an apparatus, compression device, consisting of two or more flat plates arranged so the plates are held parallel to each other by bolts or clamps and the space between the plates is adjustable to the required deflection thickness by means of spacers. The test specimens shall have parallel top and bottom surfaces and essentially perpendicular sides. Specimens shall be 50 by 50 by 25 mm unless otherwise specified. Specimens less than 25 mm in thickness shall be plied up, without the use of cement, to a 25-mm thickness. Specimens from cored foams shall have a minimum top surface area of 100 cm^2. The thickness shall be no greater than 75 % of the minimum top dimension. Specimens from uncored molded products 25 mm or less in thickness shall be 50 by 50 mm by full-part thickness and shall contain the top and bottom skin. Specimens greater than 50 mm in thickness shall be cut to 25 mm thickness from the core. Three specimens per sample shall be tested. The value reported shall be the mean of those observed [49].

The entire test procedure is performed 23 ± 2°C and in an atmosphere of 50 ± 5 % relative humidity. Deflecting the specimen to either 50 ± 1, 75 ± 1, or 90 ± 1 % of its thickness, or any other deflection agreed upon between the supplier and the purchaser.

Within 15 minutes, the deflected specimen and the apparatus are placed in the mechanically convected air oven for a period of 22 hours and after 22 hours the apparatus is removed first. Then the specimen is removed immediately from the apparatus and the final thickness is measured after allowing it to recover 30 to 40 minutes at the temperature and humidity conditions specified above [49].

The constant deflection compression set is calculated, expressed as a percentage of the original thickness, as follows;

$$C_t = [(t_o - t_f)/t_o] \times 100$$

where, C_t is the compression set expressed as a percentage of the original thickness; t_o is the original thickness of test specimen, and t_f is the final thickness of test specimen [49].

2.8.2 Density and Porosity Measurements

2.8.2.1 Density Measurement (ASTM D 1622, ISO 845)

The density of foam plastics is of considerable interest to parts designers since many important physical properties are related to foam density [48].

Density, the mass per unit volume, is a function of the weight of individual molecules and the way they pack. The hydrocarbons do not possess ‘heavy’ atoms and therefore the mass of the molecule per unit volume is rather low [22].

There are two terms relevant to the density of cellular plastic materials. These terms are apparent core density of a cellular plastic and apparent overall density. Apparent core density defines the weight in air per unit volume of a sample; after all forming skins have been removed. Apparent overall density defines the weight in air per unit volume of a sample, including all forming skins [50].

There are many procedures to determine the apparent overall density of cellular plastics. The simplest way of measuring apparent overall density of a cellular plastic material basically requires conditioning a specimen of a shape whose volume can easily be calculated. The specimen is weighed on a balance or a scale. Next, the specimen volume is calculated by measuring length, width, and height using a micrometer, a dial gauge, or a caliper. Then the apparent overall core density is calculated as follows: [48]

Apparent Overall Density (gr/cm^3) *= Weight of Specimen/Volume of Specimen*

Amorphous hydrocarbon polymers generally have specific gravities of 0.86-1.05. Where large atoms are present, e.g. chlorine atoms, the mass per unit volume is higher and so PVC, a substantially amorphous polymer, has a specific gravity of about 1.4 [22].

If a polymer can crystallise then molecular packing is much more efficient and higher densities can be achieved. The high densities of PTFE (about 2.2) and poly(viny1idene chloride) (about 1.7) are partially attributable to this fact. Polyethylenes made by different processes often differ in the degree of branching and thus can crystallise or pack to varying events. For this reason polyethylenes produced by a high-pressure process have a lower density than those produced using supported metal oxide catalysts. The amorphous ethylene-propylene rubbers have lower densities than either polyethylene or isotactic polypropylene, both of which are capable of crystallizing [22].

The conformation adopted by a molecule in the crystalline structure will also affect the density. Whereas polyethylene adopts a planar zigzag conformation, because of steric factors a polypropylene molecule adopts a helical conformation in the crystalline zone.

This requires somewhat more space and isotactic polypropylene has a lower density than polyethylene [22].

2.8.2.2 Porosity Measurement

The percentage of porosity of polymeric foams or in other words cellular plastics is a key feature by which it is understood how much air it consists of. In order to calculate the percentage of porosity in a polymeric foam material, in addition to its apparent overall density, the density of the material without air must be known. The density of cellular plastic material without air is assumed to be equal to the density of unfoamed specimen.

The unfoamed material density is measured in accordance with specific gravity test which is defined by ASTM D 792 methods. The method A, which is used in this study, requires the unfoamed cellular plastic material or blend which is intended to be measured or the ingredients of the unfoamed cellular plastic material or their blend. It also requires use of a precision analytical balance equipped with a stationary support for an immersion vessel above or below the balance pan. A corrosion-resistant wire for suspending the unfoamed specimen blend or the ingredients of the blend and a sinker for lighter specimens with a specific gravity of less than 1.00 are employed. A beaker is used as an immersion vessel. The test specimen of any convenient size is weighted in air. Next, the specimen is suspended from a fine wire attached to the balance and immersed completely in distilled water. The weight of a specimen in water (and sinker, if used) is determined. The apparent overall core density (specific gravity) of the specimen is calculated as follows: [48]

Unfoamed Specimen Density (Specific gravity) $= a/((a+w)-b)$

where, a = weight of specimen in air; b = weight of specimen (sinker, if used) and wire in water; w = weight of totally immersed sinker (if used) and partially immersed wire.

Then, the percentage of porosity of polymeric foams or in other words cellular plastics is evaluated by a formula given below;

Porosity % = [(Unfoamed Specimen Density - Apparent Overall Density) / Apparent Overall Density] x 100

2.8.3 Thermal Conductivity

2.8.3.1 Thermal Conductivity of Plastic and Cellular Plastic Materials

Thermal conductivity is defined as the rate at which heat is transferred by conduction through a unit cross sectional area of material when temperature gradient exists perpendicular to the area. The coefficient of thermal conductivity is expressed as the quantity of heat passes through a unit cube of the substance in a given unit of time when the difference in temperature of the two faces is 1 ºC [51]. More simply, thermal conductivity is just the rate at which a material will conduct heat energy along its length or through its thickness [30].

Thermal conductivity and diffusivity are discussed together because they differ only in that the former is descriptive of equilibrium or steady state conditions and the latter describes nonequilibrium or transient conditions. Under steady state conditions, the amount of heat transferred is a function of the temperature difference across the material. For transient conditions, however, the amount of the heat the material can store as internal energy must also be considered [51].

In dielectric solids and liquids, which include most polymers, heat is conducted by the interactions of thermal vibrations of molecules and their component atoms. The transmission of heat is favored by the presence of ordered crystalline lattices and covalently bonded atoms. Thus graphite, quartz and diamond are good thermal conductors, while less ordered forms of quartz such as glass have lower thermal conductivities. Most polymeric materials have k values between 10^{-1} and 10^{0} $W/m^2.K$ [52].

In comparison with the amorphous polymers, crystalline polymers are characterized by a more ordered, denser structure which yields a higher thermal conductivity [52].

The thermal conductivity of plastics depends on several variables and cannot be reported as a single factor. But it is possible to ascertain the two principal dependences, temperature and molecular orientation. In fact, molecular orientation may vary within a product, producing a variation in thermal conductivity. Thus, it is important for the designer to recognize such a situation. Certain products require skill to estimate a part's performance under steady-state heat flow, especially products made of composites. The method and repeatability of the processing technique can have a significant effect [30]. The difference between amorphous and crystalline polymers with respect to heat conduction may be characterized as a lower resistance to intermolecular transfer in crystalline polymer. Polymers may be superior thermal insulating materials at very low temperature. Thermal conductivity should increase as the square root of the weight average molecular weight and become independent of molecular weight at high molecular weights. When a polymer is oriented by stretching or by cold drawing the anisotropy of structure is reflected in a corresponding anisotropy in properties. Polymers show an increase in conductivity parallel to stretching with a decrease normal to the stretch direction [52]. The high degree of molecular order for crystalline TPs means their values tend to be twice those of the amorphous types [30].

Plastics have been readily accepted as materials for cooking utensils and automobile steering wheels. Due to their low thermal conductivities, in recent years, cellular plastics, which have the lowest thermal conductivity of all materials, have gained popularity in the field of thermal insulation. The outstanding thermal conductivity of cellular plastics is largely due to the entrapped gases and not to the polymeric material which serves merely as an enclosure for entrapment of gases. As the density of the cellular plastic decreases, the conductivity also decrease up to a minimum value and rises again due to increased convection effects caused by a higher proportion of open cells. The quantity of heat flow depends upon the thermal conductivity of the material and upon the distance the heat must flow. This relationship is expressed as:

$$Q \sim k/x$$

where, Q is the quantity of heat flow; k is the thermal conductivity constant of the material; x is the distance the heat must flow. Closed-cell structures provide the lowest thermal conductivity owing to the reduced convection of gas in the cells [48].

Thermal conductivity is also related to the specific heat capacity (C_p).This relationship expressed as:

$$\alpha = k/ C_p.\rho$$

where α is the thermal diffusivity, k is the thermal conductivity, C_p is the heat capacity and ρ is the density [52].

The thermal conductivity of cellular plastics and elastomers is conveniently defined by the k factor, which is defined by Fourier's Equation for conduction through homogenous materials. The k value is variable and dependent on the mean temperature, the temperature gradient across the sample, and the thickness. These factors are specified when reporting conductivity values. McIntire and Kennedy separated the total thermal conductivity, k, into component parts, since the different modes of heat transfer are simpler to treat individually. For example,

$$k = k_s + k_g + k_r + k_c$$

where k_s, k_g, k_r, and k_c are the contributions due to conduction through solid, conduction through gas, radiation, and convection in gas.

The change in k factor or value with a decrease in the mean temperature is attributed primarily to the decrease in k_r, which is a function of polymer composition, cell size, and configuration, and in kg, which is a function of the nature of the blowing agent [53].

In general, thermal conductivity is low for plastics and their structures do not alter their values significantly. To increase it, the usual approach is to add metallic fillers, glass fibers, or electrically insulating fillers such as alumina. Thermal conductivity can be decreased by foaming [30].

2.8.3.1.1 Factors Affecting Thermal Conductivity of Polymeric Foams

The structural variables that influence thermal conductivity can be summarized as follows:

1. Density

As density increases, k_r (contribution due to radiation) decreases; k_c is unaffected if cell size remains below 4 mm; k_s increases as the volume fraction of polymer increases; k_g decreases. The overall change in k is usually a decrease with increasing density to a minimum a 0,032 gr/cm^3 and then an increase with increasing density of the foam above 0,032 gr/cm^3 [53].

2. Cell Size

As cell size increases (at constant density), k_r increases because of fewer cells and reflecting films. Below 4 mm there is no effect on k_c, which rises abruptly above 4 mm. Both k_s and k_g remain constant and are unaffected by cell size [53].

3. Polymer Composition

With resin that is more opaque to infrared, k_r decreases, k_s depends on the polymer structure. Both k_c and k_g are unaffected by polymer composition [53].

4. Gas Phase

k_g will change according to the structure of the gas; k_r, k_c, and k_s are unaffected [53].

2.8.3.2 Thermal Conductivity Measurements by the Guarded Hot Plate Method (ASTM C 177, ISO 8302)

The primary technique for measuring thermal conductivity of insulating materials is the Guarded Hot Plate Method (ASTM C 177, ISO 8302). The equipment used for this test is fairly complex and expensive. A schematic assembly of the guarded hot plate is shown in the Figure 2.23. The guarded heaters are used to prevent the heat flow in all directions toward the specimen. The test is carried out by placing the specimen between the main heater and the cooling plate (heat sink). The time required to stabilize the input and output temperatures is determined. Thermal conductivity is calculated according to Fourier's Law of Conduction as follows:

$$k = Q\,t\ /\,A\,(T_1 - T_2)$$

where, k is thermal conductance ($W/m^2.K$); Q time rate of one-dimensional heat flow through the metering area of the test apparatus (W); t is the thickness of specimen (m); A is specimen area normal to heat flux direction (m^2); T_1 is the temperature of hot surface (ºC); T_2 is the temperature of cold surface (ºC) [48].

The equation for calculation given above depends on Fourier's Law of Conduction which is an empirical law based on observation. It states that the rate of heat flow, dQ/dt, through a homogeneous solid is directly proportional to the area, A, of the section at right angles to the direction of heat flow, and to the temperature difference along the path of heat flow, i.e dT/dx. The proportionality ratio, λ, is called thermal conductivity constant of the material. A schematic representation of Fourier's Law is given in Figure 2.24 [54].

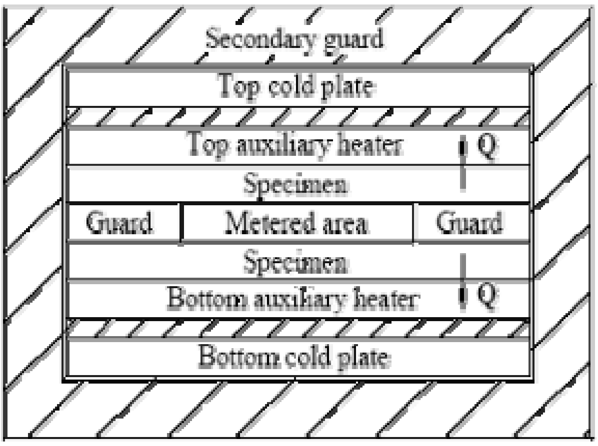


Figure 2.23 A schematic assembly of the guarded hot plate [48].

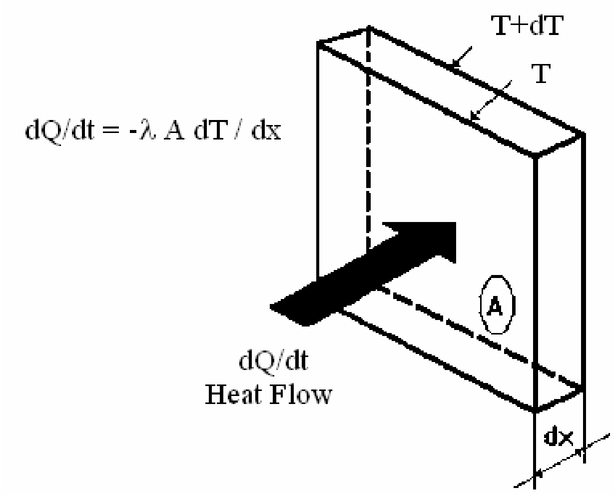


Figure 2.24 A schematic representation of Fourier's Law [54]

2.8.4 Morphological Analysis

2.8.4.1 Scanning Electron Microscopy (SEM)

SEM is particularly well suited for examining the top topography of polymer surfaces because of the large depth of field that is possible. SEM is a microscope that uses electrons instead of light to form an image. At comparable magnifications, the depth of field capacity is approximately 300 times greater than that of a conventional optical microscope. The resolution of SEM is approximately 3 nm, which is two orders of magnitude greater than the optical microscope. But the surface can be monitored as black and white images which can be fitted to x-ray instrument and elemental analysis can be made. The images can be used to make accurate conclusion about the morphology of the polymer systems [55].

In scanning electron microscopy, a fine beam of electrons is scanned across the surface of an opaque specimen to which a light conducting film (gold, platinum, silver) has been applied by high vacuum evaporation. Polymer samples can be mounted on metal stubs for SEM examination by using conductive cement. This can simply be clear nail varnish containing graphite powder. Non conductive polymer samples must be super-coated with gold to reduce the incidence of charging, which is due to high negative charges accumulating on the sample surface; these cause bright spots on the image [55].

A schematic diagram of a SEM instrument is given in Figure 2.25. The beam produced by the electron gun is condensed and demagnified by the electromagnetic lenses to produce a ‘probe’ which is scanned over the surface of the sample. Electrons emitted from the specimen surface are collected and amplified to form a video signal for a cathode-ray tube display. Typical resolutions of 10 nm may be obtained, with a depth of focus of several millimetres. It is this combination of high resolution with a large depth of focus that makes SEM well suited for examining fracture surfaces [56].

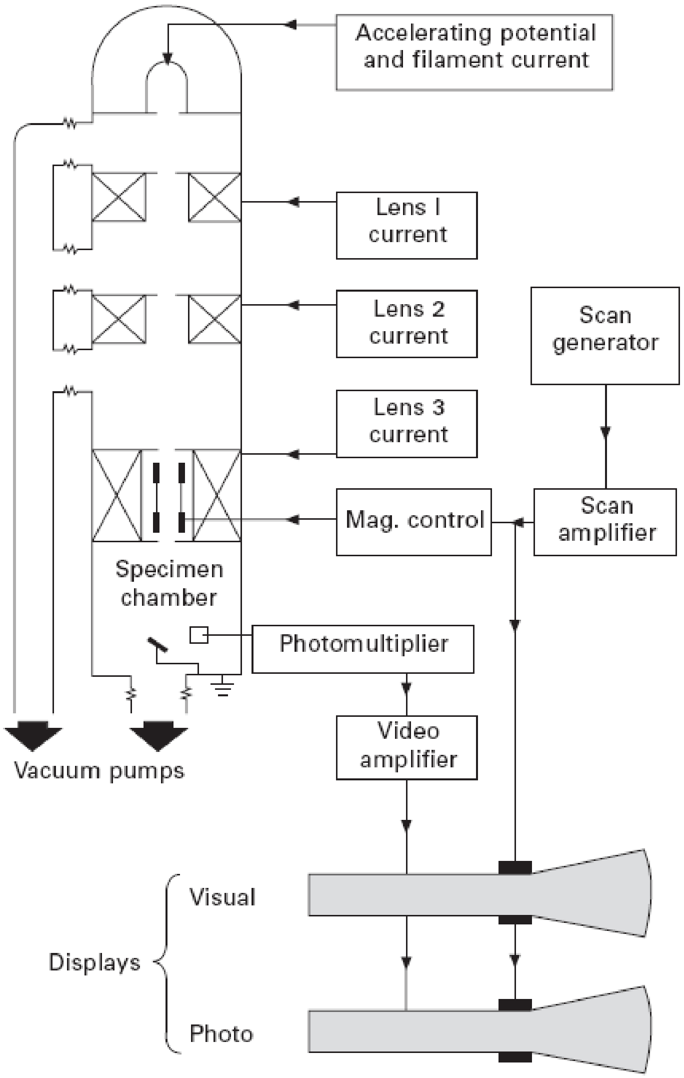


Figure 2.25 Schematic diagram of a scanning electron microscope [56].

2.9 Previous Studies

Xiaohu Lu et.al. [57] studied fundamental properties, morphology, rheology and ageing of polymer modified bitumen prepared by blending bitumen with different thermoplastic polymers (SBS, SEBS, EVA, EBA). It was concluded that morphology and the rheological properties of the modified binders were influenced by characteristics and content of the polymer and nature of the bitumen.

A. Perez-Lepe et.al. [58] investigated the effects of processing variables exert on the rheological properties of polymer-modified bitumen. They used two penetration grade bitumen, 60/70 and 50/120, as base binder. HDPE, LDPE, EPDM were used as polymer. They concluded that a rotor stator mixer device enhanced the rheological properties of binders prepared with HDPE, LDPE, EPDM and their blends as compared to a stirred tank device.

Xiaohu Lu et. al. [59] studied the rheological properties of SBS copolymer modified bitumen. The modified binders were prepared using a laboratory mixer. They studied rheological properties of the modified binders by using dynamic mechanical analysis. It was found that the addition of SBS polymer increased the binder elasticity at high temperatures and improved the binder flexibility at low temperatures.

Ulf Isacson et. al. [60] used two fillers; hydrated lime and calcium carbonate. The effect of fillers on the isothermal low temperature hardening was evaluated with the aid of physical hardening index. Burger model is used in order to understand the viscoelastic nature of the bitumen and bitumen-filler mixtures.

Pedro Partal et. al. [61] studied the modification of petroleum bitumen with four different types of waste polymers (EVA, EVA/LDPE blend, crumb tire rubber and ABS). Optical microscopy, modulated calorimeter and a set of different rheological tests were developed in order to characterize the modified bitumen. It was concluded that bitumen had significant increase in the elastic modulus and viscosity.

Gordon D. Airey et. al. [62] investigated the morphological, thermal and fundamental rheological characteristics of EVA modified bitumens. The morphologies, thermal properties and rheological characteristics of the EVA modified bitumens have been analyzed by using fluorescent microscopy, differential scanning calorimeter and dynamic mechanical analysis. EVA polymer modification increases binder stiffness and elasticity at high service temperature and low loading frequencies with the degree of modification being a function of bitumen source, bitumen-polymer compatibility and polymer concentration.

