ACCELERATED AGING OF ELASTOMERS IN AQUEOUS MEDIA

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

EKREM İNALER

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
POLYMER SCIENCE AND TECHNOLOGY

JANUARY 2007

Approval of the Graduate School of Natural and Applied Sciences.

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ABSTRACT

ACCELERATED AGING OF ELASTOMERS IN AQUEOUS MEDIA

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January 2007, 115 pages

EPDM (Ethylene-Propylene-Diene Monomer)/PP (Polypropylene) based TPV (Thermoplastic Vulcanizate) was aged in a closed system at stabilized temperature and pressure at 80, 100 and 120^oC in distilled water, detergent solution and shiner solution.

The variation in properties of TPV upon aging were followed by using DSC (Differential Scanning Calorimetry), TGA (Thermogravimetric Analysis), tensile testing, Shore A rubber hardness testing.

DSC analysis indicated that percent crystallinity of PP component in TPV increased at 100^oC whereas crystal structure was deformed at 120^oC. In addition to this, hardness test showed that the hardness of TPV remained almost constant in distilled water aging except 120^oC water aging but TPV became softer in detergent and shiner solution upon all aging temperatures used in this study. Tensile testing confirmed the hardness analysis that the loss in mechanical properties of TPV was observed except 100^oC water aging. TGA analysis showed that percent crystallinity increase causes enhancement in degradation temperature of EPDM/PP blend in air.

It is detected that TPV is quite resistant to 80^{o}C aging, but TPV loses its resistance to preserve its characteristics at 120^{o}C aging. It is also determined that aging media is as important as temperature to evaluate the performance of TPV. Moreover, it is decided that the rate of aging directly proportional to detrimental rate is arranged in an order from the slowest to the fastest as distilled water, detergent and shiner solution media.

Keywords: EPDM/PP based TPV, aqueous aging, dynamic vulcanization, aging in detergent solution, aging in shiner solution.

ÖZ

ÇÖZELTİ ORTAMINDA ELASTOMERLERİN HIZLI YAŞLANDIRILMASI

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Tez Danışmanı: Prof. Dr. Teoman Tinçer

Ocak 2007, 115 sayfa

EPDM/PP bazlı TPV kapalı bir sistemde sabit sıcaklık ve basınç altında 80,100 120 derecelerde ve damıtık su, deterjan ve parlatıcı çözeltilerinde yaşlandırılmıştır. Yaşlanma sonucu TPV'nin özelliklerinde değişim Diferansiyel Taramalı Kalorimete (DSC), Isıl Ağırlık Analizi (TGA), Çekme Testi ve Kauçuk Sertlik Testi kullanılarak takip edilmiştir.

DSC analizleri TPV'nin PP bileşeninin yüzde kristallenmesinin 100^{o}C de arttığını fakat kristal yapının 120^{o}C ise bozulduğunu işaret etmiştir. Bunun yanısıra sertlik analizi bu çalışmada kullanılan bütün yaşlandırma sıcaklıklarında su ortamında yaşlandırma sonucunda 120^{o}C'deki yaşlandırma hariç TPV nin sertliğinin neredeyse sabit kaldığını ama deterjan ve parlatıcı solüsyonu ortamında yaşlandırma sonucunda ise TPV'nin yumuşadığı bulunmuştur. Çekme testi sertlik analizini 100^{o}C su yaşlandırması hariç mekanik özelliklerdeki düşüş gözlenmesi ile doğrulamıştır. TGA analizi yüzde kristallenmedeki artışın hava ortamında termal bozunma sıcaklığında bir iyileşmeye sebep olduğunu göstermiştir.

TPV’nin 80^{o}C yaşlandırma ortamında oldukça dayanıklı olduğu ama 120^{o}C yaşlandırma ortamında ise özelliğini koruma yetisini kaybettiği bulunmuştur. TPV nin performansını değerlendirmede yaşlandırma ortamının da sıcaklık kadar önemli olduğu belirlenmiştir. Bunların yanısıra yaşlanma hızının en yavaştan en hızlıya doğru distile su, deterjan çözeltisi ve parlatıcı çözeltisi şeklinde sıralandığı belirlenmiştir.

Anahtar Kelimeler: EPDM/PP bazlı TPV, su yaşlandırması, dinamik vulkanizasyon, deterjan solüsyonunda yaşlandırma, parlatıcı solüsyonunda yaşlandırma.

To My Family

ACKNOWLEDGEMENTS

I would like to wish to express my deepest gratitude to my supervisor Prof. Dr. Teoman Tinçer for his continuous guidance, advice, criticism, encouragements and insight not only throughout this research but also about the life.

I would like to extend my sincere thanks for their valuable suggestions and comments to members of B-36 especially for Mehmet Güçlü for his help to carry distilled water and Binnur Özkan for her help to perform DSC studies.

I would like to express my sincere thanks to my family especially Sevil Ören and Filiz Kılbaş for their great sacrifice, encouragements and moral support during this research.

Also I would like to wish to extend my sincere thanks to Arçelik Ankara Bulaşık İşletmeleri A.Ş and material supplier company Elastron Kimya A.Ş.

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ABREVIATIONS

TPE : Thermoplastic Elastomer
TEO : Thermoplastic Elastomeric Olefins
PP : Polypropylene
EPDM : Ethylene Propylene Diene Monomer
TPV : Thermoplastic vulcanizate
h : Hours
80 WA : 80^{o}C Water Aging
100 WA : 100^{o}C Water Aging
120 WA : 120^{o}C Water Aging
80 DA : 80^{o}C Detergent Aging
100 DA : 100^{o}C Detergent Aging
120 DA : 120^{o}C Detergent Aging
80 SA : 80^{o}C Shiner Aging
100 SA : 100^{o}C Shiner Aging
120 SA : 120^{o}C Shiner Aging
DSC : Differential Scanning Calorimetry
T_m : Melting Temperature
TGA : Thermogravimetric Analysis
SEM : Scanning Electron Microscopy
MFI : Melt Flow Index

CHAPTER I

INTRODUCTION

Polymeric materials play an important role with an increasing rate in material science more than 50 years. Also the importance of polymers and the research on polymers to decrease the cost and to increase the performance have increased day by day.

1.1 Thermoplastic Elastomer (TPE)

One of the most important inventions in polymer science can be accepted as Thermoplastic rubbers or elastomers (TPE). The discovery of TPE was taken place in 1950s. A TPE is a rubbery material with similarity in properties and functional performance with conventional vulcanized rubber, yet it can be processed in a molten state as a thermoplastic polymer at elevated temperature [1].

Most softer TPEs, having less than 90 Shore A hardness, are accepted as true rubbers [2]. Harder TPEs, having greater than 90 Shore A or 38 Shore D hardness, are accepted as impact-modified thermoplastics because they have actual yield point or at least a pronounced ‘knee’. According to these descriptions, TPEs are existed between Thermoset rubbers and Plastics in terms of hardness [2] as shown in Figure 1.1.

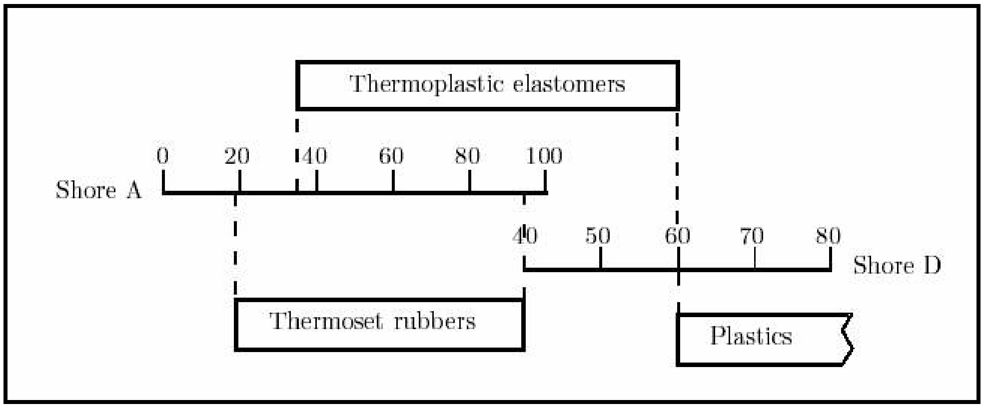


Figure 1.1 Comparison of hardness range of TPEs to those of plastics and conventional thermoset rubber [2]

TPEs based on polyolefin rubber/thermoplastic composition can be classified into two categories. First category consists of simple blends and called thermoplastic elastomeric olefin (TEO) according to ASTM D 5593. Thermoplastic vulcanizate (TPV) is the other category consisting dynamically vulcanized rubber phase and thermoplastic phase according to ASTM D 5046 [1]. In early literature dynamic vulcanizate, vulcanized alloys are the other known names of TPV.

1.2 Comparisons of TPV with TEO

In spite of TEO and TPV belonging to TPE class, there are serious differences between these two classes in terms of many aspects such as structures, mechanical properties, morphology, service temperature, fluid resistance, and usage aim etc.

There are some disadvantages of TEO restricting the usage of this material as a rubbery material. These are [2, 3]:

1. They do not have higher resistance to compression according to ASTM D 395-01 or tension set according to ASTM D 412-98a at used temperature or under prolonged deformation.
2. Manufacturing a material having 70 Shore A or lower hardness is not practical.
3. High ratio of rubber or rubber plus oil to PP decreases the flow characteristics of the mixture then the processability of the material becomes hard.
4. Because of not having crosslinked structure, TEO's swell high degree of fluid from amorphous rubber part.
5. The service temperature does not exceed 80°C.

And the advantages of TPVs over TEO are the following [4]

1. Dynamic vulcanizates eliminate the weakness of the continuous elastomer phase by the help of dynamic vulcanization causing dispersion of fine particles of the vulcanized elastomer to produce softer products with good physical properties.
2. Dynamic vulcanizates enhance the resistance against oils, gasoline or similar fluids in a way of crosslinking elastomer causing insoluble in these fluids.
3. Dynamic vulcanizates show less permanent set properties, which are the ability to stay at the extended position where the applied stress goes.

1.3 The Components of TPV

Commercially mostly used TPVs are Polypropylene (PP)/Ethylene-propylene-diene Monomer (EPDM) based TPVs [3]. They are generally composed of isotactic PP, EPDM, processing oil, reinforcing filler, stabilizers and antioxidants. PP is the thermoplastic and continuous phase while the EPDM is the elastomer and discontinuous phase [3].

PP is one of the most common used polymers in plastic industry. Low cost, low density, its crystalline structure and relatively high melting point (165^{o}C) are the main advantages of PP [4]. However, PP has high glass transition temperature from 0^{o}C to –20^{o}C and is lower in stiffness, which makes PP comparatively brittle. Therefore, in order to improve the low impact strength of PP, it has been blended with elastomers [5]. This is the reason of why TPE is also important in rubber industry.

EPDM (Ethylene-Propylene Diene Monomer) contains ethylene, propylene and a third unsaturated monomer for vulcanization purpose. Ethylene content ranging from 40 to 80%wt EPDM is generally used for commercial purposes. As the ethylene content increases, the polymer crystallinity increases. Conversely, as the ethylene content decreases and the propylene content increases, the polymer becomes more amorphous. Therefore, 62 wt% or greater ethylene containing EPDM is classified as semicrystalline while EPDM containing less than 62% ethylene content classified as amorphous. Semicrystalline EPDM shows higher green strength, higher tensile modulus, and higher hardness compared with amorphous EPDM. However, amorphous EPDM is more flexible at low temperatures, lower in hardness and more elastic compared with semicrystalline EPDM. The third unsaturated monomer is typically conjugated diene allowing the use of sulfur vulcanization. Ethylidene nonbornene (ENB), Dicyclopentadiene (DCPD) and 1, 4-hexadiene (HD) are the most common commercially used dienes. ENB is the most common one due to the allowance of fastest cure rates. All of them have two double bonds. One double bond placed in the main chain for polymerization purposes and the other double bond placed in pendant chain for vulcanization purposes. The amount of diene monomer in EPDM ranges from 0.5 % to 12 %wt. As the diene content in EPDM increases, the cure rate increases [2].

The advantages of EPDM are its thermal stability, low cost, low temperature flexibility and structural similarity (compatibility) with PP [4]. EPDM is the best commercial elastomers used for PP modification [6].

1.4 General Properties of EPDM/PP Based TPVs

TPV's show conventional rubber properties; however, TPV's are processed like thermoplastic materials [3, 7].

TPVs have hetero-phase morphology. They are composed of hard domain, which is thermoplastic component, and soft domain, which is crosslinked elastomer component [3]. The polymer matrix in most cases is semicrystalline and acts as a physical cross-linker for the elastomer phase [7]. Also both thermoplastic and elastomer domain are nonpolar [3].

In preparation of EPDM/PP based TPV, phase inversion techniques are used to make PP continuous and minor components by adjusting the volume and the viscosity of both components [6].

In order to process as a thermoplastic material the thermoplastic phase must be continuous [3]. The continuity of thermoplastic phase provides TPV with ease of processing of thermoplastics even though the amount of rubber in composition is higher or rubber particles are crosslinked [8, 9]. Also the continuous PP phase has an open fiber like microstructure [3]. This microstructure makes TPV show elastic properties [3]. Due to TPVs microstructure, they have attractive elastic properties at room temperatures, high flowability at high temperatures and remelting process for recycle use [6]. On the other hand, the elastomeric phase will be discontinuous with small diameter such as 1 μm crosslinked rubber particles dispersed in a continuous thermoplastic phase [3].

TPVs are also based on non-miscible polymer blends of rubber and thermoplastic like natural rubber and polyvinyl chloride dynamic vulcanizates [10].

The properties of saturated main chain, the excellent stability against heat oxygen and ozone can be explained by EPDM components. While high melting point, high crystallinity, the rigidity, the heat and oil resistance can be explained by PP component [10].

Dai (2003) stated that the noncrystalline region of PP and EPDM should be partially miscible because of the similarity in chemical structure of PP and EPDM having polypropylene segments. However, the stronger interaction between two phases was found in 50 or higher EPDM weight percentage. If the weight percent and crystallinity of PP are higher, the molecular chain motion is significantly restricted for the noncrystalline portion of PP. Therefore, the interaction between two phases becomes weaker because the diffusion and entanglement of molecular chains in amorphous regions for each component become more difficult [11].

Also a SEM study of the work of Katbab, Nazockdast and Bazgir showed that the continuous thermoplastic PP phase with dispersed rubber EPDM phase was seen at EPDM/PP weight ratio 80/20 and 70/30 for unvulcanized blends [8]. 60/40 weight ratio of EPDM/PP showed that two co-continuous phase were formed for unvulcanized blends [8]. As a result, 80/20 and 70/30 % ratio EPDM/PP composition is one of the best compositions for soft TPVs [3].

TPVs have a broad range of hardness from 35 Shore A to 60 Shore D [2]. The lower set or sealing applications of TPVs, softer that has 80 Shore A or below, have a lower compression sets than thermoset rubber or TEOs as seen from the Figure 1.2 [3].

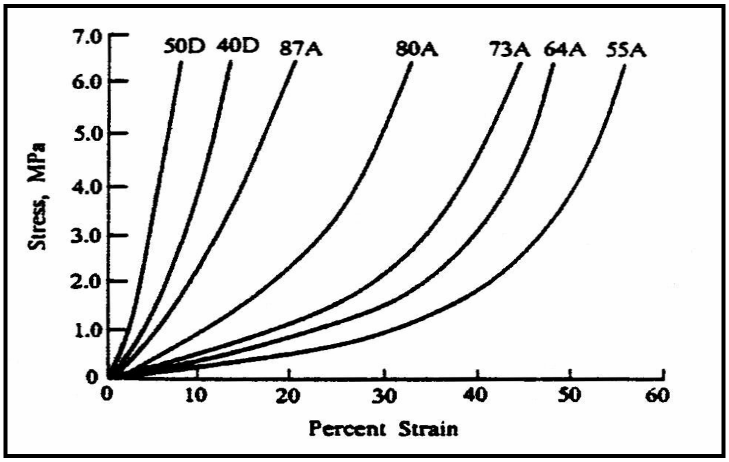


Figure 1.2 Compression stress-strain curves for different hardness EPDM/PP TPVs [3]

The upper service temperature of EPDM/PP based TPVs are up to melting point of PP phase which is almost 165°C. In air medium the upper service temperature is 150°C for limited period of time and the upper service temperature is 125 to 135°C for extended period of time according to some aging studies followed by measurement of hardness and tensile properties retention as seen from Figure1.3 [3].

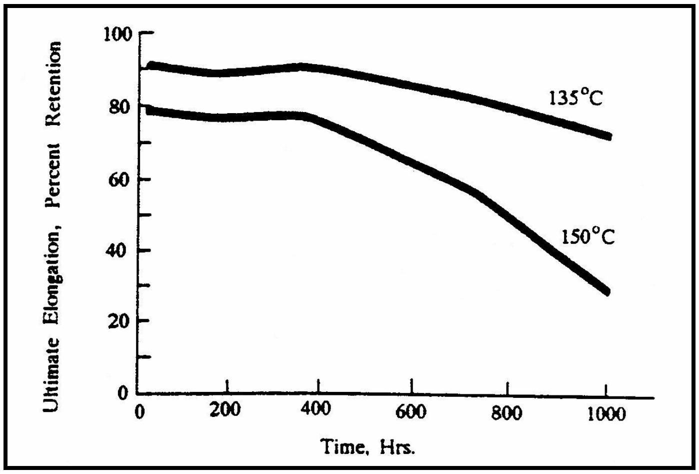


Figure 1.3 Retention of ultimate elongation according to ASTM D 412-98a as a function of time [3]

The lower service temperature of EPDM/PP based TPVs depend on the glass transition temperature of EPDM that is almost –60°C [4].

EPDM/PP based TPVs have higher resistance to polar organic fluids and aqueous media such as acids, alkalis, and salt solutions. However, they swell significantly in hydrocarbon media but even better than EPDM/PP blends or EPDM thermoset rubber if the EPDM phase is fully vulcanized. In addition to this disadvantage, EPDM/PP based TPVs exhibit lower resistance to halocarbons and highly corrosive media such as fuming sulfuric acid [3].

Butyl rubber based TPVs at about the same hardness with EPDM/PP based TPVs are twelve times less permeable to air or oxygen and four times less permeable to moisture [3].

1.4.1 The advantages of TPVs

The advantages of EPDM/PP based TPVs in the literature can be summarized as [10, 12]

- High range of usage temperature from –50 to 120-150°C
- Low value of permanent set
- Moderate stability against weathering including ozone action and various aggressive agents
- Composed of easily accessible raw materials
- Placing in the moderate region in terms of cost/performance ratio
- Having flexible production technology
- Having less waste in production compared with vulcanized elastomers and the waste being easily recycle
- Easily recyclable

The other relevant properties and processing information of TPV was given in Appendix A.

1.7 Aim of the Study

The aim of this research is to study the performance of dynamically peroxide vulcanized EPDM/PP Thermoplastic vulcanizate in distilled water media, detergent solution media and shiner solution media at different temperatures. The performance of EPDM/PP based TPV is evaluated by

-Thermal properties change
-Mechanical properties change
-Hardness change
-Morphological properties change

CHAPTER II

EXPERIMENTAL

2.1 Materials

EPDM/PP based TPV strips of 2.50 mm thickness and 2.46 cm wide were supplied by ELASTRON Kimya A.Ş. The recipe of TPV was given in Table 2.1 and the properties of TPV were summarized in the Table 2.2.

Table 2.1 The recipe of TPV

Ingredient	Weight %
EPDM	62
PP	15
Processing Oil	15
Talc	4.5
Heat Stabilizer	1.0
UV Stabilizer	0.4
Peroxide Crosslinking Agent	1.4
Carbon Black	1.0

Table 2.2 Properties of EPDM/PP based TPV used in our study

Property	Value
Density	0.9186 gram/cm^3
MFI	1.5 gram/ 10 minutes
Ash Content	8.75 %
Hardness	55 Shore A

2.2 Aging Apparatus

The aging vessel is a closed system like a pressure cooker. The vessel is composed of a heater with thermostat stabilizer and a manometer measuring the pressure of the aging medium. Total volume of the aging vessel is 50 L. 38 L of the volume was filled with water. The TPV specimens were hung perpendicular to base direction. Three different aging medium were used; distilled water, detergent solution and shiner solution.

The pH of aging medium measured at 31^{o}C are given Table 2.3 below

Table 2.3 The pH values of aging medium

Aging Medium	pH
Distilled Water	7.0
Detergent Solution	10.7
Shiner Solution	6.2

Preparation of detergent solution

In order to prepare a detergent solution for aging media 15.8 gram of dishwasher machine solid detergent was used per 4 L of pure water. Hence, 150 gram of dishwasher machine solid detergent was mixed with 38 L water.

Preparation of shiner solution

The shiner solution for aging media was prepared by adding 0.8 cc of dishwasher machine liquid shiner to 1 L of pure water. Therefore, 30 cc of dishwasher machine liquid shiner was added to 38 L water.

The aging process was done at three different temperatures, i.e. 80, 100, and 120^{o}C. Because aging studies were done in three different temperatures and three different medium the pressure in aging machine changed. The produced pressure in three different medium and three different temperatures are given in Table 2.4 below.

Table 2.4 Produced pressure with temperature change

Temperature (^{o}C)	Water Pressure (in bar)	Detergent Solution Pressure (in bar)	Shiner Solution Pressure (in bar)
80	0.4	0.5	0.45
100	0.8	1.2	1.0
120	1.2	2.5	2.0

The samples were tested at 100, 200, 300 and 350 hours (h) of aging. The solution was changed periodically for every aging.

2.3 Thermal Analysis

2.3.1 Differential Scanning Calorimetry (DSC) Analysis

DSC Thermograms were recorded on a Dupont Thermal Analyst 2000 DSC 910S. The samples were analyzed under inert N_2 atmosphere from room temperature to 200^oC with a heating rate of 20^oC/min. The melting temperature (T_m), onset temperature (T_{onset}) and melting enthalpies were obtained from the thermogram.

2.3.2 Thermogravimetric Analysis (TGA)

TGA analyses were done by the Perkin Elmer Pyris 1 TGA instrument. The samples were heated from room temperature to 800^oC with a heating rate of 20^oC/min to follow the path of chemical changes with heat.

2.4 Mechanical Testing

The tensile properties of the aged and unaged EPDM/PP based TPV were determined using a Lloyd LS 5000 computer controlled tensile testing machine. The standard dumbbell shapes strips were cut from these strips along the processing direction. The gauge length was 20 mm and the sample width and thickness were 2.75 and 2.50 mm, respectively.

2.5 Hardness Analysis

Shore A measurements were carried out by Rubber Hardness Tester made by Kori Seiko Mfc.Co.Ltd according to ASTM D 1415-05.

2.6 Scanning Electron Microscopy (SEM) Study

Surface morphologies of tensile tested fracture surfaces of EPDM/PP based TPV specimens after protective coating were inspected by a JEOL model JSM-6400 scanning electron microscope.

CHAPTER III

RESULTS AND DISCUSSION

3.1 The Effect of Aging on Thermal Properties

Thermal properties of polymer are closely related with structure and particularly thermal history of samples. DSC and TGA are the most widely and conventionally used thermal analysis techniques. In DSC technique the heat flow into or out of a small (10 – 20 mg) sample is measured as the sample is subjected to a programmed linear temperature change. It measures the heat change by the specimens while thermal transition takes places. Also it is worth mentioning DSC to determine the thermodynamic properties of the sample. It is dedicative for some properties such as heat of fusion, crystallization, melting, the glass transition temperature and other secondary transitions occurred in polymeric structures. In TGA the weight change of the sample as a function of temperature are measured for assessment of thermal stability and decomposition temperature [13].

Thermal properties of aged and unaged TPV samples were determined by Differential Scanning Calorimeter (DSC) technique and Thermogravimetric Analysis (TGA).

3.1.1 DSC Analysis

Aged and unaged EPDM/PP based TPV specimens were left in distilled water at 8 days renewing water every 24 h to get rid of detergent and shiner residues penetrated into specimens during aging. Then they were analyzed by DSC to investigate the heat of fusion, crystallinity of PP component, and T_m of PP component in specimens.

Percent crystallinity of PP in EPDM/PP based TPV can be calculated as

$$\text{Percent crystallinity} = \Delta H_{TPV} / (\Delta H_{PP} \,.\, m_{PP})$$

where ΔH_{TPV} is the actual heat of fusion of the tested specimens, ΔH_{PP} is the heat of crystallization of 100% crystalline PP accepted as 209 J/g and m_{PP} is the mass fraction of PP in TPV [6, 14].

DSC thermogram of aged and unaged TPV specimens are shown in figures from Figure B.1 to Figure B.5 in Appendix B and the graphs drawn by using these data are shown in figures between Figure 3.1 and Figure 3.6. Also variation of T_m of PP component in TPV versus aging and variation of percent crystallinity of PP in TPV versus aging time graphs drawn by using all cases aging temperatures and aging medium in one graph were given in Figure C.1 and C.2 respectively in Appendix C.

Variations of T_m of PP component in TPV at 80, 100 and 120°C water aging was given in Figure 3.1. There was a very slight increasing trend in T_m of PP component in TPV exposed to 80°C water aging (80 WA). It was noted that these changes in T_m are apparently minute but very consistent with respect to aging temperature and time. This increase started at 100 hours aging time, however, T_m values preserved until 300 h. At 350 hours aging time there was a sharp increase in T_m of PP component in TPV. On the other hand, at 100°C water aging (100 WA) an increase at 100 h aging was observed. Then, T_m of PP component in TPV decreased at 200 h and then remained almost constant at the end of aging time with small changes. At 120°C water aging (120 WA) there was a linear decrease in T_m, but a sharp increase in T_m at 300 h followed with a final decrease at the end of aging time.

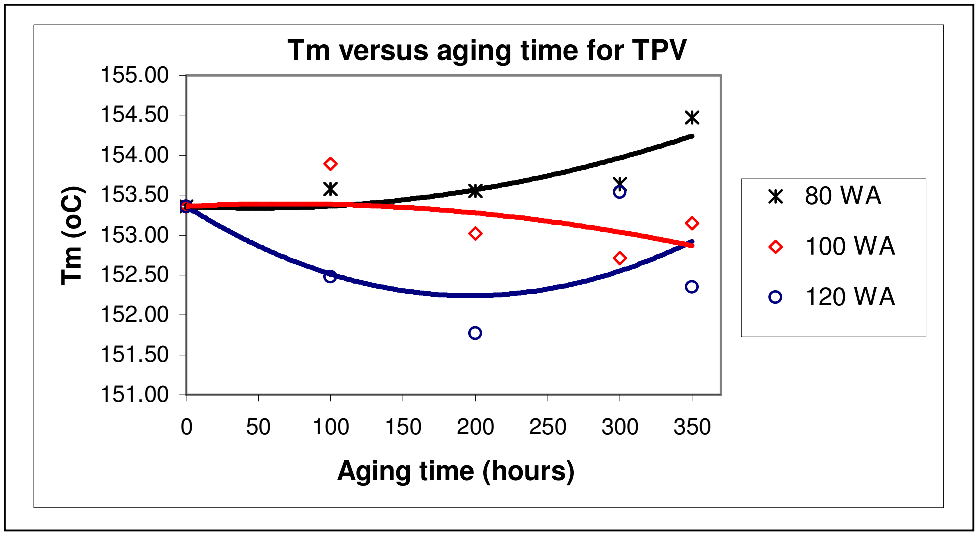


Figure 3.1 Melting temperature of PP in TPV versus aging time at water aging media

The change of T_m of PP component in TPV exposed to 80, 100 and 120°C detergent aging was given in Figure 3.2. The decrease in 80 and 120°C were similar and lower than 100°C detergent aging at the beginning. The 80°C detergent aging (80 DA) showed a sharp decrease initially and followed by a slow increase. Therefore, T_m of PP component in TPV appeared to be preserved at 350 h. The 100°C detergent aging (100 DA) showed a linear and moderate decrease in T_m. The 120°C detergent aging (120 DA) showed, almost similar to

80°C DA, a fast decrease in T_m of PP component in TPV and recovered slightly at 300 h. This increase in T_m at 300 h followed again a decrease at the end of aging time reaching lowest T_m at detergent aging media.

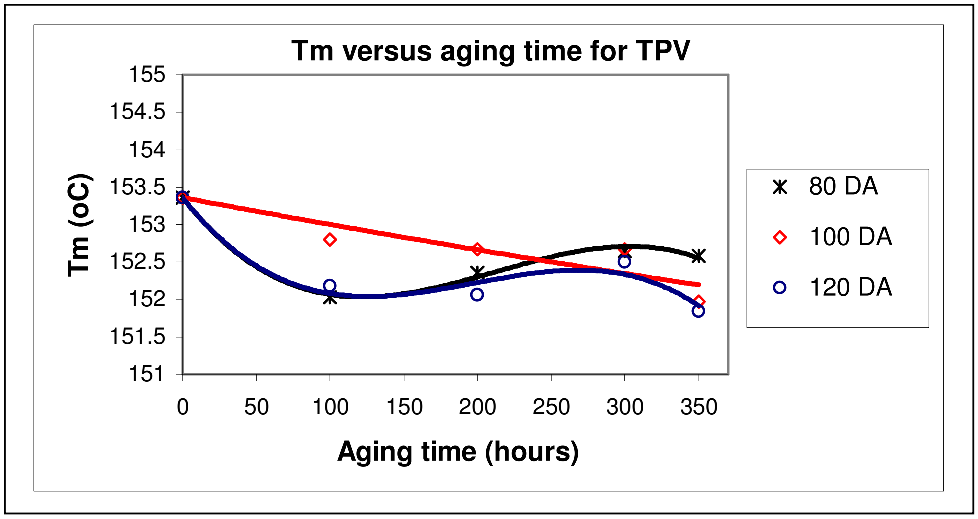


Figure 3.2 Melting temperature of PP in TPV versus aging time at detergent aging media

The decrease in T_m of PP component in TPV exposed to 80, 100 and 120°C shiner aging was seen more clearly. The decreasing trend was sharper with increasing temperature. At 80°C shiner aging (80 SA), T_m of PP component in TPV was recovered after 200 h with a slight reduction. After this minimum in T_m at 200 hours, the recovery showed an increasing trend in T_m at the end of aging time. The decrease in T_m of PP component was rather steadily and linear at 100°C shiner aging (100 SA). Although the changes at 120°C shiner aging (120 SA) showed a fast decrease in T_m initially, it appeared to remain at this low T_m.

