INFLUENCE OF SURFACE TREATMENT OF FILLERS ON THE MECHANICAL PROPERTIES OF THERMOPLASTIC POLYURETHANE COMPOSITES

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

BY

ÜMİT TAYFUN

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

DECEMBER 2015

Approval of the thesis:

INFLUENCE OF SURFACE TREATMENT OF FILLERS ON THE MECHANICAL PROPERTIES OF THERMOPLASTIC POLYURETHANE COMPOSITES

submitted by **ÜMİT TAYFUN** in partial fulfillment of the requirements for the degree of **Doctor of Philosophy in Polymer Science and Technology Department, Middle East Technical University** by,

Prof. Dr. Gülbin Dural Ünver
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Necati Özkan
Head of Department, **Polymer Science and Technology**

Prof. Dr. Erdal Bayramlı
Supervisor, **Chemistry Dept., METU**

Prof. Dr. Ülkü Yılmazer
Co-Supervisor, **Chemical Engineering Dept., METU**

Examining Committee Members:

Prof. Dr. Nursel Dilsiz
Chemical Engineering Dept., Gazi University

Prof. Dr. Erdal Bayramlı
Chemistry Dept., METU

Prof. Dr. Göknur Bayram
Chemical Engineering Dept., METU

Prof. Dr. Özdemir Doğan
Chemistry Dept., METU

Prof. Dr. Mehmet Saçak
Chemistry Dept., Ankara University

Date: December 14, 2015

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Ümit Tayfun

Signature:

ABSTRACT

INFLUENCE OF SURFACE TREATMENT OF FILLERS ON THE MECHANICAL PROPERTIES OF THERMOPLASTIC POLYURETHANE COMPOSITES

Tayfun, Ümit
Ph.D., Department of Polymer Science and Technology
Supervisor: Prof. Dr. Erdal Bayramlı
Co-Supervisor: Prof. Dr. Ülkü Yılmazer

December 2015, 125 pages

The incompatibility between filler and polymer matrix is the major restriction for the production of composites to have desirable properties. Several surface modification methods are applied to filler surface in order to improve the interfacial adhesion with polymer matrix. Easy processablity and fully recyclability character of thermoplastic polyurethane (TPU) make it cost effective for many applications. Majority of TPU application is across a range of markets including automotive, sporting goods, medical devices, tubes, hoses, wires and cables.

The objectives of this research are the enhancement of interfacial interactions between several fillers and TPU matrix by applying surface treatments and investigation the effects of these treatments on the mechanical properties of TPU based composites. The surface of fillers after modifications were characterized with fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray spectroscopy (EDX). Pristine and surface functionalized fillers were incorporated in TPU matrix by using melt-blending method. Two types of TPU composites, green polymer composites and carbonaceous fillers reinforced composites were prepared. Mechanical properties, melt flow characteristics and morphologies of the composites were evaluated by using tensile, dynamic mechanical analysis (DMA) and Shore hardness tests, melt flow index (MFI) test and scanning electron microscopy (SEM), respectively.

Surface modifications of fillers resulted in better mechanical properties for their composites as compared with untreated ones. SEM micrographs revealed that surface treated reinforcers dispersed more homogeneously than untreated fillers in the TPU matrix. Results confirmed that surface modifications improved the adhesion of fillers to TPU.

Keywords: polymer composites, thermoplastic polyurethane, surface modifications, mechanical properties

ÖZ

DOLGU MADDELERİNE YÜZEY İŞLEMİ UYGULANMASININ TERMOPLASTİK POLİÜRETAN KOMPOZİTLERİN MEKANİK ÖZELLİKLERİNE ETKİSİ

Tayfun, Ümit
Doktora, Polimer Bilimi ve Teknolojisi Bölümü
Tez Yöneticisi: Prof. Dr. Erdal Bayramlı
Ortak Tez Yöneticisi: Prof. Dr. Ülkü Yılmazer

Aralık 2015, 125 sayfa

İstenilen özelliklere sahip polimer kompozitlerin hazırlanmasındaki en büyük engel, dolgu malzemesi ile polimer matris arasındaki uyumsuzluktur. Polimer ile dolgu yüzeyleri arasındaki yapışmayı arttırmak amacıyla bir çok yüzey modifikasyon yöntemi uygulanmaktadır. Kolay işlenebilme ve tamamen geri kazanabilme özellikleri termoplastik poliüretanı (TPU), bir çok uygulamada etkin kullanım sağlamaktadır. TPU, uygulama alanı olarak özellikle otomotiv ve inşaat endüstrisinde, ayakkabı, ambalaj, koruma kıyafetleri, kablolar, tel ve boru üretimi gibi pek çok alanda kullanılmaktadır.

Bu çalışmanın temel amacı, dolgu malzemesi ile TPU arasındaki uyumun yüzey modifikasyonları uygulanarak arttırılması ve bu modifikasyonların TPU kompozitlerinin mekanik özelliklerine etkilerinin ortaya çıkarılmasıdır. Modifikasyon işlemlerinden sonra dolgu malzemesi yüzeyleri, kızılötesi spektroskopisi (FTIR) ve enerji dağılımlı X-ışını spektroskopisi (EDX) yöntemleriyle karakterize edilmiştir. Yüzey işlemi uygulanan ve uygulanmayan dolgu maddeleri TPU matrisine eriyik karıştırma yöntemi kullanılarak eklenmiştir. İki farklı TPU kompozit hazırlanmıştır; yeşil ve karbonlu dolgu içeren kompozitler. Modifiyeli ve modifiyesiz dolgular TPU matriksine eriyik karıştırma yöntemiyle eklenmiştir. Hazırlanan kompozitlerin mekanik özellikleri, erime akış karakteristikleri ve morfolojik yapıları sırası ile çekme, dinamik mekanik analiz (DMA) ve Shore sertlik testleri, erime akış indisi testi (MFI) ve taramalı elektron mikroskobu (SEM) yöntemleri kullanılarak incelenmiştir.

Dolgulara yüzey modifikasyonu uygulanması, işlem görmeyenler ile kıyaslandığında kompozitlerinde daha iyi mekanik özellikler ile sonuçlanmıştır. SEM mikrografikleri incelendiğinde, yüzey işlemi görmüş güçlendiricilerin TPU matrisi içinde işlem görmeyenlerden daha homojen dağıldığı saptanmıştır. Sonuçlar, yüzey modifikasyonlarının dolgu malzemesinin TPU polimerine yapışmasını arttırdığını doğrulamıştır.

Anahtar Kelimeler: polimer kompozitler, termoplastik poliüretan, yüzey işlemleri, mekanik özellikler

To my lovely mother

ACKNOWLEDGEMENTS

I would like express my gratitude to my thesis supervisor Prof. Dr. Erdal Bayramlı. This thesis would not have been successful without his understanding, support and guidance.

I would also like gratefully thank to my co-supervisor Prof. Dr. Ülkü Yılmazer and my thesis supervising committee members Prof. Dr. Göknur Bayram and Prof. Dr. Özdemir Doğan for their significant contributions. I would like to thank to Prof. Dr. Teoman Tinçer for his valuable advices and giving me the opportunity to study in his polymer rheology laboratory.

I wish to express my sincere thanks to Assoc. Prof. Mehmet Doğan for his kind support, encouraging advices, valuable discussions and corporation throughout my thesis beside his invaluable friendship.

It is my pleasure to thank to my colleagues Assist. Prof. Yasin Kanbur, Assist. Prof. Ümit Hakan Yıldız, Dr. Sema Demirci Uzun, Assist. Prof. Ufuk Abacı and Prof. Dr. Hasan Yüksel Güney for their friendship and research collaboration.

I express my special thanks to Osman Yaslıtaş for all his help and brotherhood. I would also thank to my former lab-mates Burhan Fuat Çankaya, Assoc. Prof. Güralp Özkoç, Dr. Yasemin Altun and my current lab-mates Tuğba Kaya Deniz and Türkan Güler for their endless friendships.

I sincerely acknowledge my friends from the PST department for making my stay in METU memorable; Fırat Hacıoğlu, Esra Oğuztürk, Vildan Sanduvaç, Esra Özdemir, Alinda Öykü Akar, Ayşegül Hisar Telli, Nehir Utku, Müberra Göktaş, Yasemin Durmuş and Barış Koltuksuz.

I am grateful to several musicians whose songs feed my soul and enlarged my vision when I needed some motivation about changing my direction to the right side and keeping on the walk that way; Yngwie J. Malmsteen (Black Star), Bruce Dickinson (Inside the Machine), Queensrÿche (Silent Lucidity), Holocaust (Death or Glory), Celtic Frost (Wings of Solitude), Savatage (Edge of Thorns), Guns N' Roses (Estranged), Tiamat (Whatever That Hurts), Die Toten Hosen (Tage Wie Diese), Chemical Brothers (The Private Psychedelic Reel), Bad Religion (Shattered Faith), Six Feet Under (As I Die), Alice in Chains (Heaven Beside You), Dr. Skull (Rain), Pearl Jam (Jeremy), Ramones (Pet Sematary), Radiohead (Morning Bell) and Blur (Out of Time).

Last but not the least; I owe my deepest gratitude to my mother and other family members for their love, support, encouragement and patience all through my life.

TABLE OF CONTENTS

CHAPTERS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

LIST OF SCHEMES

SCHEMES

ABBREVIATIONS

APTES	Amino Propyl Tri-Ethoxy Silane
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
BPO_4	Benzoyl Peroxide
BP-	Benzoyl Peroxide Treated
C_{60}	Fullerene
CF	Carbon Fiber
CFR	Carbonaceous Fillers Reinforced
CM-	Cured Isocyanate Sized
CNT	Carbon Nanotube
DMA	Dynamic Mechanical Analysis
DS-	Desized
EDX	Energy Dispersive X-ray Spectroscopy
EP-	Epoxy Sized
FF	Flax Fiber
FTIR	Fourier Transform Infrared Spectroscopy
HN-	Nitric Acid Treated
HNO_3	Nitric Acid
HW-	Hot Water Treated
$KMnO_4$	Potassium Permanganate
MD-	Isocyanate Sized
MFI	Melt Flow Index
NaOH	Sodium Hydroxide
Na-	Alkali Treated

PLA	Poly(lactic acid)
PM-	Potassium Permanganate Treated
pMDI	Polymeric Methylene Diphenyl Diisocyanate
PU-	Polyurethane Sized
RS	Rice Straw
SEM	Scanning Electron Microscopy
Si-	Silane Treated
T_g	Glass Transition Temperature
TPU	Thermoplastic Polyurethane

CHAPTER 1

INTRODUCTION

Polyurethanes are the class of polymer that found widely use in several industrial applications. They can be used with different forms such as foams, adhesives, coatings, elastomers and fibers by changing polyol structure. Thermoplastic polyurethane (TPU) is one of the most commonly used types of these forms due to the advantages of recyclability and practical processability by using traditional methods in industry. There has been increasing attention performed about TPU for devoting new approaches for synthesis of them, preparation of their blends with several polymers and producing their composites in the literature in recent years. Tuning the properties of TPU by incorporating different types of fillers has become trending issue because of the opportunity for using conventional techniques such as extrusion, injection and compression molding. Practical optimization and adaptation of these methods from lab-scale to industrial production lines rapidly open ways for researchers and producers to reach composite parts with desirable properties for versatile applications.

Mechanical strength of polymer composites is mainly depending on some parameters including size, dispersion and orientation of fillers. Since the load transfer takes place from polymer matrix to filler particle, interface between them gains importance that will be able to fulfill required level of mechanical response for polymer composites. Polar character of the most filler materials make them incompatible with polymeric matrices. The most practical and commonly used way to drawback that challenge is applying the surface modifications on the filler surfaces. Formation of effective interfacial adhesion between filler and polymer can be achieved by these modification methods. This can be improved by load transfer between polymeric matrix and reinforcement, and mechanically strong composite material can be obtained.

The composites prepared in this work were divided into two subtitles as green polymer composites and carbonaceous fillers reinforced composites. Two types of lignocellulosics, rice straw (RS) and flax fiber (FF), were used in the first kind of composites. RS is an agricultural waste that can not be used as an animal feed because of its high silica content. Different from other agricultural residues, it is generally burned after harvest. Flax fiber has found effective use mainly in textile market. Polymer composites reinforced with flax fiber have been also developed for transport and construction applications in recent years. Since natural sources were used as filler in this type of composites, new and special bio-based TPU was prefered as matrix material.

Carbon nanotube and fullerene were incorparated in TPU for the production of carbonaceous filler reinforced polymer composites. Nano dimensional fillers have great potential for the manufacturing of advanced polymeric composites. Whereas, the problems such as incompatibillity, uniform distribution and scale up to industrial fabrication were exist. Melt-mixing is rarely used method for these types of composite systems in the literature. Production of TPU/fullerene nanocomposites using melt compounding has been the first attempt in this work. Short carbon fibers were also used as a carbonaceous filler in this research. The interest for carbon fiber reinforced thermoplastic composites has been increased in recent years. Especially, the fabrication of ultra-low weight and mechanically strong automobile parts has become popular nowadays. Short carbon fibers were used either as received commercially or after modification process applied in this study. For carbonaceous fillers reinforced polymer composites, polyester type TPU was chosen since it is the most commonly used TPU type in industrial applications.

This research is focused on primarily the enhancement of interfacial adhesion between the reinforcing materials and TPU matrix by performing several surface modifications. Since the production method of composites can be readily adaptable to industrial manufacture, applied surface modification methods have been chosen for their ability to cost effectiveness, practical and compatible for large scale applications. Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), optical microscopy and scanning electron microscopy (SEM) techniques were used for the characterization of the surface properties of pristine and modified fillers.

The main target of this work is the investigation of mechanical properties of TPU based composites after these surface modification methods applied to the reinforcements. Composites were produced using melt-mixing method, and test samples were prepared by injection molding process. In addition to mechanical properties, water absorption capacity which is the characteristic property of green composites was also reported. Interfacial interactions and their effects were discussed by the means of tensile, Shore hardness, melt flow index test results. Dispersion of fillers in TPU matrix was deduced from SEM micrographs of the composites.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Fundamentals of Polymer Composites

Polymer matrix composites are the most developed type among composite materials due to their suitable specialty to easy fabrication. Thermosets or thermoplastics can be used as matrix for polymer composites. Thermoplastics have so many advantages over thermosets including processable and reshapeble easily and by using tradational processing techniques [1]. Additives are generally referred fillers and they are incorporated to polymers for the contributions of cost-lowering, property enhancement or improvement of processing [2].