A.H. Fawcett et.al. [63] prepared blends of a 100 penetration grade bitumen with four different PE having up to 29% of polymer by weight by using a Z-blade mixer at more than 160 ºC. The blends were studied by fluorescence optical microscopy, differential scanning calorimeter and dynamic mechanical thermal analysis. Optical measurements indicated the presence of bitumen rich and polymer rich phases. It is concluded that the presence of bitumen lowered the melting point of the crystallites and extent of crystallinity was reduced.

Ali Ekber Yousefi [64] studied the effects of the structural parameters of PE on its dispersion in bitumen and the performance of the resulting polymer modified bitumen was studied. It is concluded that the performance of bitumen at high temperatures increased as the MFI decreased. At low temperature the performance of bitumen decreased as the MFI of PE decreased.

Craus et al. [65] investigated factors affecting selective sorption in the bitumen-filler interface and the difference in the capacity of various fillers for selective sorption of the chemical groups combining the bitumen. They evaluated selective sorption quantitatively by using a chromatographic method and investigated that, hydrated lime and limestone were the most effective; basalt was intermediate, while sandstone and mainly glass beads showed almost no capacity for selective sorption. They stated that evaluation of selective sorption capacity of the filler is of great importance because of surface activity properties of filler constitutes influence the mechanical properties of the bitumen-filler system and the behavior of the mixture. For this reason, they studied the behavior of sand asphalt mixtures with different types of filler. They concluded that results were in agreement with the behavior of the different fillers under selective sorption.

Little et al. [66] evaluated hydrated lime as filler in bitumen and compared to similarly sized filler comprised of calcium carbonate, limestone. They made several rheological tests. According to this study, it was seen that hydrated lime as filler significantly impacts the rate and level of microcrack-induced damage, microdamage healing and plastic and viscoelastic flow in both mastics and mixtures across a wide range of temperatures. They also concluded that, the impact of hydrated lime as a filler is dependent on its interaction with a specific bitumen.

M. Murphy et al. [67] aimed to find a recycled polymer modified binder that would be similar to a proven modified binder (Polyflex 75) or would augment the properties of 100 penetration grade bitumen. In their study, a wide range of recycled polymers was tested including polyethylene, polypropylene, polyether polyurethane, ground rubber and truck tire rubber. The blend with 3 % by mass of low density polyethylene substituted for 1 % by mass of styrene-butadiene-styrene had similar properties to that of Polyflex 75 although it had a lower stiffness. A combination of ethylene vinyl acetate with low density polyethylene showed similar viscosity to that of a 100 penetration bitumen while having an increased softening point.

He Gui-Ping et al. [68] studied evaluation of moisture effects on the strength and permanent deformation of foamed asphalt (FA) mixes incorporating reclaimed asphalt pavement (RAP) materials by applying a 24-h-soaking preconditioning method, based on literature review on moisture susceptibility of hot-mixed asphalt and FA mixes. It was concluded that bitumen grade and RAP content significantly affect indirect tensile strength (ITS) result of FA mixes, and ITS will decrease with an increase of RAP content under both dry and soaked conditions. Bitumen grade and ageing of RAP material significantly affect moisture susceptibility of FA mixes in permanent deformation. Lower-grade bitumen and less aged RAP material help FA mixes to improve their moisture susceptibility in permanent deformation.

KJ Jenkins et al. [69] explored in this study new, more relevant measures and indices for characterizing the foamed bitumen based on the physics of the foam and the composition of the bitumen. Their research has included bitumen from various crude sources with different compositions, as well as a variety of additives. They concluded their study by giving recommendations for the standardization of the foamed bitumen characterization testing with due consideration given to the entire mix.

R.D.Allen et al. [70] made their research to gain knowledge of the behavior of EVA during the injection molding of shoe soles and shoe mid-soles. Their study presents a methodology for determining the expansion characteristics of EVA coupled with results relating to the initial findings for material expansion to enable the design of a method for automatically generating mold cavity geometry. They express that though there is significant experience with the general use of EVA during the injection molding process this knowledge has been gained through years of experience and molds are designed by combination of the producer’s knowledge and trial and error. They concluded that when mixed with a suitable blowing agent, EVA has the remarkable ability to expand between 30 % and 90 % compared to the injection mold size, depending on the amount of blowing agent added. Furthermore, they expressed that EVA does not expand uniformly and currently there is no precise method of predicting the expansion of components with variable thickness.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Bitumen

In this study, as a binder 20/30 penetration grade bitumen was used. It was purchased from TÜPRAS A.Ş. Some selected properties of this bitumen are shown in Table 3.1.

Table 3.1 Properties of 20/30 penetration grade bitumen used in the study.

PROPERTY	ASTM	UNIT	VALUE
Penetration at 25 °C, 100 g, 5 sec	D 5	x 0.1 mm	20/30
Softening Point (ring and ball method)	D 36	^{o}C	57-67
Solubility (dicholoroethane)	D 2042	wt %	98
Ductility at 25 ^{0}C, 5 cm/min	D113	cm	15

3.1.2 Polymer

In this study, ethylene-vinyl acetate (EVA) random copolymer is used as a polymer. EVA, which has a trade name of Alcudia® PA-461, was supplied by Alcudia. Typical properties of Alcudia® PA-461 are given in Table 3.2.

Table 3.2 Properties of EVA used in this study

PROPERTY	UNIT	VALUE
Melting point	°C	59 - 64
Density @ 23°C	kg/m^3	956
Vinyl Acetate content	%	33
Melt Flow Rate (190°C,2.16kg)	gr/10 min	45

3.1.3 Filler

In this study, calcium carbonate ($CaCO_3$) and magnesium stearate ($C_{36}H_{70}MgO_4$) are used as filler.

3.1.3.1 Calcium Carbonate ($CaCO_3$)

$CaCO_3$, used as filler in this study, has a trade name of OMYACARB 3 EXTRA-GZ. It was supplied by OMYA Madencilik A.Ş. Chemical composition and physical properties of $CaCO_3$ used in this work are given in Tables 3.3 and 3.4, respectively.

Table 3.3 Chemical composition of $CaCO_3$

Material	Composition (%)
$CaCO_3$	98.5
$MgCO_3$	1.5
Fe_2O_3	0.05

Table 3.4 Physical properties of $CaCO_3$

Property	**Value**
Average particle size	5 µm
pH value	9.5
Density	2.7 gr/cm^3

3.1.3.2 Magnesium Stearate ($C_{36}H_{70}MgO_4$)

Magnenisum stearate ($C_{36}H_{70}MgO_4$), which was used as filler in study, has a trade name of Synpro® supplied by Ferro Coop. Typical properties of magnesium stearate ($C_{36}H_{70}MgO_4$) used in this work are given in Tables 3.5.

Table 3.5 Typical properties of magnesium stearate ($C_{36}H_{70}MgO_4$)

Property	**Value**
% Ash	8.6
% Free Fatty Acid	0.5
% Moisture	3.0
Melting Point	157°C
Apparent Density	0.3 gr/cm^3

3.1.4 Chemical Blowing Agent

3.1.4.1 Celogen-OT ® [4,4’-Oxybis(benzenesulphonohydrazide)]

4,4’-Oxybis(benzenesulphonohydrazide), which was used as a blowing agent in this study, has a trade name of Celogen-OT ® obtained from Chemtura (Crompton) Corp. through Sigma-Aldrich US. Typical properties of Celogen-OT ® used in this work are given in Table 3.6.

Table 3.6 Typical properties of Celogen-OT ®

Property	**Value**
Decomposition point	160 °C
Gas yield	125 cc/gr
Specific gravity	1.55
Bulk density	496 kg/m^3
Application temperature	149 – 177 °C

3.1.5 Releasing Agent

3.1.5.1 Soft Soap

Soft soap, which is used as a mold releasing agent in this study, was produced by Nazar Kimya Sabun Ltd. Şti.

3.1.6 Cross-linking Agent

3.1.6.1 Luperox 101G45 ® [2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane]

2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane, which is used as cross-linking agent in this study, has trade name of Luperox 101G45 ® was supplied by Arkema Inc., US through Atofina I.S.Trading, Korea. Typical properties of Luperox 101G45 ® used in this work are given in Tables 3.7.

Table 3.7 Typical properties of Luperox 101G45 ®

Property	**Value**
Composition	active oxygen content, >10 wt. %
Half-life ($t_{½}$)	10 hr(108 °C)
Refractive index	*n*20/D 1.423
Boiling point	55-57 °C/7 mmHg
Melting point	≥80 °C (SADT)
Bulk density	0.877 gr/mL at 25 °C

3.2 Experimental Parameters

In this study, as a binder bitumen (20/30 penetration grade) was used. As polymer ethylene-vinyl acetate (EVA) block copolymer, as filler calcium carbonate ($CaCO_3$) and magnesium stearate ($C_{36}H_{70}MgO_4$); as blowing agent Celogen-OT ® (4,4'-Oxybis(benzenesulphonohydrazide)); as cross-linking agent Luperox 101G45 ® (2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane), and as mold releasing agent soft soap were used to prepare 24 different blend compositions. Volume percent compositions of bituminous blends prepared in this study are given in Table 3.8.

Table 3.8 Compositions of foamed polymer based bituminous composites (vol. %)

Number of Samples	**Composition of Components Blended (vol. %)**					
	CaCO$_3$	**Celogen-OT ®**	**Magnesium Stearate**	**EVA**	**Bitumen (20/30)**	**Luperox 101G45 ®**
1	10	4	1	42.5	42.5	-
2	10	4	1	31.9	53.1	-
3	10	4	1	21.3	63.8	-
4	10	4	1	10.6	74.4	-
5	15	0	1	42.0	42.0	-
6	15	0	1	31.5	52.5	-
7	15	0	1	21.0	63.0	-
8	15	0	1	10.5	73.5	-
9	15	2	1	41.0	41.0	-
10	15	2	1	30.8	51.3	-
11	15	2	1	20.5	61.5	-
12	15	2	1	10.3	71.8	-
13	15	4	1	40.0	40.0	-
14	15	4	1	30.0	50.0	-
15	15	4	1	20.0	60.0	-
16	15	4	1	10.0	70.0	-
17	15	4	1	39.5	39.5	1
18	15	4	1	29.6	49.4	1
19	15	4	1	19.8	59.3	1
20	15	4	1	9.9	69.1	1
21	20	4	1	37.5	37.5	-
22	20	4	1	28.1	46.9	-
23	20	4	1	18.8	56.3	-
24	20	4	1	9.4	65.6	-

3.2.1 Chemical Blowing Agent Ratio

In this study in order to see the effect of chemical blowing agent on morphological, thermal, and mechanical properties of foamed polymer based bituminous composites, at three different volume percentages of CBA (chemical blowing agent) twelve specimens were prepared. They are composing 0 %, 2 % and 4 % volume percentages of CBA (Cellogen-OT ®) with 15 % volume percentage of calcium carbonate (CaCO$_3$)

and 50 %, 37.5 %, 25 % and 12.5 % volume percentages of EVA were prepared and tested. The compositions of specimens are given in Table 3.9.

Table 3.9 Compositions with regard to chemical blowing agent ratio.

Number of Samples	**Composition of Components Blended (vol. %)**					
	$CaCO_3$	**Celogen-OT ®**	**Magnesium Stearate**	**EVA**	**Bitumen (20/30)**	**Luperox 101G45 ®**
5	15	0	1	42.0	42.0	-
6	15	0	1	31.5	52.5	-
7	15	0	1	21.0	63.0	-
8	15	0	1	10.5	73.5	-
9	15	2	1	41.0	41.0	-
10	15	2	1	30.8	51.3	-
11	15	2	1	20.5	61.5	-
12	15	2	1	10.3	71.8	-
13	15	4	1	40.0	40.0	-
14	15	4	1	30.0	50.0	-
15	15	4	1	20.0	60.0	-
16	15	4	1	10.0	70.0	-

3.2.2 Calcium Carbonate ($CaCO_3$) Ratio

In order to find out the effect of filler concentration on morphological, thermal, and mechanical properties of foamed polymer based bituminous composites, at three different volume percentages of calcium carbonate ($CaCO_3$) twelve specimens were prepared. They comprise of 4 % volume percentage of CBA (Cellogen-OT ®) with 50 %, 37.5 %, 25 % and 12.5 % volume percentages of EVA were prepared and tested. The compositions of specimens are given in Table 3.10.

Table 3.10 Compositions with regard to calcium carbonate ratio.

Number of Samples	Composition of Components Blended (vol.%)					
	$CaCO_3$	Celogen-OT ®	Magnesium Stearate	EVA	Bitumen (20/30)	Luperox 101G45 ®
1	10	4	1	42.5	42.5	-
2	10	4	1	31.9	53.1	-
3	10	4	1	21.3	63.8	-
4	10	4	1	10.6	74.4	-
13	15	4	1	40.0	40.0	-
14	15	4	1	30.0	50.0	-
15	15	4	1	20.0	60.0	-
16	15	4	1	10.0	70.0	-
21	20	4	1	37.5	37.5	-
22	20	4	1	28.1	46.9	-
23	20	4	1	18.8	56.3	-
24	20	4	1	9.4	65.6	-

3.2.3 Foamed vs. Unfoamed

In order to find out the differences between foamed and unfoamed polymer based bituminous composites at morphological, thermal and mechanical properties, eight different specimens comprising of 0 % and 4 % CBA (chemical blowing agent) in addition to 15 % volume percentages of calcium carbonate ($CaCO_3$), 1 % magnesium stearate, 50 %, 37.5 %, 25 % and 12.5 % volume percentages of EVA were prepared and tested. The compositions of specimens are given in Table 3.11.

Table 3.11 Compositions with regard to foamed and unfoamed specimens.

Number of Samples	Composition of Components Blended (vol. %)					
	$CaCO_3$	Celogen-OT ®	Magnesium Stearate	EVA	Bitumen (20/30)	Luperox 101G45 ®
5	15	0	1	42.0	42.0	-
6	15	0	1	31.5	52.5	-
7	15	0	1	21.0	63.0	-
8	15	0	1	10.5	73.5	-
13	15	4	1	40.0	40.0	-
14	15	4	1	30.0	50.0	-
15	15	4	1	20.0	60.0	-
16	15	4	1	10.0	70.0	-

3.2.4 Cross-linked vs. Noncross-linked

In order to find out the effects of cross-linking agent (Luperox 101G45 ®) on morphological, thermal and mechanical properties of foamed polymer based bituminous composites, four different specimens comprising 4 % CBA (chemical blowing agent) in addition to 15 % volume percentages of calcium carbonate ($CaCO_3$), 1 % magnesium stearate, 50 %, 37.5 %, 25 % and 12.5 % volume percentages of EVA and four different specimens comprising 1 % cross-linking agent in addition to 4 % CBA (chemical blowing agent), 15 % volume percentages of calcium carbonate ($CaCO_3$), 1 % magnesium stearate, 50 %, 37.5 %, 25 % and 12.5 % volume percentages of EVA were prepared and tested.. The compositions of specimens are given in Table 3.12.

Table 3.12 Compositions with regard to cross-linked and noncross-linked specimens.

Number of Samples	**Composition of Components Blended (vol. %)**					
	$CaCO_3$	**Celogen-OT ®**	**Magnesium Stearate**	**EVA**	**Bitumen (20/30)**	**Luperox 101G45 ®**
13	15	4	1	40.0	40.0	0
14	15	4	1	30.0	50.0	0
15	15	4	1	20.0	60.0	0
16	15	4	1	10.0	70.0	0
17	15	4	1	39.5	39.5	1
18	15	4	1	29.6	49.4	1
19	15	4	1	19.8	59.3	1
20	15	4	1	9.9	69.1	1

3.3 Sample Preparation

Preparation of polymer based bituminous composite samples composes of two main steps which are mixing and molding. In molding process there are two substeps which are preheating of blends and foaming of composites.

3.3.1 Mixing (Blending)

By using a counter-rotating internal mixer which is Brabender Plastic Coder PLV 151, bitumen, calcium carbonate ($CaCO_3$), polymer (EVA), magnesium stearate, chemical blowing agent (4,4’-Oxybis(benzenesulphonohydrazide)) and cross-linking agent (luperox) were mixed in order to prepare polymer based bituminous blends. As an order of mixing, first bitumen, next polymer and then the rest were added. They were mixed for fifteen minutes at 120 ºC with constant screw speed of 60 rpm.

3.3.2 Molding

3.3.2.1 Hand Lay-up Self-expanding Batch Molding (HLUSEBM)

In this study, Hand Lay-up Self-expanding Batch Molding (HLUSEBM) Technique which is a new method was firstly applied by our group. This process was for foaming process a special unique mold is designed and manufactured (See Figure 3.1).

Figure 3.1 The schematic view of Hand Lay-up Self-expanding Mold.

It works like a piston movement principle. This molding process is called Hand Lay-up Self-expanding Batch Molding. The mold used in this process composes of three main parts of which are all made of stainless steel. The technical drawing HLUSEB Mold and its details are shown on Figure A.1 in appendix. They are piston cover, piston bearing cylindrical tube and flat bottom cover. The cylindrical tube which has 10 mm wall-thickness, 60 mm depth and about 130 mm inner diameter is the piston bearing through which piston cover moves up and down. The piston cover is a stainless steel having 129 mm diameter and 10 mm thickness. It has a M10 screw valve which is used to take the air while closing the cover onto the specimen in piston bearing cylindrical tube. There are two flanges one of which is located top around the tube and the other one is located at the bottom around the tube to which the flat bottom cover is screwed by eight M5 screws. Between the flat bottom cover and the bottom flange surface, there is a rubber gasket in order to prevent any air and material leakage from the mold. In the top flange three stainless steel M5 guides are screwed. The piston cover has three cutting edges through which three guides are getting. The integration of three guides and three cutting edges provides the accurate and sensitive movement of piston cover in piston bearing cylindrical tube while polymer based bituminous blends are expanding. There are two nuts on each three guides. The first nuts are called pressurizing nuts and the second nuts over the first ones are called arresting nuts. Pressurizing nuts are used to bear against the pressure occurring during nucleation before foaming occurs. Arresting nuts are used to make the piston cover to be stopped at desired foaming height.

In Hand Lay-up Self-expanding Batch Molding Process there are two substeps. They are preheating of blends and foaming of composites.

3.3.2.1.1 Preheating of Blends

Prior to final shaping of polymer based bituminous composites; blends prepared at internal mixer must be made ready for molding in Hand Lay-up Self-expanding Batch Mold. For all 24 samples, the prior height of unfoamed blends was adjusted as 10 mm. Their weights were evaluated from their theoretical densities for each of them and then the specific amounts of blends were made ready for preheating. Before the blend was located into the mold, inner surfaces of the mold were rubbed with soft soap in order to get rid of tackiness of the blend to the mold surfaces and then blends were embedded into it. The mold was emplaced into the oven which is set to 120 °C. It was kept in the oven for one hour till softening temperature and ready to be spread. Afterwards, the mold was taken out of oven and material was made to be spread with a metal rod which has a flat circular metal surface at its tip.

3.3.2.1.2 Foaming of Composites

After making sure that blend was spread in the mold uniformly, the mold was closed with the piston like cover. Before closure, the lateral surface of the cover was clothed with Teflon® film in order to heal the small space (about 0,5 mm) between the inner wall of the mold and the cover. In addition to this, bottom surface of the cover was rubbed with soft soap in order to get rid of tackiness of the blend. The screw valve was opened while closing the mold and after it was checked not to have any air pocket between the blend and the cover bottom surface, and then the valve was closed. First of all, the pressurizing nuts were closed on the guides over the cover. Then, the arresting nuts were closed 10 mm over the pressurizing nuts. The blowing height was adjusted as 10 mm for all samples. It was adjusted to have the blends expand 100 vol. %, their densities would then be lowered by 50 % which was desired.

The mold was put into the oven which was set to 150 °C below the foaming nucleation temperature. It was kept at 150 °C for 30 minutes and next the pressurizing nuts were opened. Immediately the cover was raised by the expansion till the arresting nuts. Meanwhile the temperature was set to 170 °C at which temperature chemical blowing agent and cross-linking agent decompose. The cross-linking rate of Luperox 101G45 ® (2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane) is approximately 1.5 min/mm thickness [70]. Therefore, the mold was kept at 170 °C for 15 minutes at which cross-linking is fully complete. At the end of this period, the mold was taken out of the oven and it was cooled in icy water bath in order to cease the process.

3.3.2.2 Compression Molding

For the preparation of unfoamed specimens, the blends are molded at compression molding machine was a laboratory scale hot-press machine. Its model was Rucker PHI. Figure 3.2 is the schematic view of hot-press machine used.