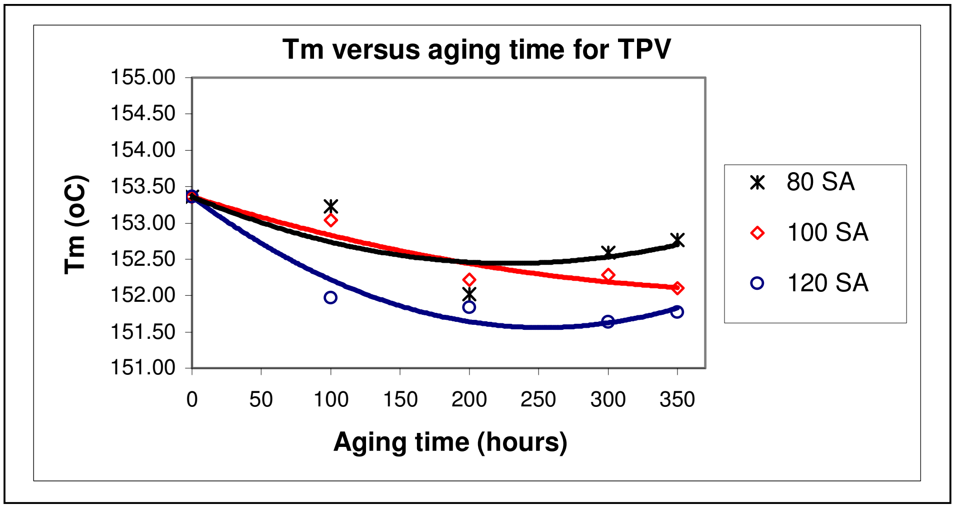


Figure 3.3 Melting temperature of PP in TPV versus aging time at shiner aging media

Within the experimental error limits, the same analyses were repeated two or three times to ensure these changes for different samples at the same aging time. Higher the aging temperature from 80 to 120^{o}C with time we observed decrease in T_m, slower in 100^{o}C but faster in 120^{o}C except in the last two aging times. Furthermore, although the range in the change of T_m of PP in the matrix is ± 2^{o}C for all cases of temperatures and medium, the trend of T_m variation seemed to be preserved in detergent and shiner solution aging.

The variation of percent crystallinity in distilled water given Figure 3.4. The percent crystallinity of PP in TPV at 80 WA had almost no change and at 120 WA percent crystallinity showed a little increase trend compared to 80 WA. However, the 100^{o}C water aging showed a significant and fast increase in crystallinity in PP of TPV.

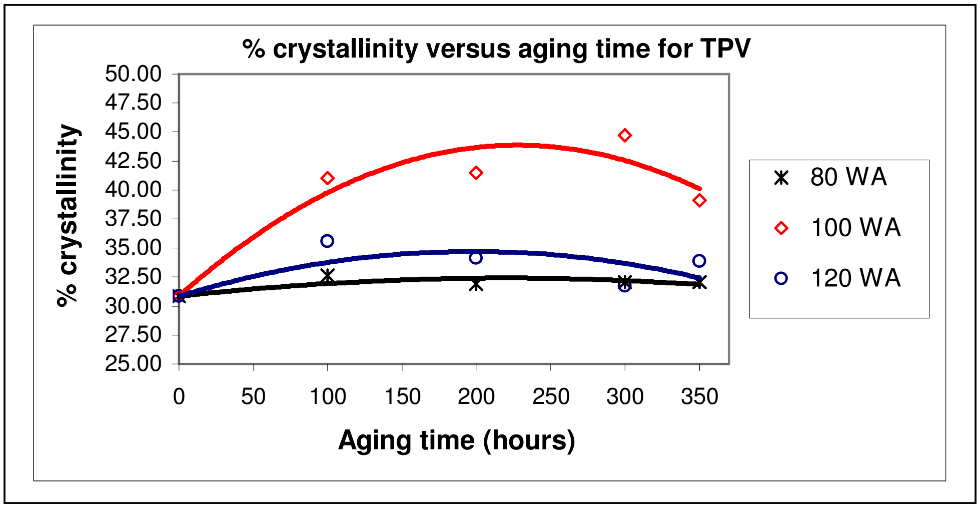


Figure 3.4 Percent crystallinity of PP in TPV versus aging time at water aging media

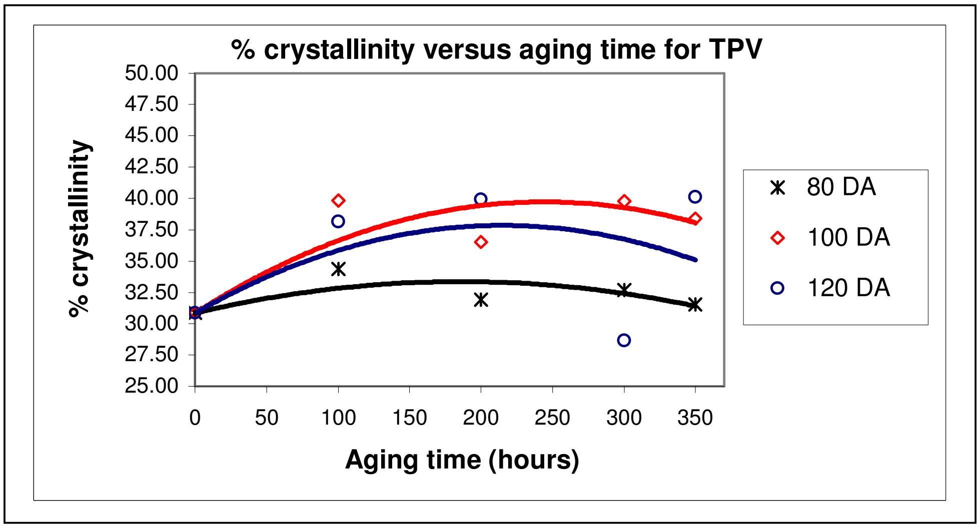


Figure 3.5 Percent crystallinity of PP in TPV versus aging time at detergent aging media

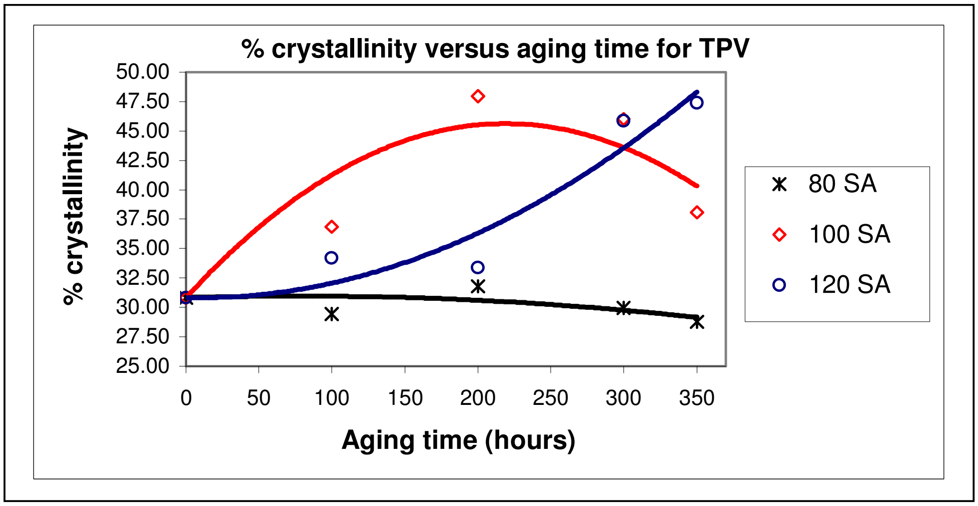


Figure 3.6 Percent crystallinity of PP in TPV versus aging time at shiner aging media

Although the 80°C detergent aging resembled to the 80°C water aging having no considerable change in percent crystallinity of PP, the minor rise of percent crystallinity of PP in detergent solution at this temperature was higher than the others. 100 and 120°C detergent aging showed very similar variation in terms of percent crystallinity of PP in TPV except 300 h datum for 120°C detergent aging. The highest and fastest increase in crystallinity of PP observed at 100 and 120°C detergent aging at 100 h. The percent crystallinity then remained almost unchanged afterwards with slight fluctuations for further aging.

Percent crystallinity variation in shiner solution is given in Figure 3.6. Slightly decreasing trend of percent crystallinity of PP in TPV at 100°C shiner aging was seen. However, an increasing trend was seen at 120°C the beginning of aging. The 100 SA showed a fast increase and reduced a little afterwards but still it is in the highest change to 350 h. The increase in percent crystallinity in shiner solution apparently competes for the 100°C and 120°C aging. This may be due to the nature of the media, having 6.17 pH, a slightly acidic compared to water and detergent solution. Drastic increase at 120 SA was observed at th mid times of aging at 300 h. Therefore, the highest and fastest increase in crystallinity of PP was observed in shiner aging for 100°C and 120°C.

Percent crystallinity of PP in TPV showed in an increasing order in terms of temperature as 80, 120 and 100°C, respectively. The biggest increase in percent crystallinity at 100°C was due to PP's cooling crystallinity observed in temperature range between 100 and 110°C given in the literature. We observed that the crystallization temperature of PP appeared in temperature range of 100-110°C during cooling scanning of DSC experiments with both heating and cooling rate of 20°C/min. Therefore, we can conclude that the aging temperature of 100°C is very favorable for crystallization of PP in the matrix. At 100°C percent crystallinity of PP in the matrix indicated a gradual increase while T_m showed a slight decrease up to 300 h of aging. Yet, the longer aging time (300-350 h) causes inevitable deterioration of the sample, yet possibly healing the defective sites of crystalline parts.

3.1.2 TGA Analysis

Aged and unaged EPDM/PP based TPV specimens were left in distilled water at 8 days renewing water every 24 h to get rid of detergent and shiner residues penetrated into specimens during aging like performing in DSC analysis. Thermal degradation oil and EPDM/PP blend were determined by using derivative of TGA thermogram. TGA analysis of only unaged, 100 and 300 h aged TPV samples were carried out in this work. 3 peaks were seen by the help of thermograms by taking the derivative of weight with respect to time. The first and the second peak observed in our TGA thermograms were due to degradation of processing oil presented in TPV to improve processability and to reduce cost [15]. The area under the first curve was more than the second one, which was due to the heterogeneity of the oil distribution in TPV. The third peak had the highest peak area. Therefore, the initial change in TGA in TPV thermograms referred [15] to oil degradation and the third peak, highest peak area, was due to the degradation of EPDM/PP blend [15]. A carbonaceous residue, approximately 8.0 % of the initial weigh, was detected at the end of each run. According to TGA thermograms of our aged samples, the residual loss of processing oil degradation was found under N_2 atmosphere about 30-40 % and in air about 20-30 %. However, the residual loss of processing oil degradation for unaged TPV was found under N_2 atmosphere about 25 % and in air about 20 % in our work. These indicated that not only oil degradation occurred initially but also EPDM/PP blend started to degradate. TGA thermograms for unaged TPV used in our study under N_2 atmosphere and in air were given in Figure 3.7 and Figure 3.8.

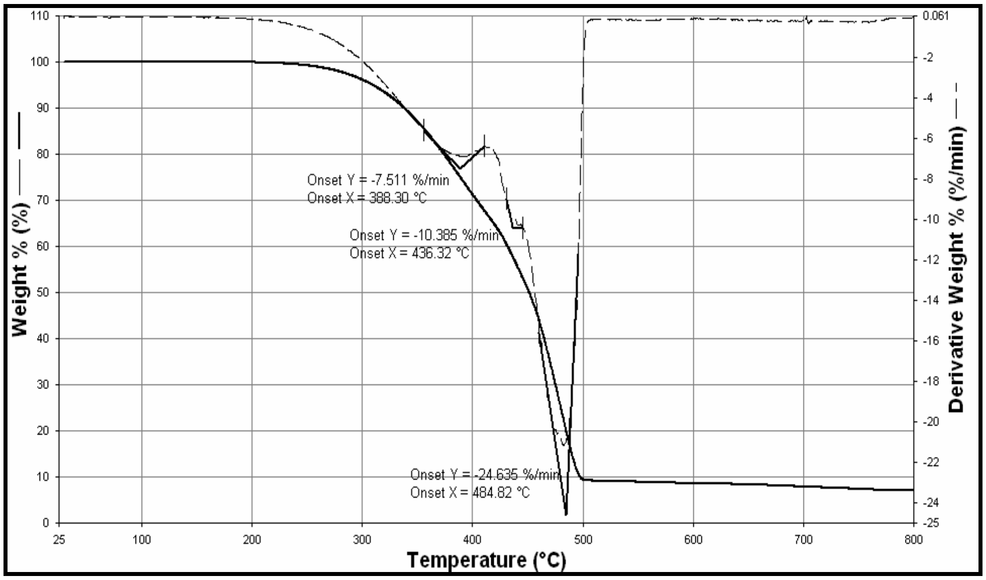


Figure 3.7 TGA Thermogram of unaged TPV in N_2 atmosphere

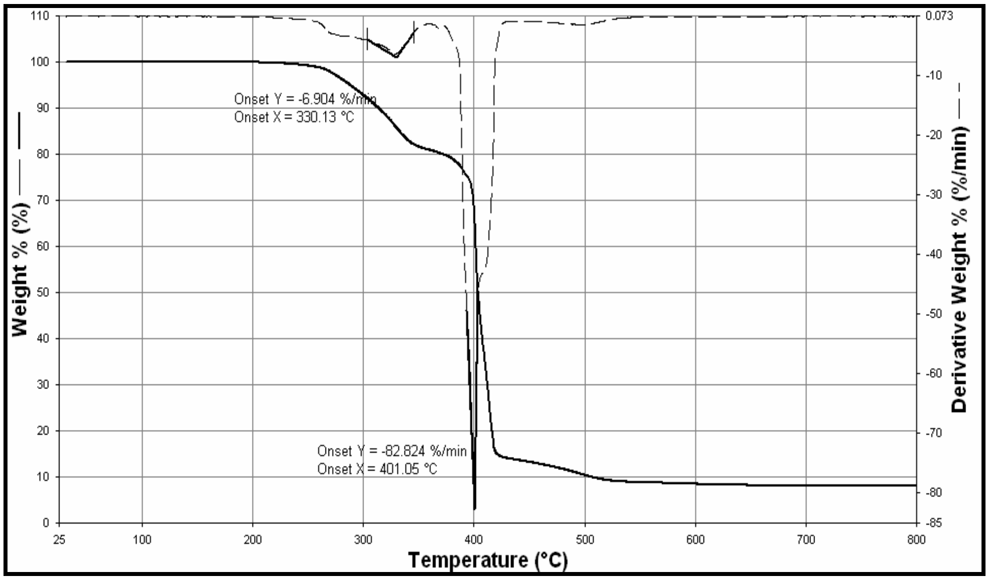


Figure 3.8 TGA Thermogram of unaged TPV in air

3.1.2.1 Oil Degradation Temperature under N_2 Atmosphere and in Air

The change at oil degradation temperature was given in Figure 3.9, Figure 3.10 and Figure 3.11.

Oil degradation temperature for 80°C DA seemed to be remained unchanged. While oil degradation temperature at 80°C WA decreased gradually, an increase was observed initially and then recovered to unaged level at 300 h for 80°C SA.

At 100°C aging, gradual decrease trend observed at 100°C WA was similar to 80°C WA but faster than 80°C WA reaching lowest oil degradation temperature among 100°C aging studies. However, a moderate decrease higher than 100 WA was observed at 100 h at 100°C for both SA and DA preserved up to 300 h.

Oil degradation temperature order at 100°C aging at 100 h was from the highest to lowest as water aging, detergent aging, and shiner aging; however, oil degradation temperature at 120°C aging at 100 h specimens was found to be just reverse of this i.e. as shiner aging, detergent aging, and water aging, respectively. Although the reduction observed at 100h seemed to be constant for detergent and shiner solution, moderate recovery at 300 h was seen for water aging being higher than detergent and shiner solution level.

The variation of oil degradation temperature depends on aging temperature in detergent solution where faster falling was observed with increasing aging temperature under inert nitrogen atmosphere. Also it was indicated that increase in temperature from 80 to 100°C in shiner solution deteriorated oil degradation temperature while temperature increase from 100 to 120°C did not affect oil degradation temperature having almost equal oil degradation temperatures at both 100 and 300 h.

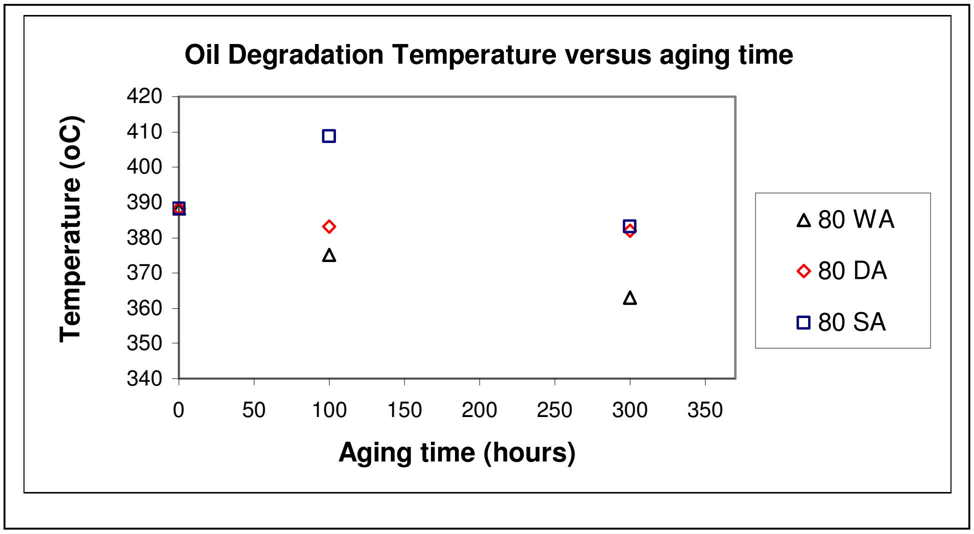


Figure 3.9 Variation of oil degradation temperature versus aging time under N_2 atmosphere at 80°C water, detergent and shiner aging

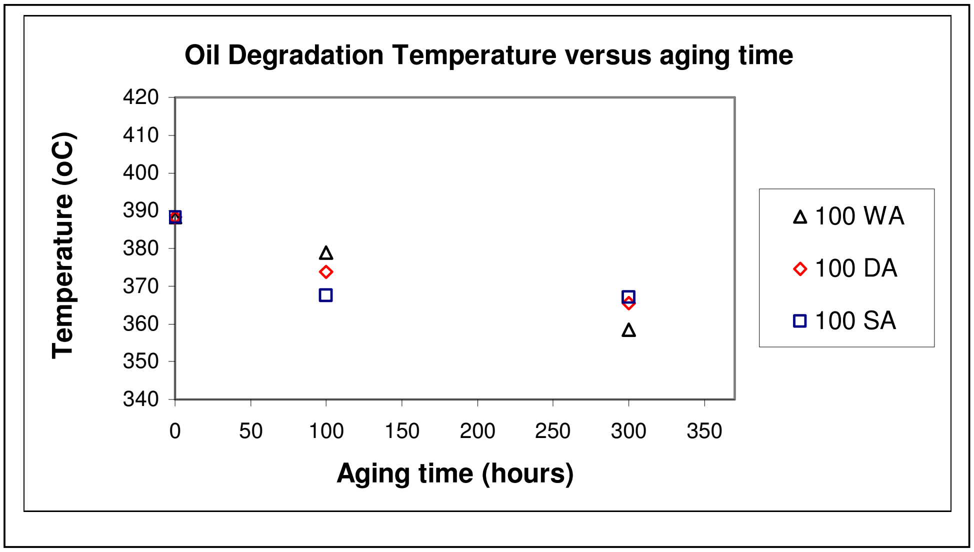


Figure 3.10 Variation of oil degradation temperature versus aging time under N_2 atmosphere at 100°C water, detergent and shiner aging

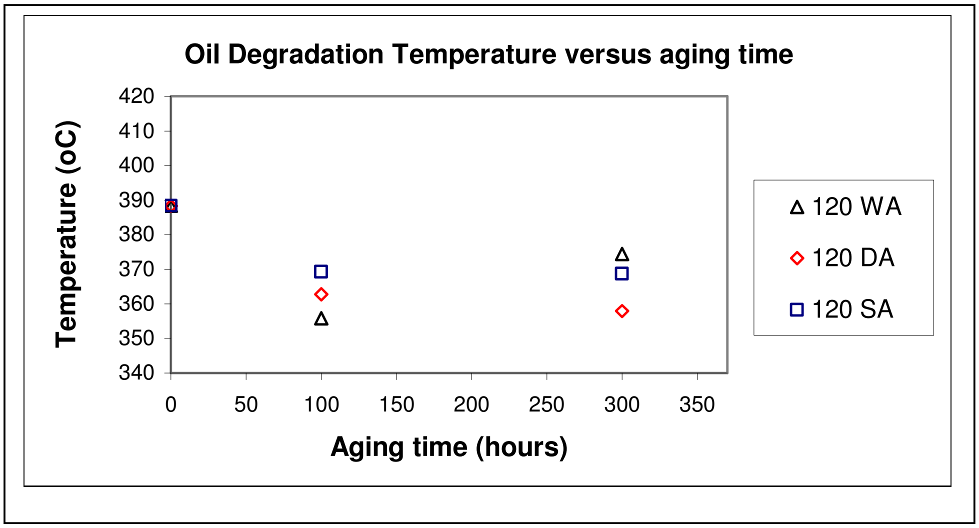


Figure 3.11 Variation of oil degradation temperature versus aging time under N_2 atmosphere at 120°C water, detergent and shiner aging

The variation of oil degradation temperature in air was shown in Figure 3.12, Figure 3.13 and Figure 3.14. Oil degradation temperatures of aged TPV in all medium at 80^{o}C were seemed to be remained constant. On the contrary, there was an increasing trend in oil degradation temperature at 100^{o}C aging TPV due to the increase in percent crystallinity confirmed by DSC analysis. Whereas, step by step augmentation observed in detergent and shiner solution caused oil degradation temperature to reach almost as 340^{o}C, the oil degradation temperature was found to reach 360^{o}C at 100 WA at 100 h and remained unchanged at 300 h aging. This is probably due to the increased crystallinity in PP matrix which acts as a protective media although it melts about 160^{o}C. Similar to 100^{o}C aging, rising of oil degradation temperature was observed at 120^{o}C aging due to percent crystallinity increase again verified by DSC analysis. The trend and the reached values for 120 DA and SA were the same as 100^{o}C ones. However, gradual and slowest increase was observed for 120^{o}C water aging having 335^{o}C oil degradation temperature at 300 h being lower than 120^{o}C DA and SA.

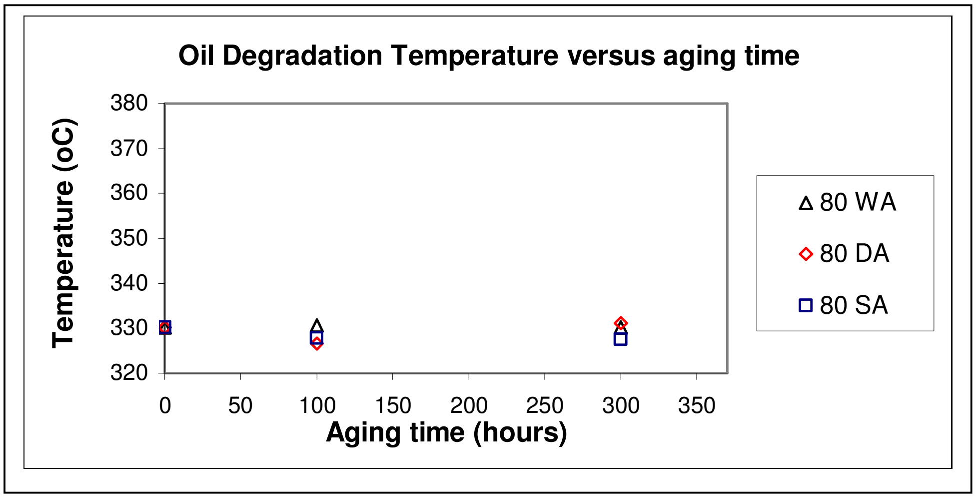


Figure 3.12 Variation of oil degradation temperature versus aging time in air at 80^{o}C water, detergent and shiner aging

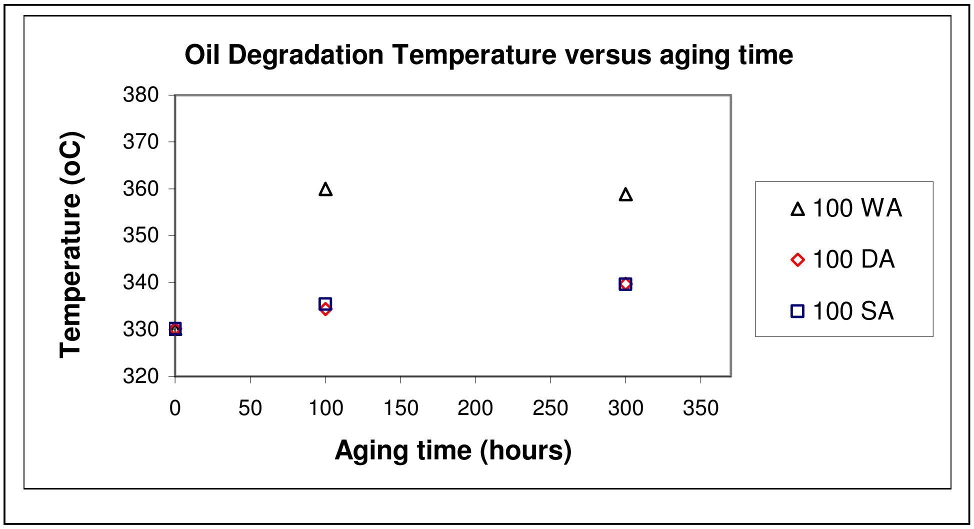


Figure 3.13 Variation of oil degradation temperature versus aging time in air at 100°C water, detergent and shiner aging

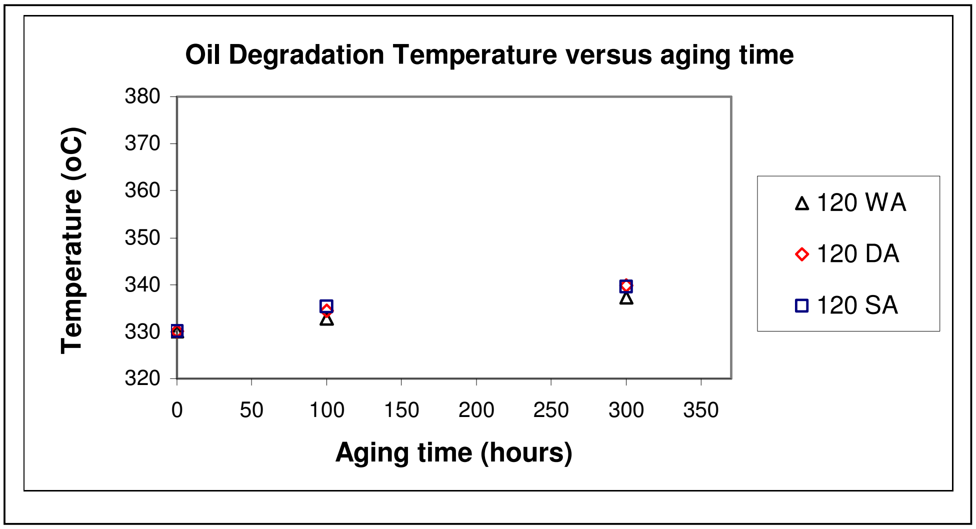


Figure 3.14 Variation of oil degradation temperature versus aging time in air at 120°C water, detergent and shiner aging

3.1.2.2 EPDM/PP Blend Degradation Temperature under N_2 Atmosphere and in Air

EPDM/PP blend degradation temperature variations under N_2 atmosphere were given in Figure 3.15, Figure 3.16 and Figure 3.17.

Though EPDM/PP blend degradation temperature preserved at 100 h in all medium (distilled water, detergent and shiner solution) at 80^oC aging, EPDM/PP blend degradation temperature in distilled water and shiner solution decreased while preservation was observed in detergent solution at 300h. Almost 5^oC fall in EPDM/PP blend degradation temperature at 80^oC shiner aging was confirmed by DSC analysis meaning slight decrease in percent crystallinity of PP component in TPV. At 80^oC aging for detergent solution, slight increase in EPDM/PP blend degradation temperature observed in TGA was verified by DSC analysis meaning slight increase in percent crystallinity of PP component in TPV. Gradual and faster falling in EPDM/PP blend degradation was observed at 80^oC WA.

In spite of gradual decreasing trends of EPDM/PP blend degradation temperature at 100^oC DA reaching the lowest value among 100^oC aging studies, the degradation temperature for 100^oC water and shiner aging after this fast decrease observed at 100 h, remained constant. The faster fall was observed in distilled water at 100^oC aging compared with shiner solution at 100^oC aging.

120^oC WA and SA testing showed a slight increasing trend after a decrease observed at 100 h. While EPDM/PP blend degradation temperature surpassed the unaged value in distilled water at 120^oC aging, EPDM/PP blend degradation temperature recovered towards unaged value at 120 SA. A fastest reduction in EPDM/PP blend degradation temperature at 300 h was observed in detergent solution at 120^oC aging reaching the lowest value among 120^oC aging studies.

It was determined that EPDM/PP blend degradation temperature behaviors at 100, 120°C DA and SA were seemed to be opposite to 80°C aging ones for each of them. While EPDM/PP blend degradation temperature in shiner solution at 100 and 120°C aging seemed to maintain due to acidic characteristic of residues of shiner molecules which caused to saturate the chain providing resistance against degradation, moderate loss at 100°C aging and substantial loss at 120°C aging was observed in EPDM/PP blend degradation temperature in detergent solution. The decrease in detergent solution was probably result of the fact that more hydrogen atoms were extracted from the saturated chain because of the basic nature of residues of detergent molecules leading to worsen of EPDM/PP degradation temperature.