The properties of polymer composites are affected by several factors such as interfacial adhesion, shape and the orientation of fillers and the properties of polymer matrix. Reinforcement/polymer interface plays key role on mechanical strength of the composite material. Reinforcement material can provide strength and stiffness by transferring load itself from the matrix as the interfacial adhesion is strong [3, 4]. Beside the mechanical properties, interfacial interactions between polymer and filler also affect several characteristics of polymer composites such as rheological behavior, resistance to environmental conditions and processing parameters [2]. There is a challange to estimate the role of interfaces that come from the mechanism and strength of interaction developing between two phases in composites. Surface modification methods must be applied specifically to each component according to their characteristic properties [5].

2.1.1 Green Polymer Composites

A composite material is referred to as green-composite when the matrix and the reinforcing material are derived from natural sources. Green composites gain considerable importance due to the increase of environmental consciousness and regulations [6]. Developing composites using polymers based on renewable resources with natural fibers make material more eco-friendly. The interest in lignocellulosic filled polymer composites has increased because of their advantages including the reduced cost and improved mechanical properties. These advantages open ways to natural fibers on potential replacement for man-made fibers in several application areas from packaging to automobile parts [7]. Among these application areas, automotive industry is the largest market and is expected to retain its leadership through 2016 according to a latest report [8]. There is an increasing trend for the use of natural fibers reinforced polymer composites in production of automotive parts mainly in door panels, seat backs, trunk liners and package trays [8]. Despite these advantages, the existing problems such as, low thermal stability of lignocellulosics, poor interfacial adhesion between polar lignocellulosics and nonpolar matrix material and moisture uptake limit their wider application [9].

2.1.1.1 Rice Straw (RS)

Rice straw contains mainly cellulose, hemicellulose, lignin, proteins and silica. Chemical composition of rice straw is represented in Table 2.1. High silica content restricts its use as animal feed and they are currently burned after farming. Burning these agricultural wastes after harvest causes some environmental issues beside their precious resources [10]. RS has hydrophilic character because of its high moisture content (about 60% on a wet base and 10-12% on a dry base) [11]. Straw based materials are generally used as filler in thermoplastic polymers and used in the manufacture of particleboard and fiberboard with thermoset resins [6, 9].

Pristine and surface treated RS were used as additive in several thermoplastic polymers including polyethylene [10, 12-19], polypropylene [20-25], polyvinylchloride [26-28], poly(lactic acid) [29-31], polystyrene [32], poly (caprolactone) [33] and poly (butylene succinate) [34].

Table 2. 1 Chemical composition of rice straw [35].

Cellulose (%)	Lignin (%)	Hemicellulose (%)	Silica (%)	Ash (%)
42-46	12-15	24-30	10-18	15-20

2.1.1.2 Flax Fiber (FF)

Flax fiber contains mainly cellulose, hemicellulose, pectin, lignin and wax. Chemical composition of FF is represented in Table 2.2. Pectin and lignin are the constituents that play key role as acting bonding agents in the structure of FF [36]. Schematic representation of a typical FF microstructure can be seen in Figure 2.1.

FF is widely used in textile and composite market [37]. FF has good mechanical properties, sufficient water resistance and biodegradability. Physical or chemical modifications can increase the mechanical properties of FF and its composites [38]. Surface treated FF was used as a reinforcement agent in several thermoplastic polymers including polyethylene [39, 40], polypropylene [41-43], poly(lactic acid) [44], poly(3-hydroxybutyrate) [45] and aliphatic polyester [46].

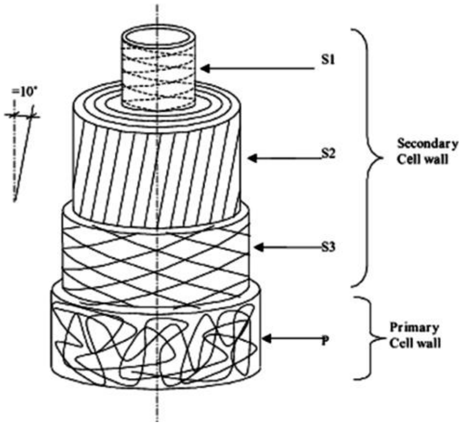


Figure 2. 1 Schematic view of flax fiber [38].

Table 2. 2 Chemical composition of flax fiber [47].

Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)	Wax (%)
71-75	18.6-20.6	2.2	2.2	1.7

2.1.2 Carbonaceous Fillers Reinforced (CFR) Polymer Composites

2.1.2.1 Carbon Nanotube (CNT)

Carbon nanotube (CNT) which has one-dimensional structure is the most popular member of carbon nanostructures family. Beside the excellent mechanical and chemical stability, high level of electrical conductivity and high aspect ratio make CNT is a special material for producing conductive polymeric materials with very low percolation thresholds [48, 49]. Incorporation of CNT into polymeric matrix has been studied by several research groups since the first polymer/CNT composite publication was reported by Ajayan *et al* [50]. CNT can add multi-functionality to composites thanks to their extraordinary mechanical and electrical properties. Thus, they are used as filler in polymeric materials. CNT reinforced polymer composites having very low density, high strength and modulus make desirable material for aerospace and transport applications [51]. However, chemical inertness of CNT surface and its tendency to form bundles are the main restrictions that limit its applications to polymer composites. Several chemical modifications are applied to CNT surface to overcome the dispersion problem in polymeric matrices [52, 53]. Another advantage of surface modification is the size reduction (shortening) of the carbon nanotubes that improves their reinforcing effect for polymers [54].

Several publications about CNT reinforced TPU composites produced by melt compounding exist in which CNT was used both as pristine [55-59] and as surface modified [60-62] forms. In these publications, several properties of these composites are reported but melt-flow behavior of CNT reinforced TPU composites have not been investigated yet. Dispersion and alignment of carbon nanotubes in polymer melt can be deduced from melt-flow index (MFI) behavior of composites in addition to control and establish of processing conditions [63].

2.1.2.2 Fullerene (C_{60})

Fullerene is a member of carbon nanostructures family that has zero-dimensional structure. Research efforts based on fullerene chemistry with combination of macromolecular chemistry led to develop easily processable fullerene-containing polymeric materials [64]. However, organic modifications are required since pristine fullerene tends to form aggregates very easily and it is difficult to handle. Formation of self-aggregation causes poor miscibility of fullerene and limits its applications [65, 66].

Polymer composites containing fullerenes have great potential for versatile applications which include optical interrupters, polymer photoconductors, electrodes in lithium batteries, and electro-optical structures in nano-electronics and nonlinear optics [67, 68].

Fullerene has been used as additive in several thermoplastic polymers including polyethylene [69, 70], polypropylene [71, 72], polyamide [73] and poly(ethylene-co-acrylic acid) [74] in which melt mixing method has been preferred.

2.1.2.3 Carbon Fiber (CF)

Since the development in the late 1950's, modern carbon fibers (CF) have been used for advanced technologies thank to their extraordinary properties such as low density, high tensile strength and Youngs' modulus [67]. Reinforcing ability of CFs for polymer composites mainly depends on interfacial adhesion between CF and polymeric matrix [75]. Formation of effecive interfacial adhesion between fiber and polymer is relatively harder for thermoplastic composites with respect to thermosetting ones. Fiber surface coated with resins should be compatible with polymer matrix to overcome that challange [76].

Research efforts based on short CF reinforced thermoplastics has been increasing trend. Opportunity to use conventional techniques (extrusion, injection and compression molding) during processing of short fibers incorporated thermoplastic melts led to develop polymeric composites parts with the combination of light weight and mechanically strong materials practically. Thermoplastic and elastomer composites containing chopped CFs have great potential for versatile applications such as seismic isolators [77, 78], aircraft structures [79, 80] and nowadays they gain importance for fabrication of ultra-low weight automobile parts [81, 82].

2.2 Thermoplastic Polyurethane (TPU)

TPU is a block copolymer that has of alternating hard and soft segments in its structure. Hard segment is composed highly polarized groups such as low molecular weight glycols or diamine reacted with diisocyanate and they provide strengthening by crosslinking [83]. The soft segment is composed of polyester or polyether units. As a result of phase separation, hard segments are dispersed as microdomains in the structure and are held together by interchain hydrogen bonding [84].

Thermoplastic polyurethanes have desirable properties for many applications like excellent mechanical properties, chemical resistance and easy processibility. Beside these specialties, TPU is a fully recyclable polymer that makes it cost effective. Major TPU applications are across a range of markets including footswear, automotive, sporting goods, medical devices, tubes, hoses, wires, cables and medical devices in the form of sheets, films, or profiles.

There are varieties of reactants derived from petroleum and/or renewable resources that are used for the production of TPU. If the polyol is produced from renewable resources, the TPUs are considered to be bio-based [6]. This property makes it possible for material researchers to develop recyclable eco-composites by incorporating natural resources into composite structures [85]. In addition to these general properties, polyurethanes can be used as an actuator with the addition of carbon based nanomaterials since they exhibit electro-striction effect [86], they can be used as electronic packaging material [87], and TPU can gain shape memory actuation when they are loaded with carbonaceous fillers [88, 89].

2.3. Surface Modification Methods of Fillers

2.3.1 Modification of Natural Fibers

Surface treatments of natural fibers are widely used for the aim of enhancing their adhesion to polymer matrix [90]. Surface modifications can be applied to natural fibers by physical and chemical methods. Physical methods do not change the chemical composition of fibers. On the other hand, chemical methods introduce an intermediate layer to fiber surface to increase its compatibility with polymer [91, 92]. Several chemical modification methods including alkaline, silane, acetylation, benzoylation, peroxide, isocyanate, permanganate treatments are applied to natural fibers in order to achieve good adhesion along the phase boundary between their surface and polymeric matrix [93, 94].

Alkaline treatment is the most common method for modifiying the surface of natural fibers. The orientation of the highly packed crystalline structure of the cellulose is modified with alkaline treatment. This method provides increase in roughness of fiber surface in addition to reduction of fiber diameter. Remarkable portion of hemicelluloses, lignin, pectin, wax and oils of the external surface of natural fiber were removed after application of this treatment which means that natural fiber surface become cleaner than its pristine form [37]. Ionization of hydroxyl group to alkoxide after reaction of sodium hydroxide with fiber cell is represented in Scheme 2.1.

$$\text{Fiber-OH} + \text{NaOH} \longrightarrow \text{Fiber-O-Na} + H_2O + \text{impurities}$$

Scheme 2. 1 The chemical reaction of sodium hydroxide with fiber cell.

Silane treatment is widely used effectively for man-made fibers as well as for natural fibers. Using silane coupling agents causes reduction for the amount of cellulose hydroxyl groups. After hydrolysis of alkoxy groups, silanol formation occurs and this group tends to react with cellulose hydroxyl group of fiber readily as represented in Scheme 2.2 [37].

$$\mathrm{RSi(OR)_3} \xrightarrow{H_2O} \mathrm{RSi(OH)_3} + \mathrm{3ROH}$$
$$\text{Fiber–OH} + \mathrm{RSi(OH)_3} \longrightarrow \text{Fiber–O–RSi(OH)}_2 + \mathrm{H_2O}$$

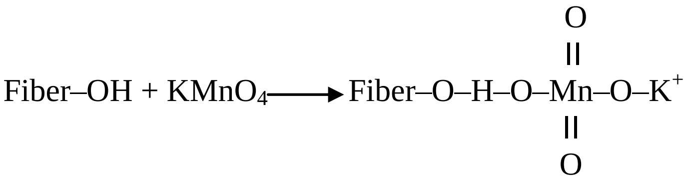
Scheme 2. 2 The chemical reaction of silane with fiber cell.

Peroxides compose of ROOR group that decomposes readily in the presence of heat to form RO radicals. This radical tends to react with hydroxyl group of fiber as shown in Scheme 2.3. Peroxide treatment is generally applied to alkali pre-treated fibers using benzoyl peroxide/acetone solution [95].

$$\text{RO–OR} \longrightarrow 2\mathrm{RO^{\cdot}}$$
$$\text{Fiber–H} + \mathrm{RO^{\cdot}} \longrightarrow \text{Fiber} + \text{R–OH}$$

Scheme 2. 3 The chemical reaction of peroxide with fiber cell.

Permanganate modification involves alkali pre-treated fibers being immersed in potassium permanganate/acetone solution for a short time. During this treatment, a Mn^{3+} ion forms which is highly susceptible to reaction with hydroxyl groups of fiber as represented in Scheme 2.4 [95].



$$\text{Fiber–OH} + \mathrm{KMnO_4} \longrightarrow \text{Fiber–O–H–O–}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{\mathrm{Mn}}}\text{–O–K}^{+}$$

Scheme 2. 4 The chemical reaction of permanganate with fiber cell.

2.3.2 Modification of Carbonaceous Fillers

Several modifications of various form of carbon have been employed by the help of scientific and technological development on carbon based polymeric materials in last decades. Development of these materials is difficult because thermodynamic and kinetic barriers inhibit the dispersal of inorganic, often hydrophilic nanoparticles in hydrophobic polymer matrices [96]. Chemical modifications of carbonaceous fillers lead to enhance dispersion and thus result in better filler-polymer interactions on composite applications [97]. The main factors affecting the final mechanical properties of polymer composites are the degree of filler dispersion and the effective stress transfer at interface between filler and matrix material. The better filler dispersion and strong adhesion between matrix and fiber can be achieved via several physical and chemical methods.

Oxidation of carbon nanotube allows the formation of new moieties on their surface wall. Thus, interfacial interactions between nanotube and other substances are improved. Chemical functionalizations after oxidation process open ways to localize several organic groups on CNT surface such as carboxylic acid, thionyl chloride, amines and organosilanes [98].

2.4 Production Methods of Polymer Composites

There are several methods used for the production of polymer composites such as solution mixing, in-situ polymerization and melt blending. Melt mixing (extrusion) is the most practical application and the most suitable for the production of polymeric composite materials in large-scale among these methods.

2.4.1 Extrusion

Thermoplastics and elastomers are compounded using extrusion process. During the extrusion process, polymer melts and then mixed with several additives including fillers, colorants, anti-oxidants and other ingredients. This process gives opportunity to handle plastic materials as required shapes such as sheets, cables, profiles, films, fibers and pellets.

During the extrusion process, polymer granules are fed into hopper part with the other additives and they are transferred by the help of rolling screw. Polymer and other ingredients are pulled by screw and go through a hole at the end of the barrel which referred as die. In addition to the external heat from outside the extruder barrel, rolling screw also causes additional heat which comes from the friction [99].

2.4.2 Injection Molding

Thermoplastic materials are shaped using injection molding process for manufacturing parts by injecting molten material into a mold. There are several kinds of materials which are generally thermoplastics polymers used for injection molding. The material is melted in pre-heated barrel and molten plastic is fed into a mold by using proper pressure. According to cavity of mold, plastic material is taken a shape after cooling [100].

CHAPTER 3

EXPERIMENTAL

Experimental part of this thesis is composed of two parts. In the first part, surface treatment procedures of RS and FF, production and characterization methods of their composites are mentioned. Surface modification procedures of CNT, C_{60} and CF, preparation and characterization parameters of their composites are explained in the second part.