Figure 3.2 The schematic view of hot-press machine.

Specimens, prepared as small balls after they were blended, were put into a 10 mm x10 mm thick steel frame-mold which was 100 mm in length and 80 in width. The molding temperature and the molding pressure were 100 °C and 10 bars respectively for each sample. Compression molding was applied for each sample at least 5 times to avoid micro bubbles formation inside materials. After specimens were compressed, they were cooled spontaneously in icy water and waited one day at room temperature to allow relaxations in the materials.

3.4 Characterization

3.4.1 Thermal Analysis

In order to measure the thermal conductivity constant of the composites prepared, a new set up was established according to Guarded Hot Plate Testing Method of ASTM C 177 at the Department of Chemical Engineering, METU (See Figure 3.3).

Figure 3.3 The schematic view of thermal conductivity measurement setup.

At this set up, two identical uniform parts whose dimensions were 40 mm x 40 mm x 15 mm were cropped from molded specimens. As a constant heat source, an apparatus, which was prepared in such a way that RED Tiger® Cr25-Al5 resistance wire, was rolled over a Teflon® plate with dimensions of 40 mm x 40 mm x 2 mm. On each two sides of this plate, two Teflon® plates with dimensions of 40 mm x 40 mm x 2 mm were clinched. The heat source whose resistance was measured as 105 Ω was placed between to cropped specimens. Four J-type thermocouples were stacked on two sides of the two cropped specimens. Two aluminum plates with dimensions of 40 mm x 40 mm x 2 mm were prepared for cooling purpose. They were placed next to the outer sides of the cropped specimens. For each specimen two thermocouples were stacked on inside and outside of the specimen. A thermocouple was stacked on one side of the heating plate and two thermocouples were stacked on inside of one of the cooler plates and outside of one of the cooler plates arbitrarily. The schematic representation of the thermal conductivity measurement setup is given in Figure 3.4.

The thermal analysis experiments were conducted at constant room temperature which was 20 °C. By the principles of ASTM standard, heat given to the system must be constant. Thus, a digital SMPS power supply made by Sunyo Electronic which was used in order to lower the voltage and reach the wanted temperature at which structures of specimens would not be changed. Desired upper limit temperature degree was 30-35 °C so that the output current given to the system was changed to DC. Seven thermocouples were connected to a digital data logger in order to read the temperatures properly. At every five minutes, temperature degrees from seven channels were gathered by Elimko Data Logger Ver.5.1 software, produced by Elimko Ltd. Şti, and all data was saved at computer. When temperature differences between two sides of the each cropped specimens were at steady-state, those values were considered as final temperature gradients.

From Fouriers Law of Conduction, “k (or λ)”, thermal conductivity constants of the composites are calculated. In order to validate the measured values, thermal conductivity of Styrafoam® was also measured. The measured thermal conductivity constant of Styrafoam® was divided to its literature value and an extrapolating constant was obtained. By this constant, the formerly measured values of foamed polymer based bituminous composites were proportionated to experimental values.

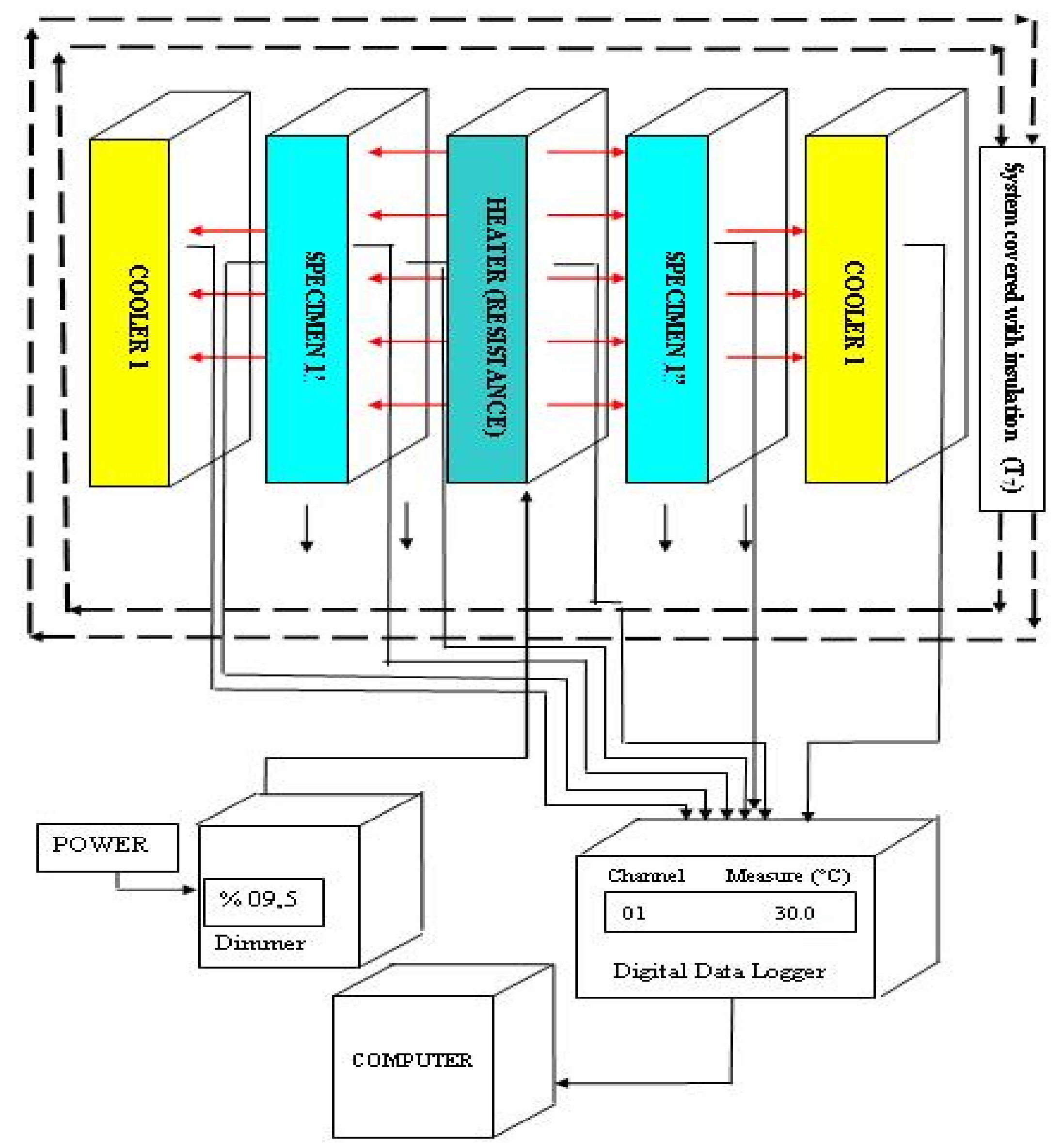


Figure 3.4 The schematic representation of thermal conductivity measurement setup.

3.4.2 Mechanical Analysis

Compression tests were carried out at Shimadzu ® Autograph (See Figure 3.5). Five samples with dimensions 10 mm x 10 mm x 10 mm from each polymer based bituminous composite were cut and they were compressed under constant 10.000 N compressive loading till 50 % of the height of the samples was compressed and maximum force applied were calculated by the software. After they were compressed, each sample was kept under room conditions for 40 minutes in order to see their recovery. Later on that period, the height of each sample was measured by a micrometer and the constant deflection set values of 5 samples from each 24 composites were calculated by using this following formula;

$$C_t = [(t_o - t_f)/t_o] \text{ x } 100$$

where, C_t is the compression set expressed as a percentage of the original thickness; t_o is the original thickness of test specimen, and t_f is the final thickness of test specimen [49].

Figure 3.5 The schematic view of Shimadzu ® Autograph.

3.4.3 Morphological Analysis

From polymer based bituminous composite samples parts with dimensions 10 mm x 10 mm x 10 mm were cut and their inner surfaces were examined by a JEOL JSM-6400 Scanning Electron Microscope. Before SEM photographs were taken, the fractured surfaces were coated with a thin layer of gold in order to obtain a conductive surface. The SEM photographs were taken at x100, x500 and x6000 magnifications.

3.4.4 Density & Porosity Measurements

3.4.4.1 Apparent Overall Density Measurements of Samples

Apparent overall density of foamed polymer based bituminous composites were calculated by dividing the weight of the specimen to its volume calculated by measuring the length, width, and the height of the specimen using a micrometer. This procedure was applied to five test samples with same dimensions cut from each composite specimen and the average value was calculated for each one in order to get accurate result.

3.4.4.2 Porosity Measurements of Samples

In order to determine how much porous the foamed polymer based bituminous composites were, the density of a foamed composite without the air in it was assumed to be equal to the density of unfoamed specimen. Densities of unfoamed specimens were measured by using electronic densitometer MD-300S, Alfa Mirage Co., Ltd. Porosities of foamed polymer based bituminous composites were calculated by the formula given below;

$$\text{Porosity \%} = [(\text{Unfoamed Specimen Density} - \text{Apparent Overall Density}) / \text{Apparent Overall Density}] \times 100$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Morphological Analysis

4.1.1 Scanning Electron Microscopy (SEM)

SEM analysis was performed in order to observe the effects of chemical blowing agent ratio and its existence, calcium carbonate ratio, and existence of cross-linking agent on the morphology of prepared polymer based bituminous foamed composites. SEM images of these samples are presented with magnifications of x100 and x500 to provide a more detailed observation.

Figure 4.1, Figure 4.2 and Figure 4.3 show the surfaces of foamed polymer based bituminous composites containing 10 %, 15 % and 20 % $CaCO_3$ with 50 % and 25 % polymer content at magnifications x100 and x500, respectively. In all specimens regarding with different $CaCO_3$ content, it is seen that at low polymer percentages, the composites have better foam structures. The best cell distribution with uniform cells is seen at foamed polymer based bituminous composites (FPBBCs) containing 15 % $CaCO_3$.

Figure 4.4 and Figure 4.5 shows the surfaces of FPBBCs containing 0 % and 1 % cross-linking agent with 50 % and 37.5 % polymer content at magnifications x100 and x500, respectively. At specimens which are cross-linked, it is seen obviously seen that there is a cellular structure with uniform cell size. On the other hand, at specimens which do not contain cross-linking agent, at high polymer content the foaming structure is not stable and cells are not uniform; at moderate polymer content the foaming structure is more apparent and the specimen has more uniform cells. However, from these two figures it can be noted that when cross-linking agent is used in a foaming mechanism, the foam has smaller cells with thicker cell walls.

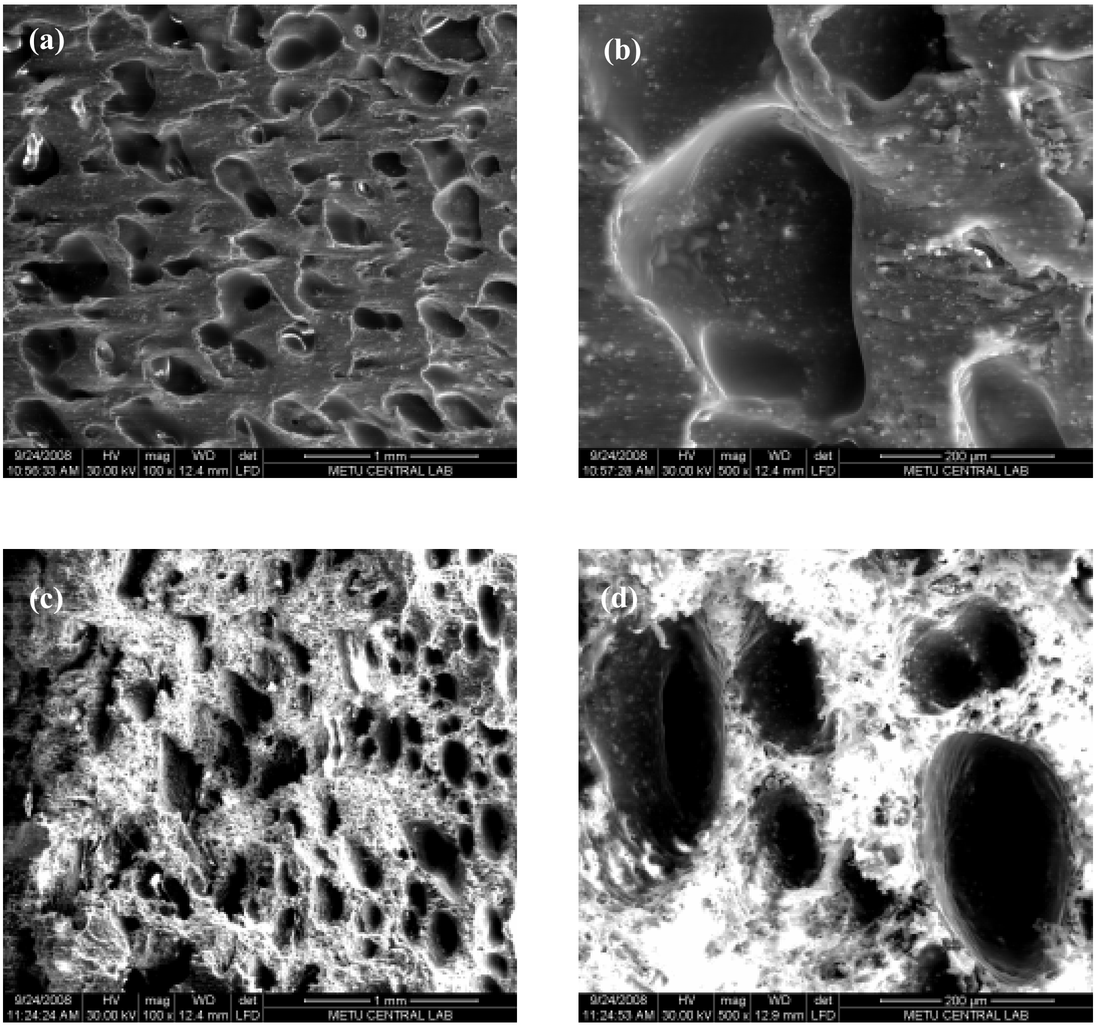


Figure 4.1 SEM micrographs of foamed polymer based bituminous composites containing 10 % $CaCO_3$, 4 % CBA and 0 % cross-linking agent with different EVA content (completing to 100 % with the bitumen content) at two different magnifications (a) 50 % EVA at x100, (b) 50 % EVA at x500, (c) 25 % EVA at x100, (d) 25 % EVA at x500.

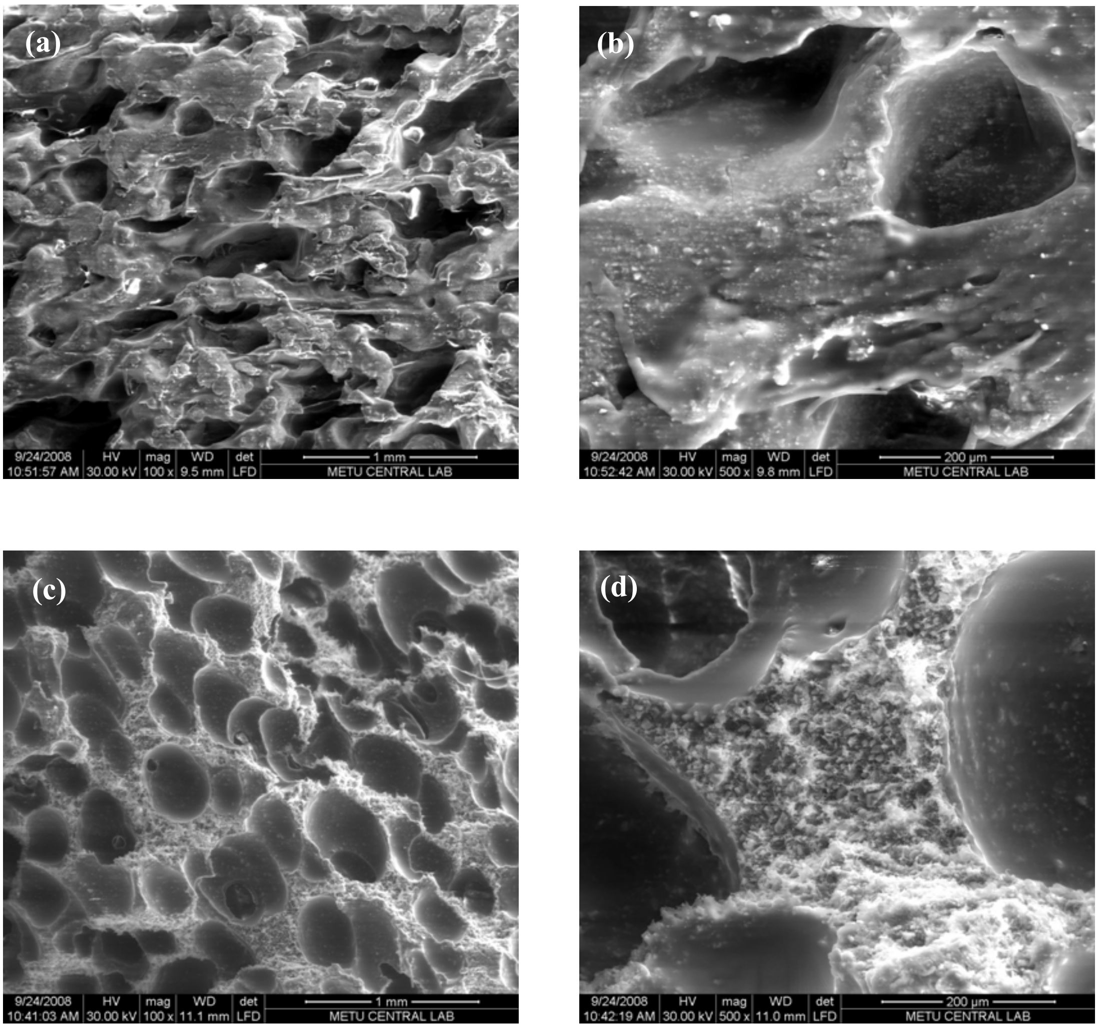


Figure 4.2 SEM micrographs of foamed polymer based bituminous composites containing 15 % $CaCO_3$, 4 % CBA and 0 % cross-linking agent with different EVA content (completing to 100 % with the bitumen content) at two different magnifications (a) 50 % EVA at x100, (b) 50 % EVA at x500, (c) 25 % EVA at x100, (d) 25% EVA at x500.

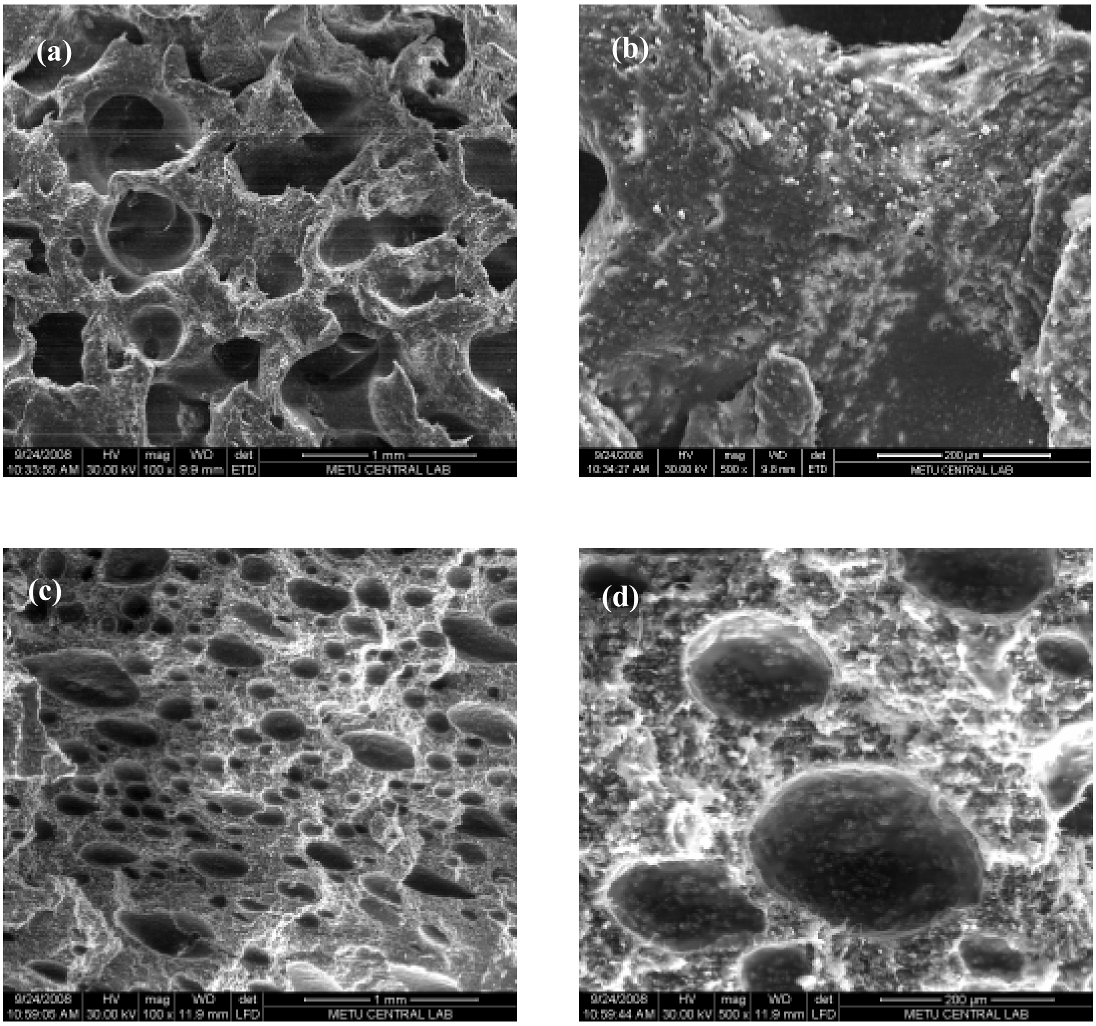


Figure 4.3 SEM micrographs of foamed polymer based bituminous composites containing 20 % $CaCO_3$, 4 % CBA and 0 % cross-linking agent with different EVA content (completing to 100 % with the bitumen content) at two different magnifications (a) 50 % EVA at x100, (b) 50 % EVA at x500, (c) 25 % EVA at x100, (d) 25% EVA at x500.