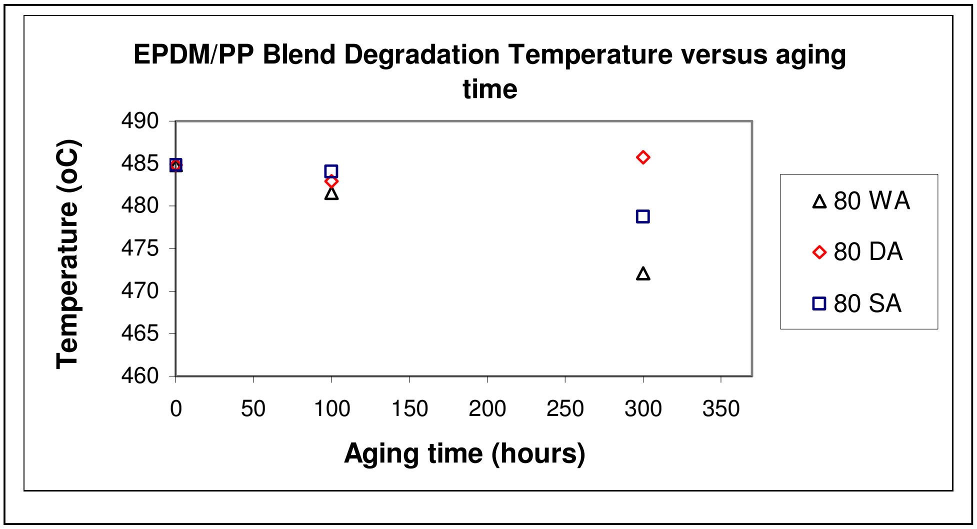


Figure 3.15 Variation of EPDM/PP blend degradation temperature versus aging time under N_2 atmosphere at 80°C water, detergent and shiner aging

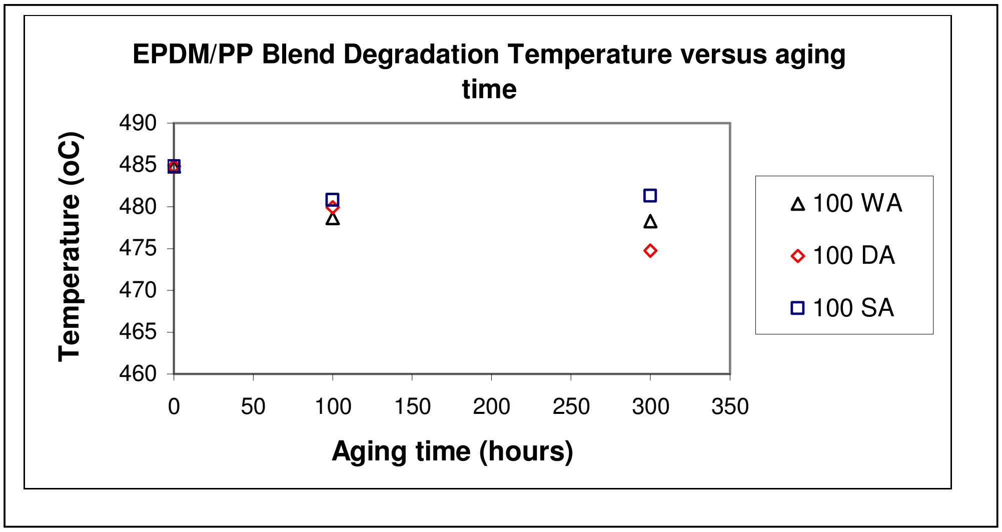


Figure 3.16 Variation of EPDM/PP blend degradation temperature versus aging time under N_2 atmosphere at 100°C water, detergent and shiner aging

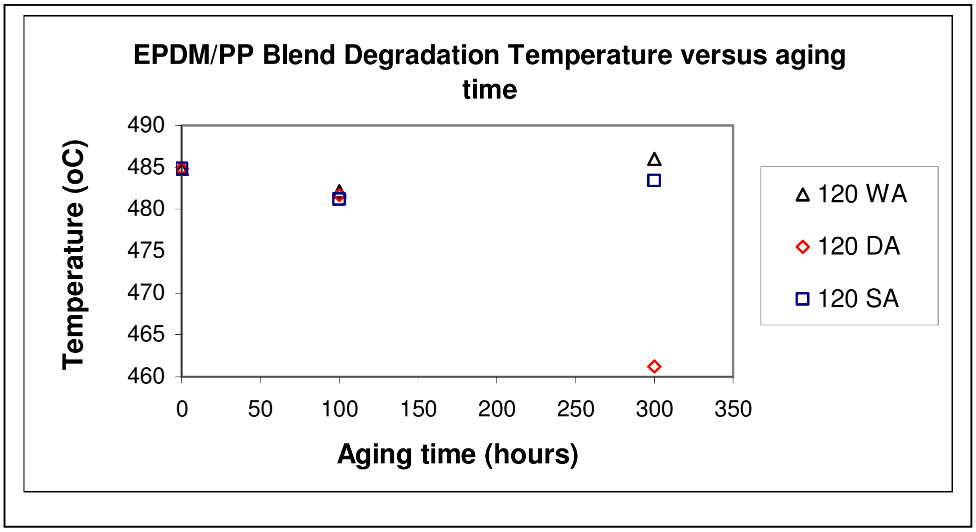


Figure 3.17 Variation of EPDM/PP blend degradation temperature versus aging time under N_2 atmosphere at 120°C water, detergent and shiner aging

The variation of oil degradation temperature in air was shown in Figure 3.18, Figure 3.19 and Figure 3.20. EPDM/PP blend degradation temperature remained almost constant at 80^{o}C aging. On the other hand, it was determined that the fast augmentation, which was observed at 100 h in EPDM/PP blend degradation temperature, maintained by slight increase at 300 h for 100 DA and SA. However, in distilled water, the degradation temperature reached 460^{o}C which was the highest ever recorded degradation temperature. This drastic rise in degradation temperature at 100^{o}C could be attributed to increase in percent crystallinity of PP in TPV which was verified by DSC studies. At 120^{o}C aging slight increase observed at 100 h in distilled water preserved up to 300 h. Although increase at 100 h at 120 DA as fast as 120 WA, EPDM/PP blend degradation temperature at 300 h decreased below the unaged value in detergent solution. At 120 SA moderate reduction in EPDM/PP blend degradation temperature almost 380^{o}C at 100 h recovered to the value of 300 h at 120 DA. Therefore, thermal degradation temperatures of EPDM/PP blend in air seemed to show more resistance compared with N_2 atmosphere, which is probably explained by the fact that oxidized oil enhanced thermal degradation temperature of EPDM/PP blend in air more than under N_2 atmosphere. This behavior is valid not only in EPDM/PP degradation temperature but also in oil degradation temperature in air.

Also it was dedicated from TGA Thermograms that as phase separation between EPDM and PP phases destroying homogeneity of EPDM/PP blends happened in TPV exposed to aging there was a shoulder on the main degradation peak of EPDM/PP blends in air. This kind of behavior was detected firstly at 100 DA and 120 SA initial aging time at 100 h. Such a shoulder formations was also observed at 120 DA at 300h.

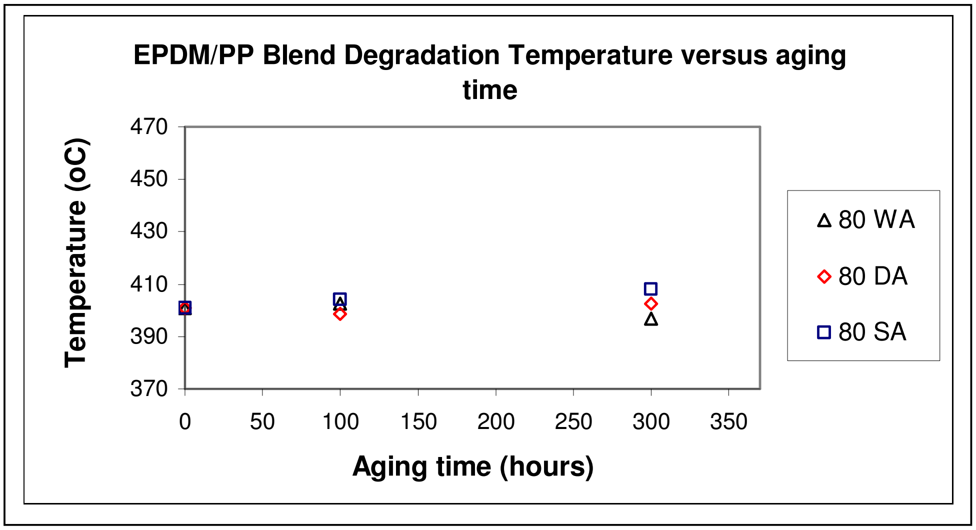


Figure 3.18 Variation of EPDM/PP blend degradation temperature versus aging time in air at 80°C water, detergent and shiner aging

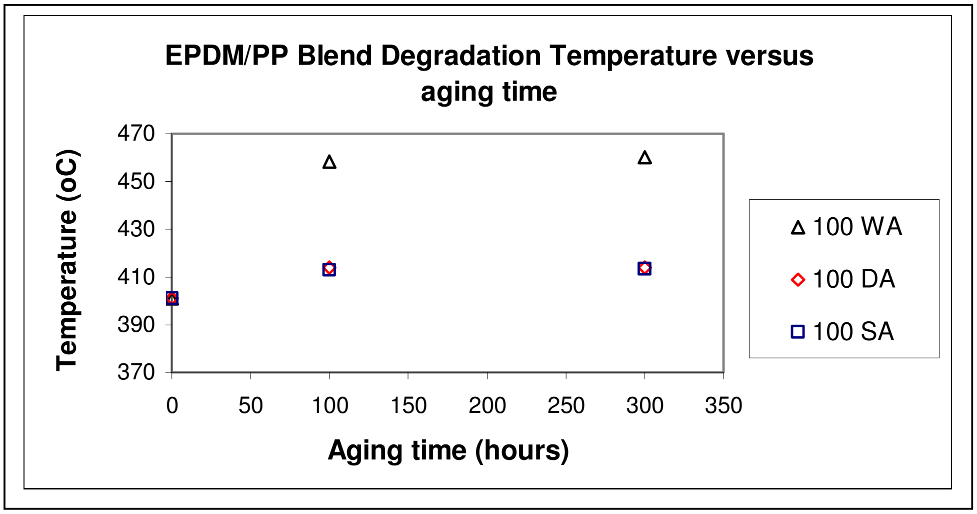


Figure 3.19 Variation of EPDM/PP blend degradation temperature versus aging time in air at 100°C water, detergent and shiner aging

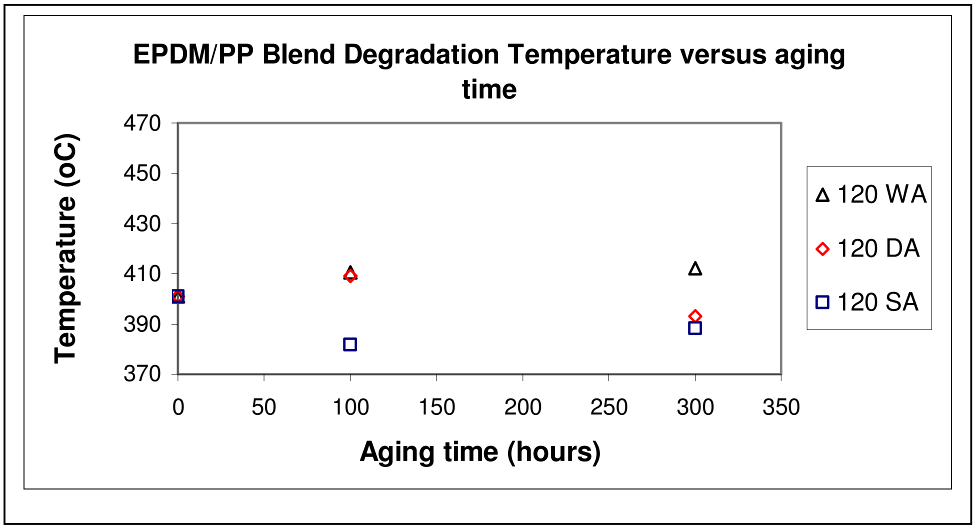


Figure 3.20 Variation of EPDM/PP blend degradation temperature versus aging time in air at 120^{o}C water, detergent and shiner aging

3.1 The Effect of Aging on Mechanical Properties

The mechanical behavior variation of aged and unaged EPDM/PP based TPV were followed by tensile testing which was carried out at room temperature at the end of 100, 200, 300 and 350 aging h collected specimens.

100% modulus (tensile strength at 100% elongation) and 300 % modulus (tensile strength at 300% elongation) according to ASTM D 412-98a, percent elongation at break and stress at break data were determined on the stress-strain curves according to tensile testing results. Additionally, the change in the hardness was followed by Shore A hardness. Graphs drawn by using all cases of aging temperature and aging medium to show the variation of mechanical properties and hardness were given in figures between Figure C.3 and Figure C.7 shown in Appendix C. Also standard deviations of tensile testing data and stress versus % gauge length curve of unaged TPV, 350 h 120°C detergent and shiner aged TPV were given in Appendix D.

Generally for the polymers especially crosslinked ones the range of stress at break for aged specimens exposed to short time aging study is very narrow scale. Only after long time aging condition the change in stress at break values are seen. In addition to this, because of the bulk matrix characteristics of TPVs percent elongation at break were more important parameters among them to determine the performance of TPV exposed to short time scale aqueous aging. Therefore, % elongation at break is a more dedicative parameter to follow for short time aging studies for evaluating the performance of EPDM/PP based TPV.

3.2.1 Percent Elongation at Break Analysis of TPV Exposed to Aging

The decreasing trend at percent elongation at break was observed generally except 100°C WA as shown in Figure 3.21, Figure 3.22 and Figure 3.23.

The sharpest fall at percent elongation at break data was seen just after 100 h aging time at 80 WA and 120 WA but no change in 100°C aging of all times in distilled water aging.

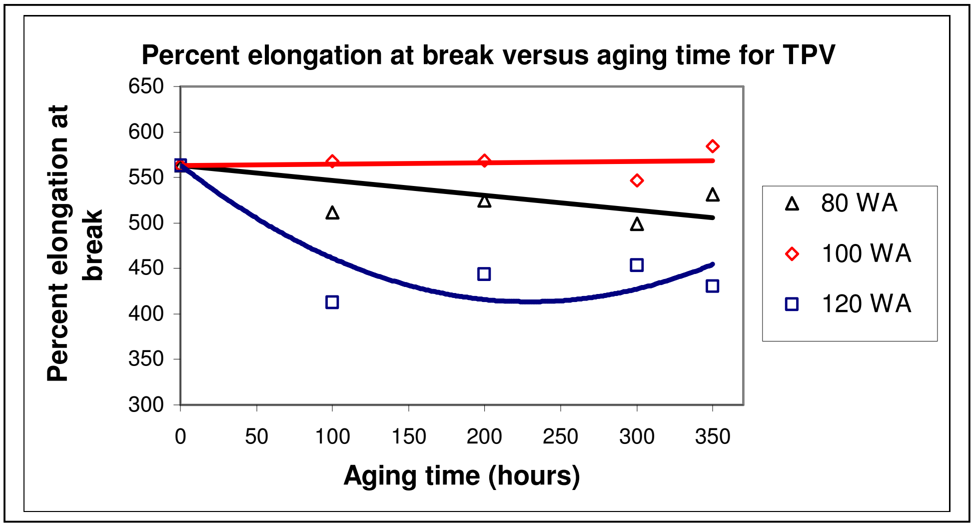


Figure 3.21 Variation of percent elongation at break versus aging time in distilled water

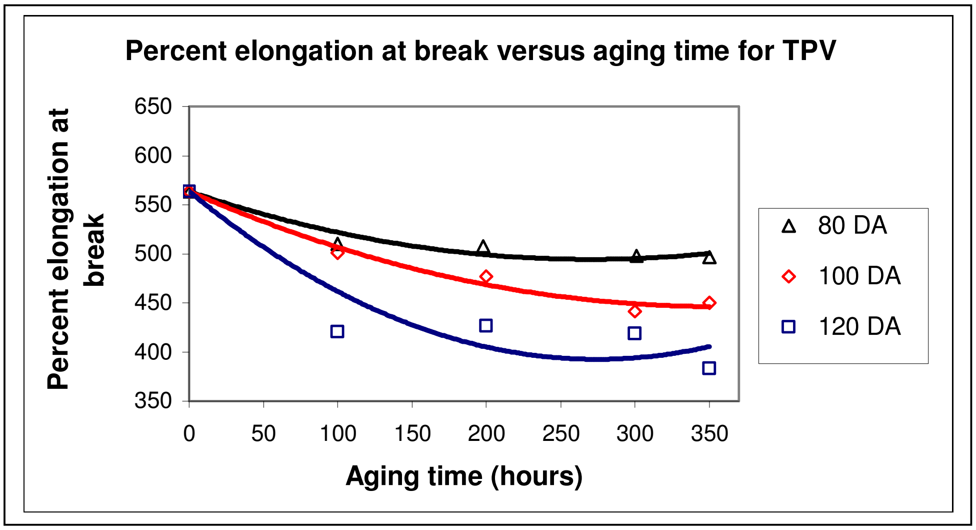


Figure 3.22 Variation of percent elongation at break versus aging time in detergent solution

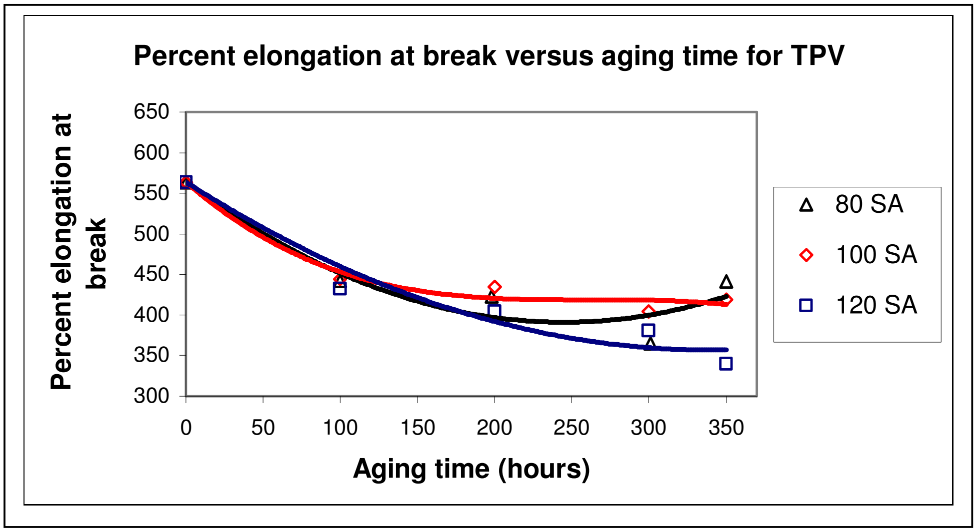


Figure 3.23 Variation of percent elongation at break versus aging time in shiner solution

In all cases of aging temperature of detergent and shiner solutions we observed an initial fast decrease of which then followed by a steady change.

At 80°C aging in water, detergent and shiner solutions although drastic decrease was observed at 100 h, percent elongation at break preserved at the end of aging with slight changes. The highest decrease in percent elongation at break at 80°C was in shiner solution because of acidity of shiner causing to reduce elasticity. However, the loss in percent elongation at break at 80°C in detergent solution, which is highly basic, was slightly higher than water.

The variation in percent elongation at break at 100°C WA seemed to remain constant during aging time. 100 WA was apparently the most resistant medium and temperature among all introduced studies. However, at 100°C detergent and shiner aging percent elongation at break reduced gradually where the loss was higher for shiner solution than detergent solution except a slight increase at 350 h.

The fastest reduction seen at 120^{o}C at 100 h in water, detergent and shiner solution was almost the same. In distilled water and detergent solution the maintenance trend of percent elongation at break was observed after sharp reduction at 100 h. On the contrary, step by step reduction trend was observed with aging period in shiner solution. Hence, the loss in percent elongation at break at 120^{o}C was substantial compared to 80 and 100^{o}C ones. Shiner aging was observed the least resistant medium and temperature for TPV in our study.

Moreover, the loss in percent elongation at break in shiner media at 80 and 100^{o}C was apparently as the same as 120^{o}C aging medium. The reason behind these decreases was probably due to the high percent crystallinity of PP. Also it was seen that the reduction of 80 DA and 120 DA was slightly higher even almost the same as 80 WA and 120 WA, respectively. Therefore, except 100^{o}C water aging it was observed that not only percent elongation at break decreased with increasing temperatures but also the loss of percent elongation at break arranged in a rising order as water, detergent and shiner solution, respectively.

3.2.2 Variation of 100 and 300 % Modulus of TPV Exposed to Aging

100 % Modulus, 300 % Modulus and Shore A values changes supported each other generally that increase in 100 % and 300 % Modulus values indicated an increase in hardness, which means increasing Shore A values. On the other hand, the relationships between 100 % Modulus, 300 % Modulus and Shore A values do not be accepted true every time since Shore A value is a bulk material measurement, which is the reply of the materials when opposed to a high compression at a point. However, 100 % Modulus and 300 % Modulus values show the elastic behavior of the material.

3.2.2.1 100 % Modulus Analysis of TPV Exposed to Aging

The variation of 100 % Modulus in distilled water, detergent solution and shiner solution were given in Figure 3.24, Figure 3.25 and Figure 3.26 , respectively.

At 80 WA decreasing trend was observed up to 200 h was followed by a slight recovery. At 80 DA, faster decrease at 100 % Modulus observed at 100 h preserved up to end of aging time with small changes and lower than 80 WA. On the other hand, at 80^{o}C shiner aging gradual decreasing trend became dominant after slight increase at 100 h. Hence, except detergent media 100 % Modulus at 80^{o}C remained almost constant within an acceptable range.

Not only 100^{o}C water aging but also 120^{o}C water aging showed severe drop observed at 100 h and recovery towards unaged 100 % Modulus up to end of aging time. However, the drop and the recovery at 100^{o}C water aging were detected faster than 120^{o}C water aging.

At 100^{o}C detergent and shiner aging 100 % Modulus was observed to reduce initially quickly, on the contrary, there was almost no change from 300 h to end of aging with slight changes.

The loss at 100 % Modulus at 120^{o}C aging in detergent and shiner solutions was faster compared to others and lead to lowest 100 % Modulus at the end of aging time. The trend of 120 DA not only resembled to 100 DA but also was lower than it. However, gradual and fastest reduction of 100 % Modulus was observed at 120 SA reaching the lowest 100 % Modulus among any of them. Hence, detergent and shiner solution at high temperature caused the highest deterioration trend at 100 % Modulus.

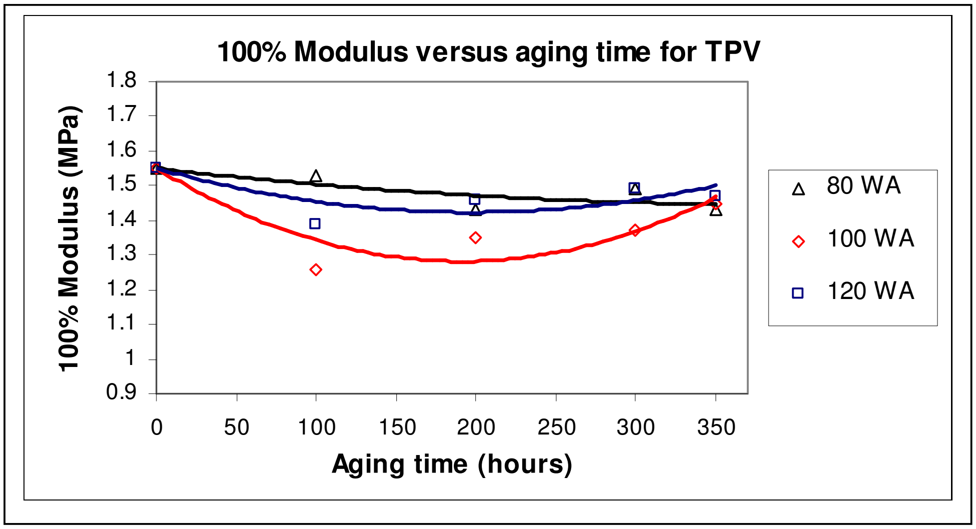


Figure 3.24 Variation of 100 % Modulus versus aging time in distilled water

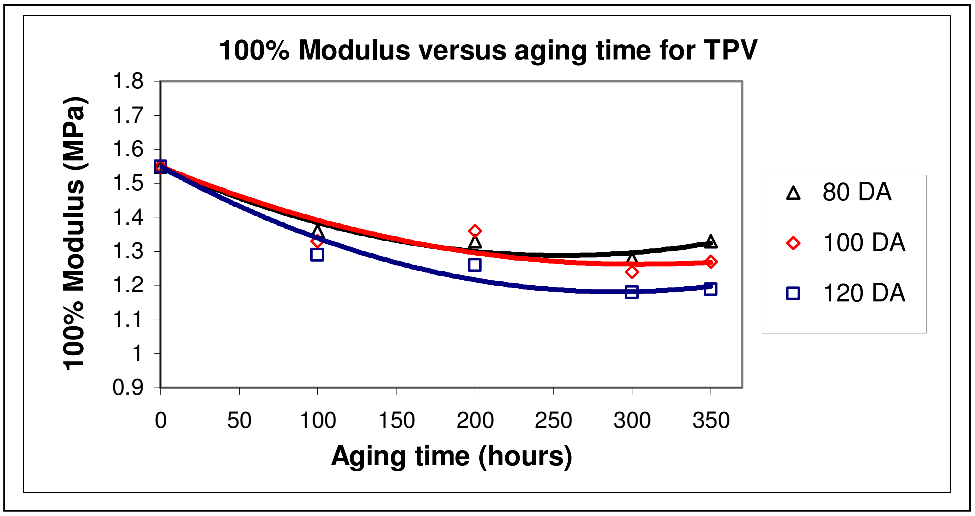


Figure 3.25 Variation of 100 % Modulus versus aging time in detergent solution

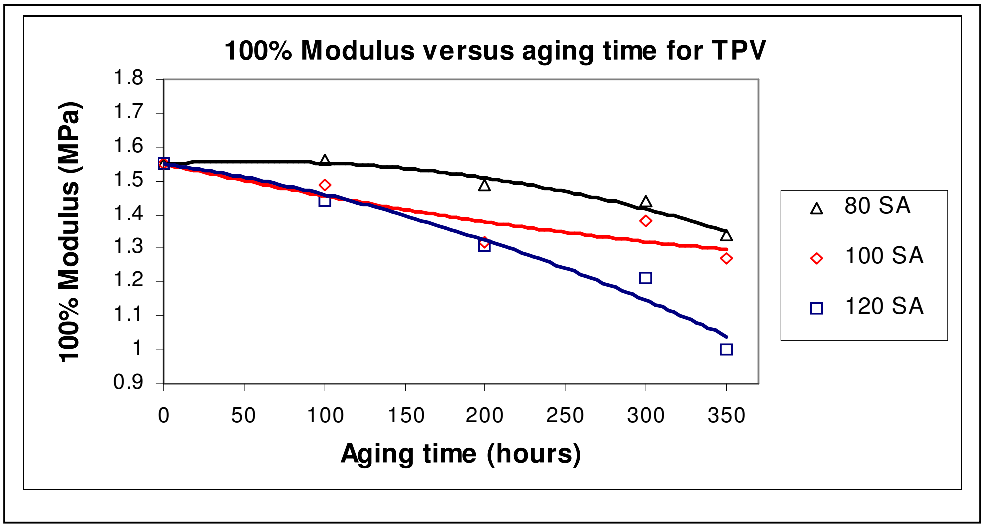


Figure 3.26 Variation of 100 % Modulus versus aging time in shiner solution

3.2.2.2 300 % Modulus Analysis of TPV Exposed to Aging

The change of 300 % Modulus shown in Figure 3.27, Figure 3.28 and Figure 3.29 indicated that 300 % Modulus and 100 % Modulus showed similarities especially at 80 WA, 100 WA, 80 SA and 120 SA, yet 300 % Modulus having some variations, and 300 % Modulus was recovered to unaged level at the end of aging time for WA except 120°C detergent and shiner aging.

300 % Modulus maintenance was observed at 80WA, 80 DA, 100 DA and 100 SA with slight fluctuations. On the other hand, fast reduction observed at 100 WA at 100 h recovered up to end of aging time reaching unaged 300 % Modulus level.

Slight and gradual 300 % Modulus up to 300 h for 120 WA dropped to the unaged level at the end of aging. A similar variation was observed at 80°C shiner aging that drastic augmentation at 100 h were lost with aging time reaching unaged 300 % Modulus level. Also increase in 300 % Modulus at 80°C shiner aging was higher than increase in 300 % Modulus at 120°C water aging. The rising trends seen at 120°C water aging and 80°C shiner aging were the reason of faster decreasing at percent elongation at break shown in Figure 3.21 and Figure 3.23, respectively, i.e. increase in rigidity, loss of elasticity.

Moreover, the loss in 300 % Modulus was the fastest in DA and SA at 120°C.

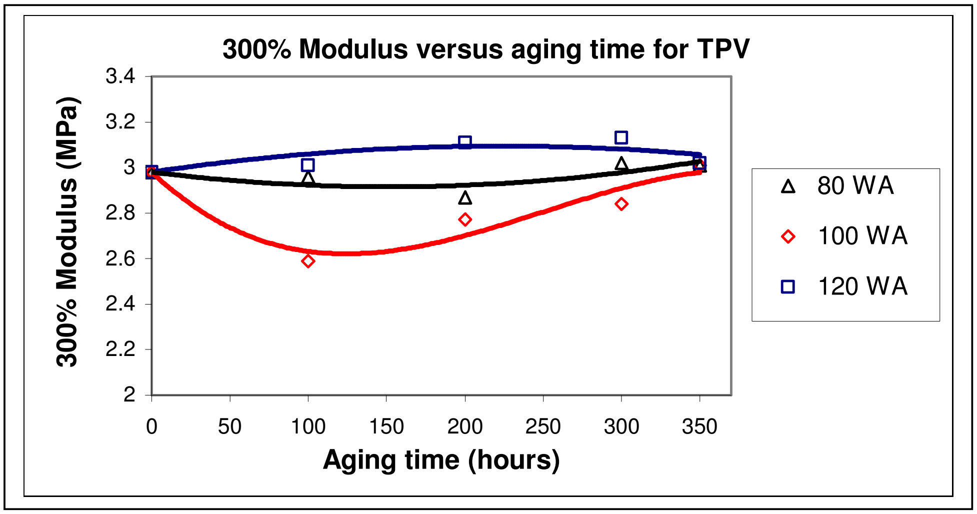


Figure 3.27 Variation of 300 % Modulus versus aging time in distilled water

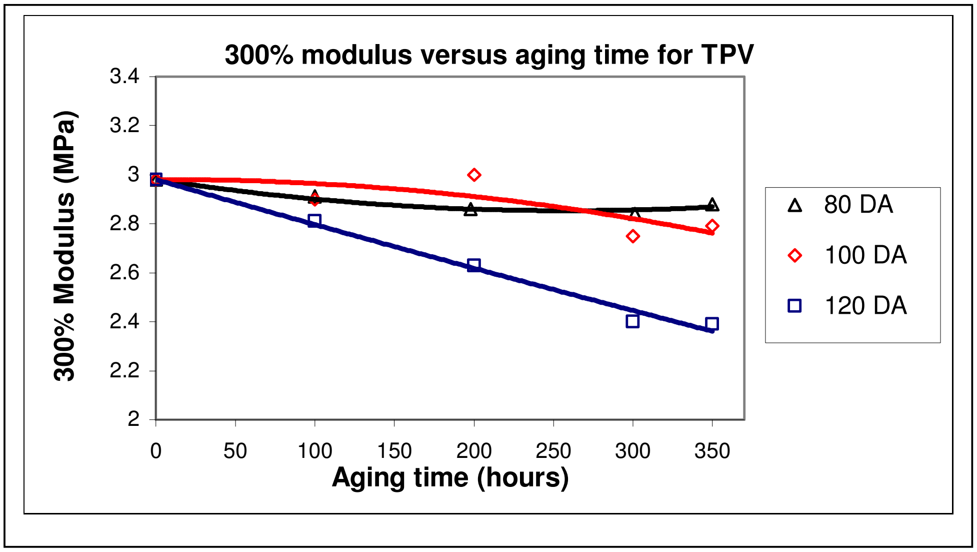


Figure 3.28 Variation of 300 % Modulus versus aging time in detergent solution

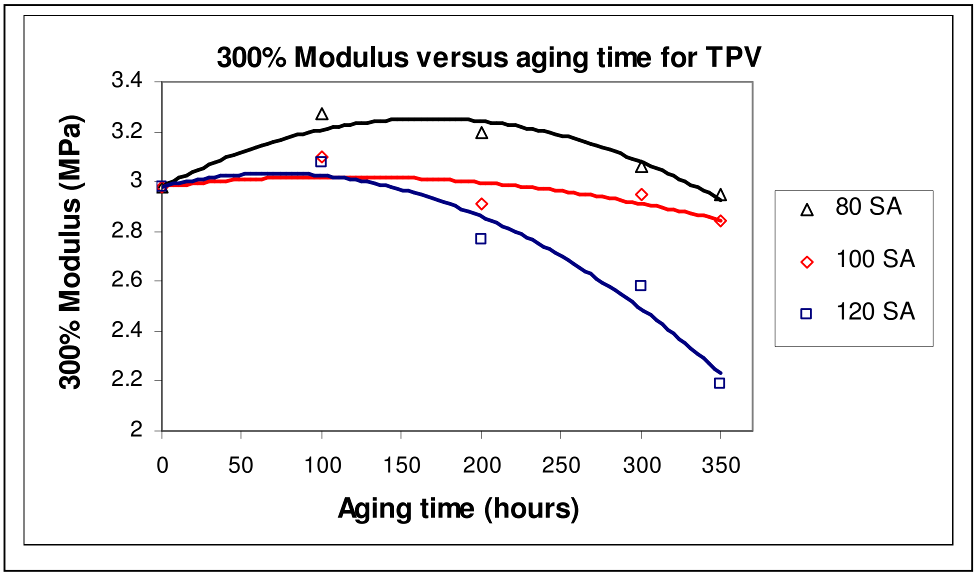


Figure 3.29 Variation of 300 % Modulus versus aging time in shiner solution

3.2.3 Stress at Break Analysis of TPV Exposed to Aging

Unlike severe drops in stress at break at 80, 100 and 120^{o}C detergent and shiner aging, water aging showed a curvature with a minimum followed by a recovery of stress at break at the end of aging.