3.1 TPU Green Composites

3.1.1 Materials

Eco grade TPU was used in green polymer composites production. The commercial thermoplastic polyurethane (Pearlthane® ECO D12T85) was obtained from Merquinsa (Barcelona, Spain). It has a density and hardness of 1.15 g/cm^3 and 85 (Shore A), respectively. It is composed of renewably-sourced polyols (Cerenol) with a content of 46% that determined according to ASTM D6866. 3-Aminopropyltriethoxysilane (APTES) and ethanol were supplied by Merck. Reagent grade sodium hydroxide (NaOH), potassium permanganate ($KMnO_4$), benzoyl peroxide (BPO_4) and acetone were purchased from Sigma Aldrich. Rice Straw was obtained from the local sources in the region of Eskisehir, Turkey. Straws were chopped into 3-4 mm length by using a lab-scale grinder. Photograph of chopped RS used in this work is represented in Figure 3.1.

Figure 3.1 The photograph of chopped RS.

Flax fiber was obtained as partially retted (brown flax) from the local sources in the region of Izmit, Turkey. Fiber portions were chopped into 3-4 mm length. Photograph of chopped FF used in this study is represented in Figure 3.2.

Figure 3.2 The photograph of chopped FF.

3.1.2 Surface Modification Procedures of Natural Fillers

3.1.2.1 Surface Modification of RS

RS was washed and dried in order to remove the impurities before grinding process. RS were milled into 1-2 mm length using laboratory scale grinder. The pristine rice straw is coded as RS. The RS was treated with 2 wt % solution of NaOH for 120 minutes under continuous mixing. The volume of the solution is 3 times that of RS. RS was then washed with water until all NaOH was eliminated. 2 ml of acetic acid were added to neutralize the last rinsing solution. The RS was air-dried at 80 ˚C for 24 hours. Same drying conditions were applied after all slurry surface treatments. The alkaline treated RS was coded as Na-RS. During hot water treatment, Na-RS was stirred with hot water at 90 ˚C for 120 minutes. The hot water treated RS was coded as HW-RS. Na-RS is further modified by silane, benzoyl peroxide, and permanganate treatments. During silane treatment, Na-RS was mixed in 2 wt% aminopropyltriethoxysilane (APTES)/ethanol solution for 120 minutes at room temperature. After silane treatment, straw was washed with ethanol several times. The silane treated RS was coded as Si-RS. During benzoyl peroxide treatment, Na-RS was immersed in 8 wt% benzoyl peroxide solution of acetone for 40 minutes at room temperature. Excess peroxide contamination was removed by washing with acetone and dried at room temperature overnight. The RS as coded as BP-RS. During permanganate treatment, Na-RS sample was stirred in 0.1 wt% of potassium permanganate/acetone solution for only 2 minutes. After fast cleaning of straws with excess acetone, they were dried at room temperature overnight and named as PM-RS.

3.1.2.2 Surface Modification of FF

After washing and drying to remove impurities, all flax fiber portions were chopped into 3-4 mm length. The pristine flax fiber is coded as FF. Alkaline treatment was applied to flax fiber by continuous mixing in 2% solution of NaOH for 120 minutes. The volume of the solution is equivalent to 3 times that of FF. After several washings, all NaOH was eliminated and a few drops of acetic acid were added to neutralize the last rinsing solution. The FF was air-dried at 80 ^{o}C for 24 hours. Same drying conditions were applied after all slurry surface treatments. The alkaline treated FF was coded as Na-FF. Na-FF was further modified by silane, benzoyl peroxide, and permanganate treatments. During silane treatment, Na-FF was mixed in 2% APTES/ethanol solution for 120 minutes at room temperature. After silane treatment, it was washed with ethanol several times and was dried at 100°C overnight for solvent removal and was coded as Si-FF. Na-FF was immersed in 8% benzoyl peroxide solution of acetone for about 40 minutes during benzoyl peroxide treatment. Excess peroxide contamination of fiber surface was removed by washing with acetone and drying at room temperature overnight. Benzoyl peroxide treated FF named as BP-FF. During permanganate treatment, Na-FF was stirred in 0.1 wt% potassium permanganate/acetone solution for only 2 minutes. After sudden cleaning of fibers with excess acetone, they were dried at room temperature overnight and coded as PM-FF.

3.1.3 Production of TPU Green Composites

TPU was dried at 100˚C for 2 hours prior to compounding. TPU based composites were prepared through the melt mixing in a counter rotating twin screw microextruder (15 ml microcompounder, DSM Xplore, Netherlands) at a screw speed of 100 rpm at 200˚C for 5 minutes (Figure 3.3). Filler loadings were kept constant at 30% by weight in all compounds. Test samples were prepared by injection molding instrument (Microinjector, Daca Instruments) at a barrel and mold temperature of 210˚C and 40˚C, respectively (Figure 3.4). Injection pressure of 5 bar were applied. Injection molded dog-bone shape specimens with dimensions of 7.4×2.1×80 mm^3 were prepared for tensile testing, hardness test, water absorption measurements and DMA.

Figure 3.2 The photograph of the lab-scale twin screw extruder.

Figure 3.3 The photograph of the micro- injection molding machine.

3.1.4 Characterization Methods

3.1.4.1 FTIR Analysis

FTIR measurements in attenuated total reflectance (ATR) mode were performed using a IR-spectrometer (Bruker VERTEX 70) at a resolution of 2 cm^{-1} with 32 scans between 600-3800 cm^{-1} wavenumbers.

3.1.4.2 Scanning Electron Microscopy (SEM)

Modified and untreated surfaces of fillers and cyro-fractured surfaces of composites were examined by a field emission scanning electron microscope (FEI Quanta 400F). Before SEM photographs were taken, sample surfaces were coated with a thin layer of gold in order to obtain a conductive surface. The SEM photographs were taken at different magnifications varied from x1,000 to x5,000.

3.1.4.3 Optical Microscopy

Surfaces of flax fiber and rice straw before and after treatments were examined using a computer-controlled optical microscope (Veho VMS-004D). Photographs were taken at x20 and x400 magnifications.

3.1.4.4 Tensile Test

The measurements of the tensile properties were carried out using Lloyd LR 30 K universal tensile testing machine with load cell of 5 kN at crosshead speed of 5 cm/min according to the standard of ASTM D-638. Tension tests were conducted on dog-bone shaped samples (7.4×2.1×80 mm^3) as represented in Figure 3.5. Tensile strength, percentage elongation at break and tensile modulus values were recorded. All the results represent an average value of five samples with standard deviations.

Figure 3.5 The photograph of tensile test machine.

3.1.4.5 Hardness Test

Shore hardness measurements were performed using Zwick digital Shore hardness tester according to ISO 7619-1 standard.

3.1.4.6 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of composites were determined by dynamic mechanical thermal analyzer (DMA 8000, Perkin Elmer) from -70°C to 150°C in dual cantilever bending mode at a constant frequency of 1 Hz and heating rate of 10°C/min. The samples with dimensions of $50\times7.5\times2.5$ mm^3 were obtained by injection molding.

3.1.4.7 Melt Flow Index Test (MFI)

Melt flow property measurements were studied using Meltfixer LT, Coesfield Material Test (Figure 3.6). The test was carried out at process temperature of composites under specified load of 5 kg. The MFI values of TPU and its composites reported are the average of ten measurements.

Figure 3.6 The photograph of melt flow indexer.

3.1.4.8 Water Absorption Test

Test specimens with dimensions of 7.4×2.1×80 mm^3 were conditioned according to ASTM D570 procedure in order to determine the water absorption properties of composites. They were immersed in water bath (Figure 3.7) at room temperature, periodically taken out from the water, wiped with tissue paper to remove their surface water, reweighed and immediately put back into water repeatedly. The pre-dried (W_0) was determined and used to calculate the degree of water absorption as the following formula:

$$\text{Water Absorption (\%)} = \frac{(W_f - W_0)}{W_0} \times 100$$

where W_f is the mass of the sample after immersion.

Figure 3.7 The photographs of water absorption test.

3.2 CFR TPU Composites

3.2.1 Materials

Polyester-based thermoplastic polyurethane (Texalan® 485A) was used in carbonaceous fillers reinforced composites. It was obtained from Pasific (Covina, USA). It has a density and hardness of 1.20 g/cm^3 and 85 (Shore A), respectively. Multiwall carbon nanotube (NC7000) was purchased from Nanocyl, USA (180–200 mesh) and fullerene carbon soot was supplied by Acros Organics (USA) (180–200 mesh). Commercially epoxy (EP-CF) and polyurethane (PU-CF) sized chopped (3 mm) carbon fibers were purchased from Dowaksa (Yalova, Turkey) used in this study. Nitric acid (HNO_3, 65%), 3-Aminopropyltriethoxysilane (APTES), ethanol, 1,2-dichloroethane and toluene were supplied by Merck. Polymeric Methylene Diphenyl Diisocyanate (pMDI) resin (Isonuh PM-200) has NCO content of 30-32 g/100 g was obtained from Nuhpol, Turkey.

3.2.2 Surface Modification Procedures of Carbonaceous Fillers

3.2.2.1 Surface Modification of CNT

CNT was annealed at 450 ˚C for 4 hours before surface treatments. The pristine nanotube is coded as CNT. Chemical oxidation of CNT was carried out using similar oxidation routes in the literature [101-103].

1.6 g of CNT was refluxed at 120 ^{0}C with 70 ml concentrated HNO_3 solution for 48 hours as shown in Figure 3.8. The mixture was diluted with distilled water and filtrated, then resulted product was washed with distilled water and dried under vacuum for 2 hours. The Nitric acid treated CNT was coded as HN-CNT. During silane treatment, HN-CNT was mixed in 2 wt% APTES/ethanol solution for 80 minutes with ultrasonication at room temperature. After silane treatment, product was washed with ethanol several times. The silane modified CNT was coded as Si-CNT.

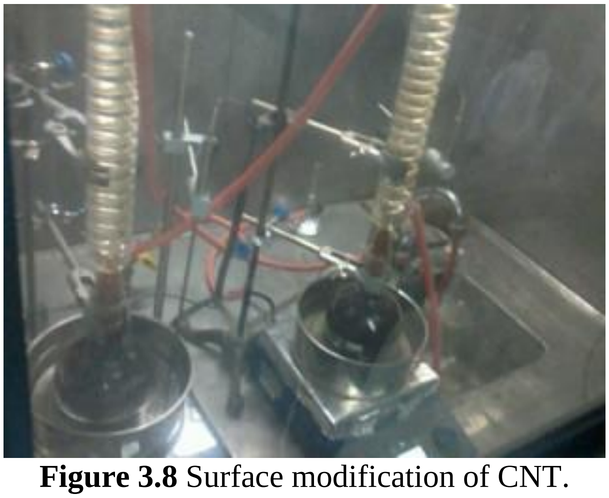


Figure 3.8 Surface modification of CNT.

3.2.2.2 Surface Modification of C_{60}

Fullerene soot was annealed at 450 ˚C for 4 hours, initially. The pristine fullerene is coded as C_{60}. Chemical oxidation of fullerene was carried by using similar methods employed by Soylemez et al. [102] and others [103, 104].

1.6 g of C_{60} was refluxed at 120 ^{0}C with 70 ml concentrated HNO_3 solution for 48 hours that can be seen in Figure 3.9. The mixture was diluted with distilled water and filtrated, and then the product was washed with distilled water and dried under vacuum for 2 hours. The nitric acid treated fullerene was coded as HN-C_{60}. During silane treatment, HN-C_{60} was mixed in 2 wt% APTES/ethanol solution for 80 minutes with ultrasonication at room temperature. After silane treatment, product was washed with ethanol several times. The silane modified fullerene was coded as Si-C_{60}.

Figure 3.9 Surface modification of C_{60}.

3.2.2.3 Surface Modification of CF

Commercially sized chopped CF was annealed at 450 ˚C for 4 hours initially for removal of sizing layer. Samples were subjected to 1,2-dichloroethane to obtain clean surface and this CF portion was named as DS-CF. Prior to surface treatment, chemical oxidation of DS-CF was carried out by applying reflux with nitric acid for 1 hour. During isocyanate treatment, acid treated DS-CF was mixed in 8% pMDI/toluene solution for 80 minutes at 55 ^{o}C. Excess pMDI contamination of fiber surface was removed by washing with toluene and was dried at 100°C overnight for solvent removal. Isocyanate treated CF was named as MD-CF. During curing process of isocyanate layer at CF surface, MD-CF was heated in oven at 180 ^{o}C for only 10 minutes and named as CM-CF.

3.2.3 Preparation of CFR TPU Composites

TPU was dried at 100˚C for 2 hours prior to compounding. TPU based composites were prepared using melt mixing in a counter rotating twin screw microextruder (15 ml microcompounder, DSM Xplore, Netherlands) at a screw speed of 100 rpm at 210˚C for 8 minutes. Carbon based fillers were incorporated at four different compositions in TPU matrix. Test samples were prepared by injection molding instrument (Microinjector, Daca Instruments) at a barrel and mold temperature of 215˚C and 40˚C, respectively. Injection pressure of 5 bar were applied. Injection molded dog-bone shape specimens with dimensions of 7.4×2.1×80 mm^3 were prepared.

3.2.4 Characterization Methods

3.2.4.1 FTIR Analysis

FTIR analysis in attenuated total reflectance (ATR) mode were performed by using IR-spectrometer (Bruker VERTEX 70) at a resolution of 2 cm^{-1} with 32 scans between 600 and 3800 cm^{-1} wavenumbers.

3.2.4.2 SEM/Energy Dispersive X-ray Spectroscopy (EDX)

Modified and unmodified surfaces of carbonaceous fillers and cyro-fractured surfaces of composites were examined by a field emission scanning electron microscope (FEI Quanta 400F). The SEM photographs were taken at different magnifications varied from x1,000 to x50,000. Elemental analysis was carried out at the indicated spots in SEM micrographs by EDX technique.

3.2.4.3 Tensile Test

Tensile test was carried out using Lloyd LR 30 K universal tensile testing machine with load cell of 5 kN at crosshead speed of 5 cm/min according to the standard of ASTM D-638. Tension tests were conducted on dog-bone shaped samples ($7.4 \times 2.1 \times 80$ mm^3). Tensile strength, percentage elongation at break and tensile modulus values were recorded. All the results represent an average value of five samples with standard deviations.

3.2.4.4 Hardness Test

Shore hardness values of composites were determined using an electrical Shore hardness tester (Zwick digital hardness tester) according to ISO 7619-1 standard.