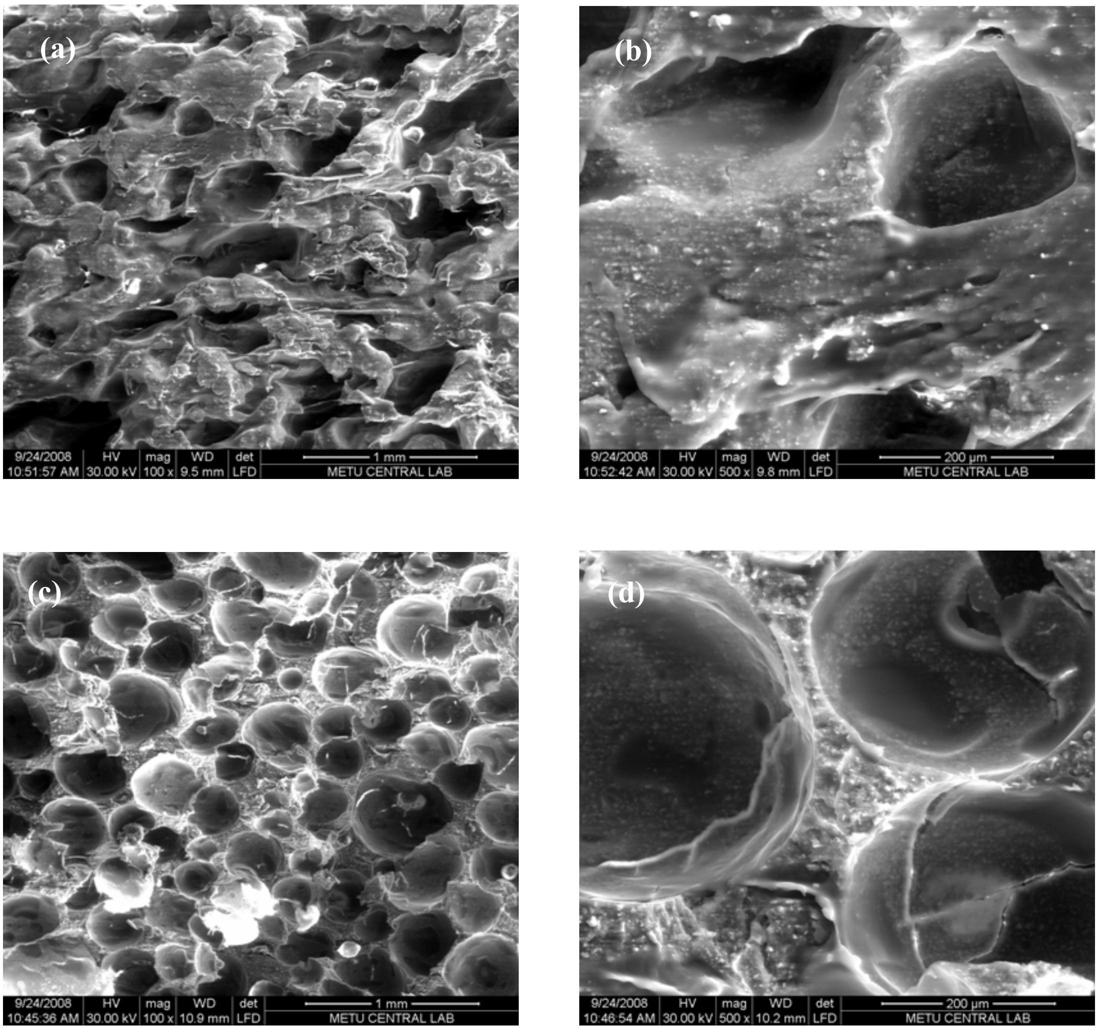


Figure 4.4 SEM micrographs of foamed polymer based bituminous composites containing 15 % $CaCO_3$, 4 % CBA and 0 % cross-linking agent with different EVA content (completing to 100 % with the bitumen content) at two different magnifications (a) 50 % EVA at x100, (b) 50 % EVA at x500, (c) 37.5 % EVA at x100, (d) 37.5 % EVA at x500.

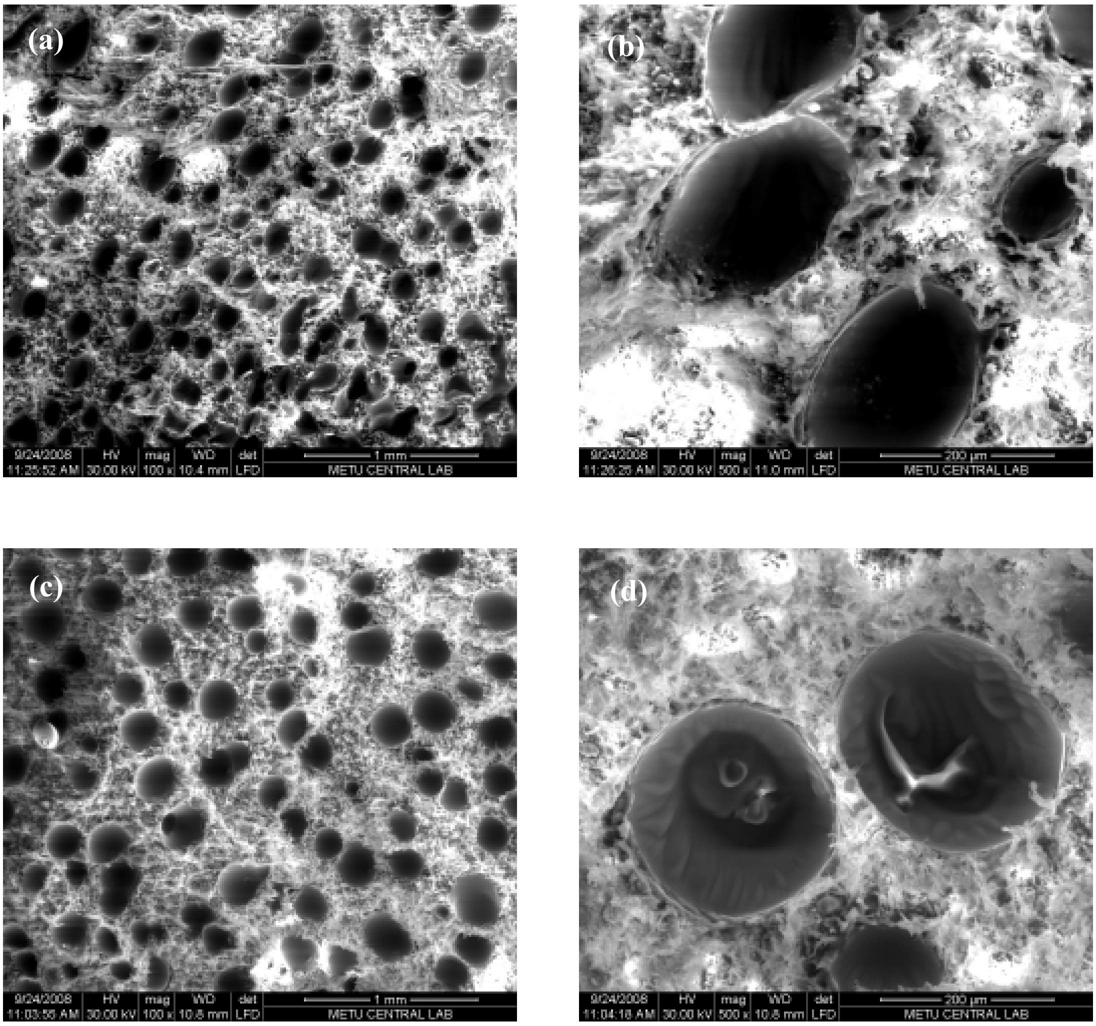


Figure 4.5 SEM micrographs of foamed polymer based bituminous composites containing 15 % $CaCO_3$, 4 % CBA and 1 % cross-linking agent with different EVA content (completing to 100 % with the bitumen content) at two different magnifications (a) 50 % EVA at x100, (b) 50 % EVA at x500, (c) 37.5 % EVA at x100, (d) 37.5 % EVA at x500.

Figure 4.6, Figure 4.7 and Figure 4.8 show the surfaces of polymer based bituminous composites and foamed polymer based bituminous composites containing 0 %, 2 % and 4 % CBA with 50 % and 37.5 % polymer content at magnifications x100 and x500, respectively. In Figure 4.6 no significant morphological difference is observed between specimens 50 % and 37.5 % EVA.

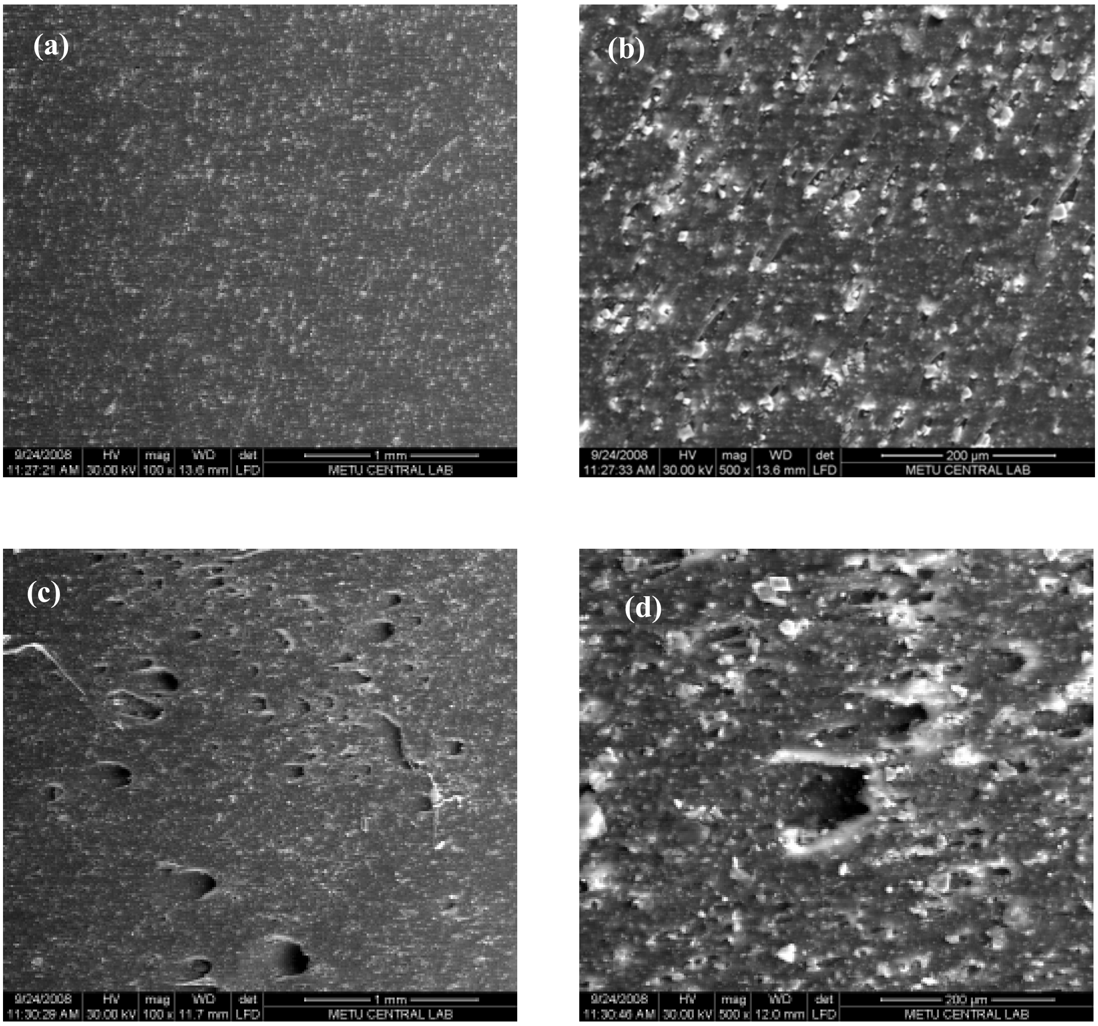


Figure 4.6 SEM micrographs of foamed polymer based bituminous composites containing 15 % $CaCO_3$, 0 % CBA and 0 % cross-linking agent with different EVA content (completing to 100 % with the bitumen content) at two different magnifications (a) 50 % EVA at x100, (b) 50 % EVA at x500, (c) 37,.5 % EVA at x100, (d) 37.5 % EVA at x500.

In Figure 4.7, it can be seen that as the polymer content is lowered the foaming structure is seen more apparent and the FPBBC has more closed-cells but with different sizes. This may be due to the homogeneity of mixing of CBA with other ingredients.

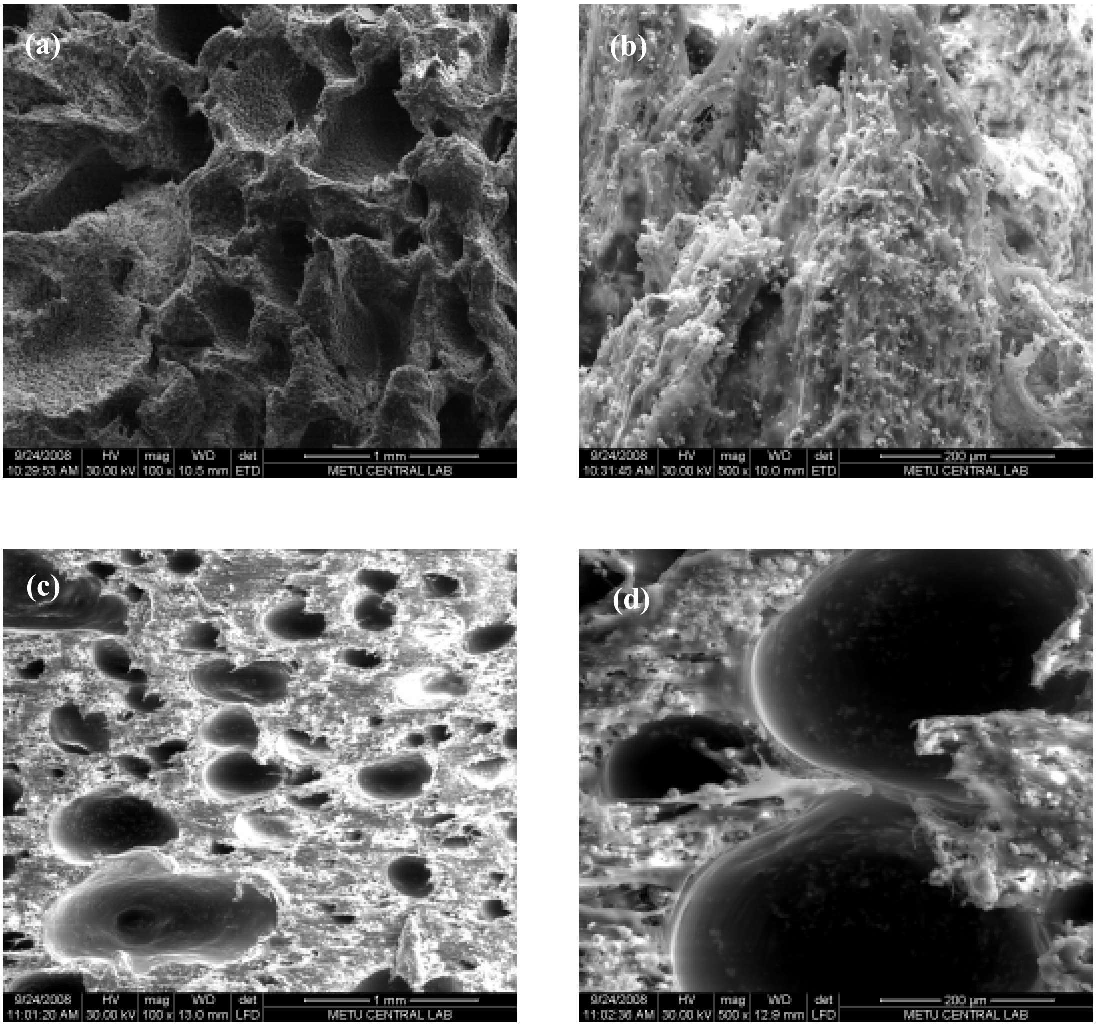


Figure 4.7 SEM micrographs of foamed polymer based bituminous composites containing 15 % $CaCO_3$, 2 % CBA and 0 % cross-linking agent with different EVA content (completing to 100 % with the bitumen content) at two different magnifications (a) 50 % EVA at x100, (b) 50 % EVA at x500, (c) 37.5 % EVA at x100, (d) 37.5 % EVA at x500.

In Figure 4.8, it is seen that as the polymer content is lowered, the FPBBC has more uniform cells with closed-cell structure.

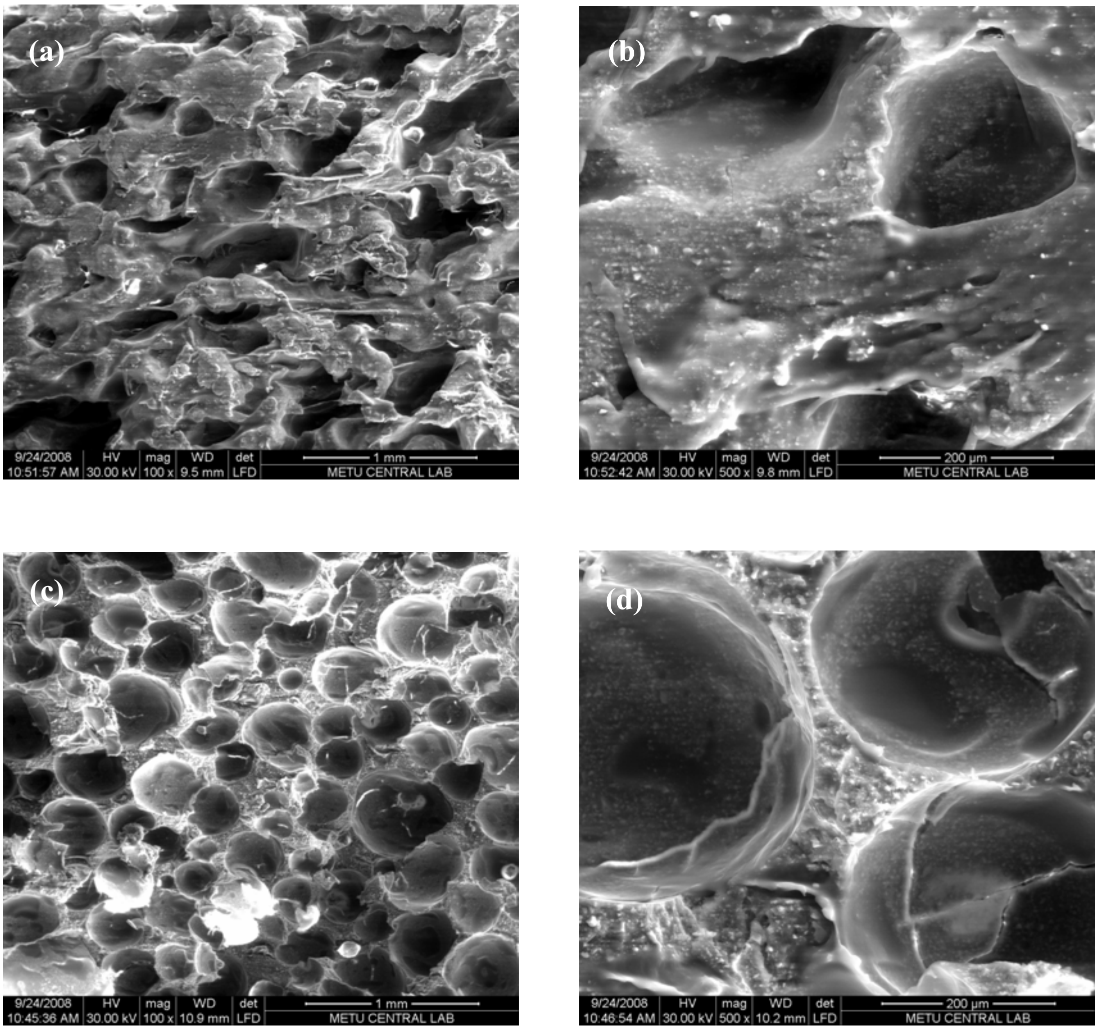


Figure 4.8 SEM micrographs of foamed polymer based bituminous composites containing 15 % $CaCO_3$, 4 % CBA and 0 % cross-linking agent with different EVA content (completing to 100 % with the bitumen content) at two different magnifications (a) 50 % EVA at x100, (b) 50 % EVA at x500, (c) 37.5 % EVA at x100, (d) 37.5 % EVA at x500.