Moderate decrease in stress at break observed at 100 h at 80 and 100^{o}C water aging recovered towards unaged one gradually at the end of aging time. While stress at break at 80 WA reached to unaged one, stress at break at 100 WA was found to be even higher than that of unaged value. Although the same trend was observed at 120^{o}C water aging, the recovery of stress at break was ceased and fallen below unaged value at 350 h.

The loss of stress at break in detergent and shiner solution was observed through the aging for all temperatures. A moderate decrease observed at 100 h was preserved with time for variation of 80^{o}C detergent aging. Similarly, up to 200 h the trend of stress at break of 100^{o}C detergent aging was almost the same as 80^{o}C detergent aging, yet after 200 h a faster reduction observed. At 120^{o}C detergent aging, a drastic reduction lower than the level attained at 300 h at 100^{o}C was observed at 100 h. Afterwards, slight and gradual reduction trend was observed up to end of aging time. Therefore, the rate of aging in detergent medium is directly proportional to temperature that is stress at break decreased faster with increasing temperature.

A steady decreasing trend was seen for 80 SA with time up to 300 h. Stress at break variations at 100^{o}C shiner aging resembled to 100^{o}C detergent aging with lower stress at break values. At 120^{o}C shiner aging sharpest and fastest decrease was observed with aging time reaching the lowest stress at break at the end of aging time.

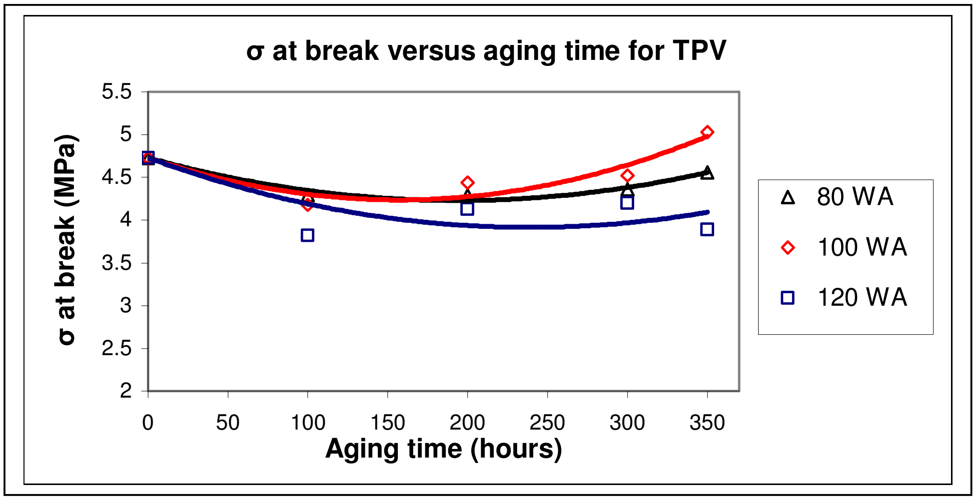


Figure 3.30 Variation of σ at break versus aging time in distilled water

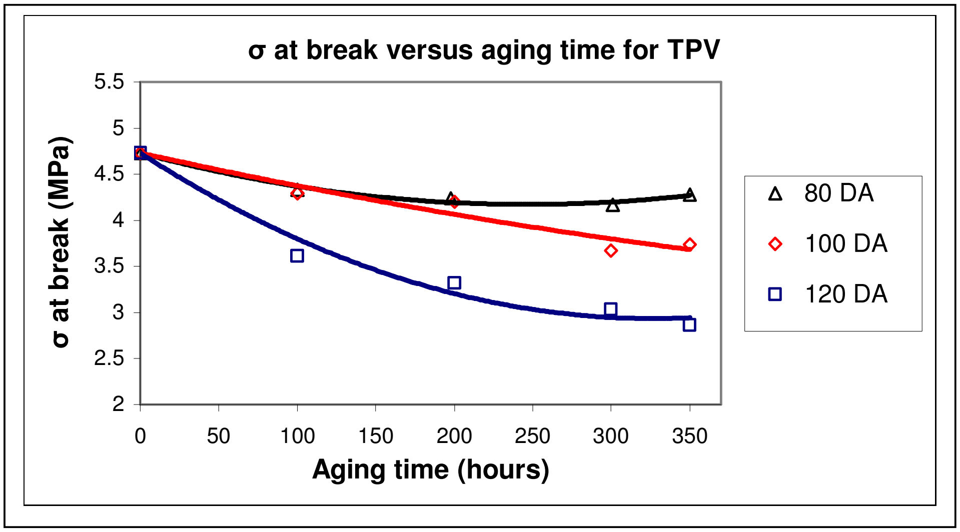


Figure 3.31 Variation of σ at break versus aging time in detergent solution

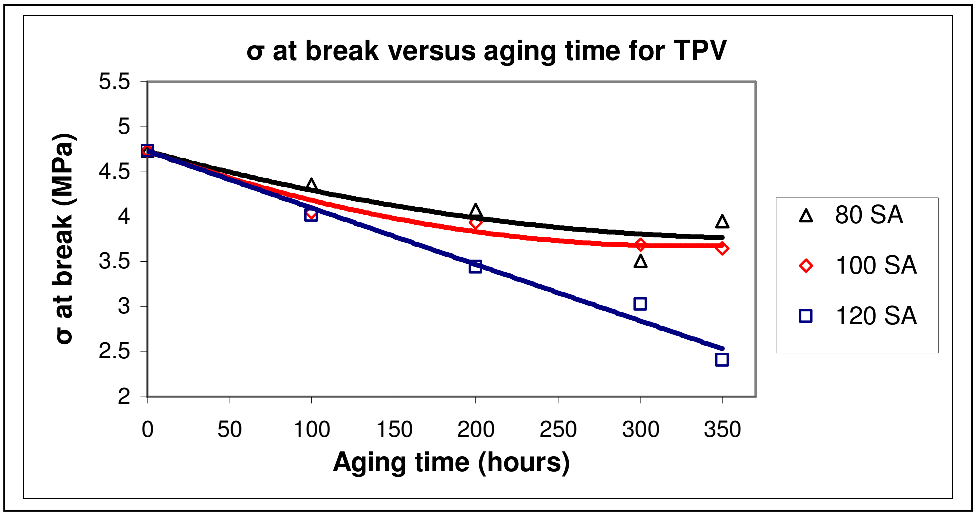


Figure 3.32 Variation of σ at break versus aging time in shiner solution

3.3 The Effect of Aging on Hardness

Hardness is defined as the resistance of material to localized deformation. Shore hardness scale was used for rubbers and plastics as given in Introduction part, page 2. Shore hardness is defined as resistance of indentation by 3 spring-loaded indenter and resistance to elastic deformation of the surface. The indentation hardness is inversely related to the entering and depends on the modulus of elasticity and the viscoelastic properties of material. While Shore A is used for soft rubbers, Shore D was used for harder plastics. If the indenter completely enters the sample, 0 is read. However, if no penetration takes place, 100 is read. The reading is dimensionless. Because of elastomeric nature of EPDM/PP based TPV Shore A scale was used to determine the variation of hardness owing to aging.

3.3.1 Shore A Analysis of TPV Exposed to Aging

Shore A variation of TPV due to exposition to aging was given in Figure 3.33, Figure 3.34 and Figure 3.35. TPV exposed to 80,100 and 120^{o}C water, detergent and shiner aging become softer generally. The hardness and 100 % Modulus verify each other in all set of aging medium and temperatures except 100 h aging time in shiner solution. There was a direct proportionality between them where one increased the other one increased or vice versa.

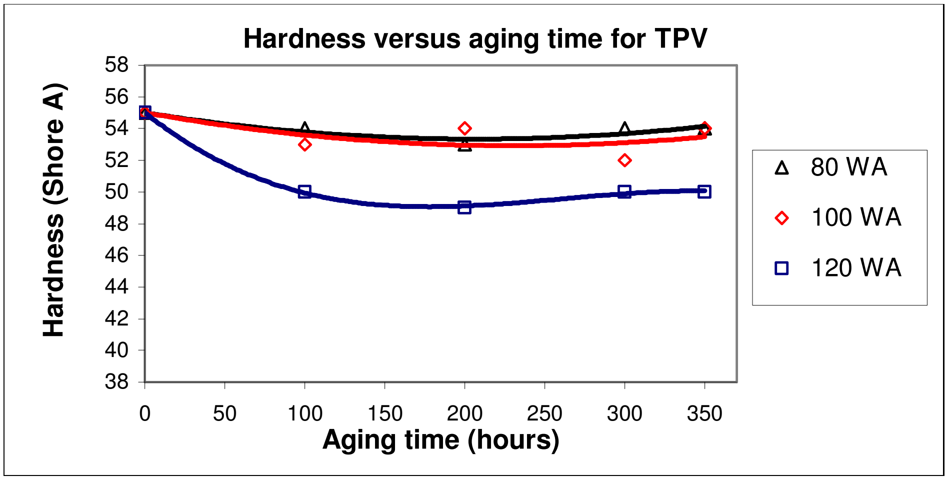


Figure 3.33 Variation of hardness versus aging time in distilled water

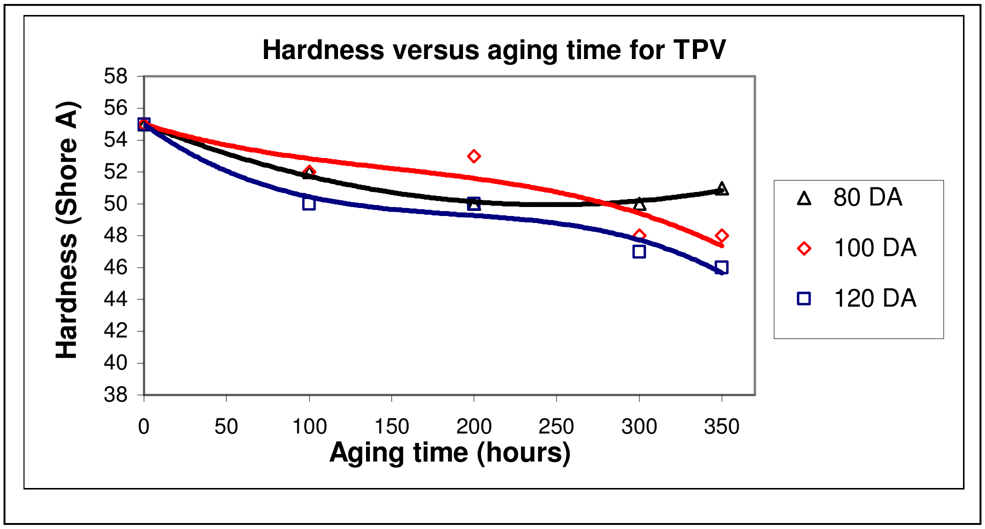


Figure 3.34 Variation of hardness versus aging time in detergent solution

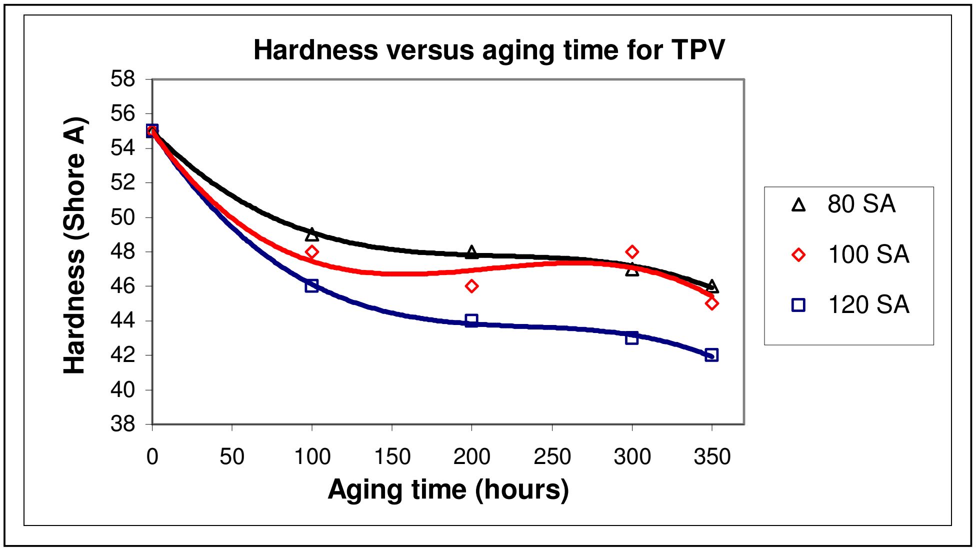


Figure 3.35 Variation of hardness versus aging time in shiner solution

Though the hardness measured at Shore A remained constant within acceptable range of variation with aging time at 80 and 100°C water aging, the drop in hardness became faster and obvious at 120°C water aging. Sharp decrease observed at 100 h at 120°C water aging was preserved during the rest of aging time with slight changes.

A sudden reduction in hardness of TPV was observed at 100 h in detergent and shiner solution. Likewise 120°C water aging, but fast decrease in hardness was measured for all DA and SA. At the end of aging same hardness was attained at 120°C water aging and 80°C detergent aging.

The sudden change in Shore A in 120°C SA was seen from 55 to 46, at 100 h, on the other hand, this change for WA and DA was found to be about 5 units decrease for 120°C.

A gradual and severe decrease was detected at 120°C detergent and shiner aging like WA at 120°C. Nevertheless, drastic decrease observed at 100 h at 120°C shiner aging was seemed to be higher and the lost during aging time was detected to be more rapid than 120°C detergent aging.

The comparison of aging medium indicated that softening obtained at 80°C detergent aging was equal to 120°C water aging and hardness drop at 80°C shiner aging was equal to 120°C detergent aging.

The softening effect of detergent and shiner solution was the result of the fact that detergent and shiner molecules diffusing into TPV possibly caused to the separation of PP and EPDM phases by weakening the connection between thermoplastic and rubber phases leading to decrease the resistance of TPV.

It was determined that the variation of hardness of TPV relied on the aging temperature as well as aging medium. The temperature dependence of hardness of TPV was explained that the hardness of TPV decreased with increasing aging temperature. It was detected that the softening effect of aging medium on the hardness of TPV was more dominant and faster than aging temperature. The softening effect of aging on EPDM/PP based TPV was arranged in order from the least one to the most one water aging, detergent aging and shiner aging, respectively.

3.4 The Effect of Aging on Morphological Properties

Morphological properties of aged and unaged fractured surface of tensile testing of TPV specimens were studied by SEM photographs given in figures from Figure 3.36 to Figure 3.41.

White parts seen in these SEM photographs was attributed to PP part and black parts seen was attributed to EPDM part. Unaged TPV SEM photograph shown in Figure 3.36 indicated that EPDM particles distributed uniformly surrounding the continuous PP phase. Although TPV was composed of two immiscible materials, phase separation between EPDM and PP components was observed very slightly from the SEM photograph of unaged TPV. This photograph indicated that morphology of unaged TPV was as homogeneous as single phase materials due to the phase mixing effect of dynamic vulcanization.

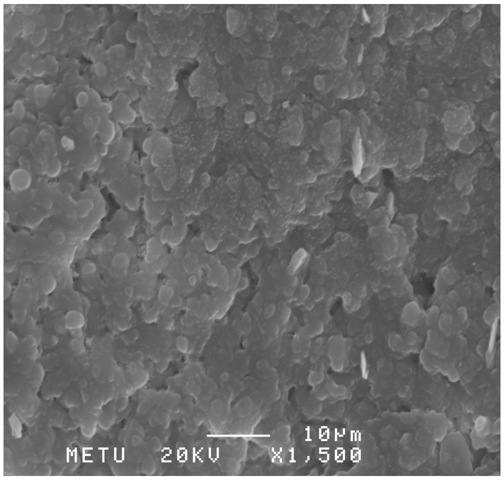


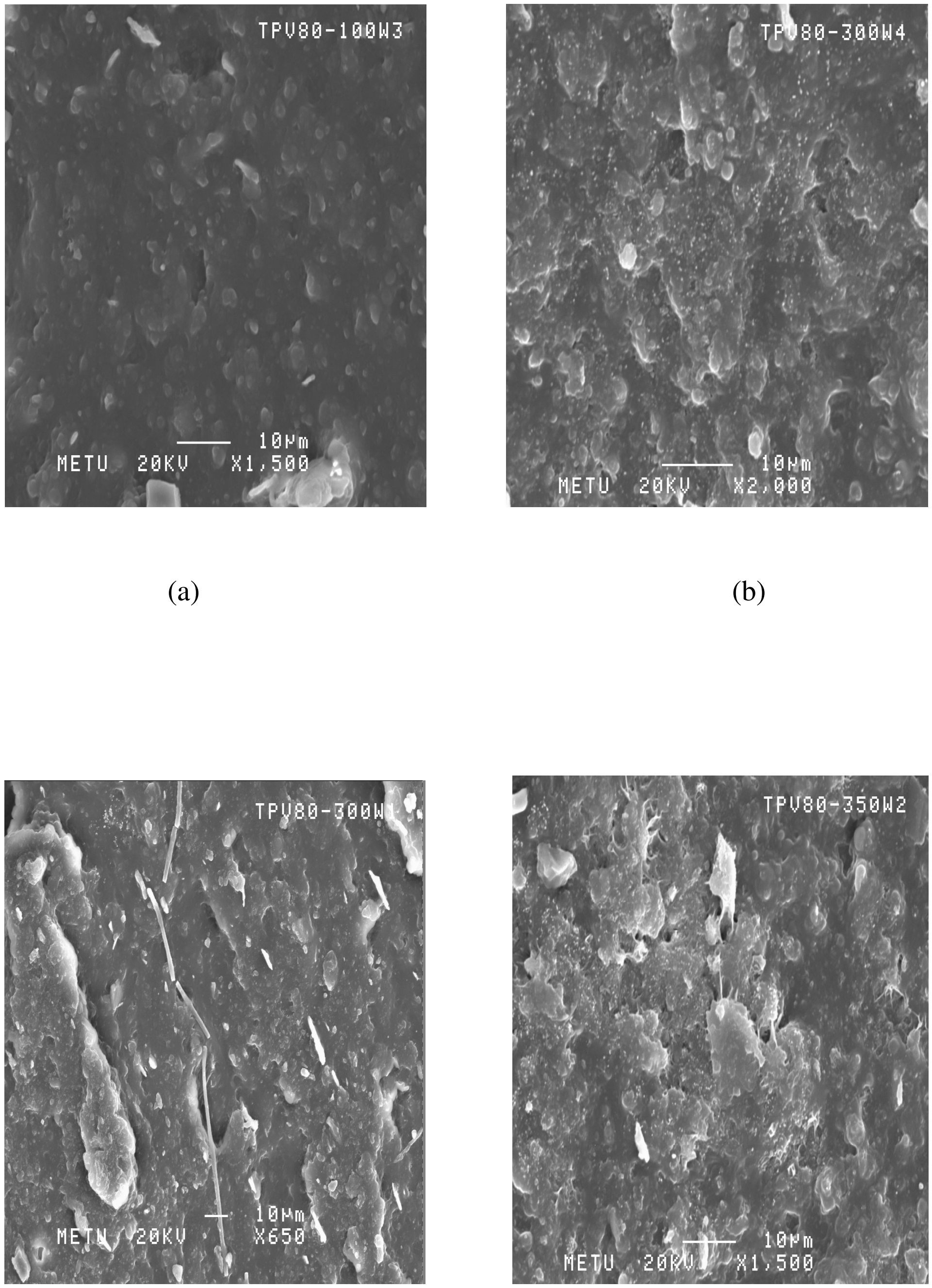
Figure 3.36 SEM Photograph of the fractured surface of tensile testing of pure EPDM/PP based TPV

SEM photographs of TPV aged at 80°C in distilled water initial aging time given in Figure 37 (a) is comparatively different from unaged TPV shown in the previous picture given in Figure 3.36; however, at the end of 80°C water aging white parts indicating PP phase became easy to distinguish seen in Figure 3.37 (c) and (d). Hollow empty spaces were observed in SEM photographs of 80°C water aging at 350 h seen in Figure 3.37, and the magnified picture of Figure 3.37 (d) was given in Figure 3.38 for a better visualization.

Fibrous PP structure formation was observed even at the beginning of aging time, 100 h, at 100°C water aging from Figure 3.39 (a) and continued up to 350 h seen in Figure 3.39 (b). Similarly, white area increases and hollow empty space appearance are observed at 120°C water aging TPV SEM photographs given in Figure 3.39 (c) and (d).

Although the homogenous structure of TPV aged at 80°C in shiner solution was maintained with rare white appearance shown in Figure 3.40, phase separation between EPDM and PP, and hollow space structure were distinguishable at 100°C shiner aging.

In general as the aging time increased, a phase separation formed between EPDM rubber and PP component. Also the decrement in elasticity when exposed to aging is the result of the phase separation. Moreover the hollow empty space seen in SEM photographs is caused by the rupture of crystalline PP which is mostly like phase separated, exposed to tensile testing. Furthermore, as the aging time increased more fibrillation upon tensile testing was seen due to PP phase separation in Figure 3.37 (c), 3.40 (a) , 3.40 (c) and 3.41 (b). The shiner aging due to its acidic characteristic had more detrimental effect on morphology than water aging, while water aging was the moderate one.



(a) (b)

(c) (d)

Figure 3.37 SEM Photograph of the fractured surface of tensile testing of TPV at $80^{o}C$ aging in distilled water at (a) 100 h, (b) 300 h, (c) 300h, and (d) 350 h

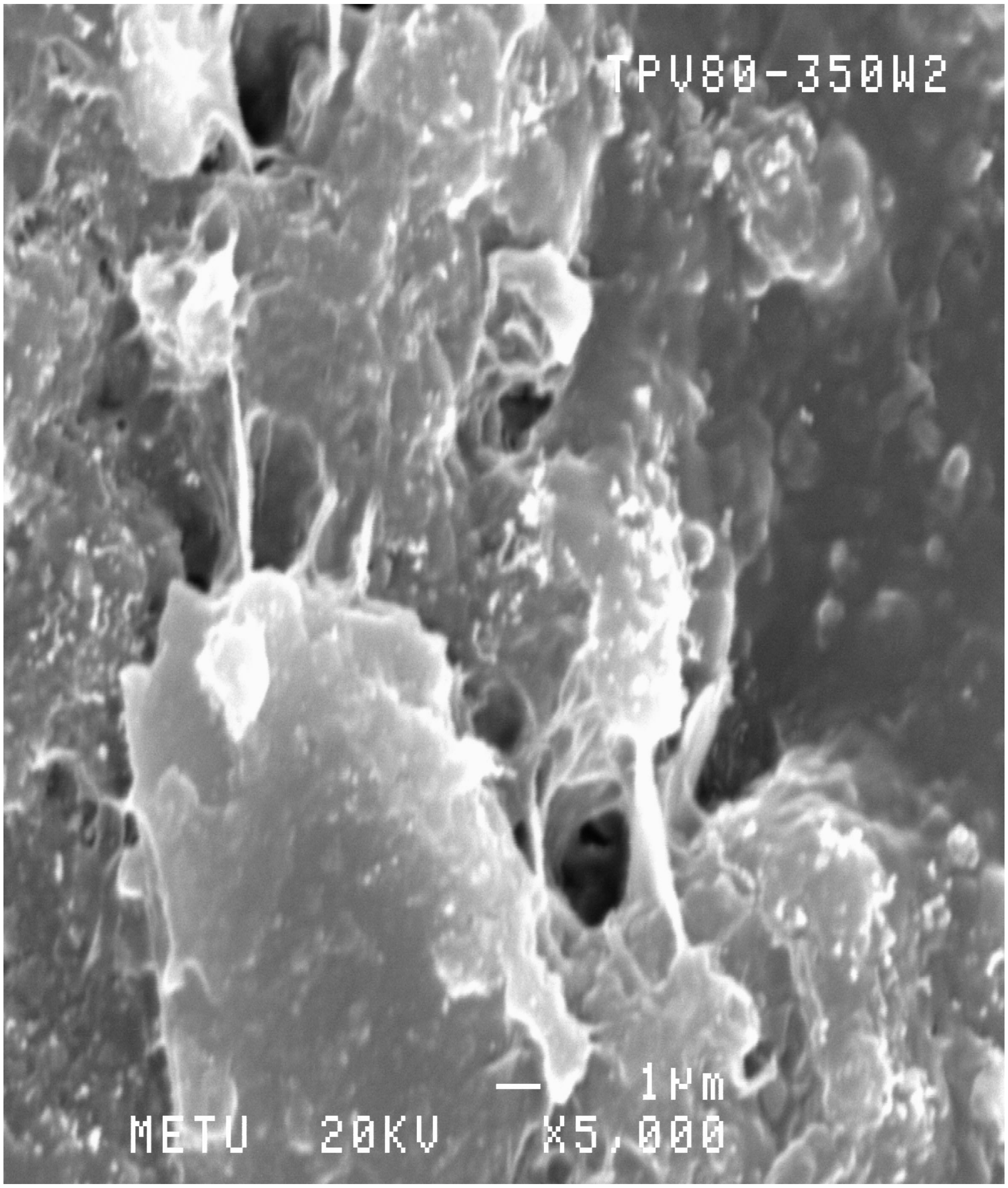
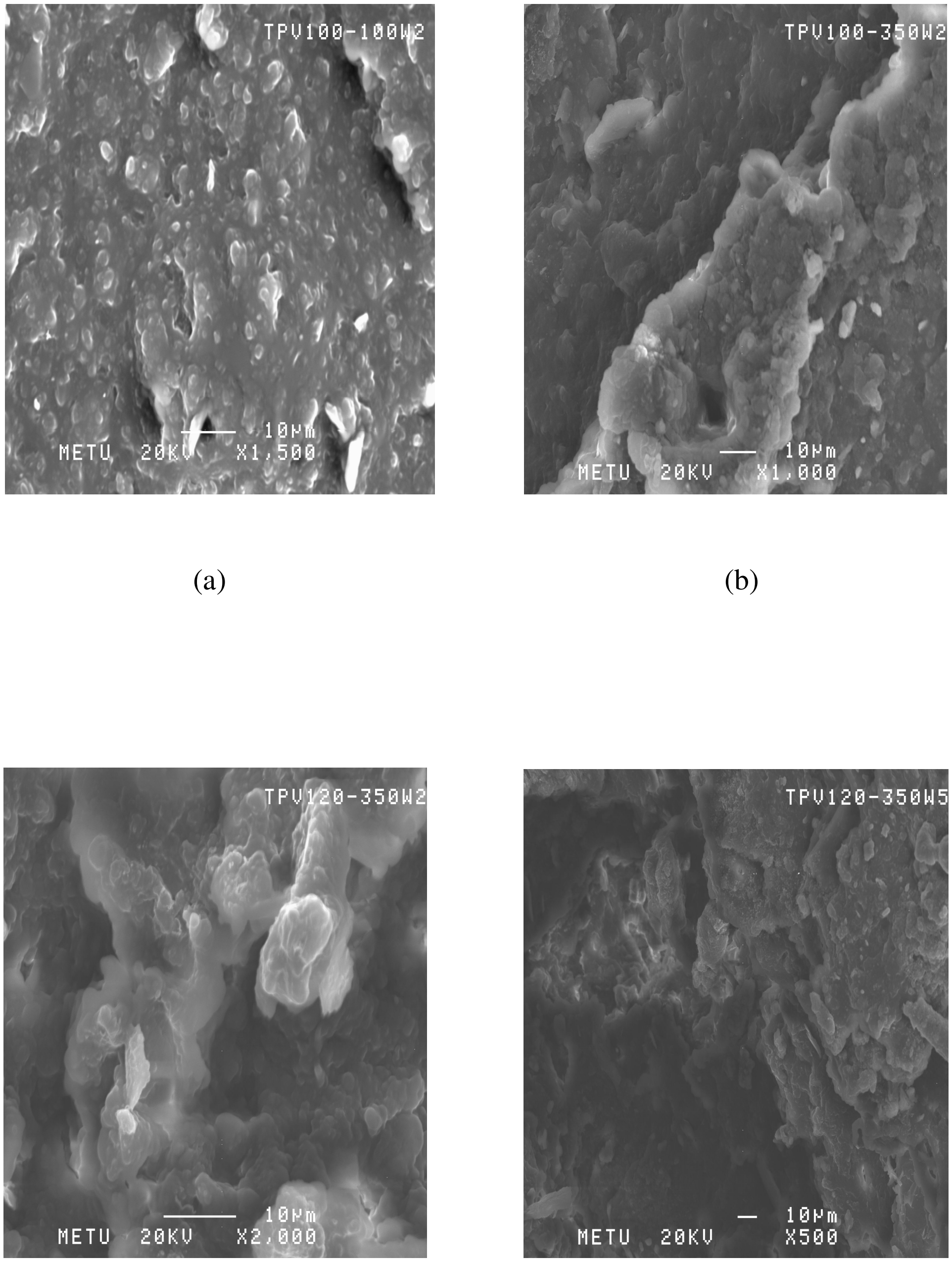