3.2.4.5 DMA

Dynamic mechanical properties of CF containing composites were determined by dynamic mechanical thermal analyzer (DMA 8000, Perkin Elmer) from -70°C to 150°C in dual cantilever bending mode at a constant frequency of 1 Hz and heating rate of 10°C/min. The samples with dimensions of $50 \times 7.5 \times 2.5$ mm^3 were obtained by injection molding.

3.2.4.6 MFI Test

Melt flow property measurements were studied by Meltfixer LT, Coesfield Material Test. The test was carried out at process temperatures of composites under specified load of 5 kg. The MFI values of TPU and its composites reported are the average of ten measurements.

CHAPTER 4

RESULTS AND DISCUSSION

Initially, the surface properties of fillers before and after treatments were investigated using several chemical and physical characterization methods. Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), optical and scanning electron microscopy (SEM) techniques were used to obtain surface characteristics of neat and modified fillers.

Mechanical properties of composites were evaluated by performing tensile and hardness tests. Dynamic mechanical analysis results were also reported for thermo-mechanical characterization of the composites. Water uptake capacities of the eco-composites were discussed. Tensile testing was also applied to green composites after water absorption test and results were compared. Melt flow rates of TPU and the composites were reported and their processabilities were examined. Dispersion of the fillers and their adhesion to TPU matrix were discussed by means of SEM micrographs of cyro-fractured surfaces of the composites.

4.1 TPU Green Composites

4.1.1 Characterization of RS Surface

4.1.1.1 FTIR Analysis

The FTIR spectra of RS and surface treated RS samples are shown in Figure 4.1. Absorption bands at 800, 1040, 1615, 2900 and 3300 cm^{-1} are the characteristic peaks for both treated and untreated samples. However, the intensities of the characteristic peaks are different. The peak at around 800 cm^{-1} arising from bending mode of C-H group in lignin is not seen in the FTIR spectra of alkali treated RS due to the partial dissolution of hemicellulose, lignin and pectin. The intensity of peaks at 1040 and 3300 cm^{-1}, which are the characteristic peaks of -OH stretching, increase with alkaline, hot water and permanganate treatments. Relatively low intensity bands are seen at 1040, and 3300 cm^{-1} for Si-RS and BP-RS due to the chemical modification of hydroxyl groups in cellulose and lignin with silane coupling agent and benzoyl peroxide [105-107].

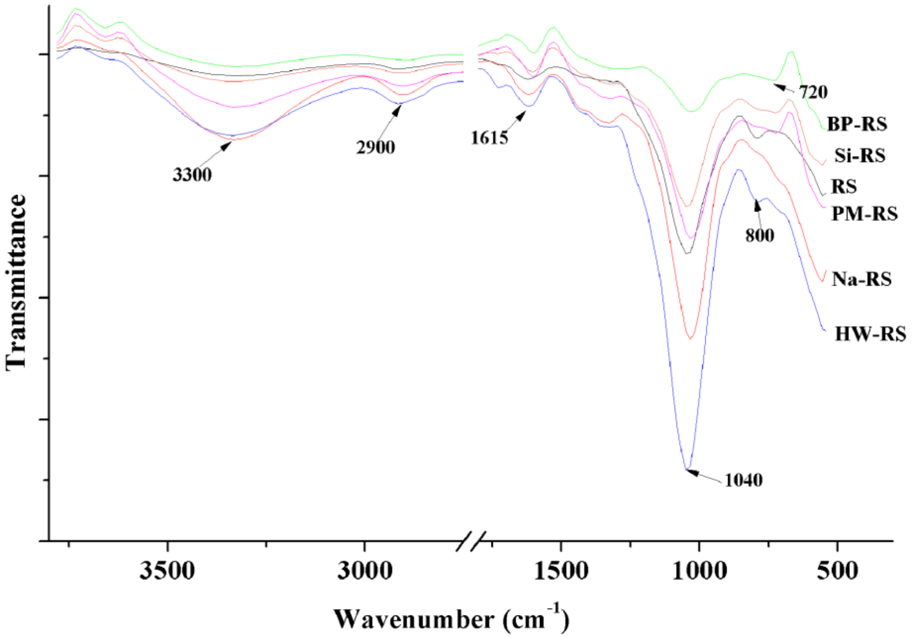


Figure 4.1 The FTIR spectra of pristine and modified RS.

4.1.1.2 Image Analysis by Optical Microscopy and SEM

Optical photographs of rice straws with magnifications of (a) x20, (b) x400; 1-Untreated RS, 2-Na-RS, 3-HW-RS, 4-Si-RS, 5-BP-RS, 6-PM-RS are shown in Figure 4.2. Color change of treated straw surfaces is the main observation that can be seen in optical photographs in Figure 4.2.

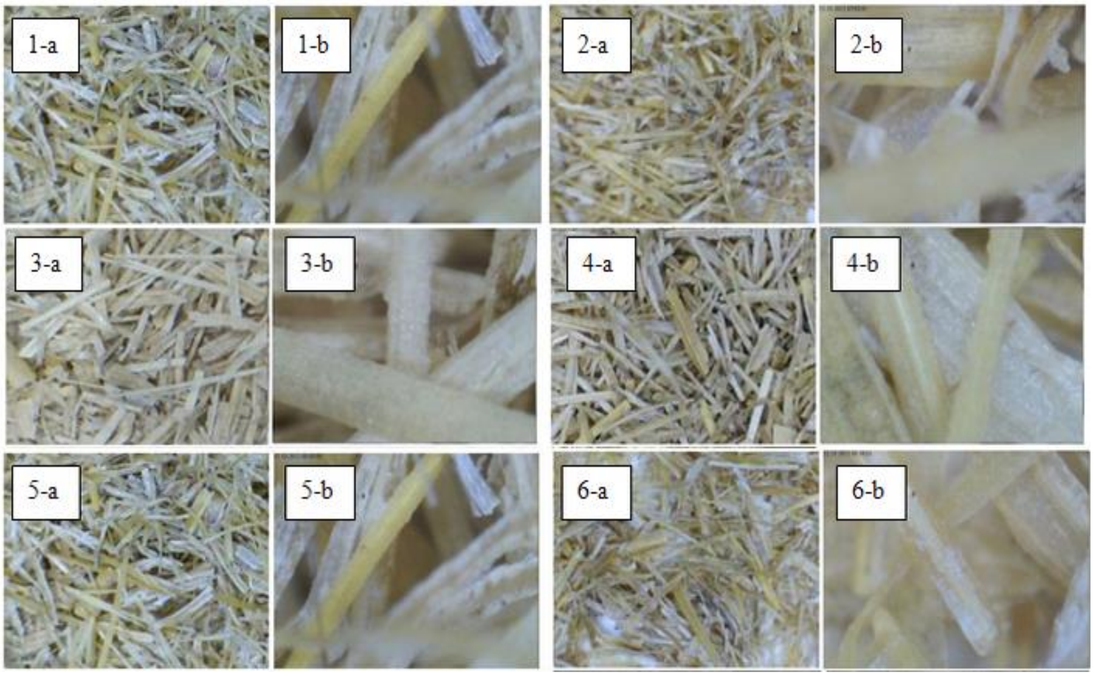


Figure 4.2 Optical photographs of pristine RS and treated RS samples.

SEM images of rice straw surfaces with magnifications of (c) x1000 (d) x5000; 1-Untreated RS, 2-NaOH treated RS, 3-Hot water treated RS, 4-Silane treated RS, 5-Benzoyl peroxide treated RS, 6-Potassium permanganate treated RS are shown in Figure 4.3. According to SEM images, the surfaces of straws become rougher and cleaner after alkaline and hot water treatments. The ordered white dots which are rich in silica [108] can be seen on the surface of treated RS with the removal of outer surface. The further treatments made on Na-RS does not alter the surface morphology of RS.

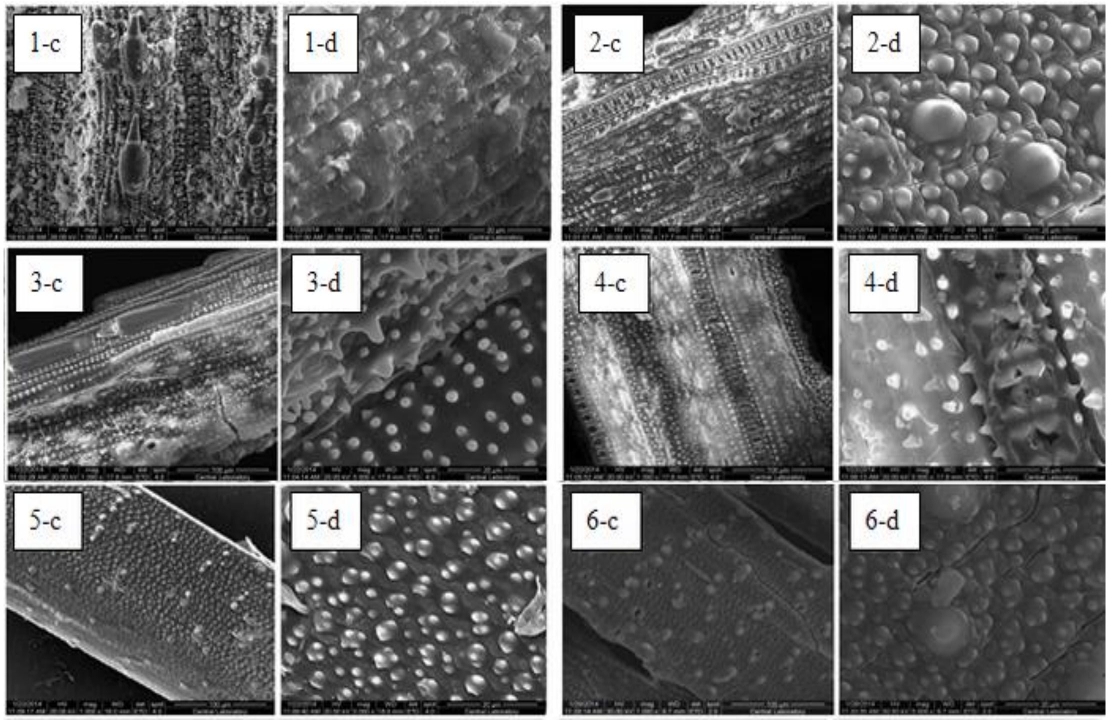


Figure 4.3 SEM micrographs of pristine RS and treated RS samples.

4.1.2 Effect of Surface Treatments on Mechanical, Physical and Water Uptake Properties of TPU/RS Green Composites

4.1.2.1 Tensile Test

The stress–strain curves of the composites are shown in Figure 4.4 and the relevant tensile test data are listed in Table 4.1.

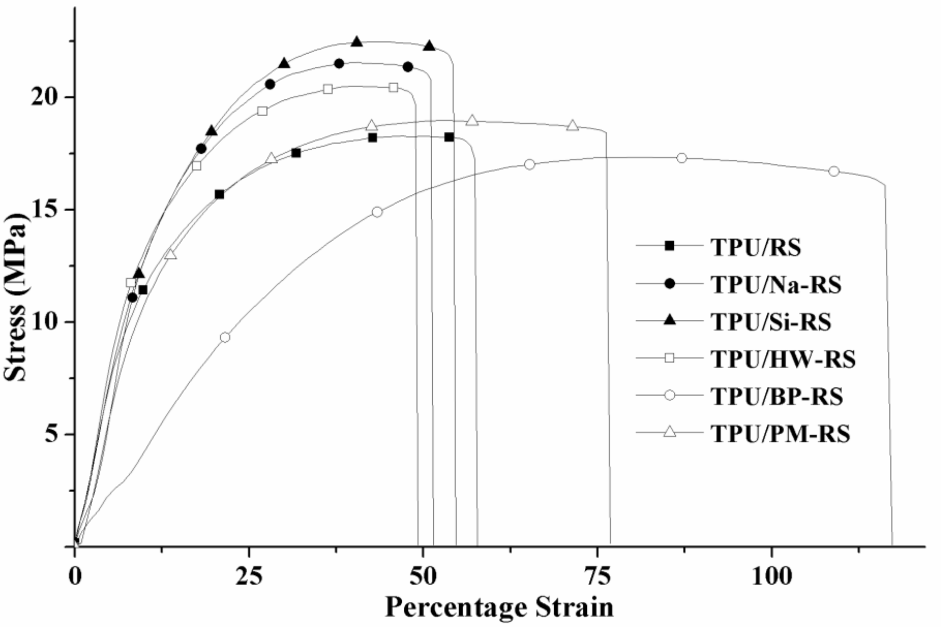


Figure 4.4 Stress-strain curves of TPU/RS composites.

It is seen from Table 4.1; the addition of both modified and unmodified RS reduces the tensile strength and elongation at break and increases the Youngs' modulus with respect to pristine TPU. The reduction in tensile strength arises from incompatibility between the hydrophilic fiber and the hydrophobic matrix [29, 30]. The previous studies show that the lignocellulosic filler with higher stiffness than the matrix can increase the tensile modulus of the composites [109-111]. With alkaline and hot water treatments, the tensile strength and Youngs' modulus are improved with respect to TPU/RS composite. After alkaline and hot water treatment, the surface of RS becomes rougher (Figure 4.3) and hemicellulose portion which reduces the adhesion between lignocellulosics and polymer matrix is removed [112]. Thus, both hot water and alkaline treatments improve the wetting of RS and increase the adhesion between phases. In order to improve the wetability and adhesion, Na-RS fiber is further modified by silane, benzoyl peroxide and permanganate treatments. Among these treatments, the greatest increase in tensile strength and Youngs' modulus is observed for Si-RS containing composite [113].

Table 4.1 Tensile properties of TPU and TPU/RS composites.

SAMPLES	**Tensile Strength** (MPa)	**Elongation at break** (%)	**Youngs' modulus** (MPa)
TPU	24.8±2.2/24.5±3.5*	424.0±22.3/421.8±20.9*	57.8±3.4/57.2±4.1*
TPU/RS	18.3±1.9/14.1±2.3*	57.4±7.8/107.3±11.0*	125.2±6.9/154.7±7.3*
TPU/Na-RS	21.6±2.0/17.1±1.6*	49.2±4.8/50.8±4.0*	167.1±5.8/165.9±5.5*
TPU/HW-RS	20.5±1.8/17.6±1.5*	48.8±5.7/45.2±6.2*	162.8±5.1/128.6±4.4*
TPU/Si-RS	22.5±2.1/18.8±1.8*	44.8±5.4/40.6±3.9*	176.8±7.0/168.3±6.4*
TPU/BP-RS	17.3±1.5/14.6±1.4*	119.3±9.8/116.8±8.9*	62.2±3.2/58.1±4.0*
TPU/PM-RS	19.0±1.9/16.3±1.7*	76.8±8.0/88.2±8.8*	112.6±5.2/86.4±4.3*

*: *Test results of samples water absorption test applied.*

Tensile test results performed after water absorption test are also reported in Table 4.1. It can be clearly seen that the tensile values of TPU are almost identical after water absorption. All composites containing RS have lower tensile strength and Youngs' modulus values than TPU after water absorption. The reductions in tensile strength and Youngs' modulus are observed in RS containing composites is, on the average, about 20 %. Water immersion of samples generally resulted in variable values. It is not possible to generalize their strain values. Untreated straw containing composite shows a bit different character that its elongation and modulus values are raised sharply. This result probably caused from penetration of water into large gaps between straw and matrix due to poor interfacial interaction [113].