On the whole about Figure 4.6, Figure 4.7 and Figure 4.8, it can be predicted that FPBBCs containing 4 % CBA has more closed-cells and they have more uniform structures.

4.2 Density & Porosity Measurements

The percentage of porosity is a fine element that should be considered in analyzing foamed polymer based bituminous composites. In order to learn how much porous the composites are, their apparent overall core densities were calculated by dividing the weight of the specimen to its volume calculated by measuring the length, width, and the height of the specimen using a micrometer. For each specimen, the arithmetic mean of apparent overall density for 5 test samples with same dimensions cut from each specimen were calculated.

In determining how much porous the foamed polymer based bituminous composites were the density of a foamed composite without air in it, was assumed to be equal to the density of unfoamed specimen. Densities of unfoamed specimens were measured by using electronic densitometer.

The percentage of porosity of a foamed polymer based bituminous composite was calculated by the following formula:

Porosity % = [(Unfoamed Specimen Density - Apparent Overall Core Density)
/ Unfoamed Specimen Density] x 100

Table 4.1 shows the results of density and porosity measurements results of 24 foamed polymer based bituminous composites.

Table 4.1 Unfoamed densities and apparent overall core densities of samples with their percentage of porosity values.

Number of Samples	Unfoamed Specimen Density (gr/cm^3)	Apparent Overall Core Density (gr/cm^3)	Percentage of Porosity (%)
1	1.16	0.99	14.23
2	1.13	0.79	30.09
3	1.14	0.78	31.10
4	1.16	1.09	6.25
5	1.24	1.24	0.00
6	1.14	1.14	0.00
7	1.24	1.24	0.00
8	1.26	1.26	0.00
9	1.27	0.63	50.76
10	1.27	0.76	40.18
11	1.28	0.59	54.30
12	1.29	0.54	58.30
13	1.25	0.57	54.80
14	1.30	0.87	33.15
15	1.22	0.96	21.49
16	1.30	0.74	43.00
17	1.33	1.14	14.68
18	1.25	0.72	42.60
19	1.27	0.67	47.32
20	1.24	1.20	3.32
21	1.26	0.76	39.98
22	1.31	0.54	58.80
23	1.36	1.16	15.10
24	1.34	1.22	8.81

Figure 4.9 shows unfoamed density values of samples comprising 0 %, 2 % and 4 % chemical blowing agent (Celogen-OT®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content. From the scheme, it can be seen that the chemical blowing agent, at pre-decomposition state, has filler effects on the densities of the specimens. While polymer content is decreasing – bitumen

percentage is increasing – the unfoamed density values are increasing. Since filler content is increasing, the densities of specimens are increasing.

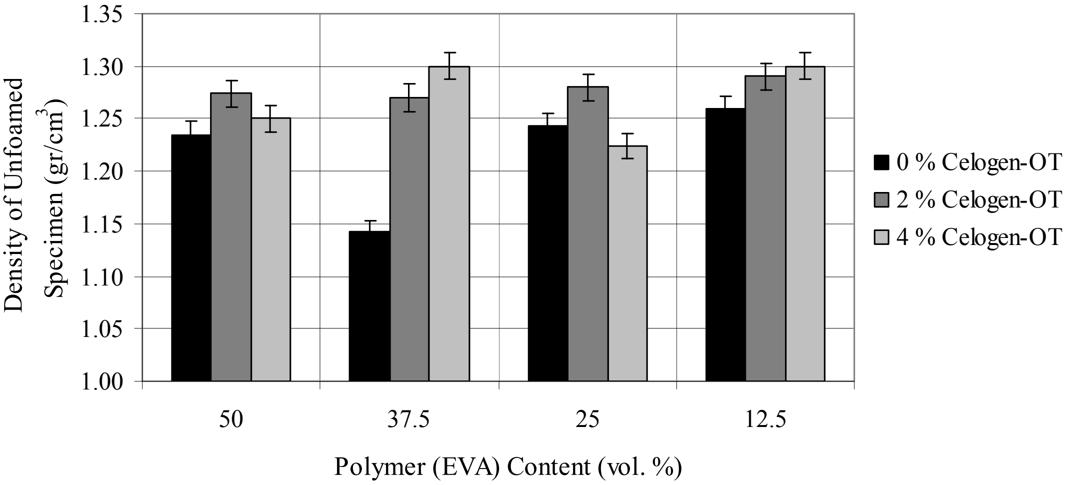


Figure 4.9 Densities of unfoamed specimens comprising 0 %, 2 % and 4 % chemical blowing agent (Celogen-OT ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.10 illustrates apparent overall core density values of samples comprising 0 %, 2 % and 4 % chemical blowing agent (Celogen-OT®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content. At 0 % blowing agent; since there is no foam formation, the apparent overall densities of composites are the highest values in comparison with the other values of foamed samples. Among the density values of unfoamed specimens, there is no critical difference except for the density of the 6th specimen.

The samples comprising 2 % blowing agent have the lowest apparent overall core density values. However if we look at SEM pictures of samples with 4 % blowing agent, it is seen that the specimens have more uniform and fine closed cells than the samples with 2 % blowing agent. Among density values of samples comprising 2 % blowing agent, there is a decreasing trend along with decreasing EVA content in the specimen. However, among samples including 4 % blowing agent there is an increasing trend of density values while polymer content is decreasing. Since CBA forms bubbles at polymer phase and this makes porosity increased, as the polymer content deceases the porosity will also be decreased and the apparent overall core density will be, too.

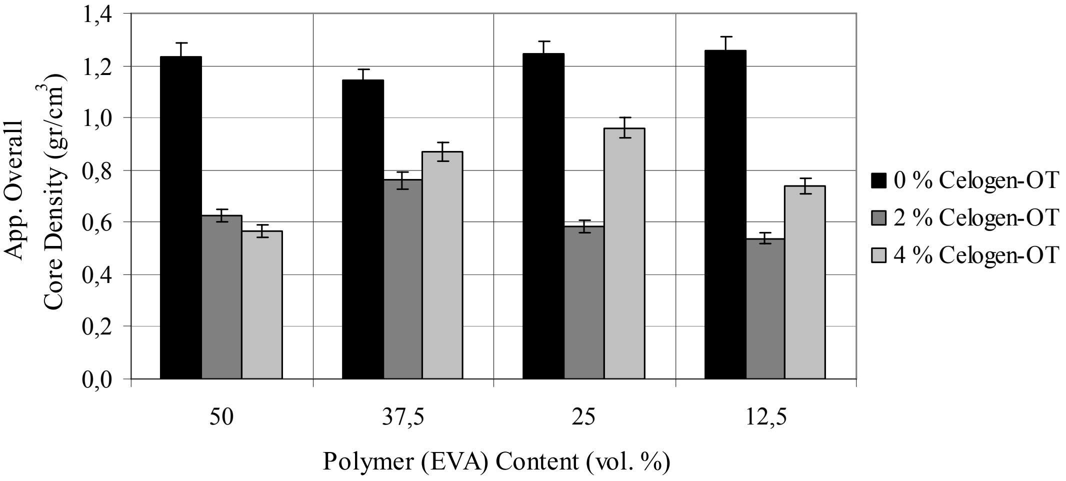


Figure 4.10 Apparent overall core densities of specimens comprising 0 %, 2 % and 4 % chemical blowing agent (Celogen-OT ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.11 shows porosity of samples comprising 0 %, 2 % and 4 % chemical blowing agent (Celogen-OT®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content. The samples with 2 % blowing agent are seen to have higher porosity content than the ones with 4 % blowing agent have. It can be seen on SEM pictures that samples with 2 % blowing agent have more pores (some of them interconnecting) as cells and also on the cell walls. This may be due to decomposition behavior of CBA at polymer phase at that molding temperature and pressure.

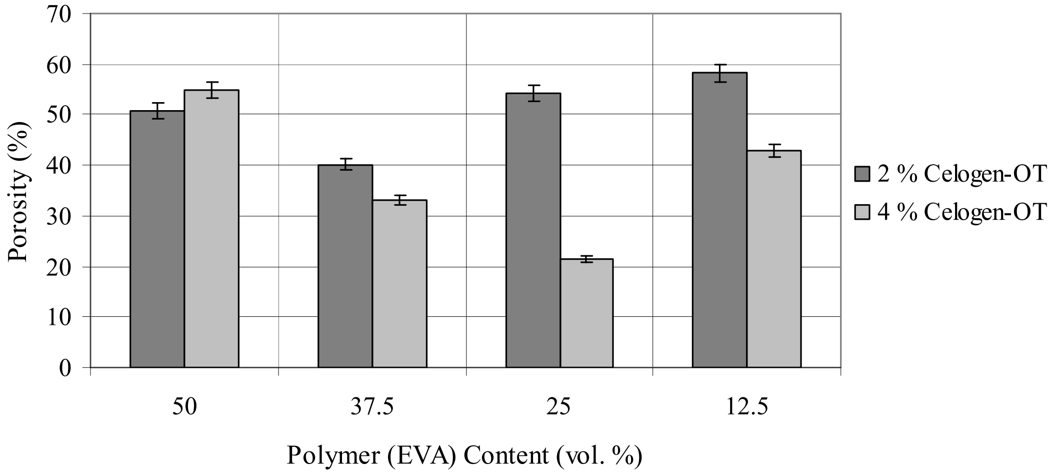


Figure 4.11 Porosity percentages of specimens comprising 0 %, 2 % and 4 % chemical blowing agent (Celogen-OT ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

In Figure 4.12, unfoamed density values of samples comprising 10 %, 15 % and 20 % calcium carbonate at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content are shown. Since calcium carbonate has a density value of 2.7 gr/cm^3, being higher than those of the other constituents in composition, its effect on unfoamed specimen is seen as increase in densities.

In Figure 4.13, apparent overall core densities of samples comprising 10 %, 15 % and 20 % calcium carbonate at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content are shown. In whole data, it is seen that for all the samples with different calcium carbonate percentages the apparent overall core densities are in an increasing trend along with decreasing EVA content. This is

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because of the fact that cell formation rate by chemical blowing agents is proportionate with the polymer content in foam formation.

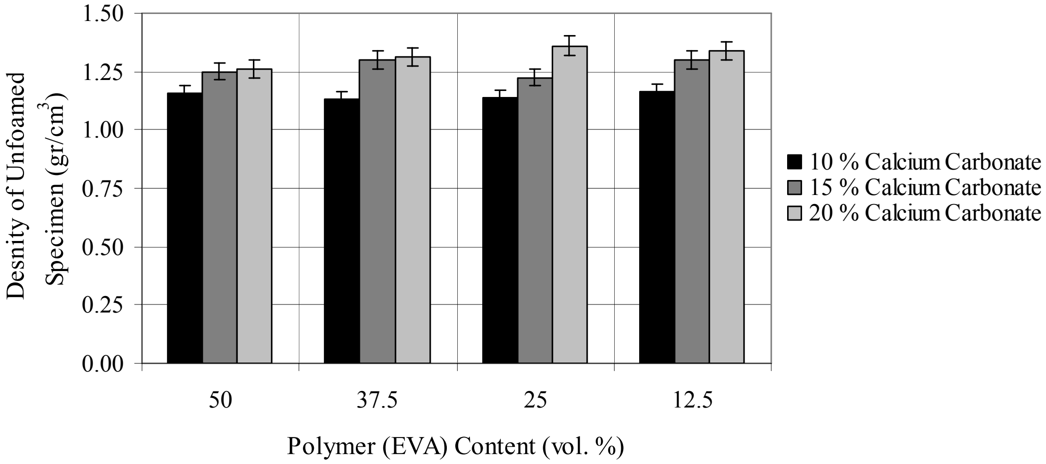

Figure 4.12 Densities of unfoamed specimens comprising 10 %, 15 % and 20 % calcium carbonate at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

In Figure 4.14, porosity of samples comprising 10 %, 15 % and 20 % calcium carbonate at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content are shown. As seen in the figure, at high polymer content, the porosity is in increasing trend while calcium carbonate concentration is increased. However on the contrary, as the polymer content is lowered, the porosity of FPBBCs decreases while calcium carbonate content increases.

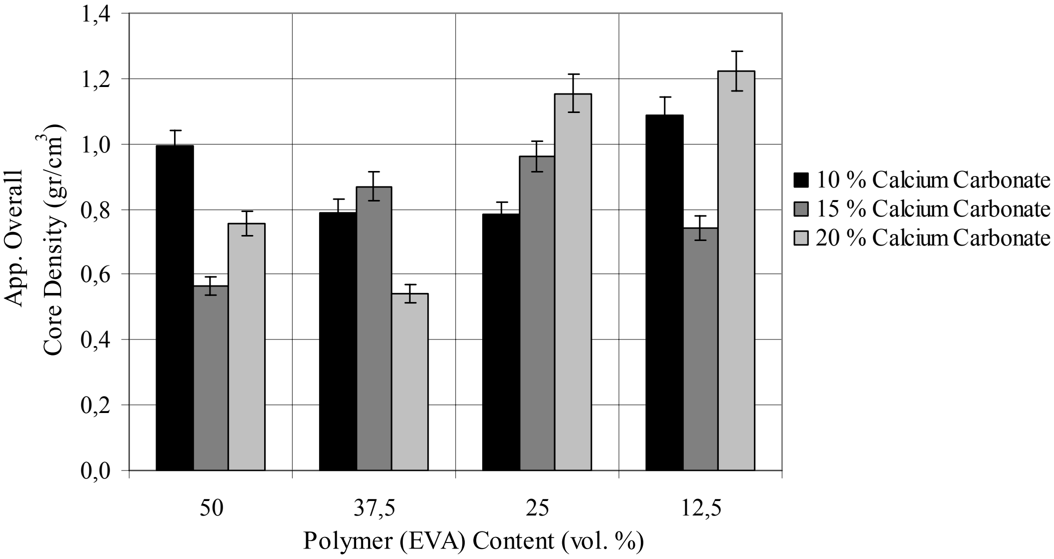

Figure 4.13 Apparent overall core densities of specimens comprising 10 %, 15 % and 20 % calcium carbonate at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

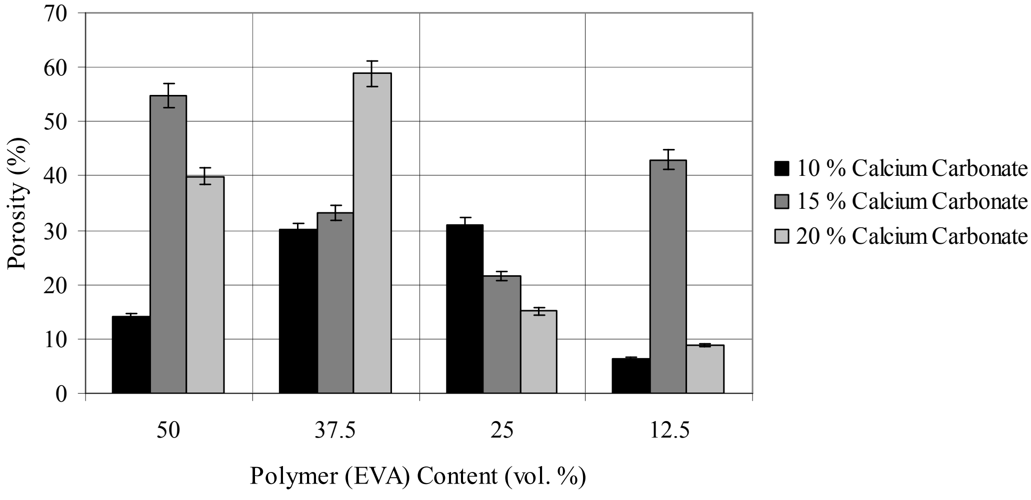

Figure 4.14 Porosity percentages of specimens comprising 10 %, 15 % and 20 % calcium carbonate at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

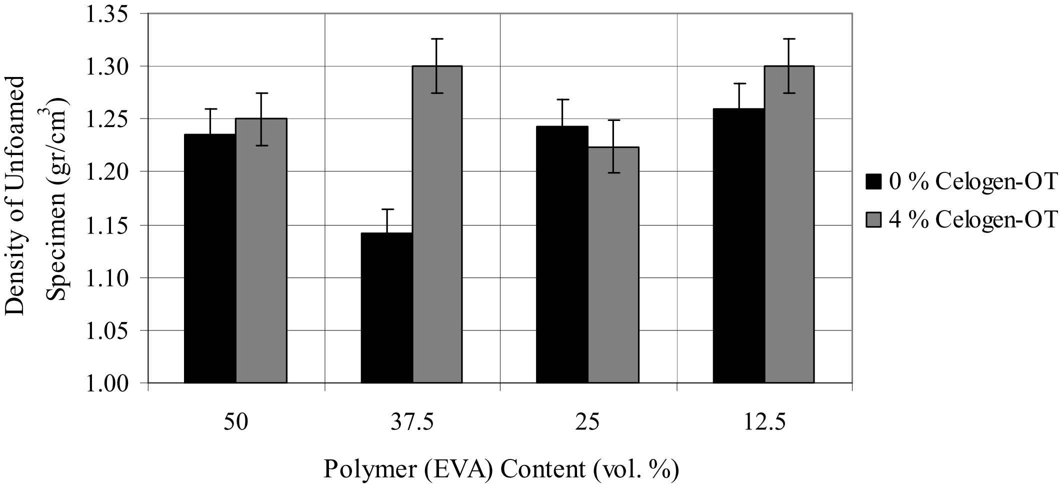

Figure 4.15 Densities of unfoamed specimens comprising 0 % and 4 % chemical blowing agent (Celogen-OT ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.15 illustrates unfoamed density values of samples comprising 0 % and 4 % chemical blowing agent (Celogen-OT®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content. Since chemical blowing agent has filler effect at its pre-decomposition state, the density of unfoamed specimens with blowing agent is higher than the ones without blowing agent.

Figure 4.16 shows apparent overall core densities of specimens with 0 % and 4 % chemical blowing agent (Celogen-OT ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content. It is seen that specimens which do not contain CBA have higher density values than the foamed ones comprising 4 %, which stems from the porous structure of foamed polymer based bituminous composites. This can be seen in Figure 4.9.