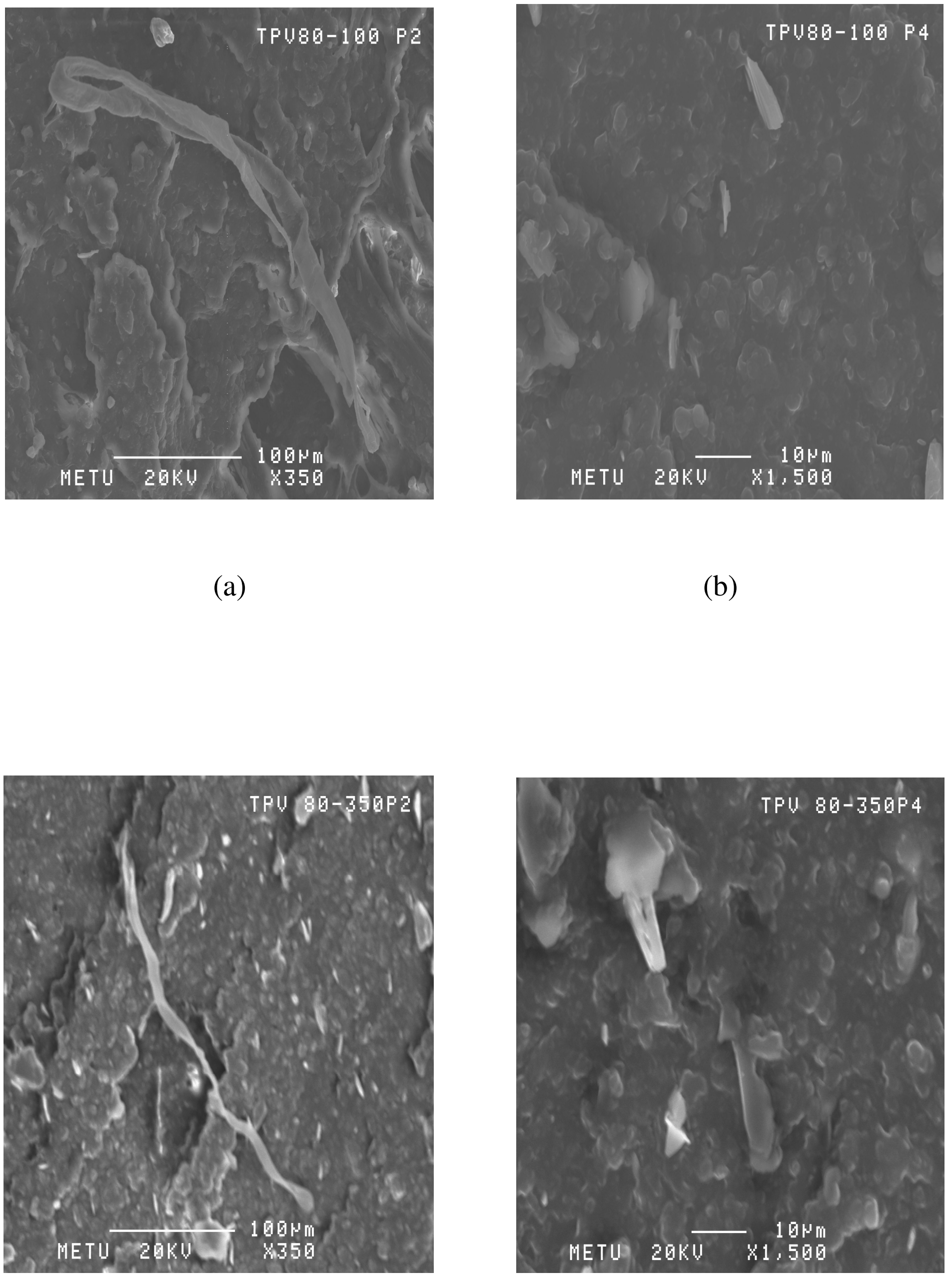
Figure 3.38 SEM Photograph of the fractured surface of tensile testing of TPV at 80^{o}C aging in distilled water at 350h



(a) (b)

(c) (d)

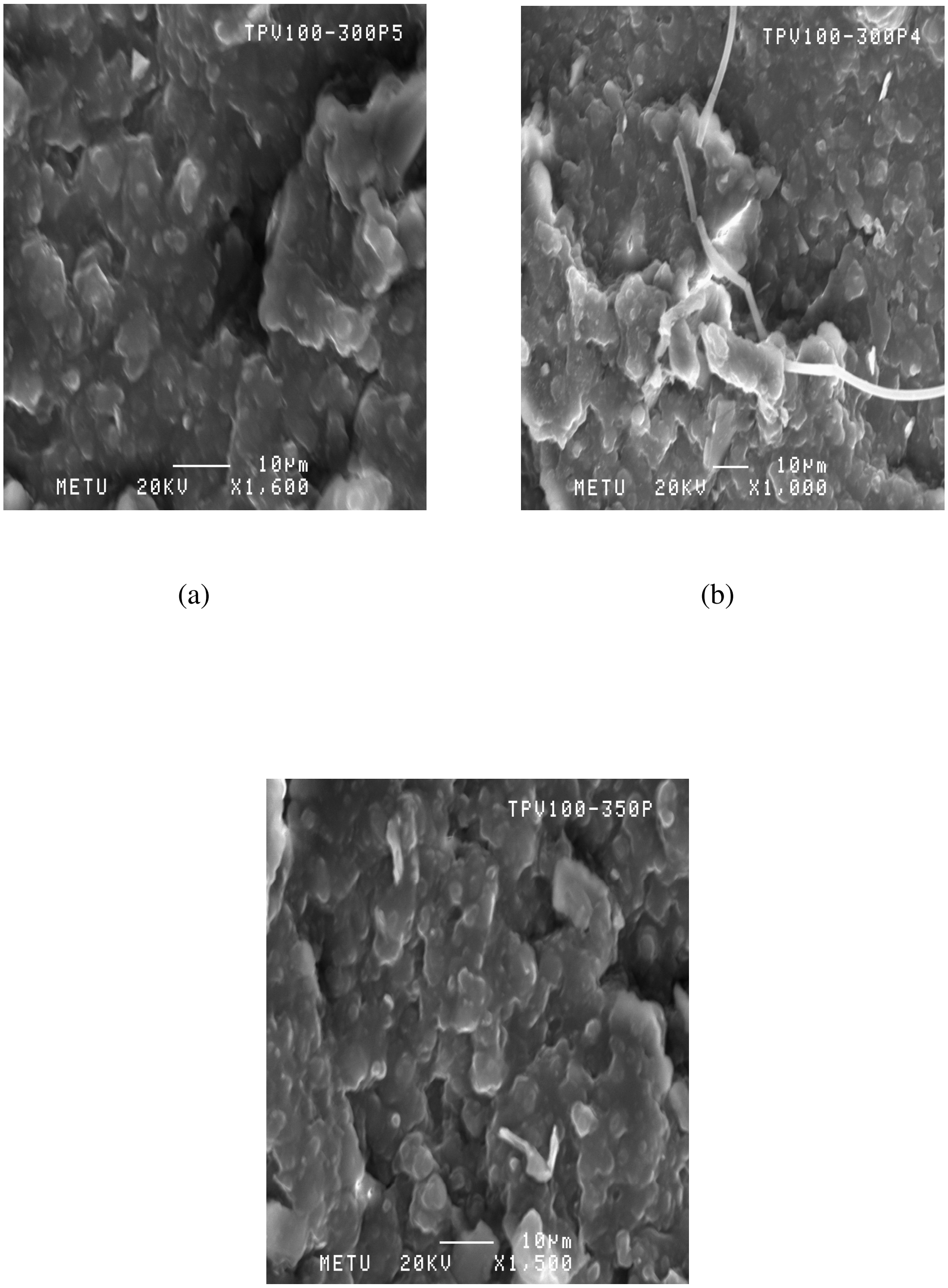
Figure 3.39 SEM Photograph of the fractured surface of tensile testing of TPV at 100°C aging in distilled water at (a) 100 h, (b) 350 h, and at 120°C aging in distilled water at (c) 350 h, (d) 350 h



(a) (b)

(c) (d)

Figure 3.40 SEM Photograph of the fractured surface of tensile testing of TPV at 80^{o}C aging in shiner solution at (a) 100 h, (b) 100 h, (c) 350h and (d) 350 h



(a)

(b)

(c)

Figure 3.41 SEM Photograph of the fractured surface of tensile testing of TPV at 100°C aging in shiner solution at (a) 300 h, (b) 300 h, and (c) 350 h

CHAPTER 4

CONCLUSIONS

Accelerated aging of TPV in distilled water, detergent and shiner solutions at 80,100 and 120^{o}C were performed in the closed system aging machine like a pressure cooker that stabilized temperature and pressure of the aging medium. The effect of accelerated aging was followed by tensile testing of TPV with respect to time. Also the thermal behavior of unaged and aged TPV with respect to time was evaluated by DSC and TGA techniques. Moreover the change in hardness and mechanical strength as well as the change in morphology were measured due to aging.

DSC analysis verified diffusion of detergent and shiner molecules into TPV. It indicated that percent crystallinity of TPV was strongly affected with both temperature and aging medium. DSC analysis showed that T_m of PP component in TPV decreased in all medium except we found an increasing trend at 80 WA. Furthermore, highest increase in crystallinity was observed at 100^{o}C aging, on the contrary, the crystal structure of PP apparently deformed at 120^{o}C aging resulting the loss in percent crystallinity of PP in TPV except 120^{o}C SA.

TGA analysis of aged TPV specimens confirmed DSC analysis that percent crystallinity increase causes enhancement in degradation temperature. Thermal degradation temperature increase of EPDM/PP blend in air was almost 5^{o}C at 100^{o}C aging in detergent and shiner solution, yet substantial increase almost 50^{o}C was observed at 100^{o}C aging in distilled water. Also TGA analysis performed under N_2 atmosphere indicated that shiner residues, being acidic, preserve chains against thermal degradation while detergent residues, being basic, accelerate thermal degradation of TPV.

Tensile testing results indicated that the loss in percent elongation at break was observed except 100 WA. The loss rate of percent elongation at break increases in a following order of shiner solution, detergent solution, and distilled water. While stress at break was observed to remain almost constant at water aging even a small increase at 100^oC water aging, stress at break in detergent and shiner solution decreased with increasing temperature. Also a substantial fall was observed at 120 DA and SA.

The loss in 100 % Modulus was seen except 80 and 100 WA which remained almost constant. The loss in 100 % Modulus in shiner solution was higher than in detergent solution. However, while 300 % Modulus in 100 WA, 80 DA was seemed to be constant, an increase was observed at 120 WA and 80 SA. Also drastic reduction in 300 % Modulus at 120 DA and SA was observed. The hardness measurements commonly were found to be directly proportional with 100 % Modulus.

Hardness measurement indicated that except 80 and 100^oC WA TPV softened when exposed to aging. It is determined that the hardness of TPV decreases with increasing temperature and the softening effect of aging arranges from the fastest to slowest in terms of aging medium as shiner solution, detergent solution and distilled water.

The morphological properties evaluated from the tensile testing fractured surface by SEM Photographs showed that PP failed in fibrillar due to phase separation with aging time.

In conclusion, EPDM/PP based TPV is quite resistant to 80^{o}C aging showing the lowest change in property. While TPV has moderate resistance against 100^{o}C aging, but it seemed to lose its resistance at 120^{o}C aging. It is also determined that aging media is as important as temperature to evaluate the performance of TPV. The rate of aging of EPDM/PP based TPV in shiner solution is decided to be the fastest one, most detrimental media, among the medium that was used in this study. While the rate of aging of TPV in detergent solution is determined to be the modest one, the rate of aging of TPV in distilled water is accepted to be slowest one.

REFERENCES

1. Naskar K., *PhD Thesis*, University of Twente, **2004**

2. Dick J.S., *Rubber Technology: Compounding and Testing for Performance*, Hanser Gardener Publications, **2001**

3. Abdou-Sabet S., Puydak R.C., Rader C.P., *Dynamically Vulcanized Thermoplastic Elastomer*, Journal of Rubber Chemistry and Technology, Vol.xx 1996, pp: 476-494

4. Geoffrey H., *Understanding Thermoplastic Elastomers*, Hanser Gardener Publications, Munich, **2000**

5. Choi W.J., Kim S.C., *Effects of Talc Orientation and Non-isothermal Crystallization Rate on Crystal Orientation of Polypropylene/Ethylene-Polypropylene Rubber/ Talc Blends*, Polymer, Vol. 45 **2004**, pp: 2393-2401

6. Wang C., Chang C.I., *Fracture Energies and Tensile Strength of an EPDM/PP Thermoplastic Elastomer*, Journal of Applied Polymer Science, Vol. 75 **2004**, pp: 1033-1044

7. Sengers W.G.F., Sengupta P., Noordermeer J.W.M., Picken S.J., Gotsis A.D., *Linear Viscoelastic Properties of Olefinic Thermoplastic Elastomer Blends: Melt State Properties*, Polymer, Vol. 45 **2004**, pp: 8881-8891

8. Katbab A.A., Nazockdast H., Bazgır S., *Carbon Black-Reinforced Dynamically Cured EPDM/PP Thermoplastic Elastomers. I.*

Morphology, Rheology, and Dynamic Mechanical Properties, Journal of Applied Polymer Science, Vol. 75 **2000**, pp: 1127-1137.

9. Ellul M.D., Tsou A.H., Hu W., *Crosslink Density and Phase Morphologies in Thermoplastic Vulcanizates*, Polymer, Vol. 45 **2004**, pp: 3351-3358.

10. Duin M.V., *Recent Developments for EPDM-Based Thermoplastic Vulcanizates*, Macromol. Symp, 233 **2006**, pp: 11-16

11. Dai Y.Q., Wang B., Wang S.J., Jiant T., Cheng S.Y., *Study on the microstructure and miscibility of dynamically vulcanized EPDM PP blend by positron annihilation*, Radiation Physics and Chemistry, Vol. 68 **2003,** pp: 493-496

12. Ivan G., *Dynamic Vulcanization: An Accessible Way to Thermoplastic Elastomers*, Iranian Journal of Polymer Science & Technology, Vol. 2 **1993**, No. 1, pp: 1-11

13. Billmeyer F.W, *Textbook of Polymer Science*, 3rd Ed, John Wiley & Sons, Inc., Singapore, **1984**

14. Sengers W.G.F, Wubbenhorst M., Picken S.J., Gotsis A.D., *Distribution of Oil in Olefinic Thermoplastic Elastomer Blends*, Polymer, Vol. xx (xxxx) **2005**, pp: 1-11

15. Navarro R., Torre L., Kenny J.M., Jime´nez A., *Thermal Degradation of Recycled Polypropylene Toughened With Elastomers*, Journal of Polymer Degradation and Stability, Vol. 82 **2003**, pp: 279-290

16. Mishra J.K., Ryou J., Kim G., Hwang K., Kim I., Ha C., *Preparation and Properties of a New Thermoplastic Vulcanizate (TPV)/Organoclay Nanocomposite Using Maleic Anhydride Functionalized Polypropylene as a Compatibilizer*, Material Letters, Vol. 58 **2004**, pp: 3481-3485

17. Mishra J.K., Kim G., Kim I., Chung I., Ha C., *A New Thermoplastic Vulcanizate (TPV)/Organoclay Nanocomposite: Preparation, Characterization, and Properties*, Journal of Polymer Science, Part B: Polymer Physics, Vol. 42 **2004**, pp: 2900-2908

18. Naskar K., Kokot D., Noordermeer J.W.M., Influence of Various Stabilizers on Ageing of Dicumyl Peroxide-cured Polypropylene/ Ethylene-Propylene-Diene Thermoplastic Vulcanizates, Journal of Polymer Degradation and Stability, Vol. 85 **2004**, pp: 831-839

APPENDIX A

PROPERTIES AND PROCESSING INFORMATION OF TPV

A.1 Dynamic Vulcanization and TPV

Dynamic vulcanization is a process that the elastomer phase is cured during continuous mixing of the blend [7]. Cross-linking of rubber phase is required to prevent coalescence and to achieve optimum elasticity, tensile properties and oil resistance [1, 10].

Gessler developed the dynamic vulcanization process in 1962. W.K Fisher is the first scientist to achieve not only the partial crosslink of the EPDM phase of EPDM/PP TPV with peroxide in 1972, but also controlling the degree of vulcanization by limiting the amount of peroxide to maintain thermoplastic processability. Later Coran, Das and Patel were able to vulcanize the rubber phase fully under dynamic shear to maintain thermoplastic processability [1]

Non-rotational elongational flows producing more effective break up and dispersion than rotational shear flows shows us that the co-continuity phase of both rubber and thermoplastic components are required [1]. As the rubber phase is dynamically vulcanized during mixing, rubber viscosity becomes higher than that of PP viscosity. Increasing viscosity of EPDM due to crosslinking not only cause high stress in the material [1] but also prevents the movement of rubber particles [8]. In other words, viscous liquid EPDM phase becomes elastic solid during dynamic vulcanization [7]. Therefore the co-continuous rubber phase is forced to break up into small size particles under shear field [1, 8]. The dispersion of EPDM particles doesn't depend on the EPDM ratio composition of TPV [7].

Dynamic vulcanization is same as static vulcanization in terms of producing 3-D polymer structures. The difference between dynamic and static vulcanization is that crosslinked rubber particles are dispersed in the uncrosslinked thermoplastic polymer as microgel. Coran, Das, Patel exhibit that the stress values of TPVs increase with decreasing diameter of microgel as seen in Figure A.1 [3].

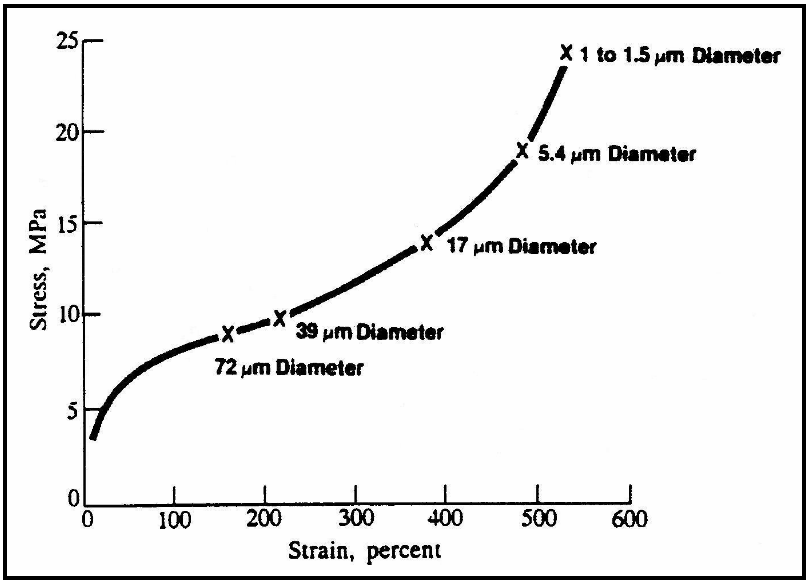


Figure A.1 Effects of rubber particle size on stress strain properties of TPVs

Dynamic vulcanization process is performed under high shear and above the melting point of thermoplastic material to activate and complete vulcanization

[3]. The high shear stresses in the process of dynamic vulcanization leads to phase mixing of both PP and EPDM phases [6].

Good interfacial strength between EPDM and PP phases is obtained due to the process of dynamic vulcanization that promotes the miscibility of PP and EPDM [6]. Also, it has been pointed out that partial miscibility of EPDM and PP occurs during dynamic vulcanization due to elevation of lower critical solution temperature at high shear stresses [6].

Modest enhancement is provided by the partially crosslinked TPVs, yet fully cured and 1-2 µm diameter rubber microgel TPV has [3]

higher ultimate tensile strength
better elastic recovery(tension and compression)
higher properties retention at elevated temperatures
greater resistance to swelling by fluids
greater flex fatigue resistance
more consistent processability

The relationships between extent of cure with oil swell or ultimate tensile strength or stress at 100% elongation are seen from the Figure A.2 [3].

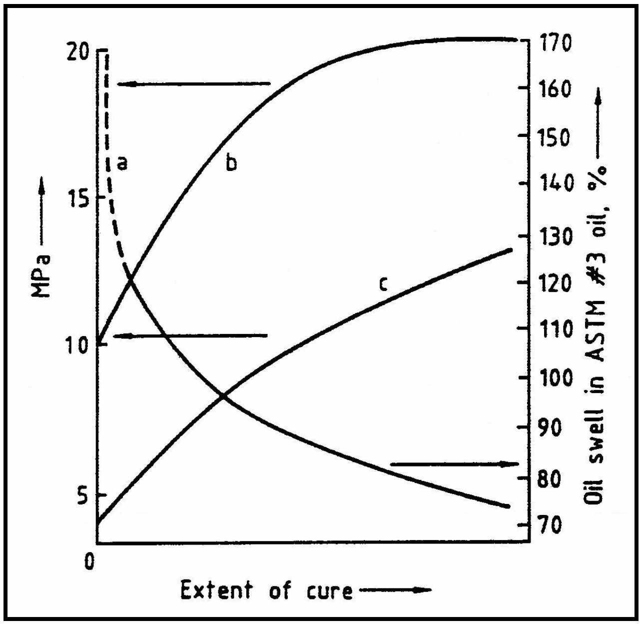


Figure A.2 Effects of degree of cure on properties of TPVs; curve a, oil swell at 152°C/22 h; curve b, ultimate tensile strength; curve c, stress at 100 % elongation [3]

The extent of cure is inversely related to oil swell. There is a parabolic decrease in oil swell with increasing extent of cure. However, ultimate tensile strength and stress at 100 % elongation increases with increasing extent of cure. Moreover extent of cure increases the hardness of the TPVs [3].

A.1.1 Type of Curatives

There are many types of curatives that are used in dynamic vulcanization. Sulfur, activated phenolic/formaldehyde resins, co-agent assisted peroxides, platinum catalyzed hydrosiloxane, vinyl trialkoxysilane/ moisture, catalyzed quinonedioxime and bisthiols are some examples [1, 3].

By the help of curing group nature high tensile strength and elongation at break TPVs with satisfactory permanent set are produced with moderate crosslinking density [12].

Curing group nature influences the curing rate and final curing degree [12]. Because of the high melting temperature of PP, the static sulfur curing system is not useful having low thermal and UV stability [1]. Dimethyloloctylphenol curing resin as activated phenolic/formaldehyde resins provides TPVs with improvement in compression set, oil resistance and processing characteristics. These improvements are due to graft copolymer between EPDM and PP that enhances the interfacial adhesion between the microgel rubber particles and PP matrix. The graft copolymer is produced through the functionalization of PP with dimethyloloctylphenol that then react with EPDM [3]. Therefore, phenolic types of curatives enhance the flow characteristics and rubber like properties of TPVs [3]. On the other hand, acid activated resol crosslinked mechanism is used for white color TPVs while Platinum-catalyzed hydrosilane and peroxide/co-agent mechanism are used for black color TPVs [10].

A.1.2 Peroxide Crosslinking

The types of peroxide are dialkyl peroxides (most thermally stable one), alkyl-aralkyl peroxides, diaralkyl peroxides, peroxy-ketoles and peroxy esters [1].

The crosslink efficiency, ε_c, is the main parameter to determine the cure level of peroxide. The crosslink efficiency of peroxides is defined as the number of moles of chemical crosslinks formed per mole of reacted peroxide. It depends on type and amount of termonomer, Ethylene/Propylene ratio, randomness of monomer distribution, polymer molecular weight and molecular weight distribution. Higher Ethylene/Propylene ratios EPDM TPVs have higher efficiency values. Also the crosslink efficiency for terminal unsaturated EPDM including TPVs is higher than the internal ones [1].

t-amyl type of peroxides, e. g 1,1-di(t-amyl peroxy) cyclohexane, are useful in the manufacture of various thermoplastic elastomers (TPE, TPV) via dynamic vulcanization. The first reason for this is that t-amyl type of peroxides being suited with high saturation or formulation containing monomers, coagents as well as unsaturated polymers together. The other reason is that, t-amyl type of peroxides produce selective free radicals that target double bonds and significantly reduce residual monomer or co-agent levels [2].

A.1.2.1 Peroxide Crosslinking Mechanism

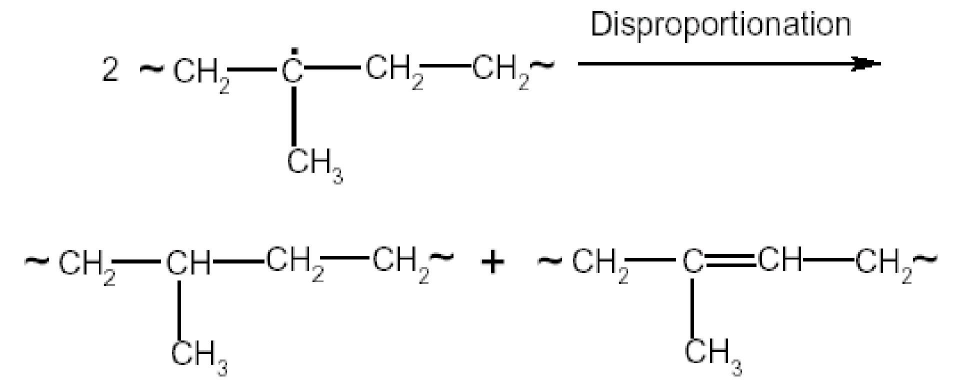
Peroxide crosslinking mechanism is divided into three parts [1]. The first step is the rate-determining step of the overall reaction, which is the hemolytic decomposition of peroxide and generation free radicals.

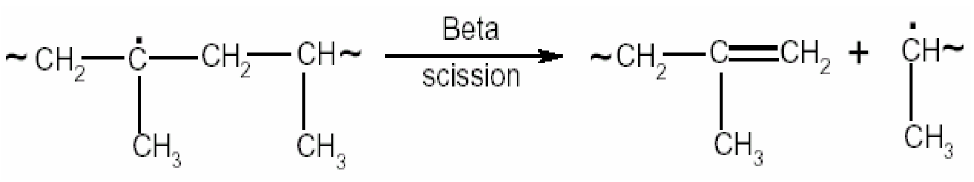
$$\mathrm{R{-}O{-}O{-}R} \longrightarrow 2\,\mathrm{RO}^{\bullet}$$

The second step is the abstraction of hydrogen atom from the polymer chain to produce stable peroxide decomposition product and polymer radicals [1].

$$\mathrm{RO}^{\bullet} + \sim\mathrm{CH_2}\sim \longrightarrow \sim\dot{\mathrm{C}}\mathrm{H}\sim + \mathrm{ROH}$$

The final step is the combination of two polymer radicals to form a C-C crosslink [1]. Also some side reactions, which are disproportionation or β-scission, can take place during the crosslinking process where β-scission causes PP degradation by abstraction of tertiary hydrogen atoms from the main chain [1].





In order to avoid β-scission the amount of peroxide is increased. However, it has some detrimental effect on the morphology of the TPV. So co-agents are used to [1]

-Remove the steric hindrance for coupling
-Minimize the chain scission by stabilizing macroradicals via resonance
-Modify the tight C-C crosslink formed by the peroxy radical
-Suppress unwanted side chain reactions of the polymeric radicals like termination via disproportionation.

Co-agents are investigated into two parts. Examples of first type are acrylates, methacrylates, and bismaleimides. They have unsaturation without allylic hydrogen that increases the rate of cure by addition reaction by reacting in addition reaction mechanism. Examples of second type are triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), triallyl phosphate (TAP), divinyl benzene (DVB) and small amount of sulfur having readily accessible vinyl unsaturation and sites for radical addition and ample amount of easily abstractable allylic hydrogens [1].

The benefits of co-agents are [1]

- improving heat aging,
- higher modulus tensile and tear strength TPV
- higher harness TPV
- improving compression set
- increasing abrasion resistance

A.1.2.2 The Advantages of Peroxide Crosslinking on Sulfur Based One

These are as given in Reference [1, 2]

- Simple formulation
- Ability to store the peroxide-containing compound over a long time without scorching
- Rapid vulcanization without reversion
- Ability to crosslink saturated as well as unsaturated rubber
- High temperature resistance of the vulcanizates
- Good compression set properties of the vulcanizates (elastic recovery) at elevated temperature by creating Carbon-Carbon type crosslink bonds that are stronger than Carbon-Sulfur and Sulfur- Sulfur bonds created by sulfur vulcanization
- No moisture uptake of TPVs
- No staining or discolorination of the finished TPV

A.1.2.3 The Disadvantages of Peroxide Crosslinking on Sulfur Based One

- Peroxide crosslinking is sensitive to oxygen under curing conditions and has temperature dependence in terms of acceleration and retardation [1].
- Additives such as extender oils that are highly aromatic for low or high concentration, antioxidants that are aromatic or amine, Silica (SiO_2) or clay as an acid filler for low or high concentration reduce the crosslink efficiency so paraffinic oils and non-acidic Burges type clay fillers should be used [2]
- 15% less tensile and tear strength are gathered compared with sulfur based crosslinking systems [1]
- Peroxide crosslinking is worse than sulfur one in terms of flex fatigue [1]
- Diffusion processes are required to get rid of unpleasant smell by post cure [1]

A.1.3 Crosslinked Density

By the help of Flory-Rehner equation solvent swelling measurement is the basic technique used to determine crosslink density [3].

The work of Ellul on EPDM/PP TPVs by scanning electron microscope showed that in reducing the tensile set and increasing the tensile strength of TPVs are more dependent on crosslinking density [6].

Crosslinks introduced during dynamic vulcanization lowers the tension set and raise the tensile strength of the TPV [9].

Curing group nature (curing agent, accelerator, and activator) is another parameter affecting the crosslinking density [12]. Fisher states that the degree of vulcanization is controlled by limiting the peroxide amount to maintain thermoplastic processability [3].

With increasing curative content the crosslink density of EPDM in TPV increases [9]. An increase in curative content reduces the population of the large dispersion [9]. Also an increase in curative content could cause the thickening of PP ligament, so there is a upper limit for the curative quality to maintain elastic properties [9]. The rise in EPDM crosslink density does not only narrow of EPDM domain size, but also raising the PP ligament number-average thickness [9].

Ultimate elongation and tensile strength of a TPV depend upon both the crosslink concentration in the rubber phase and its dispersion morphology in terms of the rubber domain sizes and distribution [9]. Moreover, as the crosslink density of EPDM phase is increased [3], i.e more rigid EPDM domains dispersed in the continuous PP-phase [1], TPVs show higher retention of ultimate tensile strength and modulus compared with the thermoplastic elastomer olefins (TEOs) [3]. Also an increase in EPDM crosslink density with curative content lead to an increase in TPV viscosity, the drop in its swelling and an increase in its dynamic modulus [9]. However, even though higher tensile strength than TEOs their ultimate tensile strength is significantly lower than most of thermoset rubbers with the same hardness [3].