4.1.2.2 Hardness Test

Shore hardness is the characteristic parameter for elastomers and their composites. Hardness values of TPU and TPU/RS composites are listed in Table 4.2. Hardness of TPU increases with the incorporation of both untreated and treated RS. Composite containing alkali treared RS give slightly higher hardness value than that of TPU/RS.

HW-RS loaded composite exhibit the highest value which leads to about 10 units increase in Shore A hardness of TPU. It is clearly seen from Table 4.2 that the addition of silane treated RS addition to TPU also causes sharp increase, and hardness values of TPU/RS and TPU/BP-RS are almost identical. Composite containing PM-RS give the lowest value among treatments but it has higher hardness value than neat TPU [114].

Table 4.2 Shore A hardness of TPU and TPU/RS composites.

TPU	**TPU/RS**	**TPU/ Na-RS**	**TPU/ HW-RS**	**TPU/ Si-RS**	**TPU/ BP-RS**	**TPU/ PM-RS**
85.9±0.2	89.3±0.1	89.7±0.2	95.5±0.2	92.2±0.1	89.2±0.2	88.4±0.2

4.1.2.3 DMA

The storage modulus versus temperature graphs of TPU and its composites are shown in Figure 4.5. The inclusion of pure and surface modified RS in TPU matrix except for BP-RS increase the storage modulus of pure TPU. The storage modulus results are in accordance with the tensile modulus results. The highest storage modulus is observed for Si-RS containing sample due to the increase in compatibility between RS and TPU [113].

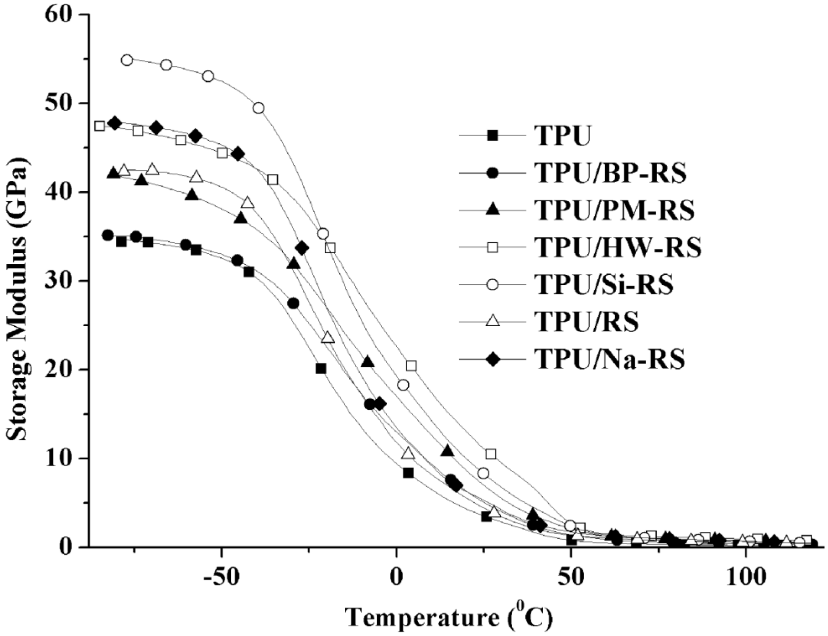


Figure 4.5 Storage modulus-temperature curves of TPU and TPU/RS composites.

Damping properties of composites were analyzed with their Tan δ versus temperature curves which are shown in Figure 4.6. It can be seen from these graphs that Tan δ increases with all surface treatments. Glass transition temperature (T_g) of the composites shifts to a bit higher temperatures with the addition of surface treated rice straws. The shiftings of T_g are more significant for Na-RS, HW-RS and Si-RS loaded composites. Another observation from Figure 4.6 is TPU/Na-RS and TPU/Si-RS showed two peaks in the graphs. This may be caused from the stabilizing capability of rice straw after glass transition temperature. Similar result was also observed by A. Shakoor et al. for PLA/hemp fiber composites [115]. These observations can be explained by the hindrance of chain motions of TPU due to increased interfacial interactions.

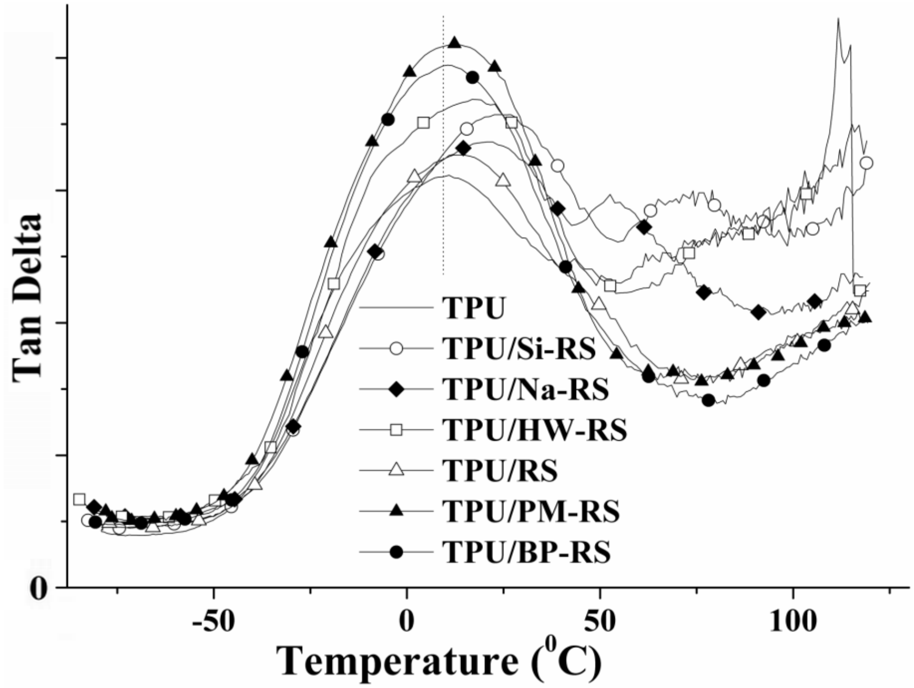


Figure 4.6 Tan δ-temperature curves of TPU and TPU/RS composites.

4.1.2.4 MFI Test

MFI values are important in order to determine the processing parameters of the polymer composites in industrial applications where extrusion of the material is the preferred processing method. MFI values of pure TPU and its composites at process temperature (200 ˚C) are given in Figure 4.7. It is clear that MFI values of all the composites are much higher than that of neat TPU due to the orientation of RS along the flow line. Alkaline, hot water and silane treatments cause gradual increase in MFI values with respect to TPU/RS composite. On the other hand, benzoyl peroxide and permanganate treatment cause slight decrease in MFI values. It is seen that there is a correlation between the adhesion and MFI values. Melt viscosity decreases by addition of surface treated RS which tend to interact stronger with TPU due to fiber-matrix adhesion rather than fiber-fiber adhesion [113].

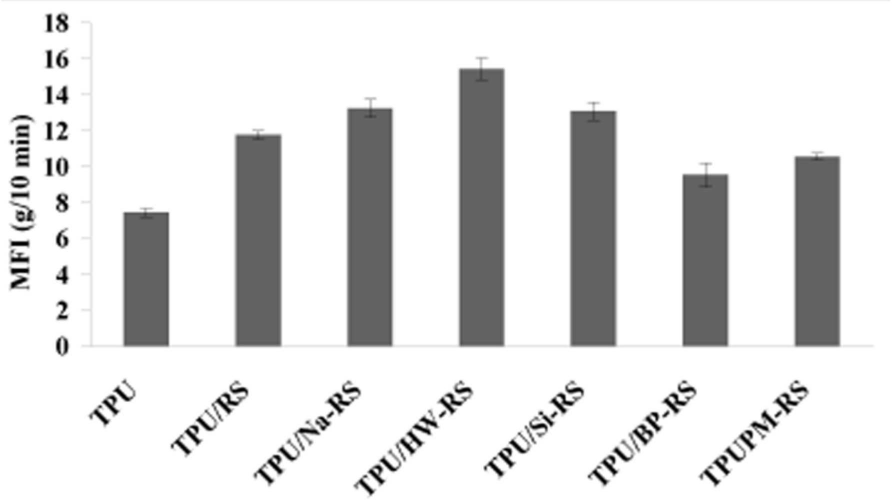


Figure 4.7 MFI values of TPU and TPU/RS composites.

4.1.2.5 Water Absorption Test

The water uptake of TPU and its composites in 60 days period of time is shown in Figure 4.8. According to Figure 4.8, TPU absorbs at about 1 wt% water in a few days and reaches its maximum capacity. All surface modifications reduce the water uptake with respect to TPU/RS. Water absorption is mainly related to hydrogen bonding of water molecules to the hydroxyl groups present on lignocellulosics and the compatibility between matrix and the reinforcing material. Although NaOH and hot water treatments make RS more hydrophilic, the water uptake is reduced after these treatments due to the reduction in the number of capillaries (pores) in the composite structure which makes suction effect. It is clearly seen that the composite containing Si-RS absorbs much less water due to well-known hydrophobicity of silane coupling agent and the increase in compatibility. Because of poorer adhesion and formation of gaps between fiber and matrix for BP-RS and PM-RS containing composites as claimed from SEM images, their water uptake capacities are found as higher with respect to other treated RS loaded composites [114].

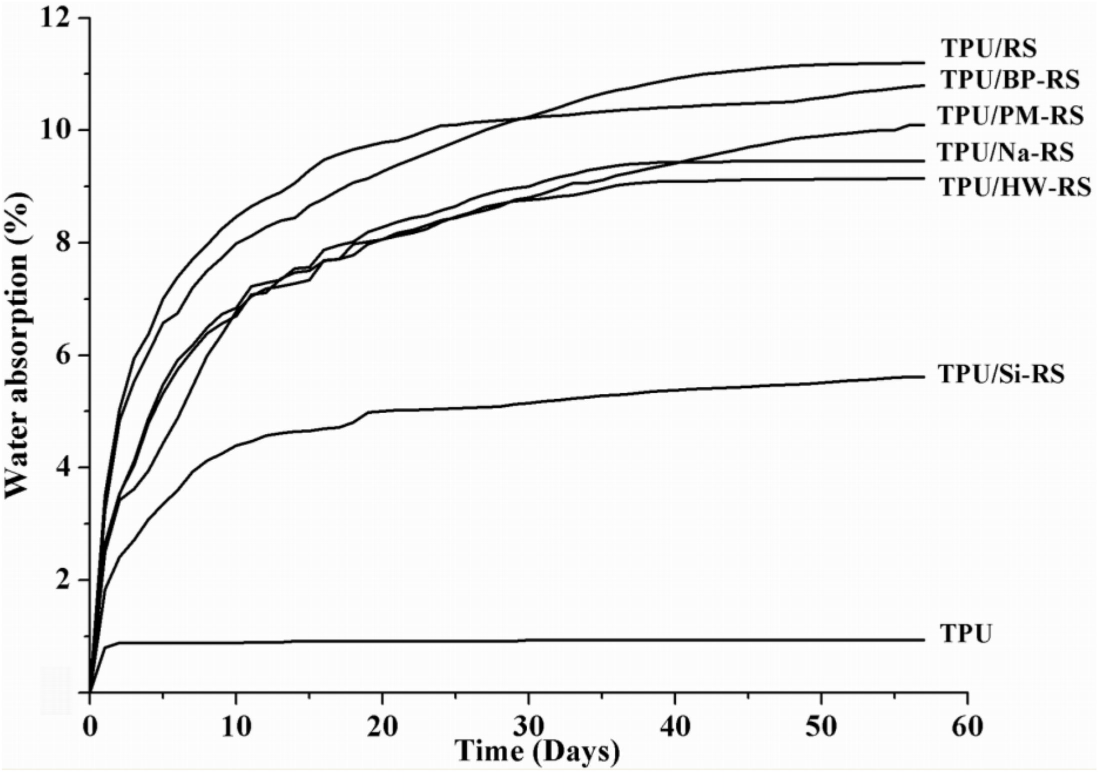


Figure 4.8 Water uptake curves of TPU and TPU/RS composites.

4.1.2.6 SEM Analysis

The effect of surface treatments on the morphology of the composites is studied by SEM. Representative SEM micrographs of fracture surfaces of selected TPU/RS composites are shown in Figure 4.9. It is observed that gaps formed between straw particles and TPU matrix in RS, BP-RS, PM-RS containing composites due to poor adhesion between TPU and RS. TPU covers the surface of Na-RS, HW-RS and Si-RS. This observation indicates that alkaline, hot water and silane treatment greatly improve the interfacial adhesion between straw and polymer matrix. These findings provide qualitative evidence for the mechanical, flow and water absorption properties of composites.