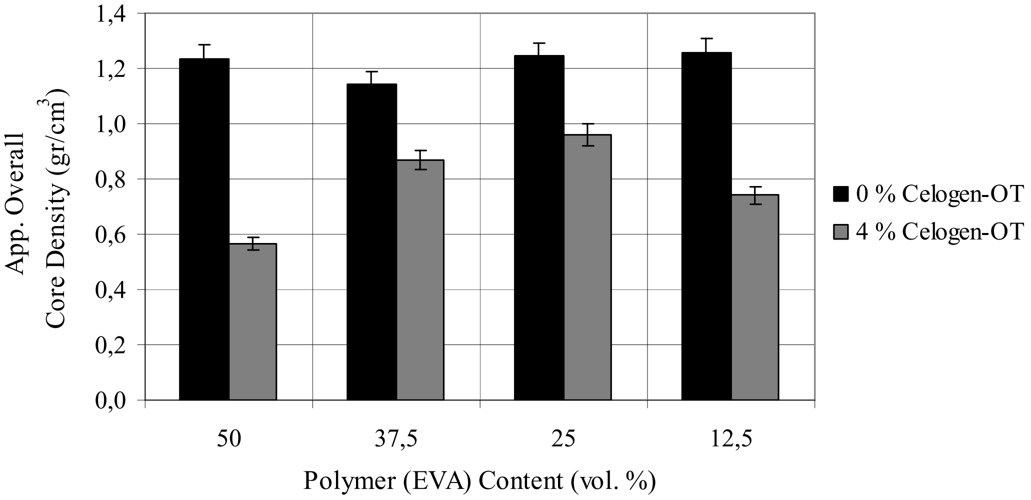

Figure 4.16 Apparent overall core densities of specimens with 0 % and 4 % chemical blowing agent (Celogen-OT ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

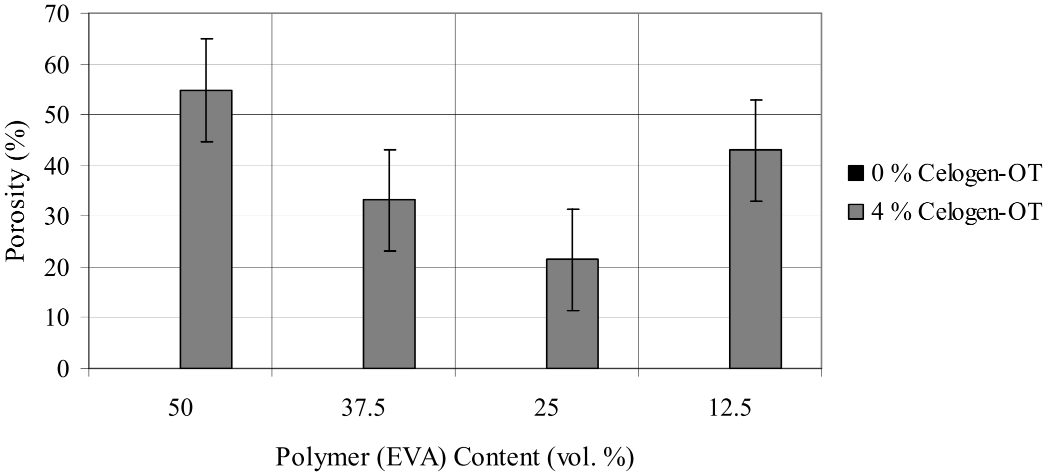

Figure 4.17 Porosity percentages of specimens with 0 % and 4 % chemical blowing agent (Celogen-OT ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

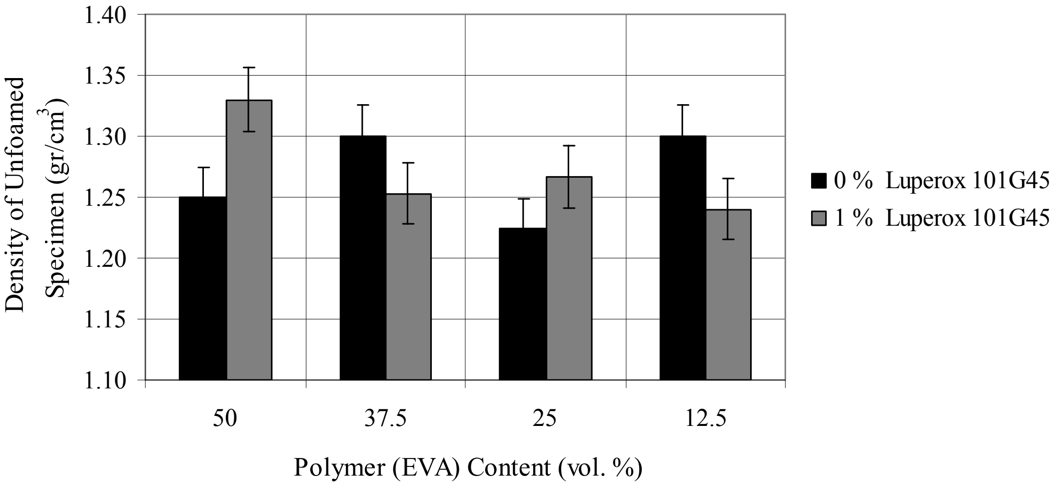

Figure 4.18 Densities of unfoamed specimens comprising 0 % and 1 % cross-linking agent (Luperox 101G45 ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

In Figure 4.18, the effect of cross-linking agent on the densities of unfoamed specimens. At unfoamed state, cross-linking agent acts as filler in the composition and it increases the density of composites. However, noncross-linked composites containing 37.5 % and 12.5 % EVA have higher densities than the cross-linked ones have.

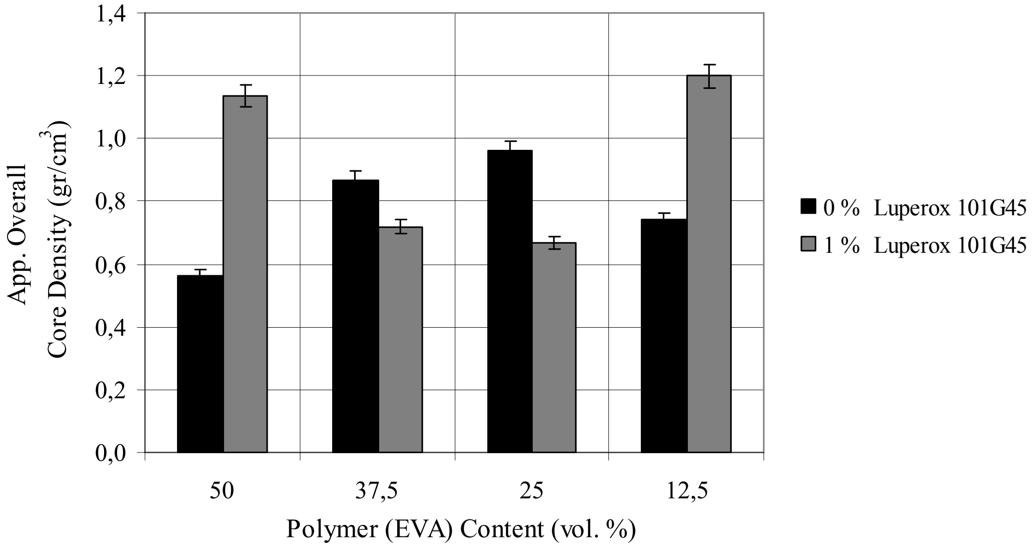

Figure 4.19 Apparent overall densities of specimens comprising 0 % and 1 % cross-linking agent (Luperox 101G45 ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content

In Figure 4.19 the effect of cross-linking agent on the apparent overall core densities of specimens is shown. At 50 % and 12.5 % EVA content, the cross-linked foamed polymer based bituminous composites (FPBBC) have much higher densities than the ones noncross-linked ones have. However, at 37.5 % and 25 % EVA content, the noncross-linked FPBBCs have higher densities than the ones cross-linked FPBBCs have. This data is not enough to explain this difference. It is expected from cross-linked polymers to have higher apparent overall core densities than the ones noncross-linked ones have since the cross-linking agent prevents the formation of more cells.

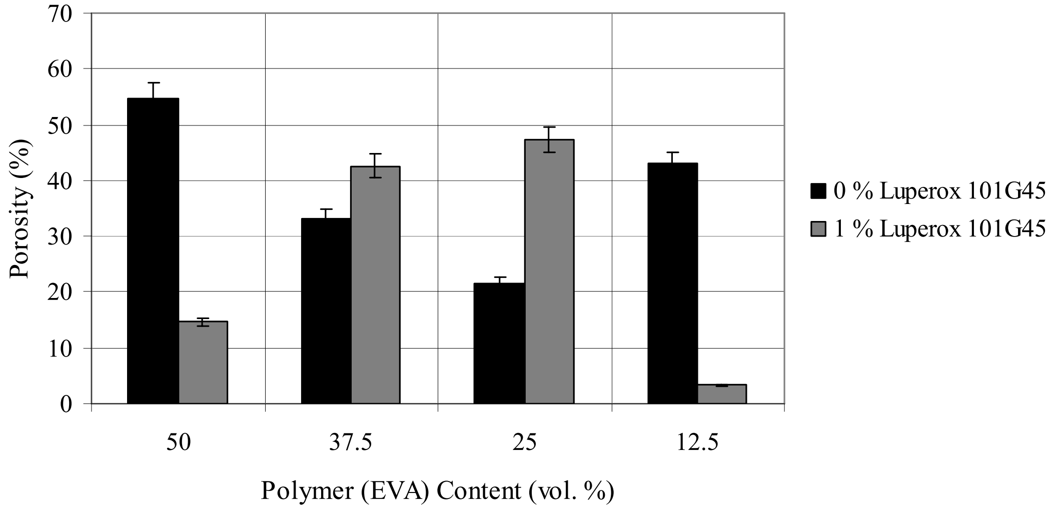

Figure 4.20 Porosity percentages of specimens comprising 0 % and 1 % cross-linking agent (Luperox 101G45 ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.20 illustrates the porosity percentage of specimens containing 0 % and 1 % cross-linking agent (Luperox 101G45 ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content. As it is mentioned for Figure 4.11, the porosity content of a FPBBC is expected to be disproportional with the cross-linking content. This can be validated for the specimens with 50 % and 12.5 % EVA.

4.3 Mechanical Test

4.3.1 Compression Test

In order to investigate the effects of chemical blowing agent (CBA) and its concentration, $CaCO_3$ concentration and cross-linking agent with varying polymer (EVA) contents on mechanical properties of FPBBCs, compression tests were performed. Five samples with dimensions 10 mm x 10 mm x 10 mm from each polymer based bituminous composite were cut and they were compressed under constant 10.000 N compressive loading till 50 % of the height of the samples was compressed. Maximum force applied to each samples were calculated by the software. From maximum force at maximum displacement vs. displacement data, stress-strain curves were obtained. Stress-strain curves provide information about the response of materials to applied stress during the compression tests. Figure 4.21 represents the typical stress-strain curves of the composites.

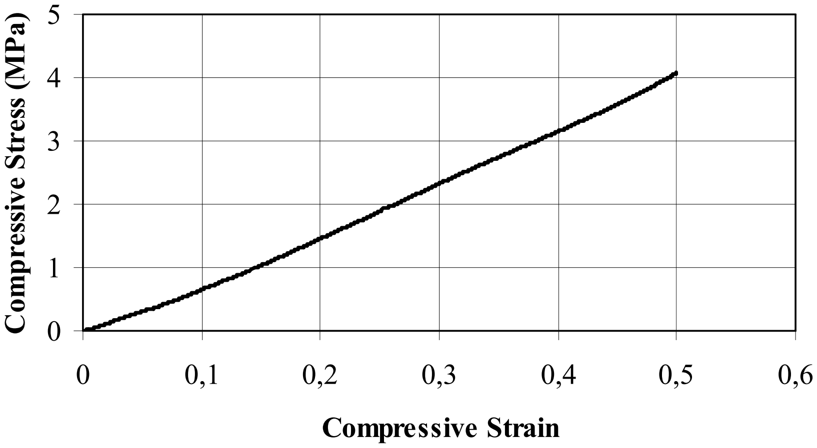

Figure 4.21 Compressive strain vs. Compressive stress curve of FPBBC comprising 10 % $CaCO_3$, 4 % CBA, % 50 EVA (content completing to 100 % with the bitumen content.

Figure 4.22 and Figure 4.23 illustrate the effect of chemical blowing content on the compressive strength and maximum force at maximum displacement of the composites. For both unfoamed and foamed materials, it can be seen that as EVA content decreases, the compressive strength that the composite can resist decreases, too. The unfoamed polymer based bituminous composites have the highest compressive strength. This is because of the fact that cellular structure decreases the materials' compressive strength. On the other hand, at high CBA content, the composites show high compressive strength at high polymer content. However as the polymer content decreases, the compressive strength of FPBBCs decreases.

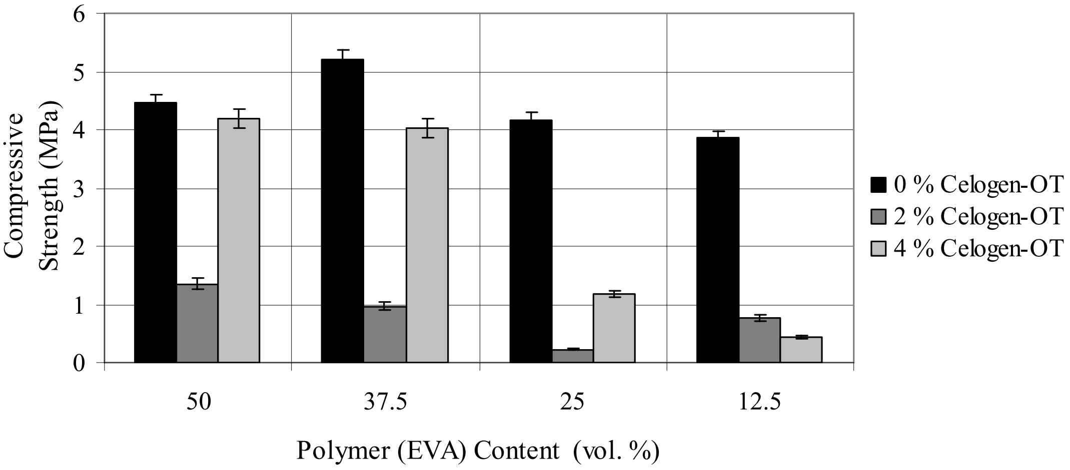

Figure 4.22 Compressive strength of specimens comprising 0 %, 2 % and 4 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

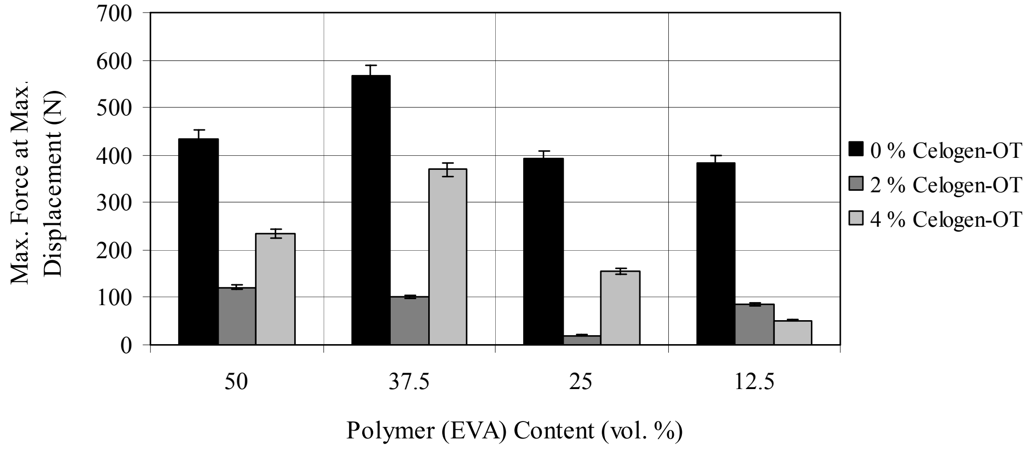

Figure 4.23 Maximum forces at maximum displacement of specimens comprising 0 %, 2 % and 4 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.24 shows the effect of CBA on the compressive modulus of foamed and unfoamed composites with varying polymer content. From this data, it can be predicted that at FPBBCs having high CBA content there may be less cells with small sizes.

Figure 4.25 illustrates the effect of CBA content on the constant deflection compressive set values of composites with varying polymer content. As the polymer content decreases but CBA content increases, the elastic recovery of materials decreases. This is an expected result from the polymer side, because the elasticity of the composite would be given to the material by EVA. However, from CBA side, it is so interesting. Because, this shows that at high CBA content, the composite has more cells or same number of cells with bigger sizes.

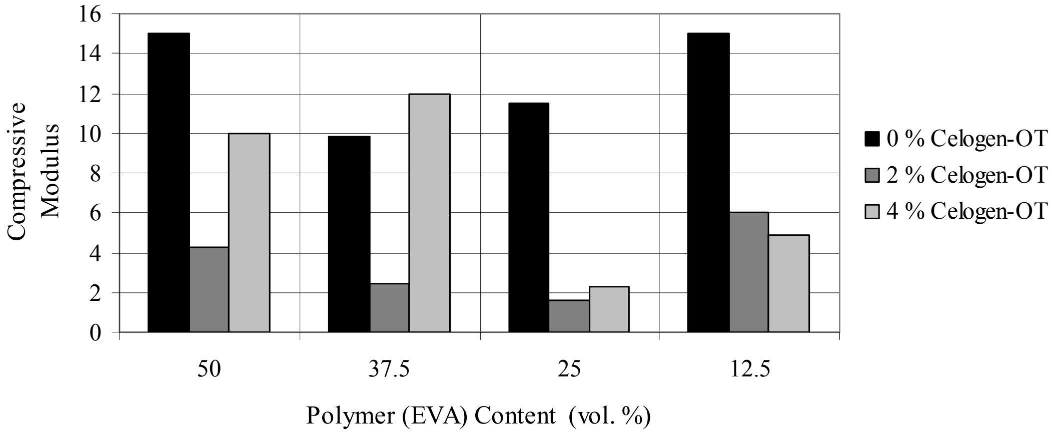

Figure 4.24 Compressive modulus of specimens comprising 0 %, 2 % and 4 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

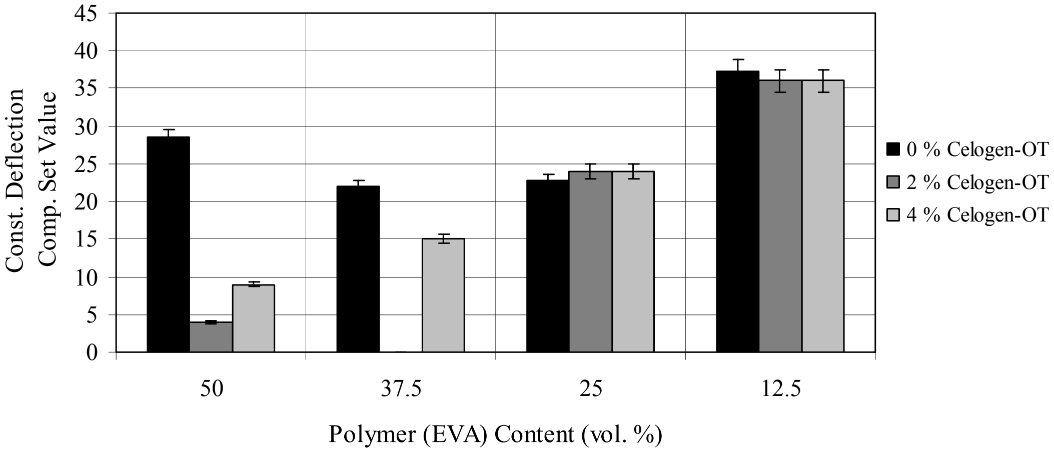

Figure 4.25 Constant deflection compressions set values of specimens comprising 0 %, 2 % and 4 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.26 and Figure 4.27 illustrate the effect of $CaCO_3$ content on the compressive strength and maximum force at maximum displacement of the composites. In general for all materials having different $CaCO_3$ composition, it can be seen that as EVA content decreases, the compressive strength that the composite can resist decreases, too. FPBBCs containing 15 % $CaCO_3$ have the highest compressive strength with respect to others containing different calcium carbonate content. Materials containing 20 % $CaCO_3$ with low polymer content have high compressive strength. On the other hand, at high polymer content FPBBCs having moderate $CaCO_3$ have much high compressive strength.

Figure 4.28 shows the effect of $CaCO_3$ content on the compressive modulus of FPBBCs with varying polymer content. From this data, it is seen that at low polymer content, materials having high $CaCO_3$ content have high compressive modulus. This may be due to less cell content with smaller sized cells. Moreover, this is an expected result because $CaCO_3$ acts as nucleating agent during foam mechanism causing more cells to be formed.