The decrease in crosslinking density causes low tensile strength and elongation at break and permanent set of elongation is achieved by N_a (the size of the chain segment between two successive points of the network) values higher than 600 [12].

A.2 Compatibility of TPVs

If the material is miscible or thermodynamically compatible, the material has single-phase morphology [3]. However, PP/EPDM based TPVs have hetero phase morphology [3]. Therefore, a special compatibilizer can be used to reduce interfacial tension between two polymeric phases, leading to enhanced dispersion of discrete phase in the matrix with important enhancement on physical properties of composite materials [12].

Because of the nonpolarity of TPV in order to improve the dispersibility of nano filler, polar maleic anhydrate functionalized PP is used as a compatibilizer in the nanocomposite preparation [16]. Also compatibilizer is used to enhance miscibility required for modest dynamic vulcanization [3].

A.3 Morphology of TPVs

The morphology and the properties of TPVs are affected by the parameters that are [3]

- viscosities of phases
- the shear rate during mixing
- polymer ratio
- relative surface energies
- crosslinking density
- type of crosslink
- the presence of compounding additives

In order to have efficient mixing the viscosities of the used phases should be the same or similar [3]. On the contrary, the viscosities of EPDM and PP are different for EPDM/PP based TPVs.

For immiscible liquid phase one phase becomes dispersed phase. When the fraction of dispersed phase exceeds a critical value, there is a region where the blend exhibits phase co-continuity. The co-continuous morphology can be accepted as intermediate structure where phase inversion takes place and dispersed phase becomes the matrix phase and vice versa [1].

When the dynamic crosslinking starts, two co-continuous phases are generated firstly. During mixing as the crosslink density increases, the continuous rubber phase is broken up into fine droplets and PP becomes the continuous phase. Therefore, phase inversion is occurred and thermoplasticity of the TPVs is gathered [3]. Also dispersed rubber phase morphology is due to the tendency of the less viscous phase to encapsulate the most viscous phase to minimize the mixing energy [8].

Although the elastomer phase in TPVs is dispersed, some parts of the PP phase are entrapped by the agglomerated structures resulting particles touching each other. Thus, TPV behaves like continuous structure [7].

A.4 Elasticity of TPVs

First of all, the EPDM phase is responsible for the recovery from deformation at short time scales [3]. Also if EPDM is semicrystalline or highly branched, this EPDM phase is helpful for the elasticity of the TPVs [3].

At the beginning of dynamic vulcanization small amount of PP is dissolved in EPDM phase because of the similarity in the structures of PP and EPDM. Then EPDM phase are fully crosslinked so the PP is trapped in the rubber particles. Moreover, small amount of EPDM particles doesn’t let the size of PP grow. These fragmented PP lamellae may serve as the tie points to connect the amorphous PP segments [6].

Young et al. investigated that fragmented PP crystallites serving as the tie point are the result of excellent strain recovery of EPDM/PP TPVs [6]. Kikuchi's research on deformation of EPDM/PP based TPVs at high strain exhibited that the other reason for strain recovery is the ligament matrix between EPDM particles [6].

According to the TPV deformation mechanism proposed by Boyce, thinner PP ligaments and their ability to yield, bend, rotate, and buckle are critical pseudo-elastic network development and the elasticity in TPV [9].

Fourier Transform-Infrared (FTIR) studies have shown that not only EPDM domains but also PP crystallites and amorphous PP phase orient upon elongation. However; upon relaxation only EPDM domains relaxes to some extent only [10].

Also Atomic Force Microscopy (AFM) studies have shown that thin thermoplastic layers at the equator of the rubber particles are subjected to plastic yielding upon elongation. And upon relaxation thermoplastic layers are drawn back by the elastic rubber domains and fold back to a harmonic-like buckling [10].

Moreover the other important parameter for lower residual deformation upon release of deformation is a high degree of long-chain branching PP phase. Long chain branching PP-phase causes dual network with chemically crosslinked rubber phase [1].

The attractive elastic performance of EPDM/PP based TPVs is due to the physical crosslinks, domain formation, resulting from the segregation of different phases [6].

A.5 Rheology of TPVs

TPVs show a non-Newtonian fluid behavior in terms of Rheology [3, 12]. The melt viscosity of TPV exceeds the viscosity of thermoplastic using in the composite material [12]. Thermoplastic viscosity being 5-10 times lower than the elastomer viscosity at the same temperature supplies continuous thermoplastic phase [12]. TPV has a shear thinning behavior [7]. The viscosity of TPV shows power law behavior even though at low deformation rate and a zero shear viscosity is impossible [7]. Therefore, the melt viscosity of TPVs is highly shear rate dependent. TPVs exhibit high flow characteristic at high shear rates while TPVs exhibit low flow characteristic at low shear rates as seen from the Figure A.3 [3]. The shear rate should be about 10^2 s^{-1} and the process temperature should be 20-60°C higher than the melting temperature of the thermoplastic component [12].

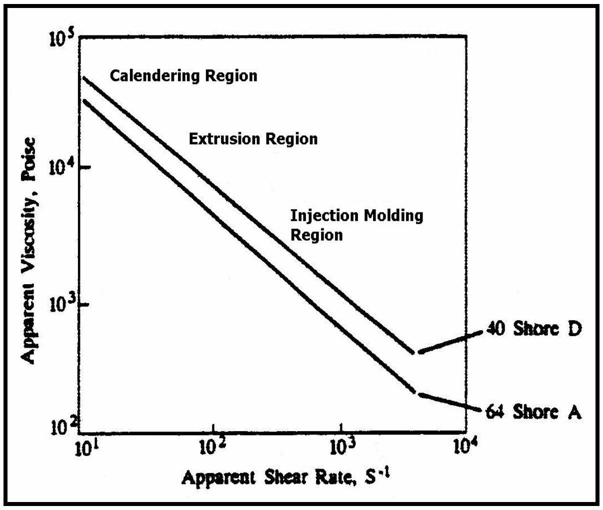


Figure A.3 TPV viscosity variation with shear rate at 204°C

At high shear viscosity, the viscosity difference between EPDM and PP are reduced, which is desired to decrease the size of the dispersed rubber particles in the blends of the two polymers [8].

The rheological behavior of TPV consisting densely packed elastomer particles in a thermoplastic matrix resembles highly filled polymers [7, 8], so that the interface between the less mobile dispersed rubber particle and the thermoplastic phase increases leading to increase in shear viscosity [8].

At low shear stress the system behaves like an elastic network of rubbery particles having yield stress whereas at intermediate shear stress TPVs behave likes a PP melt filled with rubber particles after passing the yield stress [1, 10]. For the high shear stress the PP matrix becomes dominant in terms of rheological properties that are required for TPV production. In other words; if the local shear stress is higher than the yield stress of the rubbery network, the rubber particles will turn over each other. Therefore, deformation required for melt processing occurs. If the shear stress is lower than the yield stress of the rubbery network, plug flow will occur [10].

A.5.1 Torque Profile

According to Figure A.4 [12] at the beginning of the mixing there is a high torque value. With starting of thermoplastic melting the torque value decreases and reaches a plateau. After addition of curing agents starting the vulcanization process, the viscosity of mixture raises increases the torque value increases until mechano-chemical destruction of the crosslinked elastomer. The mixing time after vulcanization is to be advised 2-3 minutes to improve the dispersion of the vulcanized phase in the thermoplastic matrix.

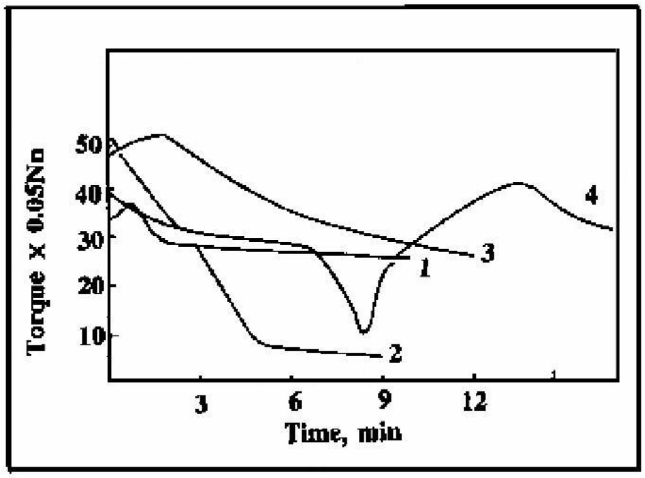


Figure A.4 Variation of torque in Brabender Plastograph (mean curve) during mixing of EPDM (1), polypropylene (2) and their mixture with ratio 5:2 (3), and of the compound (4) with the following recipe (mass parts): 100 EPDM, 40 PP, 2 stearic acid, 0.5 MBT, 1 TMTD, 2 sulfur, initial temperature 10°C, rotor speed 90 rpm [12].

A.6 Mechanical Features of TPVs

Mechanical features of TPVs depend mainly on [12]

- the nature of the components
- the ratio of the components

Another important parameters influencing mechanical features of TPVs are polymer viscosity, mechano-chemical processes and interaction at interfaces [12]

The performance of TPVs is dependent on [1, 12]

- the characteristics of starting polymers (molecular mass, distribution of molecular mass, crystallinity…)
- compound recipe (polymer ratio, nature of the curing group, nature and amount of the filler and plasticizer, addition of special components)
- the condition for producing & processing of TPV
- the phase morphologies and the interactions between phases (Only a fine dispersion of the relatively high amount of rubber in to small particles < 0.5 μm surrounded by the thermoplastic matrix guaranties an elastomer-typical and high mechanical property level).

Having good balance property TPVs' three important criteria should be thought [12]. Those are

1-the degree of crystallinity of thermoplastic (W_p)

Crystallinity in the thermoplastic phase is required for TPVs [4]. High degree of crystallinity of thermoplastic material provides TPVs with an increase in tensile strength and elongation at break while sacrifying in permanent set and in elongation [12].

2-interfacial tension ($\Delta\gamma_s$) ensuring mutual wetting of the phases

The surface energies of both hard thermoplastic phase and soft elastomer phase must match for wetting [4]. Interfacial tension values should be low to maintain high tensile strength and elongation at break with low permanent set [12].

3-the size of the chain segment between two successive points of the network (N_a)

N_a is formulated like below where; A and B are constants, μ_o is the molar mass of the monomer unit and z is the number of atoms in the backbone of the monomer unit [12].

$$N_a = A + B(\mu_o/z))$$

When the value of N_a increases the network density decreases [12]. The molecular weight between inter-chain entanglements in the elastomer phase must be low [4].

4-thermal stability at mixing temperature

Both phases must be thermally stable at the mixing temperature at which the elastomer phase must be able to be vulcanized [4].

EPDM/PP TPVs having a relatively high tearing strength at room temperature is explained that small scale yielding of PP matrix at fragmented PP lamellae takes places for tear deformation [6]. Also the EPDM particles have lamellae of PP crystals near the interface so the dispersed phase contributes to the enhanced interfacial strength. On tearing, the amorphous PP segments between the fragmented PP lamellae are stretched to a highly extended status and breaking of the PP chains across the interface initiates the fracture process. Moreover, good tearing strength is still preserved until 150^{o}C where some PP crystals are melted and start to flow [6]. The energy for cutting for TPVs is twice larger than for the rupture of C-C bonds at room temperature is decided by cutting test that is used for intrinsic strength [6].

Also the fatigue resistance of softer EPDM/PP TPVs is better than thermoset rubber. Because of the fact that generally good compression set thermoset rubbers show poor fatigue properties or vice versa as seen from the Figure A.5 and Figure A.6 [3].

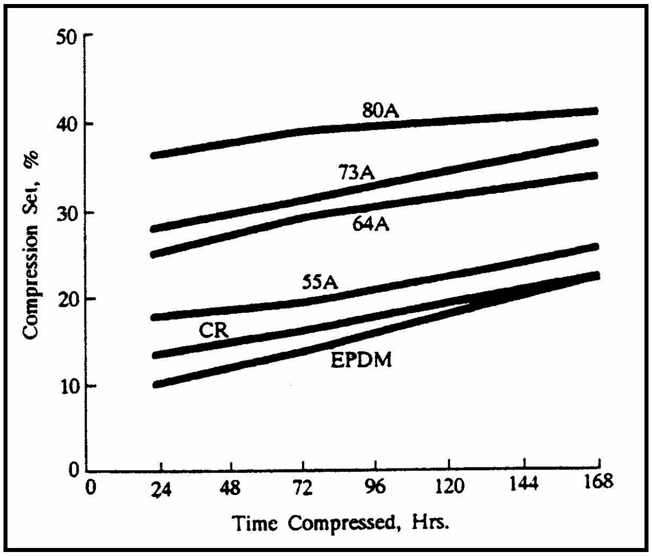


Figure A.5 Compression set variation with time; TPVs compared to thermoset rubbers; ASTM D 395, Method B, 25% deflection, 100 °C

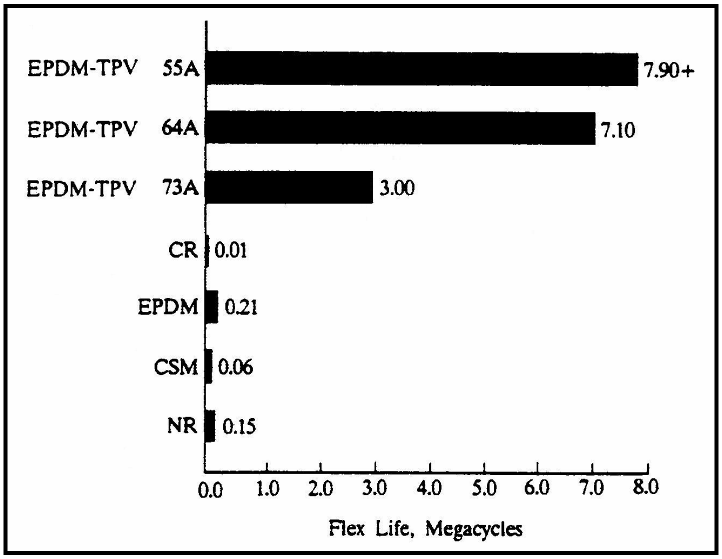


Figure A.6 Direct comparison of tensile flex fatigue of TPVs to that of thermoset rubbers; 100% extension; 100 cycles/min [3]

A.6.1 Tensile Properties and Ultimate Elongation

When thermoplastic domain melts at elevated temperature, the material starts to flow. While the material is cooled, the thermoplastic part solidifies. Thus, the material exhibits tensile strength at normal used temperature [3].

One of the most important properties TPVs is its anisotropy. Tensile strength and ultimate elongation of a TPV measured in flow direction is 20 to 35% lower than that measured in perpendicular direction. This property is generally occurring in injection molded specimens. The orientation of polymer chains during molding process causes this anisotropy [2].

The tensile strength of TPV can depend on the composition ratio of EPDM according to Figure A.7 [8]. For highly PP concentrated TPV exhibits increasing in stress with strain sharply and then gradually after passing through the yield point of the PP. On the other hand, for highly EPDM concentrated TPV PP yielding disappears at 80/20 EPDM/PP ratio and TPV shows more elastomeric mechanical properties. The increase in EPDM content causes a decrease in tensile strength due to the decrease in the continuous semicrystalline PP concentration and increase in the size of the dispersed rubber particles [8].

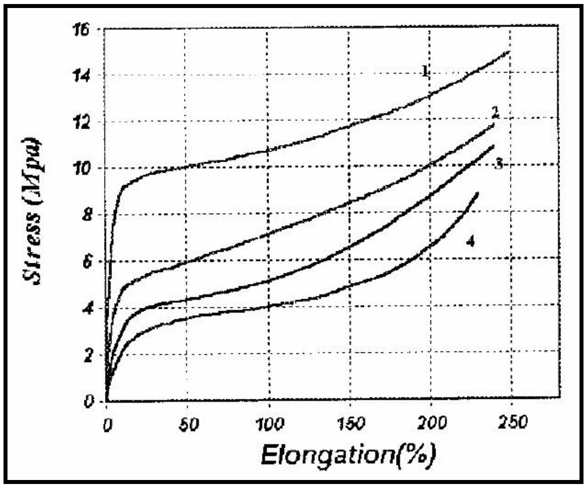


Figure A.7 Tensile stress-strain curves of dynamically vulcanized EPDM/PP blend at various composition: (1) 50/50 EPDM/PP; (2) 60/40 EPDM/PP; (3) 70/30 EPDM/PP; (4) 80/20 EPDM/PP [8]

Highest tensile strength of phenolic–resin cured EPDM/PP TPVs is produced with high ethylene content, high diene content of EPDM phase. The viscosity of EPDM rubber is less significant in this case. However, better rubber properties are achieved with low ethylene content, low diene content, low viscosity of EPDM-rubber, smaller rubber particle size and uniform crosslink density [1].

According to Figure A.1 tensile properties are improved dramatically as the particle sized decreased [4].

The tensile stress-strain curves of EPDM/PP based TPVs are similar to rubber and do not show defined yield points. The tensile stress-strain curves of EPDM/PP based TPVs strongly depend on temperature. These curves become significantly linear, i.e. rubber-like, with increasing temperature while knee formation at yield point is seen, i.e. thermoplastic-like, with decreasing temperature as seen from Figure A.8 [3].

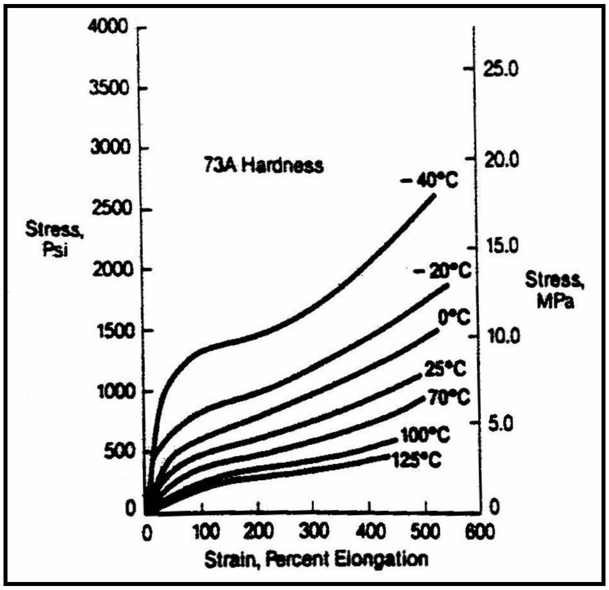


Figure A.8 Tensile stress-strain curves for 73 Shore A EPDM/PP TPE at different temperatures

When the strain rate increases, the breaking stress slightly increases but the elongation at break decreases according to Figure A.9 [6].

The elongation at break increases with temperature rise according to Figure A.10 while the stress at break decreases with temperature rise according to Figure A.11 [6]. The elongation increase is due to pulling out of PP chains from the lamellae crystals giving drawability of EPDM/PP TPVs [6].

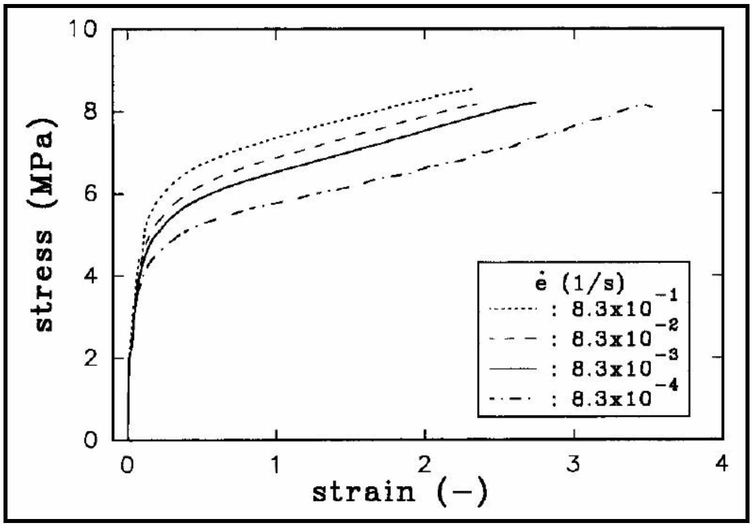


Figure A.9 Stress-strain relation of EPDM/PP TPE at different strain rates (room temperature)

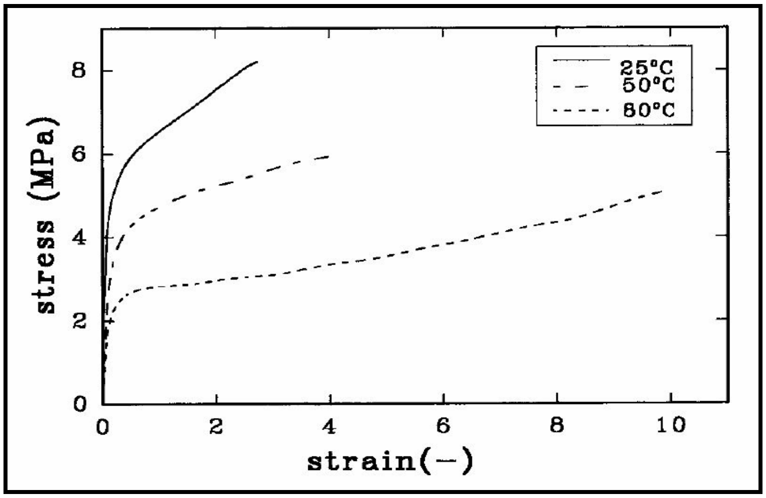


Figure A.10 Stress-strain relation of EPDM/PP TPE at different temperatures at 8.3 x 10^{-3}/s strain rate [6]

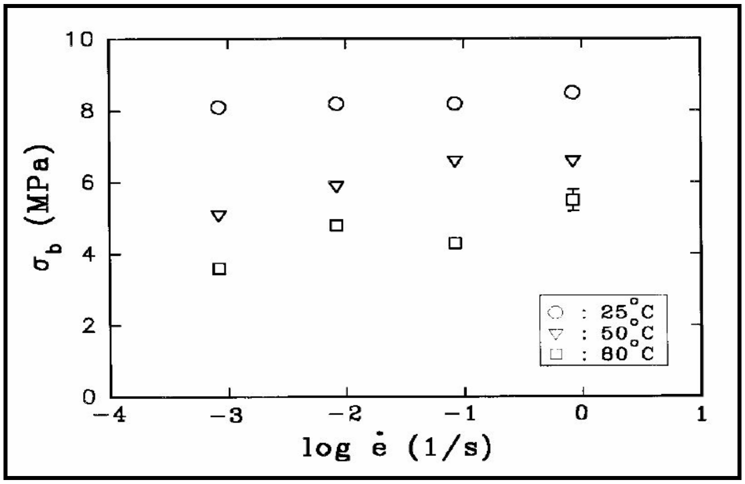


Figure A.11 Breaking stress, σ_b, of EPDM/PP TPE versus strain rate at different temperatures [6]

A.7 Fillers, Plasticizers and Additives within TPV

Reinforcing fillers are used to enhance the strength of polymeric materials. The extent of property enhancement depends on many factors including [17]

- the aspect ratio of fillers
- their degree of dispersion in the matrix
- their degree of orientation in the matrix
- the adhesion of fillers to the matrix interface

White fillers such as talc and other additives such as anti-oxidants, UV-stabilizers, pigments can be used at low level only for TPVs [10].

A.7.1 Carbon Black as Reinforcing Filler

The addition of reinforcing fillers such as carbon black raises the hardness, ultimate tensile strength, modulus and tension set, while it lowers elongation [3, 8]. In TPVs, carbon black is generally only used to give black color to products [3]. However; sufficient amount of carbon black can be used to increase the mechanical properties of TPVs. Greater carbon black affinity toward EPDM and the stronger interactions between the active groups on the surface of carbon black and unsaturated rubber segments result in the higher tendency of carbon black toward EPDM [8]. On the other hand, carbon black also appeared partially within the interface of two phases [8]. Used carbon black particles preferentially diffuse into the more viscous rubber phase and the size of the dispersed rubber particles increases with carbon black loading in a way increasing viscosity differences between rubber and thermoplastic phase [8]. Also the increase in size of the dispersed rubber particles could be explained by the carbon black's disturbing effect the uniformity in size and dispersion for EPDM phase by diffusing into the more viscous EPDM phase [8].

The tensile strength increase with loading carbon black occurs until 60 phr carbon black loading which is due to less wetting of the black particles by the rubber chains for 80/20 weigh ratio of EPDM/PP TPVs [8].

For the elongation at break property, it decreases slowly until 60 phr carbon black loading but there is a sharp decrease after this points for 80/20 weigh ratio of EPDM/PP TPVs [8].

A.7.2 Talc as a White Filler

Talc is one of the most used conventional white fillers such as mica and $CaCO_3$ [17]. Talc, $[Mg_3Si_4O_{10}(OH)_2]$, is a platelet form of magnesium silicate with a high aspect ratio [2]. Because the platelets can orient in the extrusion process, it provides rubber extrudates with smooth surfaces that can be extruded at high rates [2]. Because of this reason it is commonly used in compounds that have critical surface appearance requirement, which is smooth [2]. Also the large platelets of talc provide a barrier to gas and moisture permeability in compounds [2]. Like barrier property talc leads to restrict the solvent uptake so it improves the solvent resistance of TPV [17]. Furthermore, particulate filler such as talc does not only increase the hardness and stiffness of rubber compounds but also it reduces the cost with having low level of flame retardancy [2]. Although talc increases the hardness and stiffness of TPVs while also increasing weight and melt viscosity, it decreases toughness and optical clarity [17].

The study of Winters on EPDM/PP TPVs having both oil and talc exhibits interesting point. According to this study it is stated that one third of oil is neither mixed within the EPDM nor in the PP therefore oil can form a very thin layer around talc filler particles [1].

The effects of high talc loading, nearly 20%, to TPV in terms of mechanical properties are explained that it improves both tensile modulus and tensile strength with sacrifiying elongation at break [17].

Talc is anisotropic filler such as fiber, mica so the characteristic of talc is similar to glass fiber. Because of the talc particles having disc shape, the talc orientation depends on the type of flow. Vincent and Agassant reported that shear rate reaches a maximum near the mold wall, whereas the elongational rate reaches maximum at the center of the wall. In a simple shear flow near the mold wall, anisotropic fillers such as talc, glass fiber are nearly parallel to the flow direction. On contrary, in a simple elongational flow in the core, anisotropic fillers such as talc, glass fiber are nearly perpendicular to the flow direction or randomly oriented. Moreover according to the research of Choi and Kim [5] the

PP lamellae were arranged perpendicular to the cleavage surface of talc due to the transcrystallization of PP for injection molded PP/EPR/talc blends. In other words, PP could be transcrystallized on the cleavage surface of talc and the PP crystal was oriented perpendicular to the surface of talc [5]. Therefore, PP lamellae were arranged perpendicular to flow direction near the mold wall whereas they were arranged parallel to flow direction or randomly oriented in the core.

A.7.3 Processing Oil as a Plasticizer

Also oil is used in the composition of TPVs to manufacture softer composition, i.e. oil lowers the hardness of TPVs [7, 10, 14], with significant enhancement in processability and elastic recovery [3].

Furthermore, processing oil has low molecular weight. This causes the oil to plasticize both the PP and the EPDM phases [7, 14]

However the quantity and the type of oil is important in terms of cure state. All the oils and the plasticizers reduce the relative degree of crosslinking. Since in the peroxide curing peroxide free radicals abstract labile hydrogen from aromatic species leading to create non-reactive free radicals, the aliphatic type additives display higher cure states than aromatic counterparts [2].

Because the polarities of PP, EPDM and oil are not so high, the oil can be present in both PP and EPDM phases [14].

In order to indicate the quantity of oil presence in both PP and EPDM phases the distribution coefficient, K, as the ratio of the oil concentration in the PP phase over the oil concentration in the EPDM phase is defined by Ohlsson. The work of Picken [14] shows that K value is slightly less than 1 in solid state because of both elastomer and oil having ethylene components. In fact, the oil could be accepted as EP oligomer having higher than 70% ethylene content due to the paraffinic nature of the oil [14]. Also this research indicates K value being independent of blend composition in solid state. However, it is shown that in the melt state the oil concentration in PP phase decrease with increasing PP content in the blend. Also the oil in PP phase is presented in the amorphous region not in the crystalline region. As a result, the oil resides significantly in the elastomer and less preferably in noncrystalline PP phases [14]. This partition of oil improves the elasticity of the TPVs [3].

The processability of the material for TPV production in injection molding and extrusion becomes easy because of the fact that in the melt state the oil is shared between the EPDM and amorphous PP phases and not only lowers the viscosity of molten plastic, but also expands the volume fraction of the solid crosslinked rubber phase [3].

A.7.4 Stabilizers and Antioxidants

When TPV is exposed to heat or shear or etc in the presence of Oxygen the carbon radicals of the polymer chains are first converted to peroxy-radicals. Then these peroxy-radicals react with labile hydrogen of the polymer to form hydroperoxides that start the auto-catalytic reactions [18].

Antioxidants are used to prevent the degradation of polymers due to detrimental effects of Oxygen to improve the useful lifetime of polymers. In fact, the aim of usage of antioxidants does not completely eliminate the oxidation, but they prevent the auto-catalytic reactions [18].

Two types of antioxidants are used. The primary type antioxidants, which are hindered phenols and amines, are used to neutralize alkoxy and peroxy radicals causing abstraction of labile hydrogen in polymers. The secondary type antioxidants, which are thio compounds or phosphites, are used to decompose hydroperoxides that causes to stop propagation of radicals [18].

The used antioxidants in peroxide crosslinking is very important in that antioxidants result in reduced crosslink efficiency by deactivating the radicals formed after decomposition of the peroxide if they are used excess [18]. It was found that the quinoline-type antioxidant had the least effect on cure state, followed by the amine type, with the hindered phenol type antioxidant resulting in the largest reduction in final cure state [4].

Three important criteria should be thought to select suitable stabilizer for peroxide cured PP/EPDM TPVs [18]

1. The interaction and consumption of peroxide-radicals by stabilizers during the production stage
2. The effectiveness of antioxidant in stabilizing against oxidation during the process of aging
3. The color of the stabilizers and consequently of the TPV-end products

A.8 Processing of TPVs

The general production scheme of TPV [12] is located in the Figure A.12.

The process parameters are determined due to thermoplastic material, yet the properties and performance are determined due to elastomeric phase [3].