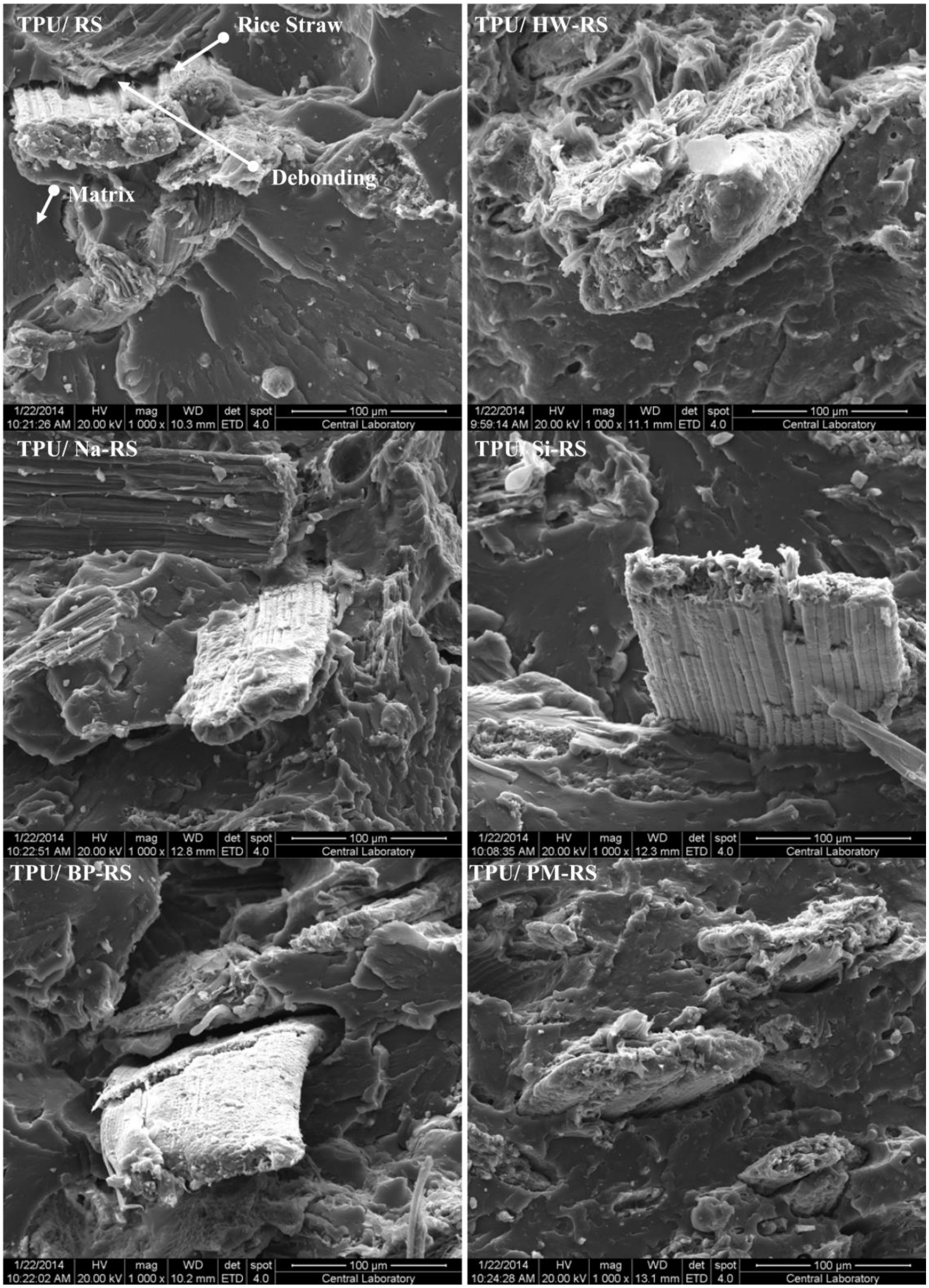


Figure 4.9 SEM micrographs of TPU/RS composites

4.1.3 Characterization of FF Surface

4.1.3.1 FTIR Analysis

The FTIR spectra of FF and surface treated FF samples are shown in Figure 4.10. Absorption bands from 400 cm^{-1} to 1800 cm^{-1} range in which oxygen functionalities observed such as C–O stretching at broad peak from 900 cm^{-1} to 1200 cm^{-1}, COO– asymmetric stretching and C=O stretching vibrations at 1620 cm^{-1} and 1730 cm^{-1}, respectively. Absorption increments of these oxygen related peaks for Na-FF, PM-FF and BP-FF are clearly seen from the spectra. Intensities of these peaks are relatively low for Si-FF that may indicates the silane coupling agent chemically modified the surface hydroxyl groups of cellulose and lignin. The carbonyl stretching vibration peak at 1730 cm^{-1} present for PM-FF only due to the oxidation of alcohol groups to C=O groups during permanganate treatment [116, 117]. The intensity of band at 1420 cm^{-1} assigned to COO- group is slightly increased because of the alkali treatment. The band at 1270 cm^{-1} indicates the C–O stretching mode of COO– group of hemicellulose that is observed for all of the treated fibers [118].

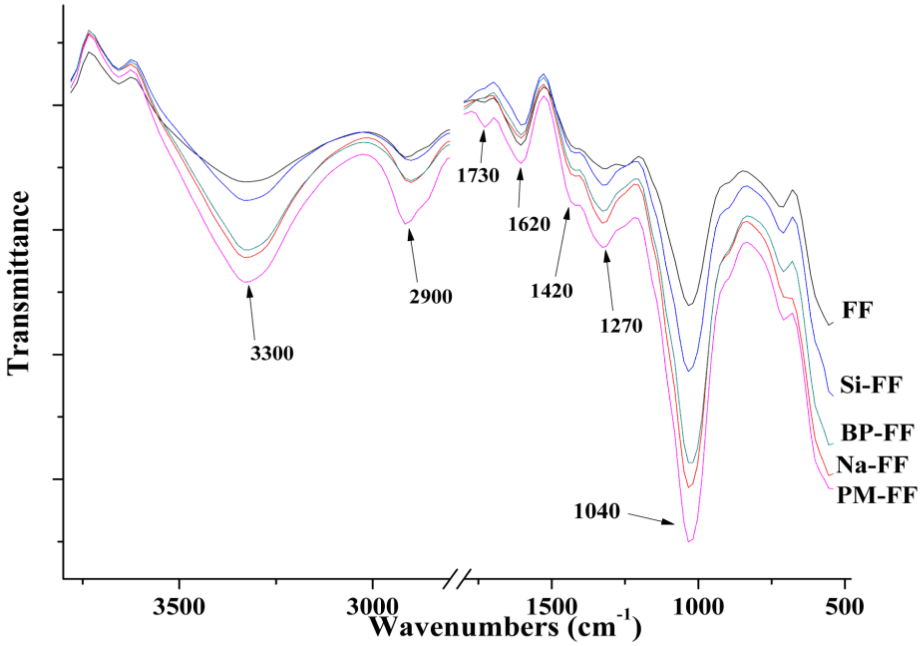


Figure 4.10 FTIR spectra of FF samples.

Broad band that centered at around 3300 cm^{-1} is the characteristic hdroxyl group stretching that observed as more intense for Na-FF, PM-FF and BP-FF. Relatively low intensity of this band for Si-FF is the observation that indicates the chemical modification of cellulose and lignin hydroxyl groups with silane coupling agent and formation of siloxane units. Appearance of another broad absorption band in the range of 2800 cm^{-1} and 3000 cm^{-1} is attributed to $–CH_2$ fluctuations of lignin [119]. Shifting of C–H stretching absorption band at 2900 cm^{-1} for PM-FF may due to hemicellulose removal during permanganate treatment [117]. These observations indicate that all treatments except for silane treatment resulted in increase of hydoxyl groups.

4.1.3.2 Image Analysis by Optical Microscopy and SEM

Optical photographs of pristine FF and alkaline treated FF are shown in Figure 4.11. It can be observed in these images that alkaline treatment caused fibrillation along the individual fibers beside the color change.

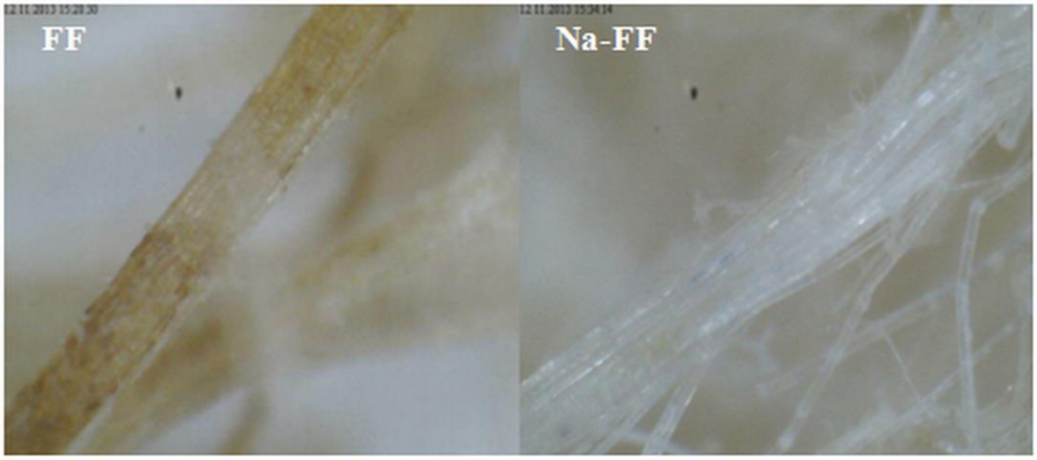


Figure 4.11 Optical photographs of pristine and alkali modified FF.

SEM images of untreated FF and surface treated FFs are shown in Figure 4.12. According to SEM images, the surfaces of fibers become rougher after alkaline and other treatments due to the partial removal of soluble components.

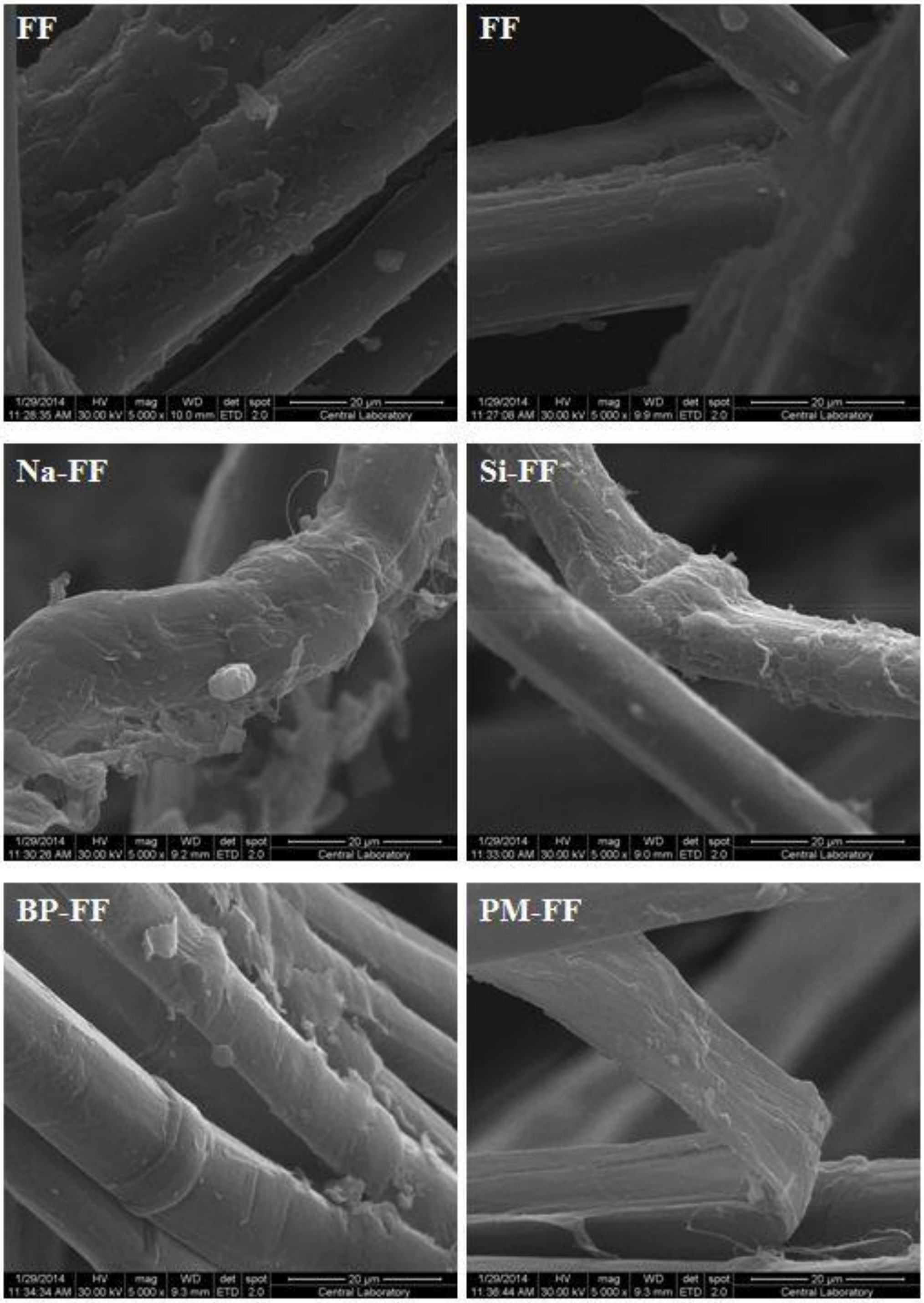


Figure 4.12 SEM micrographs of FF surfaces.

4.1.4 Effect of Surface Treatments on Mechanical, Physical and Water Uptake Properties of TPU/FF Green Composites

4.1.4.1 Tensile Test

The stress–strain curves of TPU/FF composites are shown in Figure 4.13 and the relevant tensile test data are listed in Table 4.3.

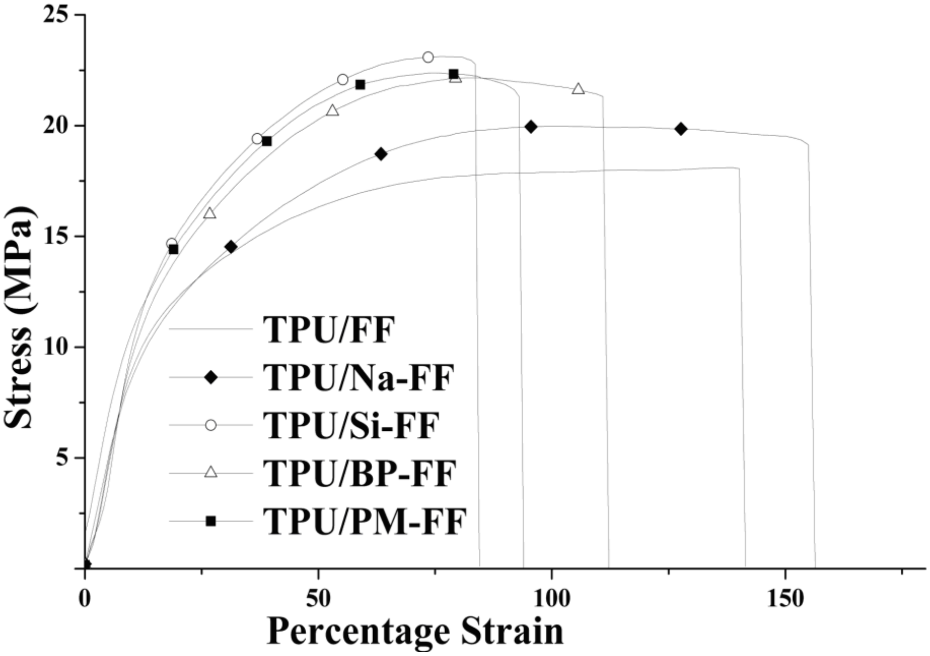


Figure 4.13 Stress-strain curves of TPU/FF composites.