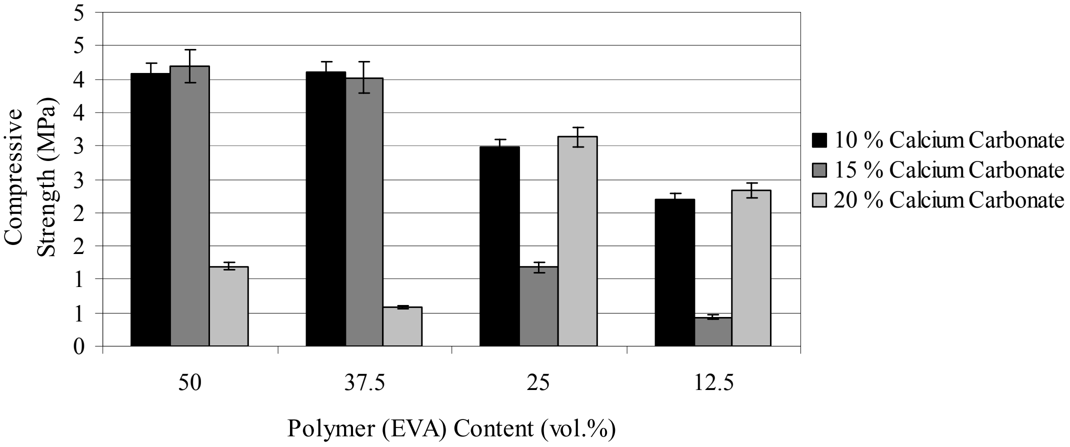

Figure 4.26 Compressive strength of specimens comprising 10 %, 15 % and 20 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

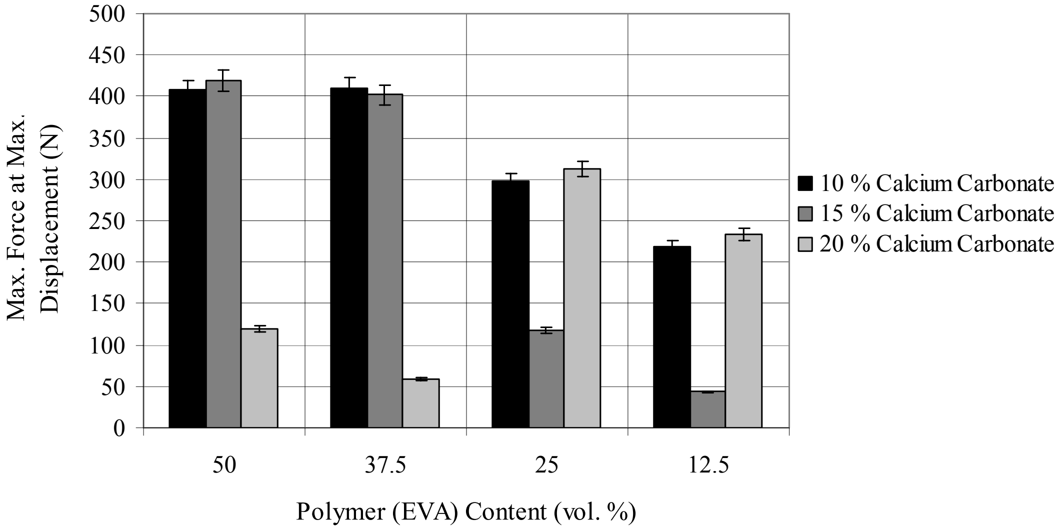

Figure 4.27 Maximum forces at maximum displacement of specimens comprising 10 %, 15 % and 20 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

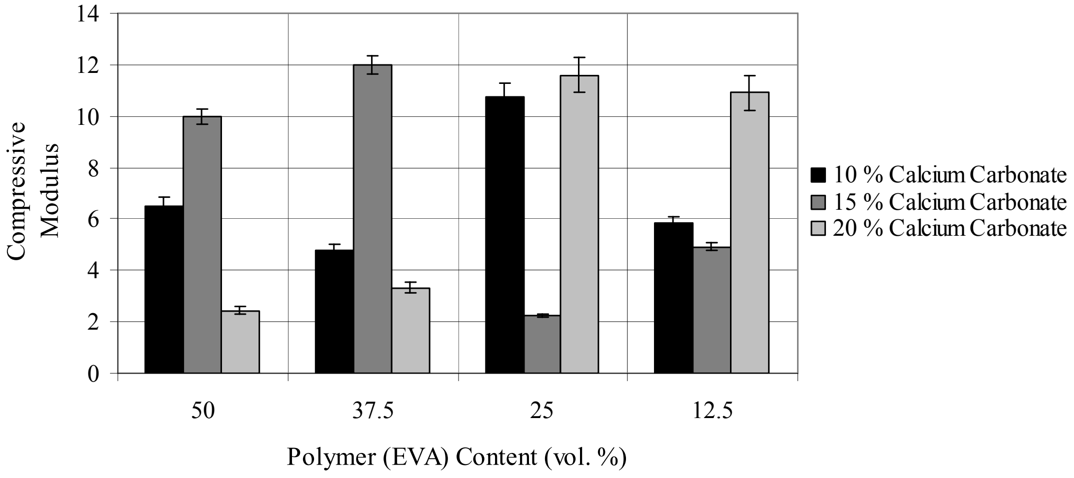

Figure 4.28 Compressive modulus of specimens comprising 10 %, 15 % and 20 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.29 illustrates the effect of $CaCO_3$ content on the constant deflection compressive set values of composites with varying polymer content. As the polymer content decreases but the $CaCO_3$ content increases, the elastic recovery of materials decreases. This is an expected result from the polymer side, because the elasticity of the composite would be given to the material by EVA. Moreover this shows that at higher $CaCO_3$ contents, formed cells are either bigger cells with thin cell walls are formed or the cells formed are mostly interconnected.

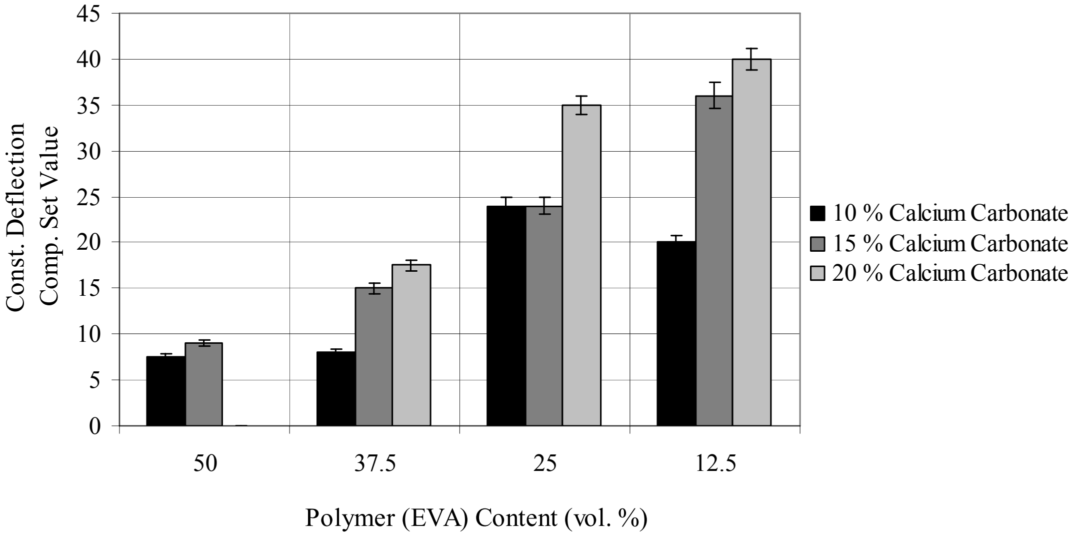

Figure 4.29 Constant deflection compressions set values of specimens comprising 10 %, 15 % and 20 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

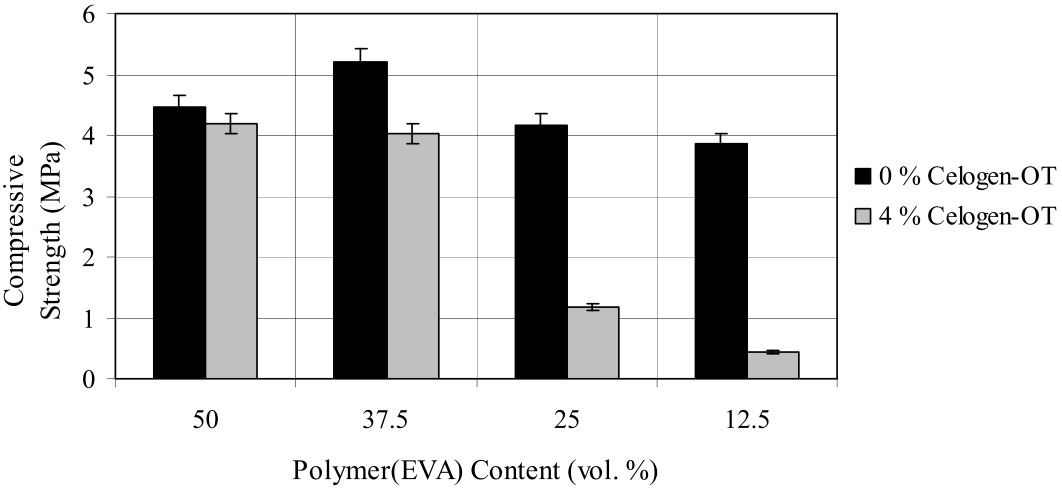

Figure 4.30 Compressive strength of specimens comprising 0 % and 4 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

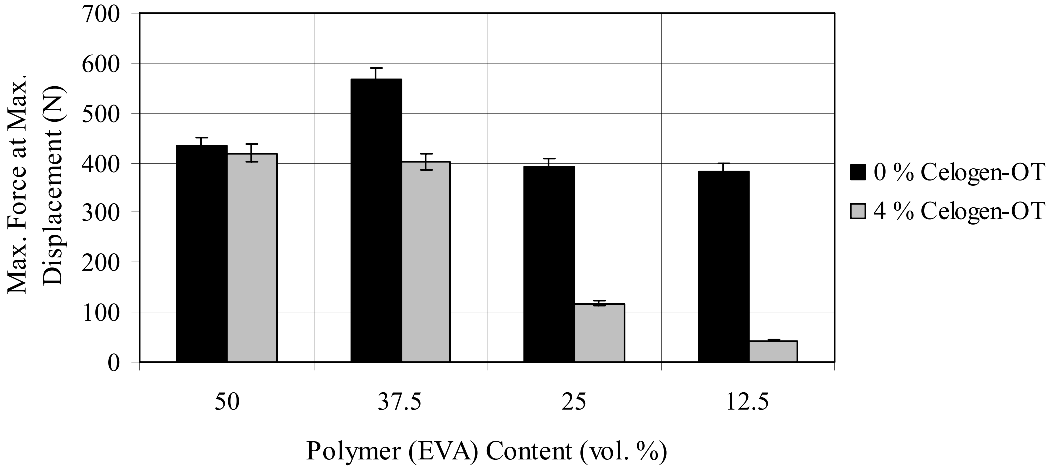

Figure 4.31 Maximum forces at maximum displacement of specimens comprising 0 % and 4 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.30 and Figure 4.31 illustrate the effect of chemical blowing agent content on the compressive strength and maximum force at maximum displacement of the composites. For both unfoamed and foamed materials, it can be seen that as EVA content decreases, the compressive strength that the composite can resist decreases, too. The unfoamed polymer based bituminous composites have the highest compressive strength. This is because of the fact that cellular structure decreases the materials' compressive strength. On the other hand, at higher EVA content, the composites show higher strength.

Figure 4.32 shows the effect of CBA on the compressive modulus of foamed and unfoamed composites with varying polymer content. Figure 4.33 illustrates the effect of CBA content on the constant deflection compressive set values of composites with varying polymer content. As the polymer content decreases, the elastic recovery of materials decreases. This is an expected result from the polymer side, because the elasticity of the composite would be given to the material by EVA.

Figure 4.34 and Figure 4.35 illustrate the effect of cross-linking agent content on the compressive strength and maximum force at maximum displacement of the composites. For both cross-linked and noncross-linked FPBBCs, it can be seen that as EVA content decreases, the compressive strength that the composite can resist decreases, too. Although it is expected higher compressive strength from cross-linked foams, FPBBCs containing cross-linking agent have lower strength values. However, at the lowest polymer content the cross-linked material has the highest compressive strength value. This may be occurred because of the order of mixing materials before the molding stage. In this study, cross-linking agent is mixed with the materials as the last one. Since cross-linking agents shows their affinity while their decomposition at polymer phase more, they should be mixed with the polymer first and then with other materials.

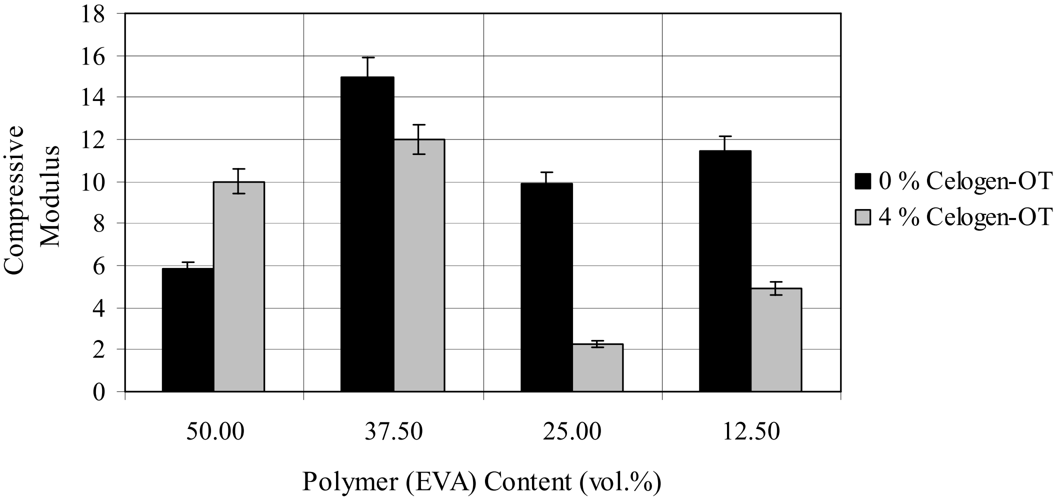

Figure 4.32 Compressive modulus of specimens comprising 0 % and 4 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

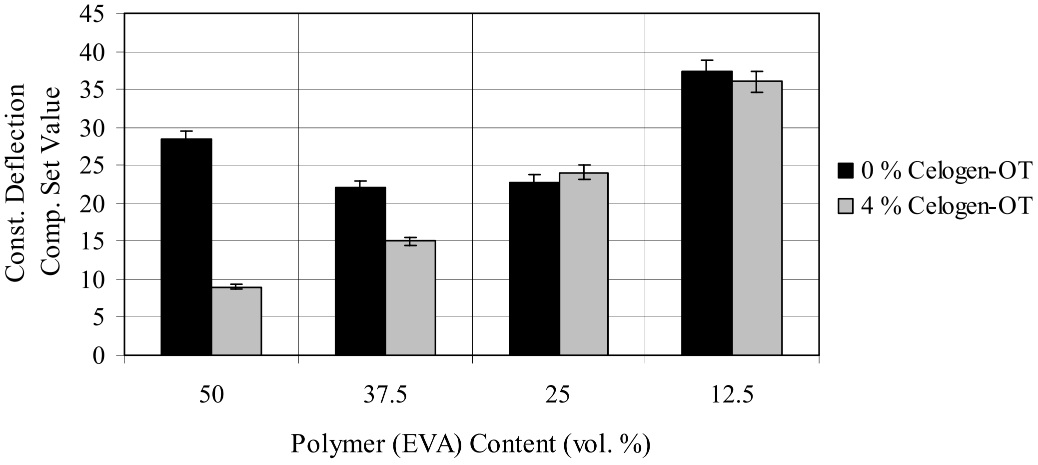

Figure 4.33 Constant deflection compressions set values of specimens comprising 0 % and 4 % CBA at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

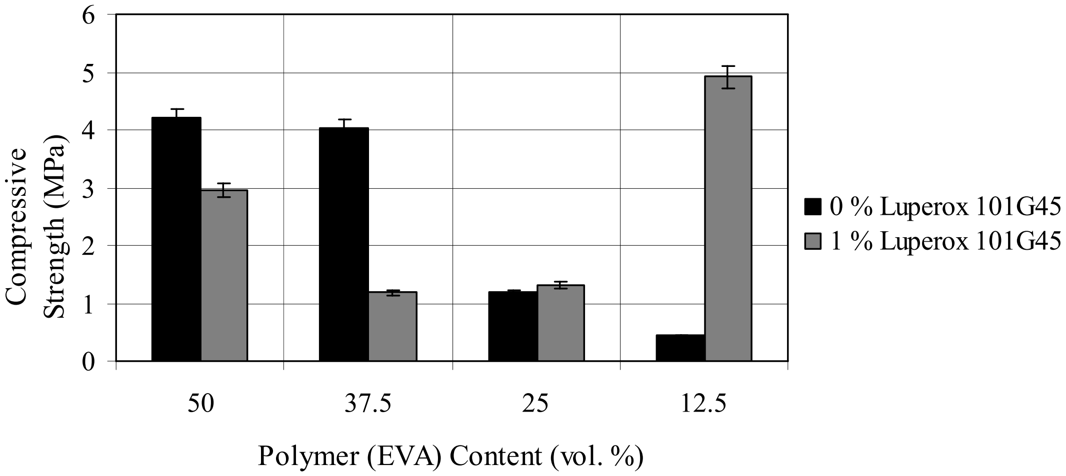

Figure 4.34 Compressive strength of specimens comprising 0 % and 1 % cross-linking agent at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

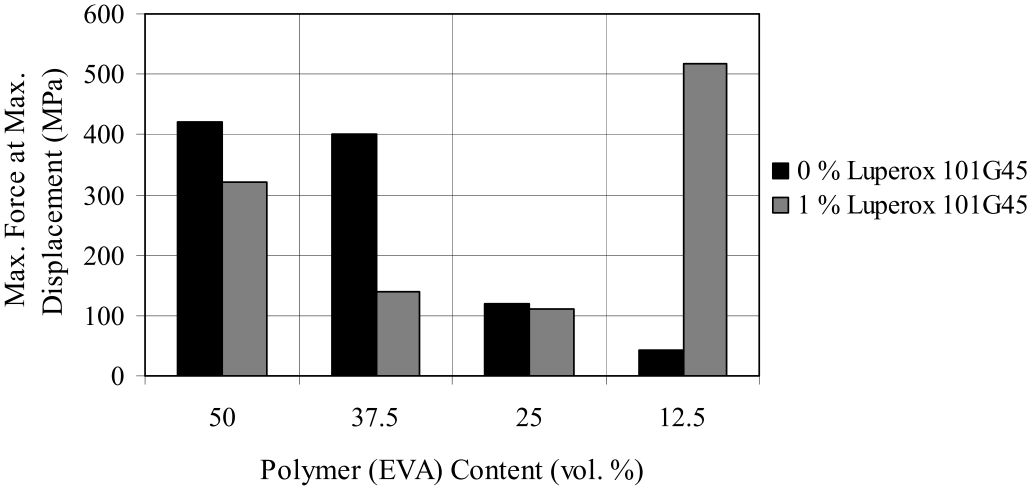

Figure 4.35 Maximum forces at maximum displacement of specimens comprising 0 % and 1 % cross-linking agent at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

Figure 4.36 shows the effect of CBA on the compressive modulus of foamed and unfoamed composites with varying polymer content. Figure 4.37 illustrates the effect of CBA content on the constant deflection compressive set values of composites with varying polymer content. As the polymer content decreases, the elastic recovery of materials decreases. This is an expected result from the polymer side, because the elasticity of the composite would be given to the material by EVA.