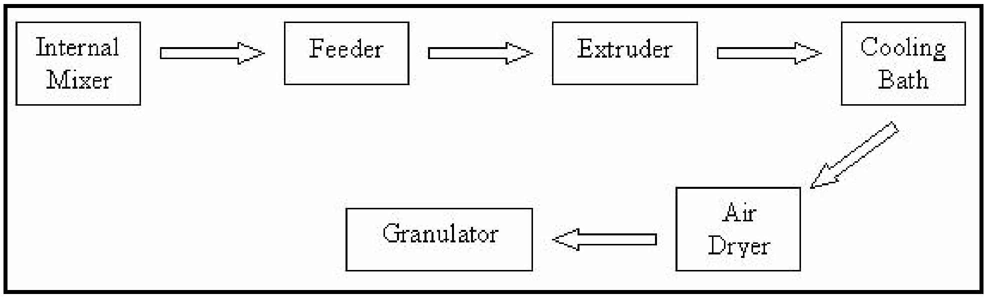


Figure A.12 TPV production scheme

When thinking the production methods we have to take into consideration on viscosity of the melt material. There is a viscosity decrease with increasing the processing temperature as it is seen in Figure A.13. On the contrary, the effect of temperature is lower than the shear effect [3].

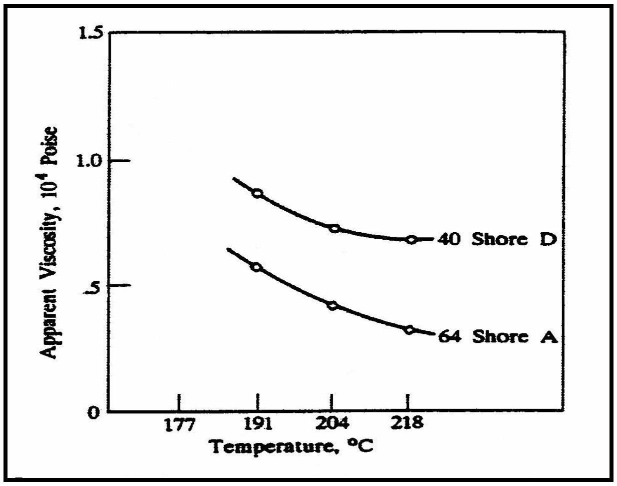


Figure A.13 TPV viscosity variation with temperature at 100 s^{-1} shear rate [3]

Calendaring, extrusion and injection molding are the important manufacturing methods used for the TPVs production. Shear rates profile differs from one method to another. The used shear rates for the manufacturing of TPVs are lowest for calendaring, moderate for extrusion and highest for injection molding according to Figure A.3. Moreover seen from the Figure A.3 the lines for 40 Shore D TPVs is located upward compared to 64 Shore A TPVs [3].

Extrusion is another widely use manufacture method to fabricate sheeting, intricate profiles, tubing, hose and electrical insulation and jacketing from TPVs. In addition to this, productions of foamed TPVs via extrusion with water as the foaming agent become popular recently [3]. Extrusion process variables such as throughput, rpm, set temperatures effects significantly the properties of produced TPVs [10]. L/D ratio for the extruder should be setted 15 or higher value convenient thermoplastic materials for efficient TPV production. The rubber networks have formed before all thermoplastic content is melted. Melt temperature increases very rapidly in the first kneading zone for high EPDM included TPV due to viscous dissipation at about 280^{o}C [10].

If we compared injection molding methods used for TPVs manufacturing to thermoset rubber manufacturing, there is no need for vulcanization process for TPVs that are applied for thermoset rubber. Also the cycle times for TPVs are less than thermoset rubber with higher curing time. On the other hand, the use of higher temperature makes the control over the vulcanization process hard for TPVs manufacture [3].

Blow molding, thermoforming and heat welding are the other manufacturing methods used for TPVs production and cannot be applied for thermoset rubber production. The hollow articles produced by TPVs by the help of blow molding are more efficient than the injection molded thermoset rubber ones [3].

The production cost of TPVs is lower than the thermoset rubber production cost but the price of equipment used for TPVs manufacture is higher than the thermoset rubber ones [3].

One of the main disadvantages of TPVs production is the moisture problem. Although TPVs has a hydrocarbon nature, it can easily pick up moisture and this causes a decrease in the performance of produced TPVs. In order to prevent this defect the used materials should be dried before processing [3].

A.9 Applications of TPVs

Since 1981 TPVs have been replaced with thermoset rubber day by day. Especially for the softer rubber products the popular materials become TPVs in case of thermoset rubbers [3]. Today, TPVs become one of the known elastomeric products with 150 kton usage in a year and 8%/year increase trend [10].

One of the mostly used application area of TPVs is the under-the hood automotive application where the service temperature can reach as high as 135 to 150^{o}C [3].

Other important application areas of TPVs are in motor vehicles, building construction as insonorization sheets [3, 12],sealing profiles [12], household appliances, electrical cable as insulating materials [3, 12], food packaging, hospital operating rooms, medical/pharmaceutical use [12], physicians' offices, sports [12], leisure items [12] and numerous other areas [3].

Moreover TPVs' thermoplastic nature makes TPVs recycle easily compared to thermoset rubber [3]. Thus, the production volume of TPV increases day by day.

APPENDIX B

DSC THERMOGRAMS OF UNAGED AND AGED TPV

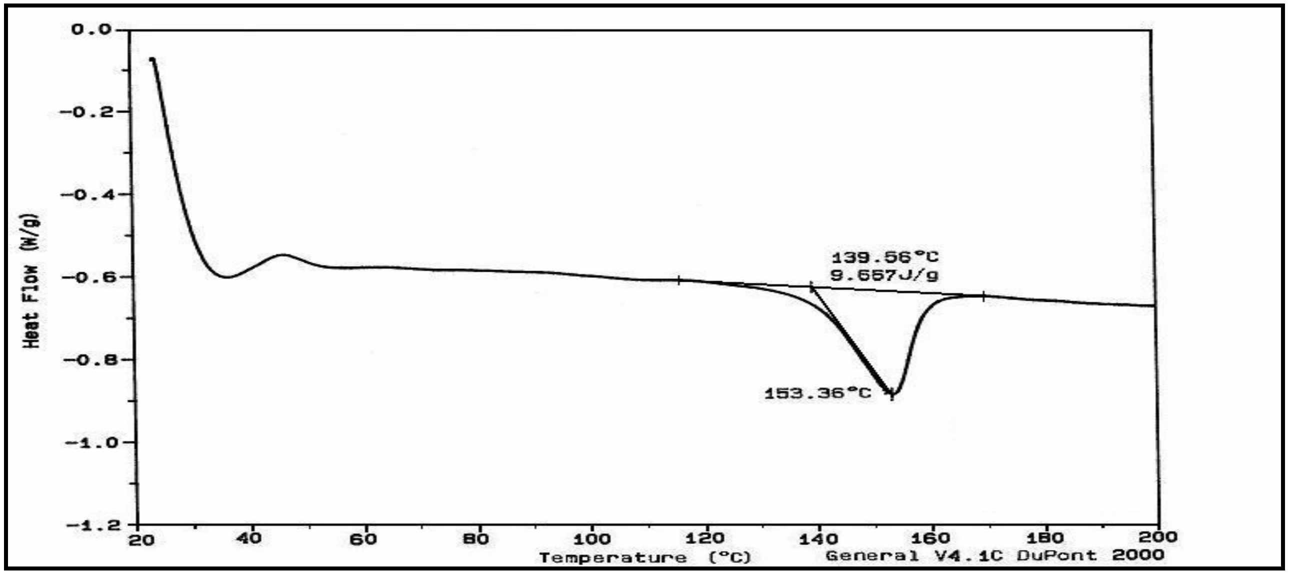


Figure B.1 DSC Thermogram of pure TPV

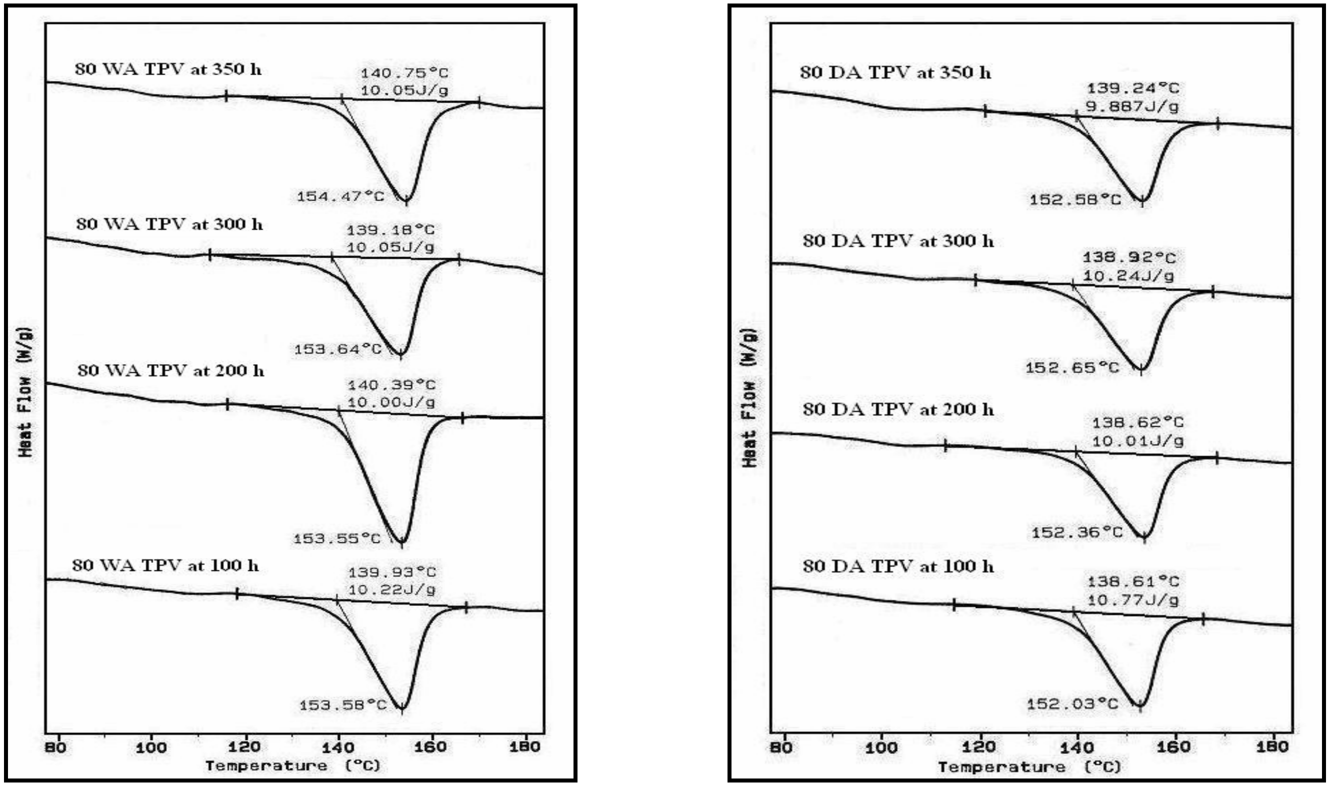


Figure B.2 DSC Thermograms of TPV specimens at 80 WA and 80 DA exposed to 100, 200, 300 and 350 h aging

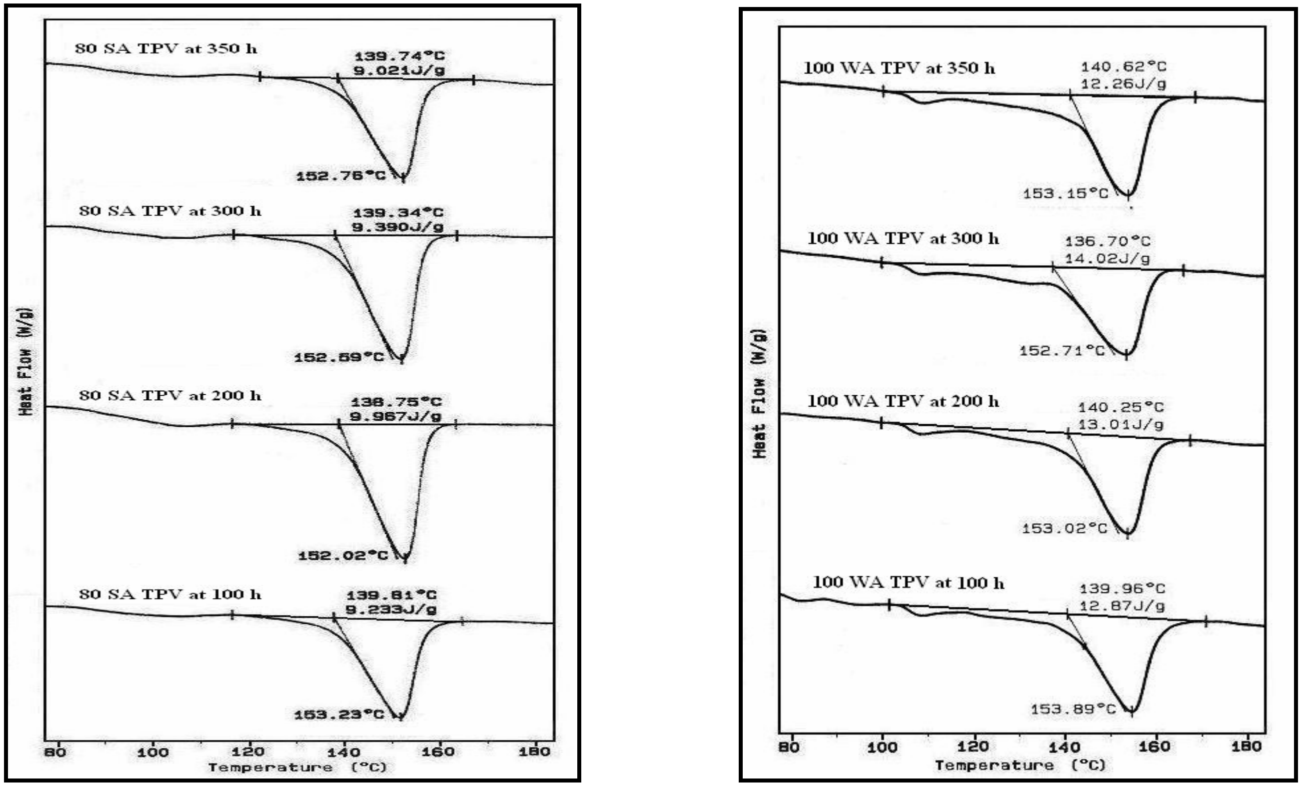


Figure B.3 DSC Thermograms of TPV specimens at 80 SA and 100 WA exposed to 100, 200, 300 and 350 h aging

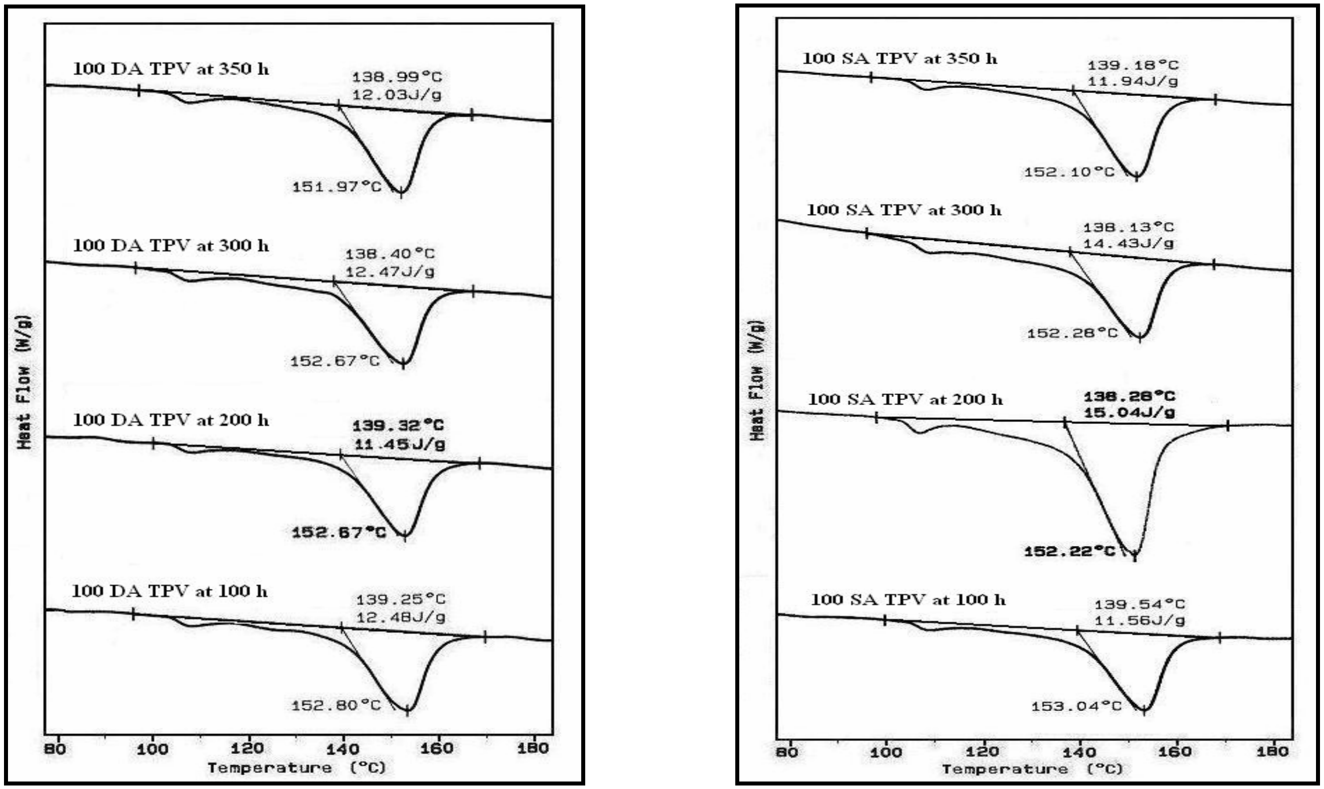


Figure B.4 DSC Thermograms of TPV specimens at 100 DA and 100 SA exposed to 100, 200, 300 and 350 h aging

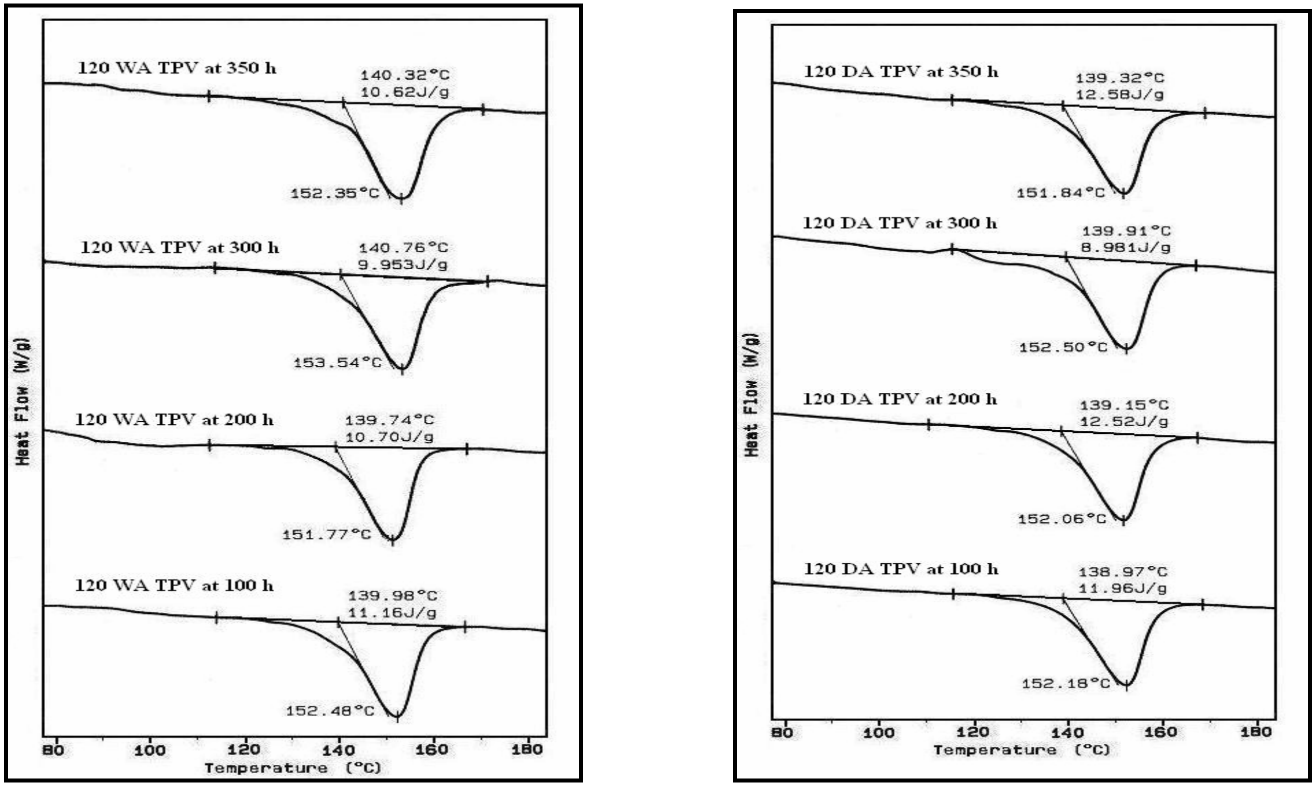


Figure B.5 DSC Thermograms of TPV specimens at 120 WA and 120 DA exposed to 100, 200, 300 and 350 h aging

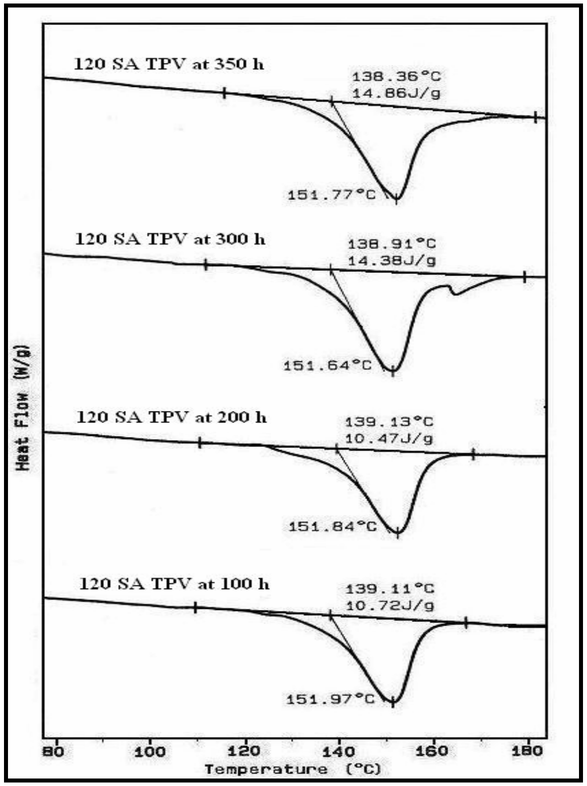


Figure B.6 DSC Thermograms of TPV specimens at 120 SA exposed to 100, 200, 300 and 350 h aging

APPENDIX C

IN ONE GRAPH ANALYSIS

In this section all DSC, Tensile testing and Hardness testing measurements were given in one graph for each type of measurements at all cases of temperatures and aging medium. DSC graphs were composed of variation of T_m of PP in TPV versus aging time and variation of percent crystallinity of PP in TPV versus aging time. Tensile testing graphs were composed of Variation of percent elongation at break of TPV versus aging time, variation of 100 % Modulus of TPV versus aging time, variation of 300 % Modulus of TPV versus aging time and variation of σ at break of TPV versus aging time. Hardness testing graph was composed of variation of hardness of TPV versus aging time.

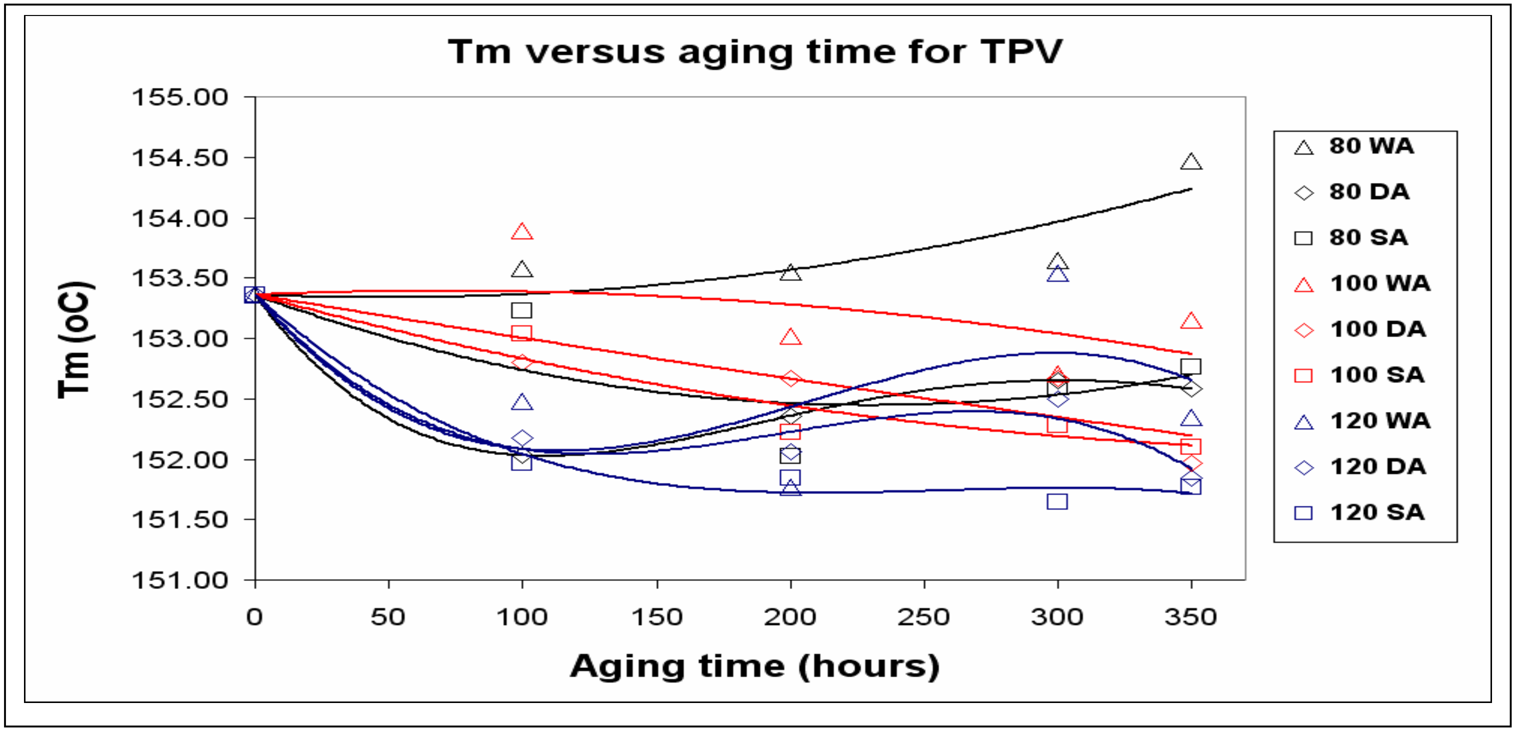


Figure C.1 Variation of T_m of PP in TPV versus aging time at 80, 100 and 120^{o}C aging in distilled water, detergent and shiner solution

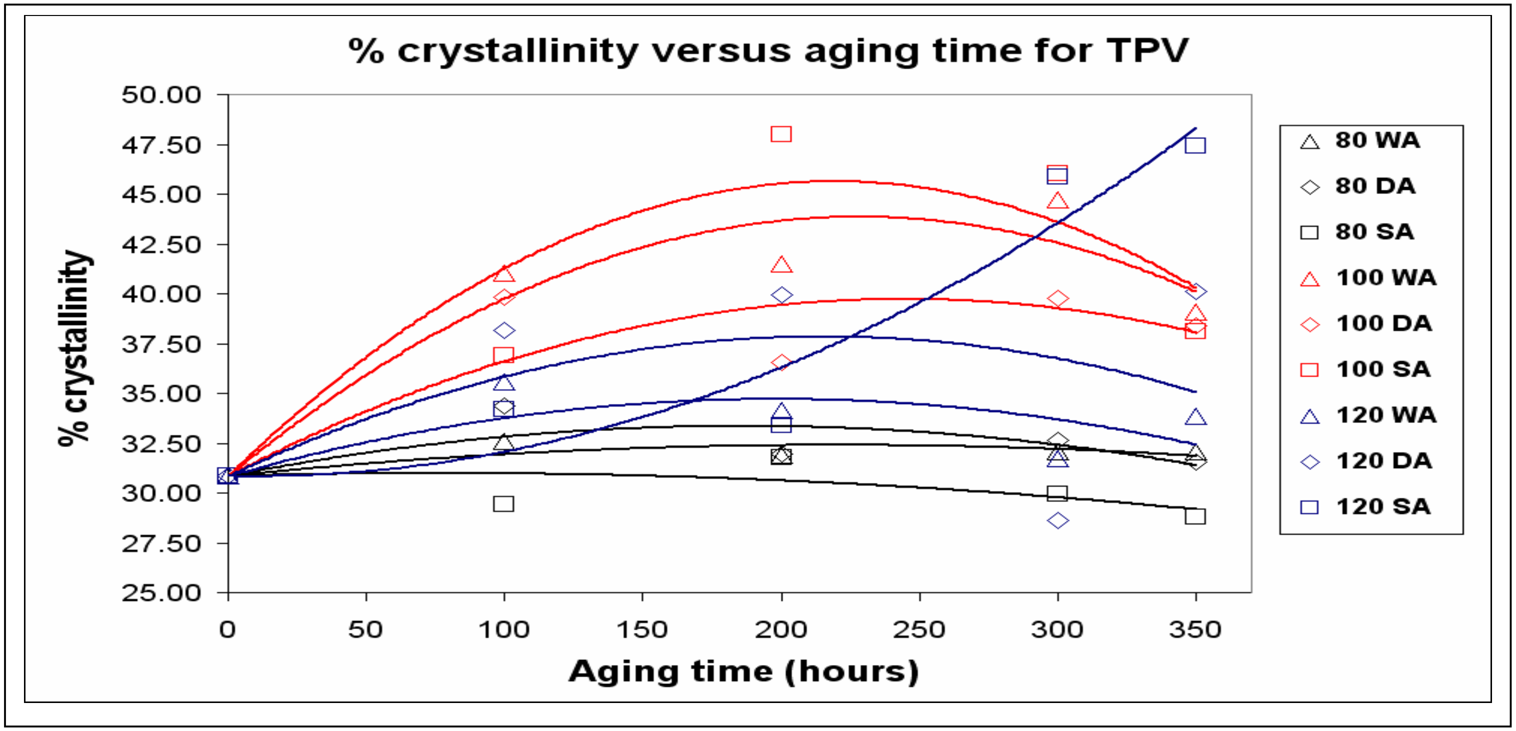


Figure C.2 Variation of percent crystallinity of PP in TPV versus aging time at 80, 100 and 120°C aging in distilled water, detergent and shiner solution