It is seen from Figure 4.13 that all treatment methods sharply increases the tensile strength values of composites with respect to untreated FF. This result shows that applied surface treatments improved the fiber-matrix interactions. The greatest increase in tensile strength is observed for Si-FF containing composite with approximately 28% increase compared to that of untreated FF containing composite. It is also seen that permanganate and peroxide treatments resulted in significant increase in tensile strength values. Surface treatments cause fibrillation of flax along the main axis at the fibers as mentioned earlier (Figure 4.11). This fibrillation also increases the strength of the composites physically in addition to enhanced chemical interactions between fiber surface and polymeric matrix [120]. In the case of percent elongation values; alkali-treated FF containing composite has the highest strain where other treatments resulted in a decrease compared to untreated FF containing composite. It is clearly seen that surface modifications cause some increase in Youngs' modulus and all the composites have greater modulus than the unfilled TPU [121].

Table 4.3 Tensile properties of TPU and TPU/FF composites.

SAMPLES	**Tensile Strength** (MPa)	**Elongation at break** (%)	**Youngs' modulus** (MPa)
TPU	24.8±2.2/24.5±3.5*	424.0±22.3/421.8±20.9*	57.8±3.4/57.2±4.1*
TPU/FF	18.1±1.7/17.4±2.0*	141.0±8.4/240.7±10.5*	121.6±6.1/57.7±6.6*
TPU/Na-FF	20.0±2.4/18.2±1.4*	155.9±5.7/303.9±6.9*	104.8±4.5/47.6±3.2*
TPU/Si-FF	23.1±2.2/19.1±1.3*	87.6±4.0/105.0±5.2*	115.8±6.1/62.3±4.9*
TPU/BP-FF	22.1±1.9/18.6±1.8*	110.9±7.3/123.6±7.0*	114.5±4.2/60.6±3.8*
TPU/PM-FF	22.4±2.0/18.8±1.5*	96.3±6.4/127.9±7.6*	100.5±5.3/60.5±3.7*

**: Test results of samples water absorption test applied.*

The basic stress–strain characteristics like tensile strength, Youngs' modulus and elongation at break values of the composites are compared with those that are after water absorption and reported in Table 4.3. It is not surprising that immersion of TPU in water even for a long time did not affect the mechanical properties. All the tensile values of neat TPU are identical to those that are after water absorption. Water immersion of the composites generally results increase in strain while decreasing in strength and Youngs' modulus. Si-FF containing composite is the one that strain with no significant increase took place because of hydrophobic nature of silane-treated surface [121]. Some studies reported that immersion of polymer/flax fiber composites in water caused significant decrease in mechanical properties which was not the case in our experiments [122-124].

4.1.4.2 Hardness Test

Hardness values of TPU and TPU/FF composites are listed in Table 4.4. It can be seen from these values that hardness of TPU increases with the addition of both untreated and treated FF. Hardness values of TPU/FF and TPU/Na-FF are almost identical. Silane treated FF loaded composite exhibited the highest value which leads to 6.4 units increase in Shore A hardness of TPU. Composite containing BP-FF gave slightly lower hardness value than that of TPU/FF. It is clearly seen from Table 4.4 that permanganate treatment caused sharp decrease that hardness of its composite is lower than unmodified FF containing composite.

Table 4.4 Shore A hardness of TPU and TPU/FF composites.

TPU	TPU/FF	TPU/Na-FF	TPU/Si-FF	TPU/BP-FF	TPU/PM-FF
85.9±0.2	90.1±0.1	89.9±0.2	92.3±0.1	89.6±0.1	82.5±0.3

4.1.4.3 DMA

The storage modulus versus temperature graphs of TPU and its composites are shown in Figure 4.14. Storage modulus of TPU and its composites drop down sharply around -40 ^{0}C that corresponds to glass transition temperature of polymer. Storage modulus of surface modified FF filled composites is higher than unfilled TPU and TPU/FF. The storage modulus results are in accordance with the tensile modulus results. The highest storage modulus is observed for Si-FF containing composite due to enhanced interfacial compatibility of fiber with TPU. These strong chemical interactions result improvement in stiffness and elastic modulus [121].

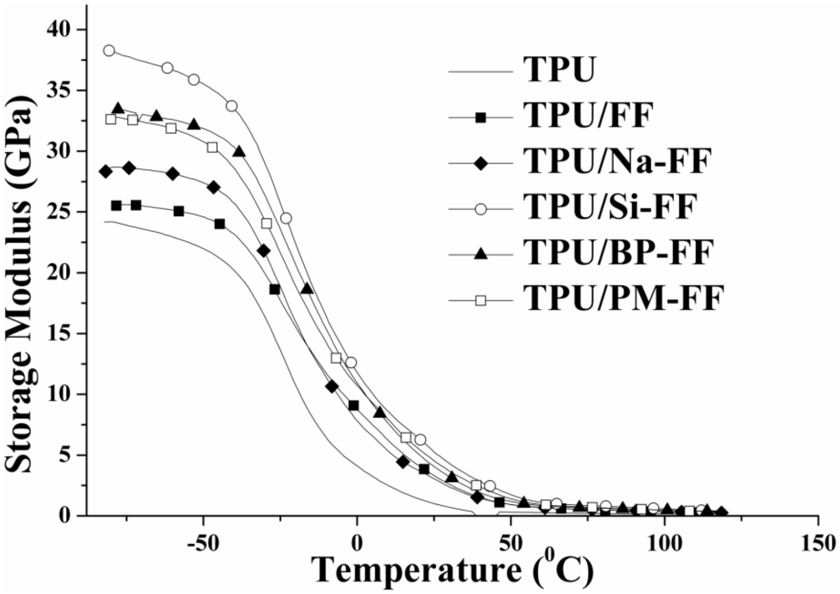


Figure 4.14 Storage modulus-temperature curves of TPU and TPU/FF composites.

Damping properties of composites are analyzed with their tan δ versus temperature curves which are shown in Figure 4.15. It can be seen from these curves that tan δ increases with all surface treatments. T_g of the composites shifts to a bit higher temperatures with the additon surface treated flax fibers. This observation can be explained by the hinderance of chain motions of TPU due to increased interfacial interactions. The study made by Wielage et al. supports this conclusion. They investigated the dynamic mechanical properties of FF reinforced polypropylene composites. In their study, coupling agent was added to improve wetting of fibers with polypropylene matrix. They showed that the T_g and tan δ values of the composites increase by the addition of coupling agent [125].

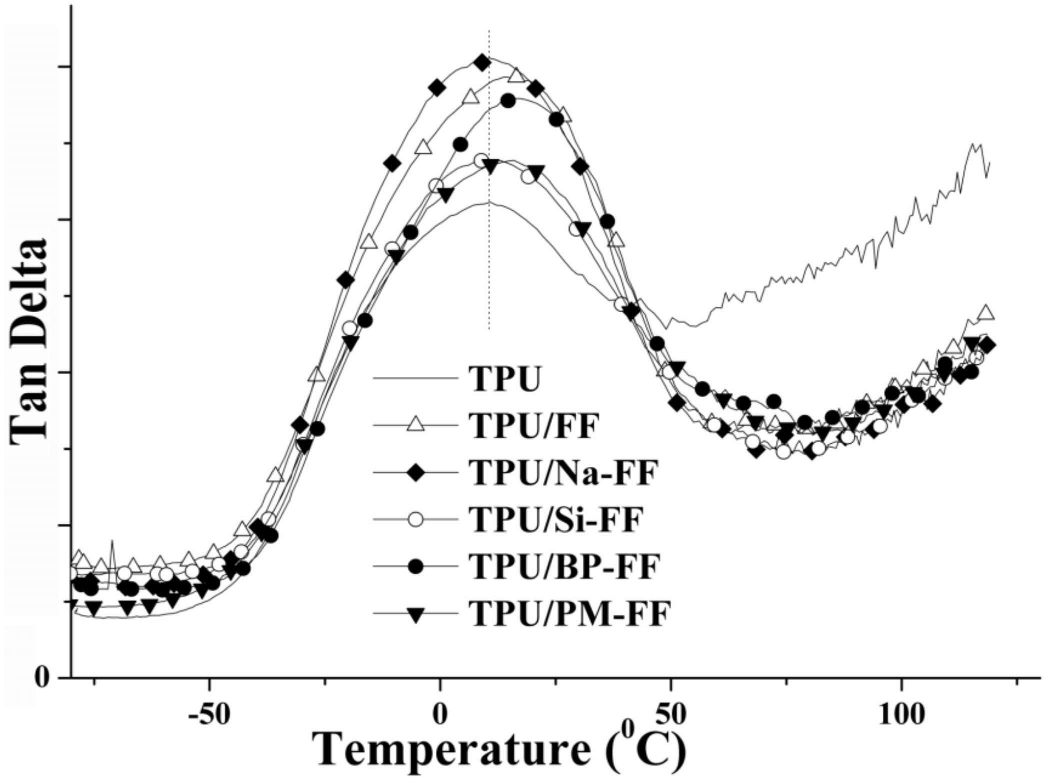


Figure 4.15 Tan δ-temperature curves of TPU and TPU/FF composites.

4.1.4.4 MFI Test

MFI values of pure TPU and its composites at process temperature (200 ^{o}C) are given in Figure 4.16. It is clear that MFI values of all the composites are much higher than that of neat TPU due orientation of flax fibers along the flow lines owing to their high aspect ratio. Alkaline and silane treatments cause slight decrease where benzoyl peroxide and permanganate treatment cause sharp decrease in MFI values with respect to untreated FF loaded composite. The most probable reason for this observation may be the stronger interactions of surface treated elementary fibers due to fiber-matrix adhesion rather than fiber-fiber adhesion. On the other hand, melt viscosity of composites increase due to bundle formation of untreated fibers in TPU matrix [121].

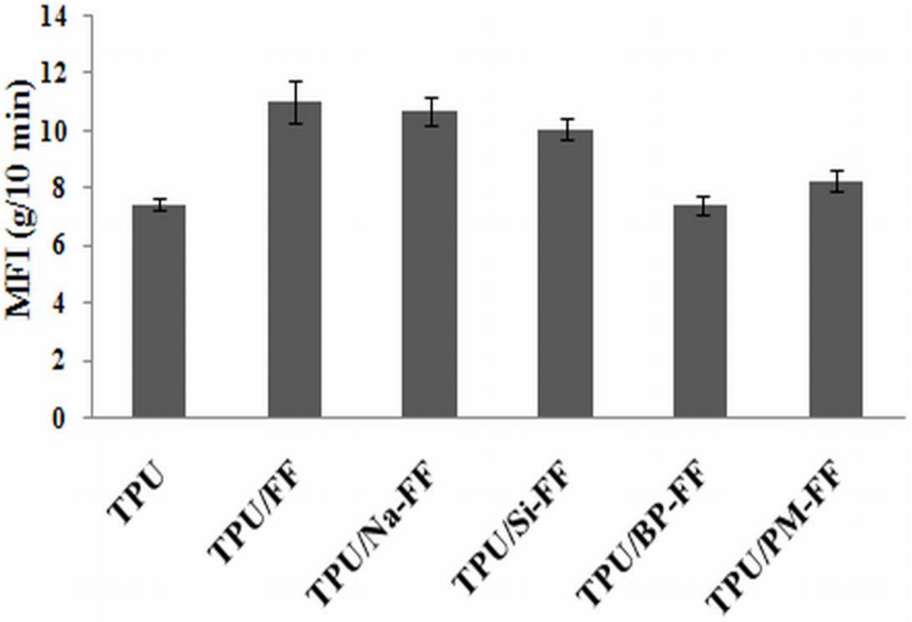


Figure 4.16 MFI values of TPU and TPU/FF composites.

4.1.4.5 Water Absorption Test

The water absorption curves of TPU and TPU/FF composites in 30 days period of time are shown in Figure 4.17. As can be seen in these curves, TPU absorbed about 1 % water rapidly in a few days and reached its maximum capacity. Untreated flax fiber containing composite gives the greatest water uptake value at around 6% at the end of the test due to formation of micro voids between fiber surface and polymer matrix. Permanganate and peroxide treatments cause almost no change in water absorption results as compared with alkaline treatment. It is found that all these three treatments are almost identical at around 5% at the end of the experiment. It is clearly seen that the composite containing silane treated flax fiber absorbs much less water with respect to other composites at around 4%. This result may not be surprising because of the well-known hydrophobicity of silane coupling agent [121].

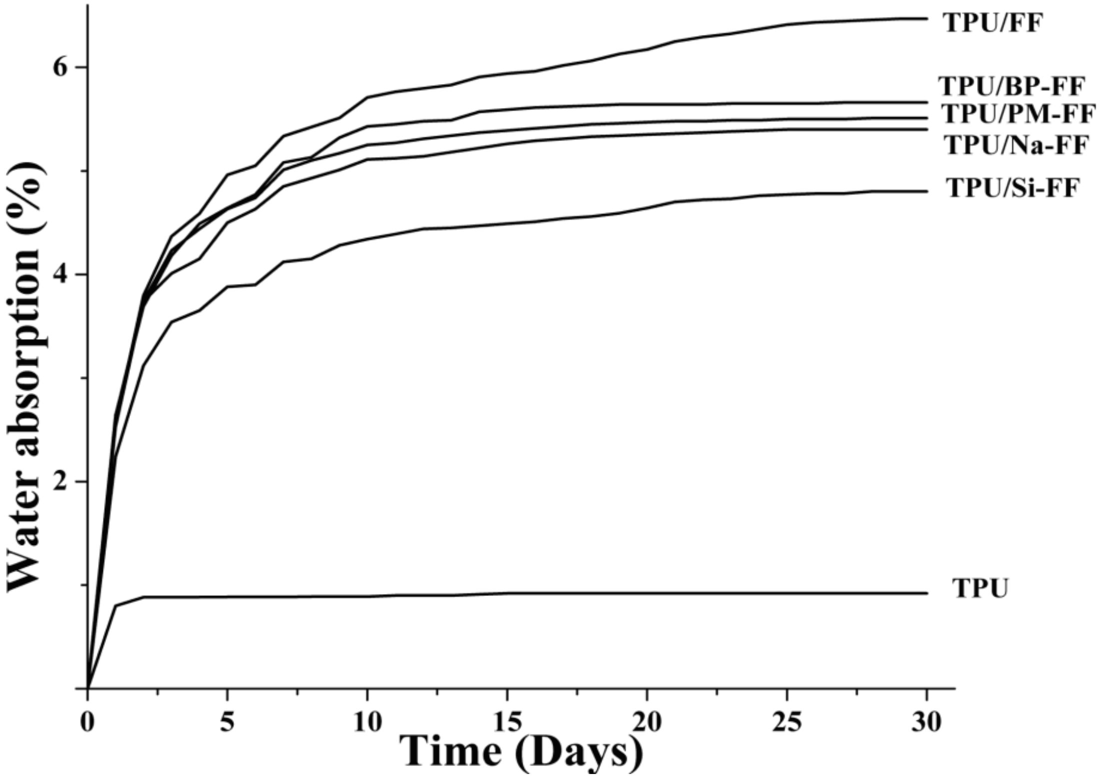


Figure 4.17 Water uptake curves of TPU and TPU/FF composites.