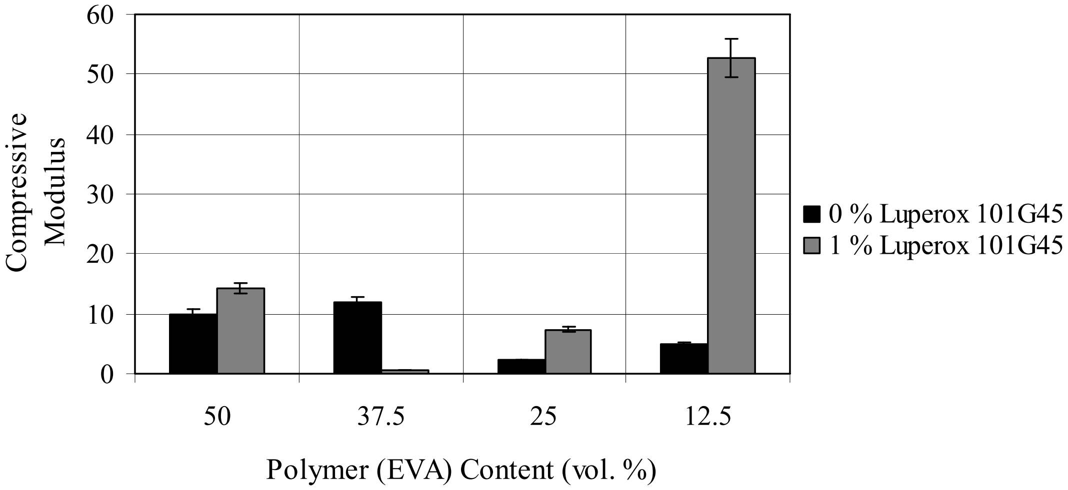

Figure 4.36 Compressive modulus of specimens comprising 0 % and 1 % cross-linking agent at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

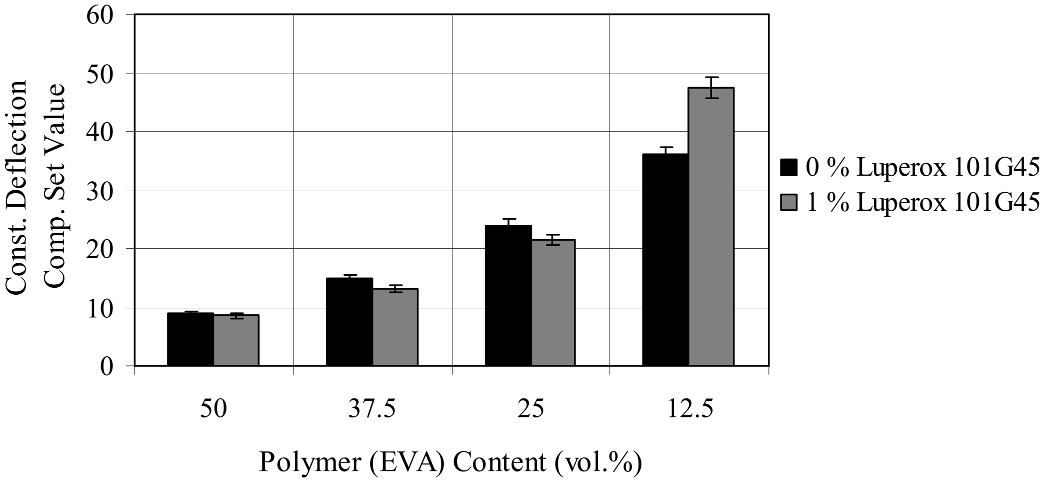

Figure 4.37 Constant deflection compressions set values of specimens comprising 0 % and 1 % cross-linking agent at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content

4.4 Thermal Tests

4.4.1 Thermal Conductivity Test

Via data obtained from the thermal conductivity measurements of FPBBCs, the effects of chemical blowing agent (CBA) and its concentration, $CaCO_3$ concentration and cross-linking agent with varying polymer (EVA) contents were examined. The addition of polymers in general reduces the thermal conductivities. In addition to this, having closed-cell foam structure reduces the thermal conductivity more. For bitumen, $CaCO_3$, are used in composites, thermal conductivities of these substances are 0.17 W/m.K, 1.26-1.33 W/m.K, respectively. Heat capacities of these substances are 0.19 kcal/kg.°C, 0.2 kcal/kg.°C. No data for EVA is found.

Table 4.2 Extrapolated average thermal constant values (k) of specimens and reference material*.

Number of Specimen Measured	**Extrapolated Average Thermal Conductivity Constant (k) (W/m.K) of the Material**
1	0.05
2	0.04
3	0.04
4	0.04
5**	0.07
6	0.06
7	0.04
8	0.05
9	0.04
10	0.03
11	0.04
12	0.05
13	0.04
14	0.05
15	0.06
16	0.04
17	0.07
18	0.07
19	0.06
20	0.05
21	0.07
22	0.04
23	0.06
24	0.08

* Thermal Conductivity of Styrafoam® as a reference material = 0.03 W/m.K

** Thermal Conductivity of Unfoamed Specimen = 0.07 W/m.K

In Table 4.2 extrapolated average thermal constant values of specimens are shown. On the whole, thermal conductance of FPBBCs is found to be expected and desired. In Figure 4.38 thermal conductivity constant values of some selected FPBBCs are shown with respect to their porosity percentage values. From this graph it can be seen that the phenomenon of decreasing thermal conductivity with increasing porosity is validated. However, not for all porous materials this fact will be valid. Because the porous structure of that materials must be composed of closed-cell bubbles in order to designate thermal insulative behavior.

Figure 4.39 shows the effect of CBA and its concentration on the thermal conductivity of FPBBCs. From the figure, for foamed specimens it is seen that as the CBA content increases but on the other hand EVA content decreases, thermal conductivity increases. This is because of the fact that, at high CBA content the polymer is not enough for stable closed-cell formation. Most of the cells are formed at bitumen rich phase and they are all either collapsed or interconnected. Figure 4.40 illustrates the effect of $CaCO_3$ and its concentration on the thermal conductivity of FPBBCs. From the figure, it is seen that at 50 % and 12.5 % EVA with higher $CaCO_3$ content the materials have the highest thermal conductivity values.

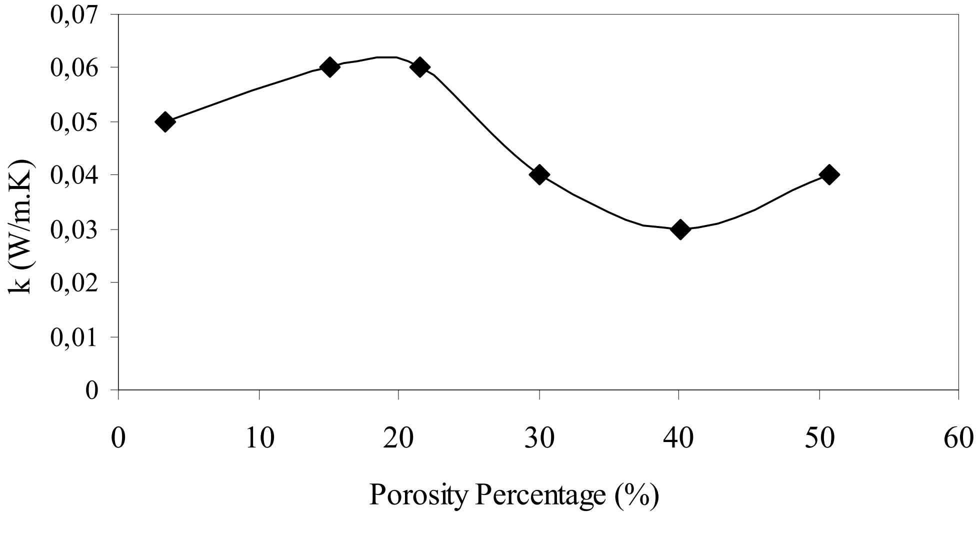

Figure 4.38 Thermal conductivity constant values (k) of some selected FPBBCs compared with their porosity percentage.

Figure 4.41 shows the effect of cross-linking agent on the thermal conductivity of FPBBCs. It can be seen that cross-linking makes decrease in the thermal conductivity of FPBBCs. However as EVA content decreases, the decreasing effect of cross-linking agent on thermal conductivity lowers. This may be because of the fact that since cross-linking occurs between polymer chains, as polymer content decreases the number of cells to be cross-linked will be less and they will be less stable. This will cause more interconnected cells to be formed.

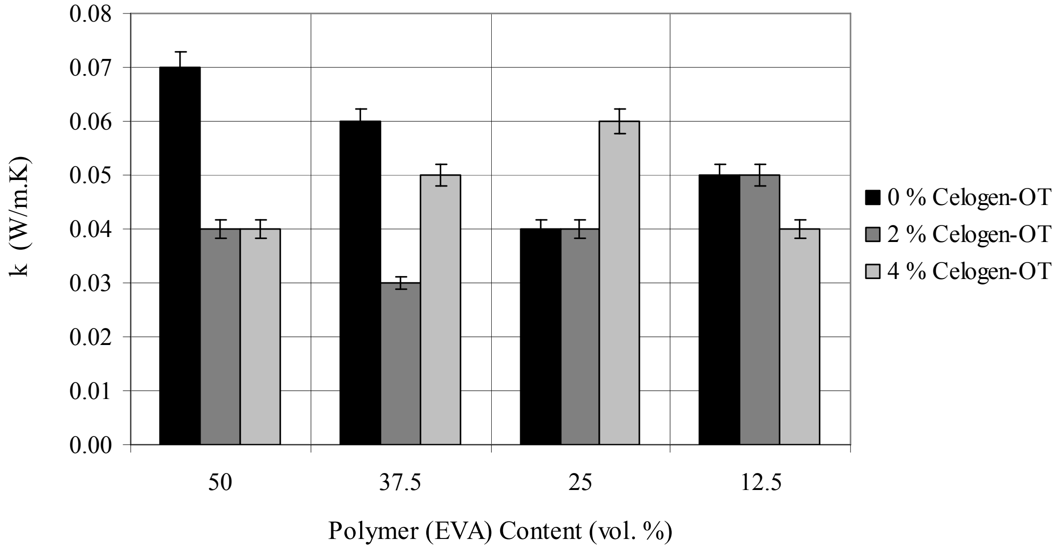

Figure 4.39 Extrapolated average thermal conductivity constant (k) of specimens comprising 0 %, 2% and 4% chemical blowing agent (Celogen-OT ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

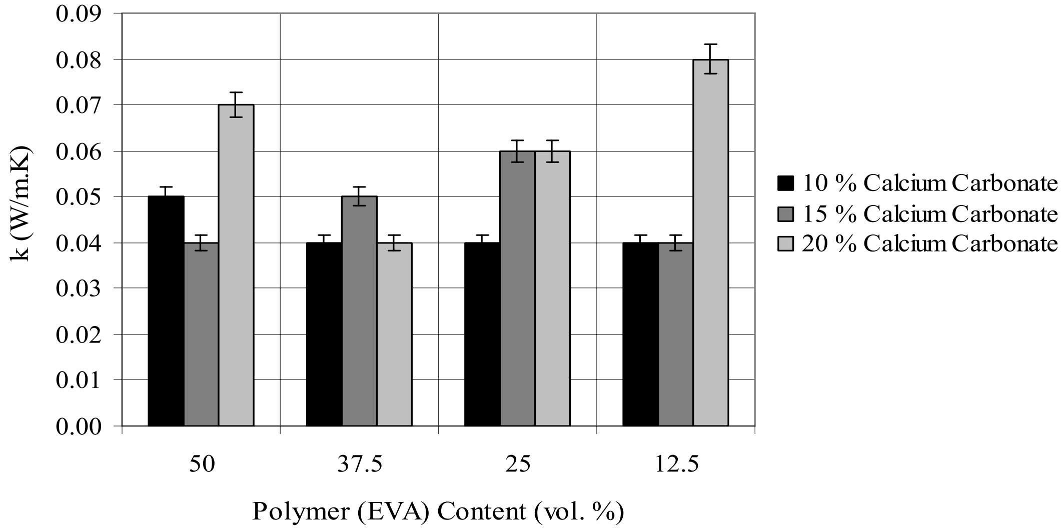

Figure 4.40 Extrapolated average thermal conductivity constant (k) of specimens comprising 10 %, 15 % and 20 % calcium carbonate at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

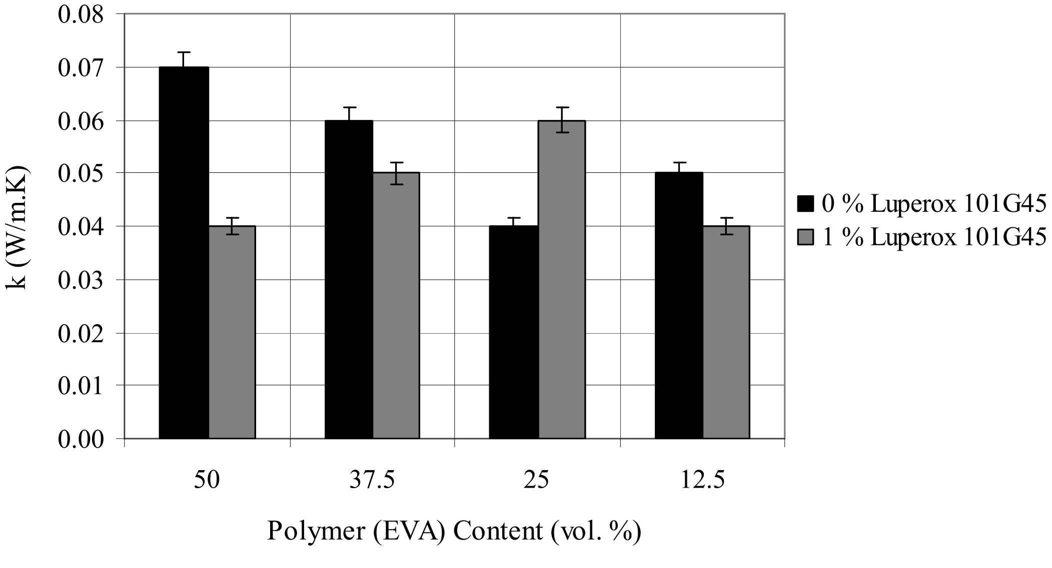

Figure 4.41 Extrapolated average thermal conductivity constant (k) of specimens comprising 0 % and 1 % cross-linking agent (Luperox 101G45 ®) at 50 %, 37.5 %, 25 % and 12.5 % polymer (EVA) content completing to 100 % with the bitumen content.

CHAPTER 5

CONCLUSIONS

In this study, the effects of inorganic filler concentration of calcium carbonate and the effects of cross-linking on the thermal, mechanical and morphological properties of foamed and unfoamed EVA based bituminous blends and composites are investigated. The aim of this study is to make a new insulating material having good thermal properties.

One of the aims of this study is to investigate the concentration of chemical blowing agent which makes closed-cell foam structure in the composite. Closed-cell structure is known as an effective morphology causing low thermal conductivity. This was investigated through the porosity tests, thermal conductivity tests and from SEM micrographs. As a result, the best closed-cell morphology was obtained with 15 % $CaCO_3$, 4 % CBA at 25 % EVA content. Moreover, the thermal conductivity test results with SEM graphs confirm this finding. On the other hand, at 2 % CBA content with high EVA concentration, the composites have high strength with high compressive modulus. Moreover, from SEM micrographs it can be predicted that FPBBCs containing 4 % CBA has more closed-cells and they have more uniform structures. From the mechanical points of view, foams containing high CBA at high polymer content have higher compressive modulus. In addition to this, elastic recovery of FPBBCs decreases with lowering CBA content and EVA concentration.

Another aim of this study was to investigate the effects of $CaCO_3$ concentration on various properties of PBBCs. The composites have high apparent overall densities with high $CaCO_3$ concentration at low EVA content due to low porosity. On the other hand, the porosity values of specimens increase with increasing filler content at higher EVA content. Validating these findings, thermal conductivity of these materials decreases with increasing filler content and EVA concentration. In addition to these, from SEM micrographs it is seen that at low polymer percentages, the composites have better foam structures. The best cell distribution with uniform cells is seen at FPBBC containing 15 % $CaCO_3$. From the mechanical points of view, it is seen that at low polymer content, materials having high $CaCO_3$ content have higher compressive modulus. In addition to this, elastic recovery of composites is lowered as the filler content increases.

The last aim of this study was to examine whether the cross-linking agent affects the compressive mechanical properties of foamed EVA based bituminous composites. In order to strengthen the cell walls of foams, at EVA phase cross-linking was applied via peroxide based cross-linking agent. The results showed that as EVA content is lowered, the compressive modulus of the composites decreases. However, although it is expected from cross-linked foamed specimens to have high compressive strength values, the compressive strength decreases in specimens. But on the other hand at the lowest EVA content with cross-linking agent, the composite has the highest compressive strength. This is basically due to the unfomaed nature of specimen at low EVA content. If the material is not adequately foamed we naturally expect high compressive strength value. Furthermore, there is a decreasing effect of cross-linking agent on the elastic recovery of specimens while EVA content decreases. This is an expected result. From SEM micrographs, it is seen that composites which were cross-linked have small cells with homogeneous and uniform distribution. This causes the specimens with high EVA content to have low thermal conductivity values. At especially 25 % EVA content the composite becomes more porous (at about 48 %) compared to Luperox free material. The increase is more than twice to the peroxide containing composite. What is also very promising is that the increase in porosity does not reduce the compressive strength. At 25 % EVA content there is a slight improvement in compressive strength together with an increase in porosity.

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APPENDIX

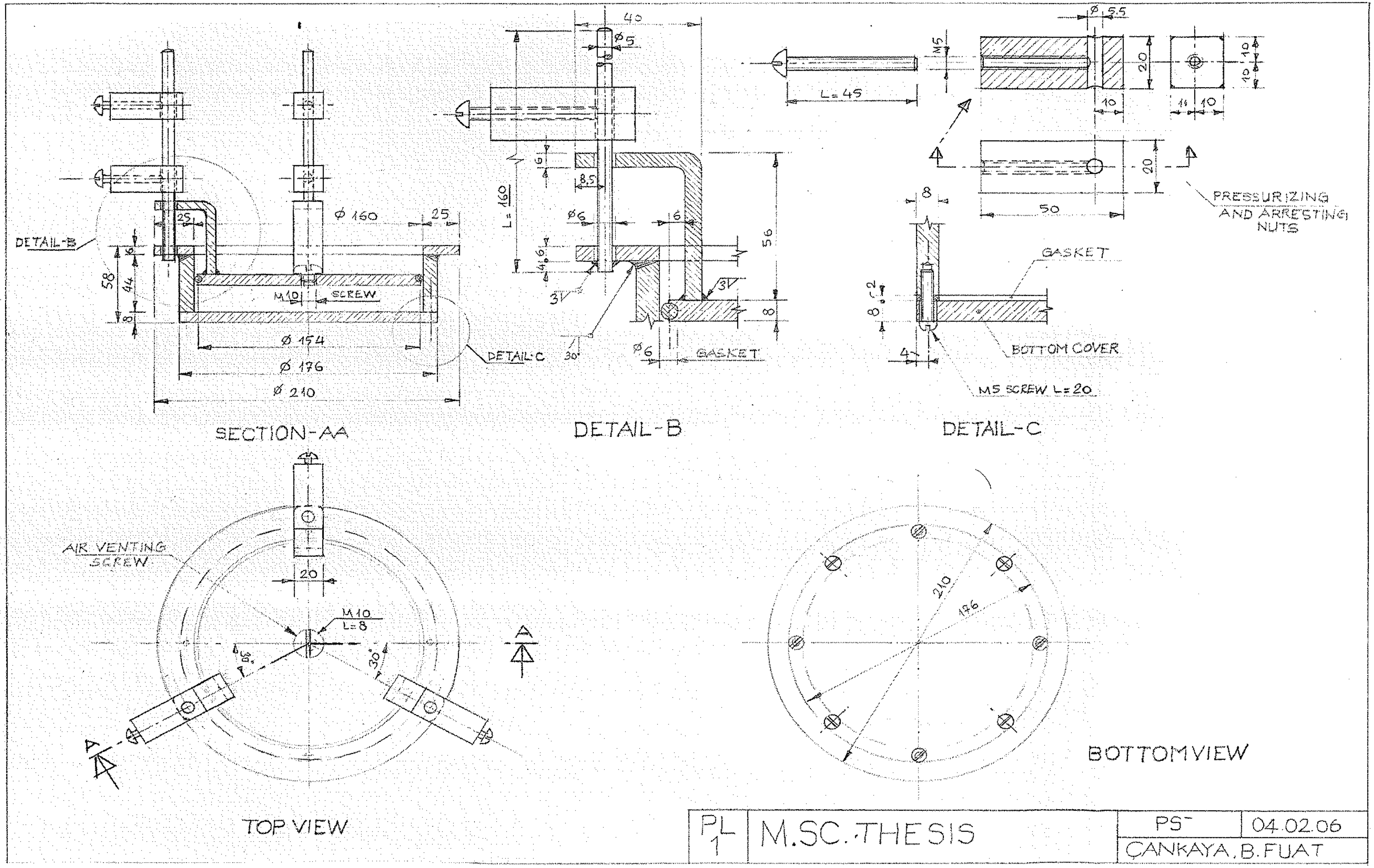

Figure A.1 Technical Drawing of Hand Lay-up Self-expanding Mold