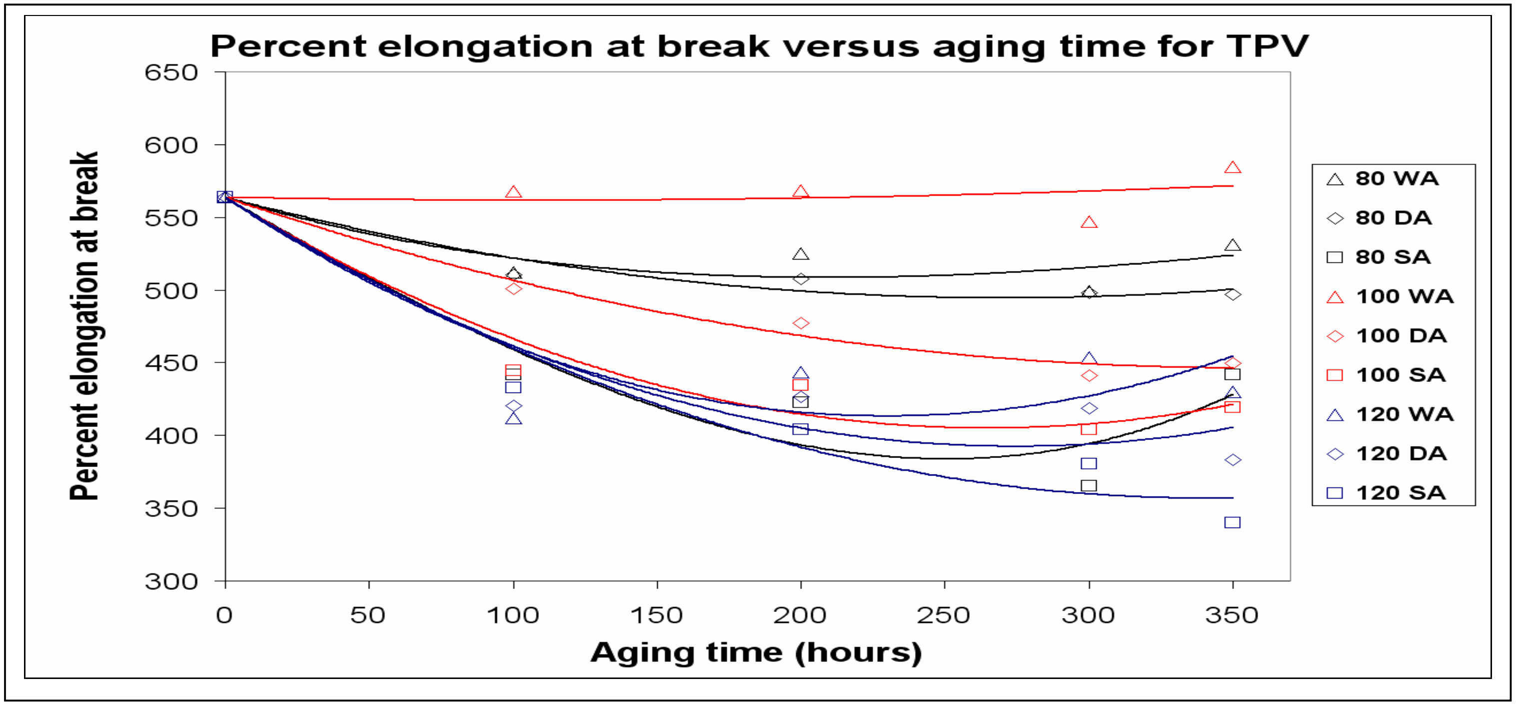


Figure C.3 Variation of percent elongation at break of TPV versus aging time at 80, 100 and 120^{o}C aging in distilled water, detergent and shiner solution

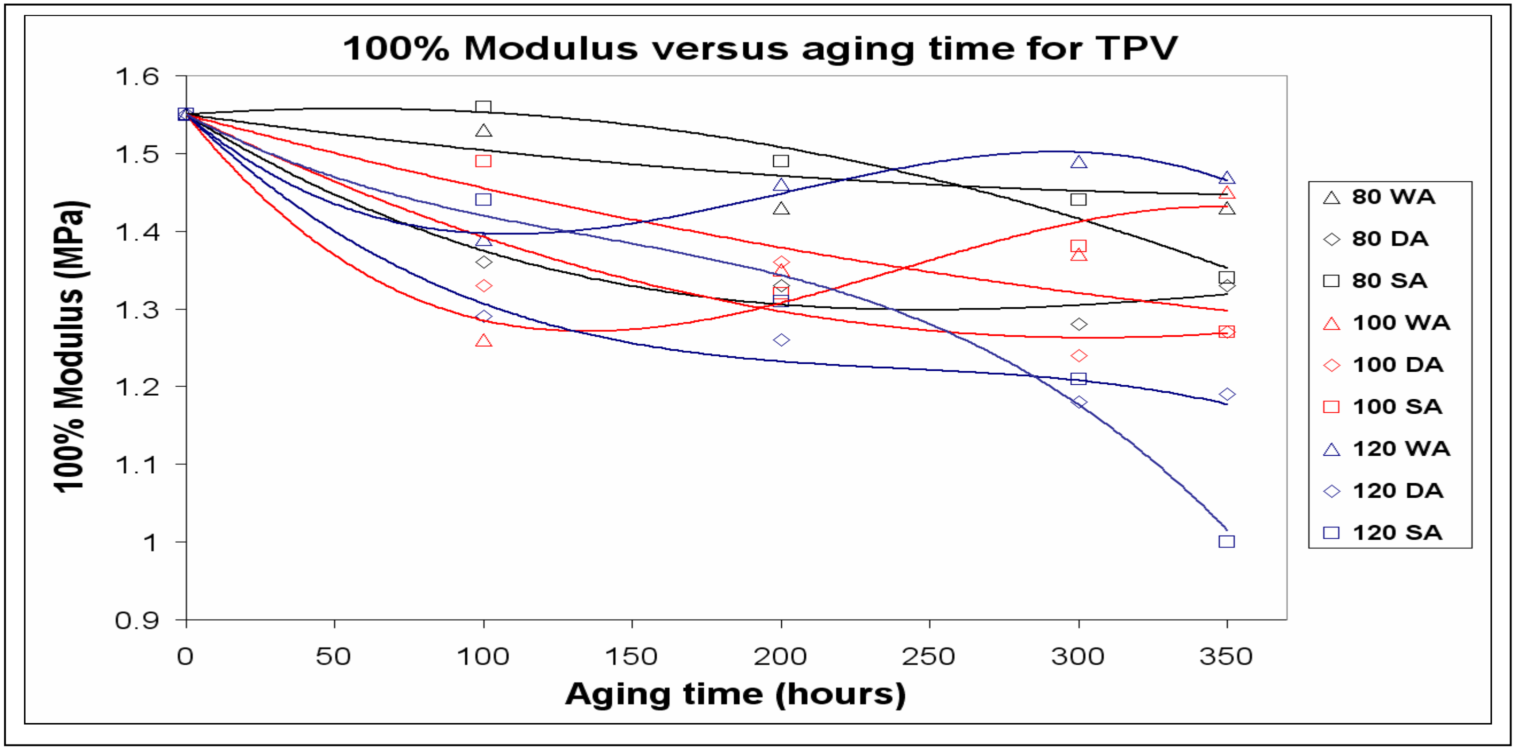


Figure C.4 Variation of 100 % Modulus of TPV versus aging time at 80, 100 and 120°C aging in distilled water, detergent and shiner solution

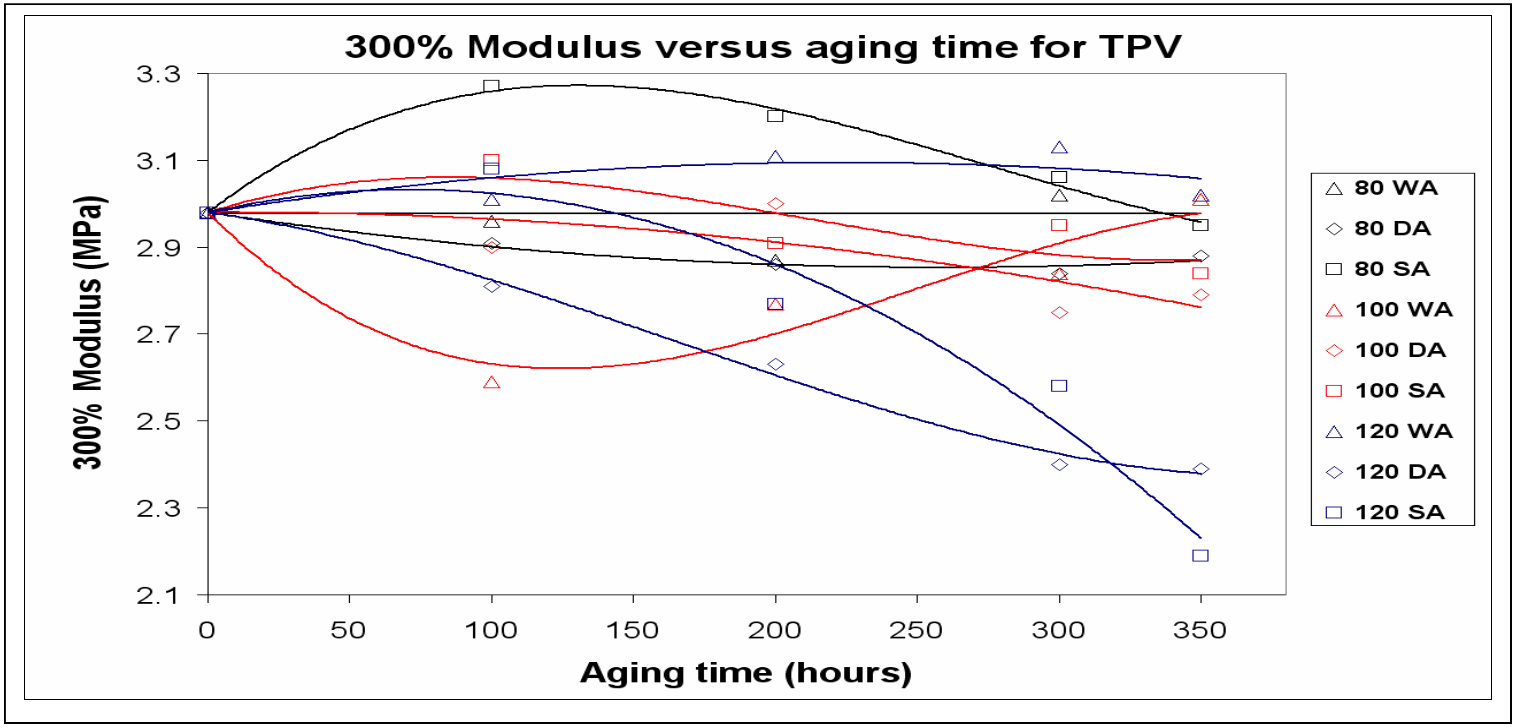


Figure C.5 Variation of 300 % Modulus of TPV versus aging time at 80, 100 and 120°C aging in distilled water, detergent and shiner solution

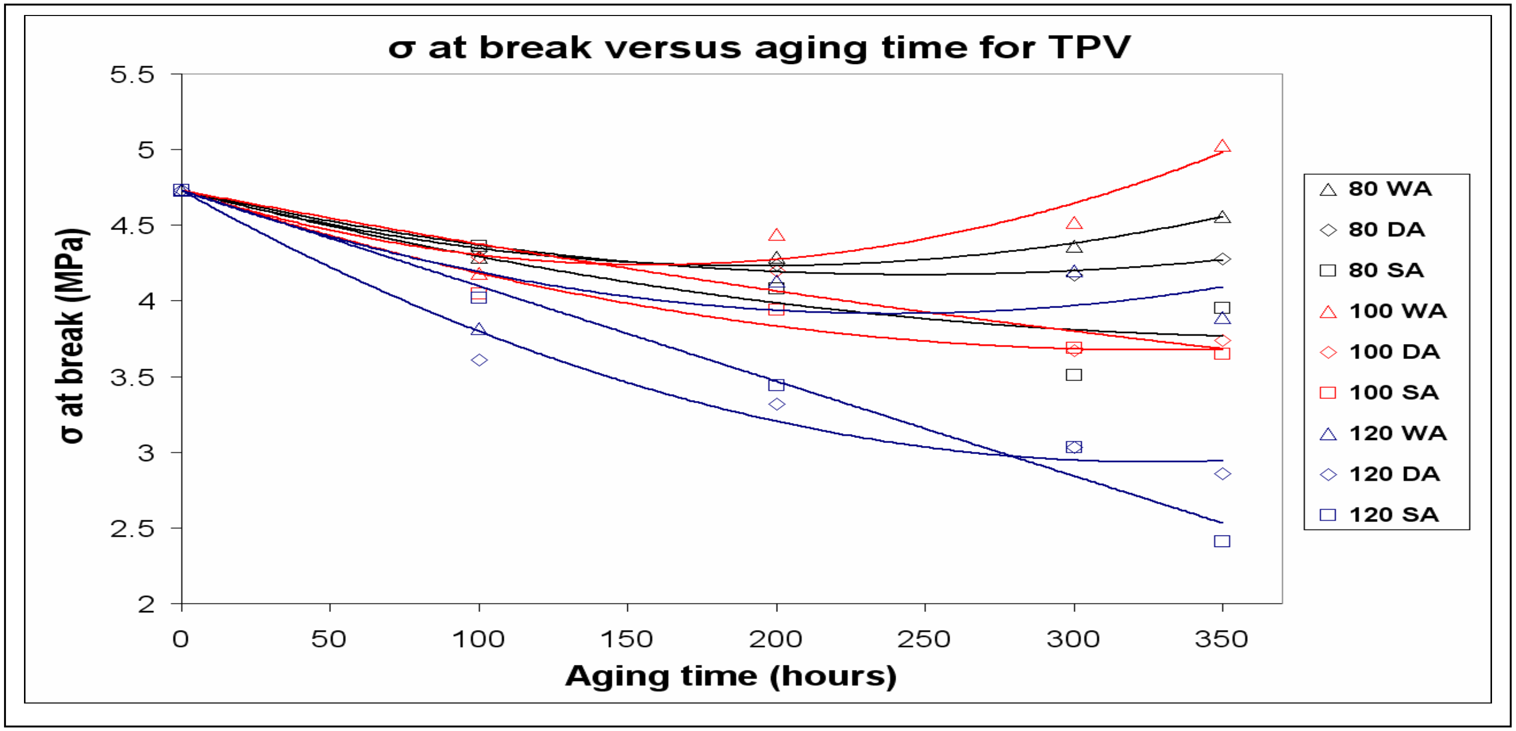


Figure C.6 Variation of σ at break of TPV versus aging time at 80, 100 and 120°C aging in distilled water, detergent and shiner solution

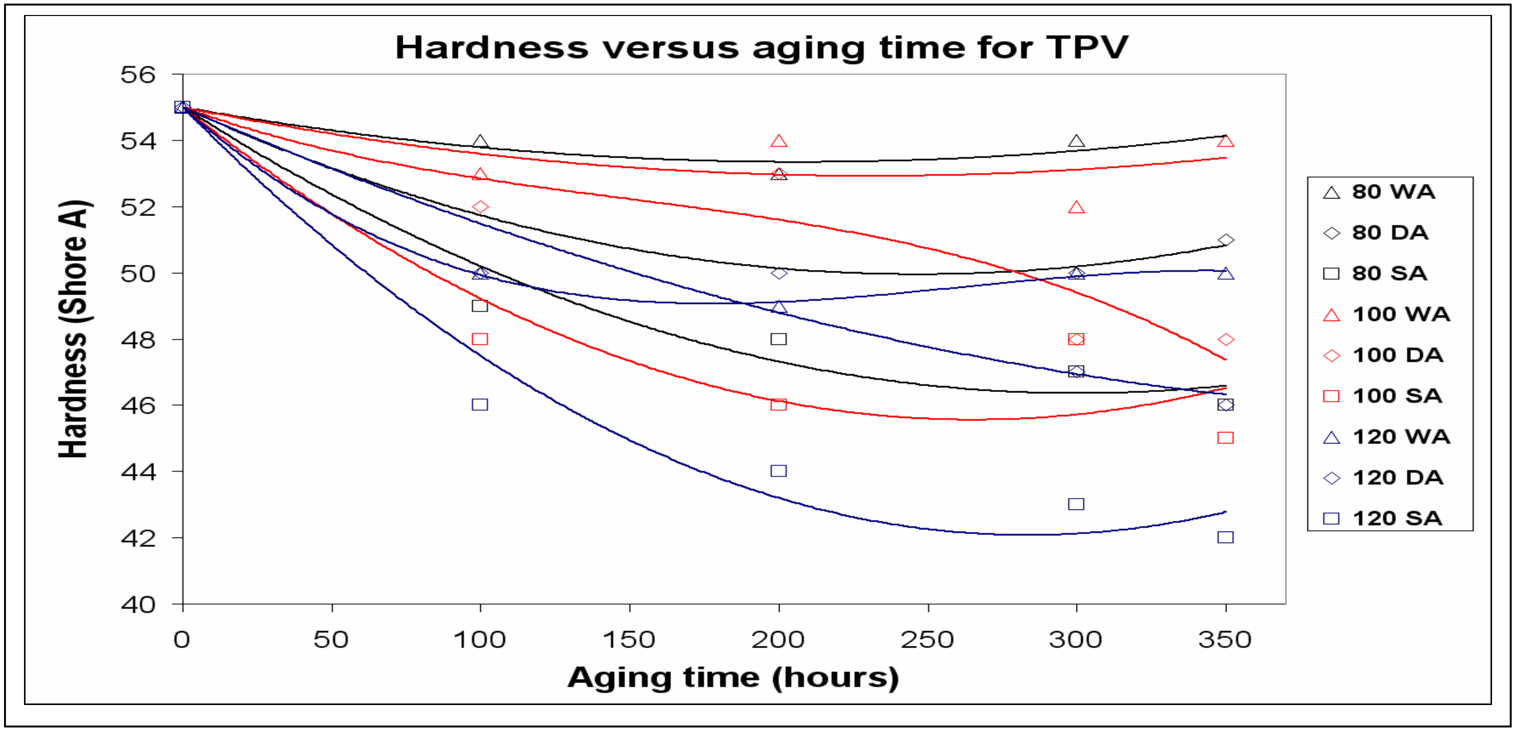


Figure C.7 Variation of hardness of TPV versus aging time at 80, 100 and 120°C aging in distilled water, detergent and shiner solution

APPENDIX D

TENSILE TESTING DATA

Table D.1 Standard deviations of Percent Elongation at Break data in Figure 3.21

Percent Elongation at Break	80 WA	100 WA	120 WA
Pure TPV	563.65 ± 33.55	563.65 ± 33.55	563.65 ± 33.55
100 h	511.98 ± 23.54	567.71 ± 25.66	412.24 ± 14.15
200 h	525.11 ± 9.89	568.49 ± 25.54	443.59 ± 7.79
300 h	499.02 ± 15.23	546.94 ± 37.95	453.61 ± 5.79
350 h	531.46 ± 10.44	584.74 ± 19.22	430.24 ± 10.93

Table D.2 Standard deviations of Percent Elongation at Break data in Figure 3.22

Percent Elongation at Break	80 DA	100 DA	120 DA
Pure TPV	563.65 ± 33.55	563.65 ± 33.55	563.65 ± 33.55
100 h	510.31 ± 10.63	501.11 ± 7.66	420.63 ± 8.74
200 h	507.52 ± 15.90	477.15 ± 8.21	426.84 ± 9.52
300 h	498.04 ± 10.20	441.29 ± 10.15	418.85 ± 8.02
350 h	496.69 ± 5.59	449.85 ± 7.22	383.42 ± 6.67

Table D.3 Standard deviations of Percent Elongation at Break data in Figure 3.23

Percent Elongation at Break	80 SA	100 SA	120 SA
Pure TPV	563.65 ± 33.55	563.65 ± 33.55	563.65 ± 33.55
100 h	441.73 ± 11.92	444.66 ± 9.98	432.77 ± 15.79
200 h	422.6 ± 24.98	434.64 ± 0.64	404.17 ± 21.07
300 h	365.22 ± 21.38	404.22 ± 16.97	380.74 ± 37.10
350 h	441.62 ± 12.23	419.39 ± 11.40	339.87 ± 8.90

Table D.4 Standard deviations of 100 % Modulus data in Figure 3.24

100 % Modulus	80 WA	100 WA	120 WA
Pure TPV	1.55 ± 0.06	1.55 ± 0.06	1.55 ± 0.06
100 h	1.53 ± 0.07	1.26 ± 0.02	1.39 ± 0.06
200 h	1.43 ± 0.04	1.35 ± 0.02	1.46 ± 0.06
300 h	1.49 ± 0.07	1.37 ± 0.07	1.49 ± 0.06
350 h	1.43 ± 0.04	1.45 ± 0.05	1.47 ± 0.05

Table D.5 Standard deviations of 100 % Modulus data in Figure 3.25

100 % Modulus	80 DA	100 DA	120 DA
Pure TPV	1.55 ± 0.06	1.55 ± 0.06	1.55 ± 0.06
100 h	1.36 ± 0.06	1.33 ± 0.05	1.29 ± 0.03
200 h	1.33 ± 0.03	1.36 ± 0.05	1.26 ± 0.04
300 h	1.28 ± 0.04	1.24 ± 0.07	1.18 ± 0.02
350 h	1.33 ± 0.01	1.27 ± 0.03	1.19 ± 0.05

Table D.6 Standard deviations of 100 % Modulus data in Figure 3.26

100 % Modulus	**80 SA**	**100 SA**	**120 SA**
Pure TPV	1.55 ± 0.06	1.55 ± 0.06	1.55 ± 0.06
100 h	1.56 ± 0.06	1.49 ± 0.08	1.44 ± 0.07
200 h	1.49 ± 0.03	1.32 ± 0.07	1.31 ± 0.04
300 h	1.44 ± 0.06	1.38 ± 0.06	1.21 ± 0.06
350 h	1.34 ± 0.07	1.27 ± 0.03	1.00 ± 0.01

Table D.7 Standard deviations of 300 % Modulus data in Figure 3.27

300 % Modulus	**80 WA**	**100 WA**	**120 WA**
Pure TPV	2.98 ± 0.06	2.98 ± 0.06	2.98 ± 0.06
100 h	2.96 ± 0.09	2.59 ± 0.04	3.01 ± 0.07
200 h	2.87 ± 0.09	2.77 ± 0.05	3.11 ± 0.06
300 h	3.02 ± 0.06	2.84 ± 0.10	3.13 ± 0.09
350 h	3.01 ± 0.11	3.01 ± 0.06	3.02 ± 0.08

Table D.8 Standard deviations of 300 % Modulus data in Figure 3.28

300 % Modulus	**80 DA**	**100 DA**	**120 DA**
Pure TPV	2.98 ± 0.06	2.98 ± 0.06	2.98 ± 0.06
100 h	2.91 ± 0.06	2.90 ± 0.05	2.81 ± 0.03
200 h	2.86 ± 0.03	3.00 ± 0.04	2.63 ± 0.04
300 h	2.84 ± 0.04	2.75 ± 0.06	2.40 ± 0.05
350 h	2.88 ± 0.02	2.79 ± 0.05	2.39 ± 0.03

Table D.9 Standard deviations of 300 % Modulus data in Figure 3.29

300 % Modulus	**80 SA**	**100 SA**	**120 SA**
Pure TPV	2.98 ± 0.06	2.98 ± 0.06	2.98 ± 0.06
100 h	3.27 ± 0.06	3.10 ± 0.05	3.08 ± 0.07
200 h	3.20 ± 0.04	2.91 ± 0.06	2.77 ± 0.03
300 h	3.06 ± 0.07	2.95 ± 0.10	2.58 ± 0.11
350 h	2.95 ± 0.06	2.84 ± 0.05	2.19 ± 0.05

Table D.10 Standard deviations of σ at break data in Figure 3.30

σ at break	**80 WA**	**100 WA**	**120 WA**
Pure TPV	4.73 ± 0.22	4.73 ± 0.22	4.73 ± 0.22
100 h	4.29 ± 0.11	4.18 ± 0.19	3.82 ± 0.12
200 h	4.29 ± 0.08	4.44 ± 0.15	4.13 ± 0.05
300 h	4.36 ± 0.08	4.52 ± 0.22	4.20 ± 0.07
350 h	4.56 ± 0.17	5.03 ± 0.18	3.89 ± 0.15

Table D.11 Standard deviations of σ at break data in Figure 3.31

σ at break	**80 DA**	**100 DA**	**120 DA**
Pure TPV	4.73 ± 0.22	4.73 ± 0.22	4.73 ± 0.22
100 h	4.33 ± 0.12	4.29 ± 0.08	3.61 ± 0.06
200 h	4.24 ± 0.13	4.20 ± 0.07	3.32 ± 0.04
300 h	4.17 ± 0.08	3.67 ± 0.07	3.03 ± 0.05
350 h	4.28 ± 0.03	3.74 ± 0.12	2.86 ± 0.07

Table D.12 Standard deviations of σ at break data in Figure 3.32

σ at break	80 SA	100 SA	120 SA
Pure TPV	4.73 ± 0.22	4.73 ± 0.22	4.73 ± 0.22
100 h	4.36 ± 0.09	4.05 ± 0.08	4.02 ± 0.10
200 h	4.08 ± 0.23	3.94 ± 0.09	3.44 ± 0.11
300 h	3.51 ± 0.09	3.69 ± 0.14	3.03 ± 0.36
350 h	3.95 ± 0.16	3.65 ± 0.05	2.41 ± 0.09

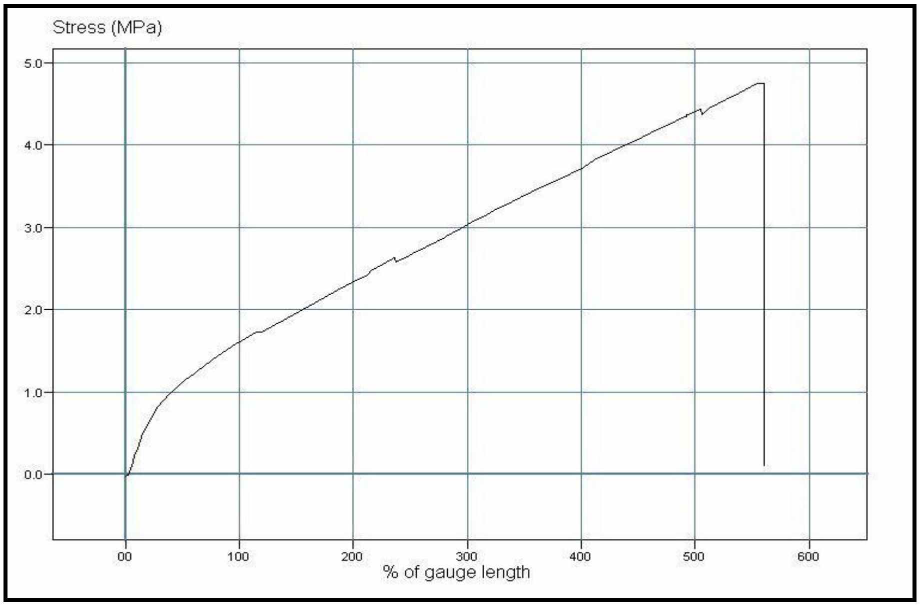


Figure D.1 Stress versus % gauge length curve of unaged TPV

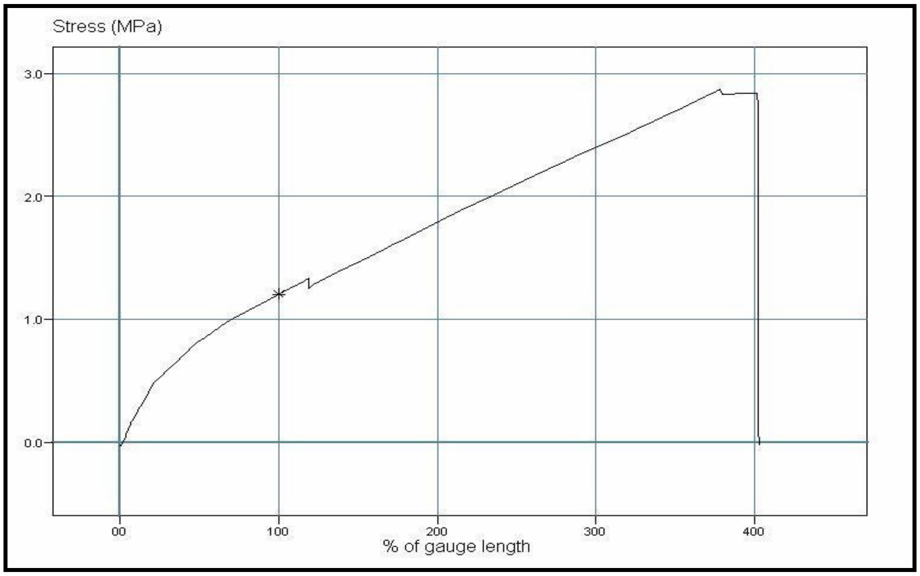


Figure D.2 Stress versus % gauge length curve of 120^{o}C 350 h detergent aged TPV

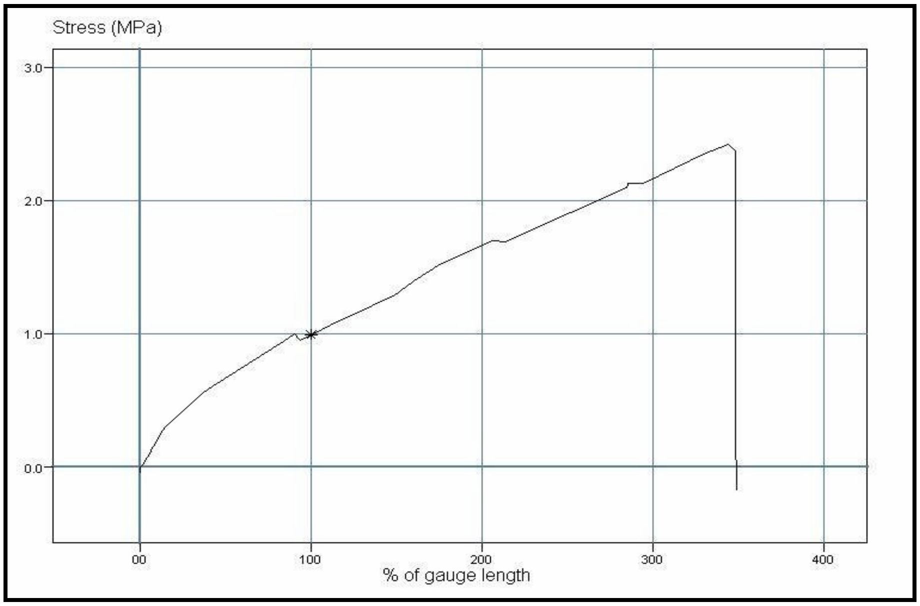


Figure D.3 Stress versus % gauge length curve of 120^{o}C 350 h shiner aged TPV