4.1.4.6 SEM Analysis

SEM micrographs of fracture surfaces of selected TPU/FF composites are shown in Figure 4.18. It is clearly seen that gaps formed between untreated fiber and matrix which indicates poor adhesion between TPU and flax fiber. TPU covers and wets the surface of fibers where in the case of surface modified fibers. This observation indicates that alkaline and silane treatments greatly improve the interfacial adhesion between flax fiber and polymer matrix. These findings provide qualitative evidence for the mechanical, flow and water absorption properties of composites that are discussed in earlier sections.

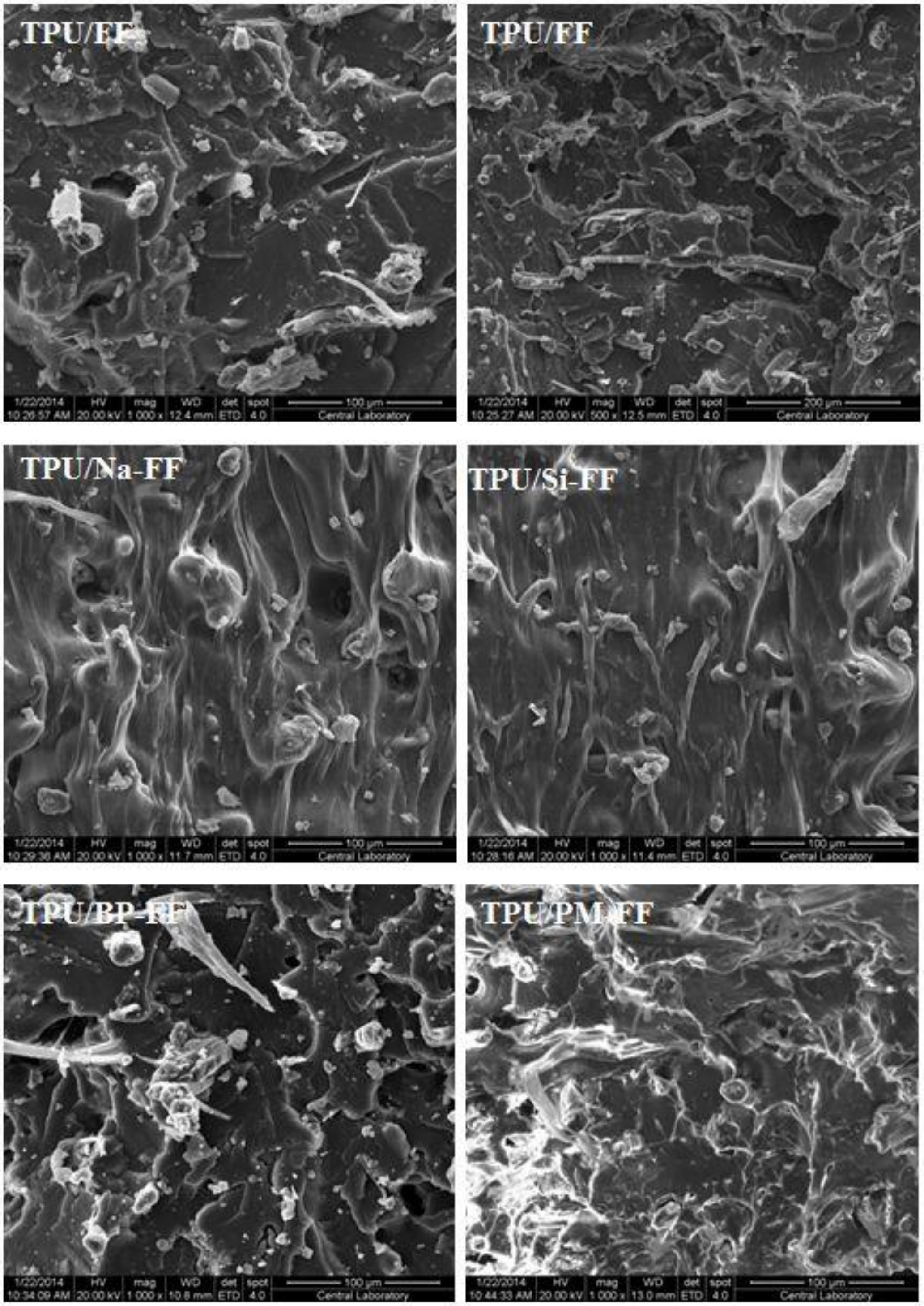


Figure 4.18 SEM micrographs of TPU/FF composites.

4.2 CFR TPU Composites

4.2.1 Characterization of CNT Surface

4.2.1.1 FTIR Analysis

FTIR spectra of CNT and surface treated CNT samples are shown in Figure 4.19. The three intense peaks at 1580, 1630 and 2860 cm^{-1} are the characteristic CNT peaks that correspond to C–C stretching vibration, C=C stretching vibration and symmetric $–CH_2$ stretching vibrations, respectively [56]. Absorption band from 1000 cm^{-1} to 1200 cm^{-1} range in which oxygen functionalities observed such as C–O stretching at broad peak around 1000 cm^{-1}. This peak is indicative of the presence of oxygen on pristine CNT surface. The peak for adsorbed oxygen for HN-CNT is clearly seen. Si–O–Si and Si–O–C vibration bands at 1050 cm^{-1} and 1100 cm^{-1} for Si-CNT are only due to formation of siloxane units after silane treatment [126, 127]. Absorption band at 800 cm^{-1} indicates the Si–OH bond which corresponds to hydrolyzed silane portion during silanization [128].

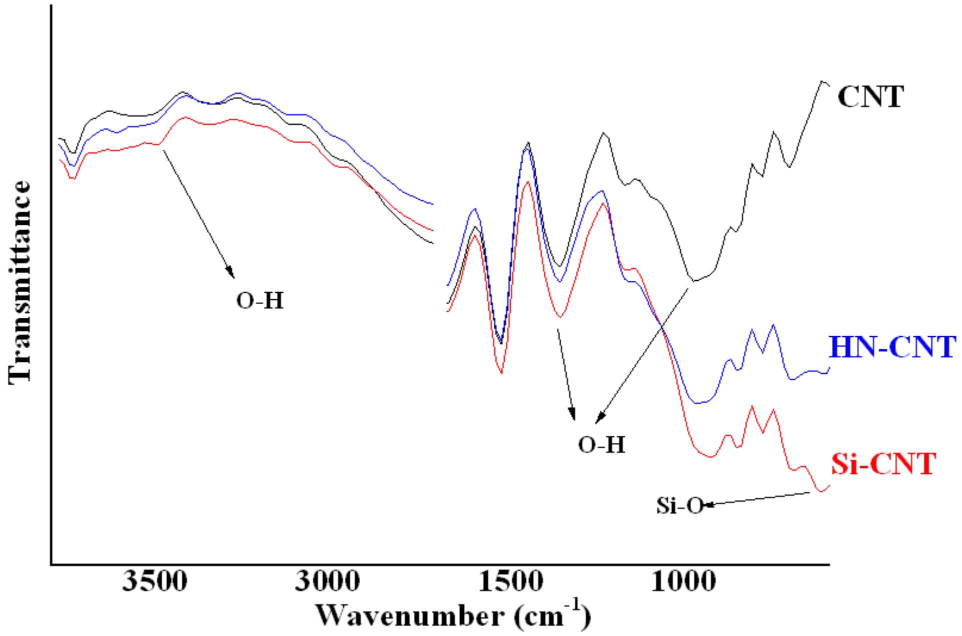


Figure 4.19 FTIR spectra of CNT samples**.**

Broad band that centered at around 3200 cm^{-1} is the characteristic hydroxyl group stretching that is observed as a more intense peak for HN-CNT than Si-CNT. Appearance of another –OH functionality band at 1380 cm^{-1} is observed as broader for acid treated CNT. Relatively low intensity of this band for Si-CNT is caused from the chemical modification of surface hydroxyl groups with silane coupling agent. These observations indicate that all the treatments resulted in increase of hydoxyl groups where silane modification caused slight reduction of these groups by chemical bond formation.

4.2.1.2 SEM/EDX Analysis

According to elemental analysis in Table 4.5 (see also Appendix A) it is clearly observed that oxygen content raise about two-fold for HN-CNT which indicates the hydroxyl group formation on CNT surface after nitric acid modification. Remarkable silicon percentage was observed for Si-CNT may be due to the formation of siloxane units at CNT surface after silanization.

Table 4.5 SEM/EDX results of CNT and surface modified CNTs.

SAMPLES	C Wt%/At%	O Wt%/At%	Si Wt%/At%
CNT	91.87 /94.28	6.38 /4.92	0 /0
HN-CNT	87.59 /90.51	11.99 /9.30	0 /0
Si-CNT	79.14 /85.41	14.13 /11.45	5.01 /2.31

SEM images with 50,000 magnifications of pristine and surface treated CNT samples are shown in Figure 4.20. According to SEM images, HN-CNT and Si-CNT are seen in more bulky form relative to pristine CNT which may be caused from the increasing of intermolecular forces such as formation of hydrogen bonding with functionalizations of carbon nanotubes.

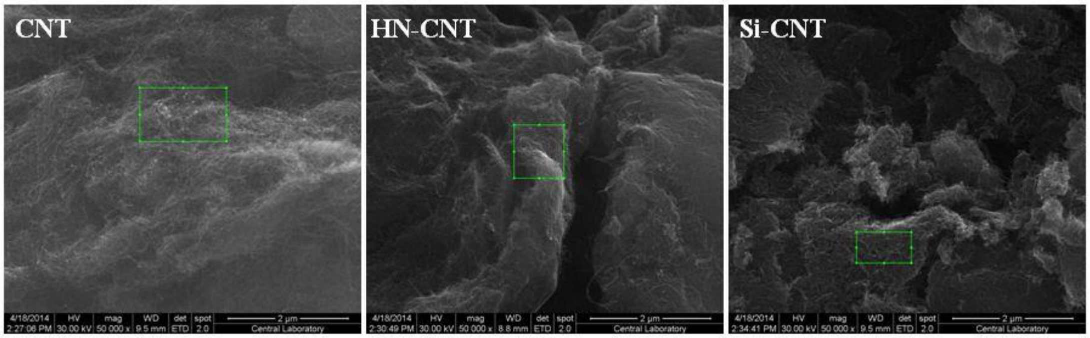


Figure 4.20 SEM micrographs of pristine and modified CNTs.

4.2.2 Effect of Surface Modifications on Mechanical and Physical Properties of TPU/CNT Composites

4.2.2.1 Tensile Test

Tensile test data of TPU and its composites are listed in Table 4.6. It is seen from the Table 4.6 that addition of both modified and unmodified CNT raised the tensile strength, elongation at break and Youngs' modulus values with respect to pristine TPU. Tensile strength increase with surface treated CNT addition compared to unmodified CNT filled composite. Thus, both nitric acid and silane treatments improve the wetting of CNT surface may attributed to increase of the adhesion between CNT and TPU at low loading levels. The highest strength result is obtained for Si-CNT containing composite at the lowest concentration (0.5 %). Tensile strength exhibits decreasing trend with further modified CNT loadings. The reduction in tensile strength at higher concentrations may arise from the starting of bundle formations due to decrease in interfacial interactions between two phases.

Both pristine and surface funtionalized CNT additions to TPU are resulted in remarkable increase in elongation at break and Youngs' modulus. Incorporating CNT to TPU leads to increase of Youngs' modulus may due to restriction of chain motions. Contrary to tensile strength results, percent elongation and Youngs' modulus values of TPU/CNT are slightly higher than those of surface modified CNT filled composites. It is not possible to generalize elongation and modulus behavior of unmodified and modified CNTs with respect to composition from tensile test data.

Table 4.6 Tensile test results of TPU and TPU/CNT composites.

SAMPLES	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Youngs' Modulus (MPa)**
TPU	24.8±1.7	331.8±4.3	33.4±3.0
TPU/0.5% CNT	30.5±1.8	510.0±5.1	74.8±3.3
TPU/1% CNT	29.3±1.6	510.3±5.5	83.2±3.8
TPU/1.5% CNT	28.4±2.1	482.6±6.4	70.7±3.5
TPU/2% CNT	27.2±1.9	531.0±5.2	74.8±3.1
TPU/0.5%HN-CNT	35.0±2.2	462.9±6.3	63.1±3.4
TPU/1% HN-CNT	31.0±2.4	411.7±5.7	65.4±3.1
TPU/1.5%HN-CNT	29.6±1.7	432.5±5.9	69.6±3.7
TPU/2% HN-CNT	28.5±2.0	423.0±5.4	67.4±3.2
TPU/0.5% Si-CNT	35.1±2.3	489.1±6.5	67.9±3.3
TPU/1% Si-CNT	32.0±1.8	462.7±6.1	60.0±3.6
TPU/1.5% Si-CNT	30.6±2.4	388.0±5.6	65.0±2.9
TPU/2% Si-CNT	30.0±2.1	422.5±6.2	70.0±3.5

4.2.2.2 Hardness Test

Shore A hardness values of TPU and TPU/CNT composites are listed in Table 4.7. It can be seen from these values that hardness of TPU drops down with unmodified CNT addition. Pristine CNT interacts mostly with hard segment of polyurethane chain. CNTs have tendency to form bundles and this restricts their dispersion in polymeric matrix. Because of these facts unmodified CNT inclusion to TPU causes reduction in hardness values. On the other hand, Shore hardness values of TPU, HN-CNT and Si-CNT loaded composites are almost identical at the lowest loading level and hardness increased with HN-CNT and Si-CNT concentration. Si-CNT containing composite exhibits slightly higher hardness values than that of TPU/HN-CNT.

Table 4.7 Shore A hardness of TPU and TPU/CNT composites.

CNT Content (%)	TPU	TPU/CNT	TPU/ HN-CNT	TPU/ Si-CNT
0.5	84.8±0.2	83.6±0.2	84.4±0.1	84.8±0.1
1	84.8±0.2	82.3±0.1	84.9±0.1	85.5±0.2
1.5	84.8±0.2	79.7±0.3	85.8±0.2	86.3±0.2
2	84.8±0.2	77.1±0.3	86.5±0.1	87.1±0.1

4.2.2.3 MFI Test

MFI values of TPU and its composites at 215 ^{0}C are given in Figure 4.21. It is clear that melt flow index decreases for 0.5% CNT and HN-CNT containing composites with respect to neat TPU. Further additions of unmodified CNT cause sharp reductions on MFI values because of large agglomerates formation. CNT tends to form bundles readily due to interparticle adhesion rather than CNT-matrix adhesion that cause restriction for flow of polymer melt. Reduction on MFI values of polymer composites by addition of pristine CNT was also observed in several publications [129-131].

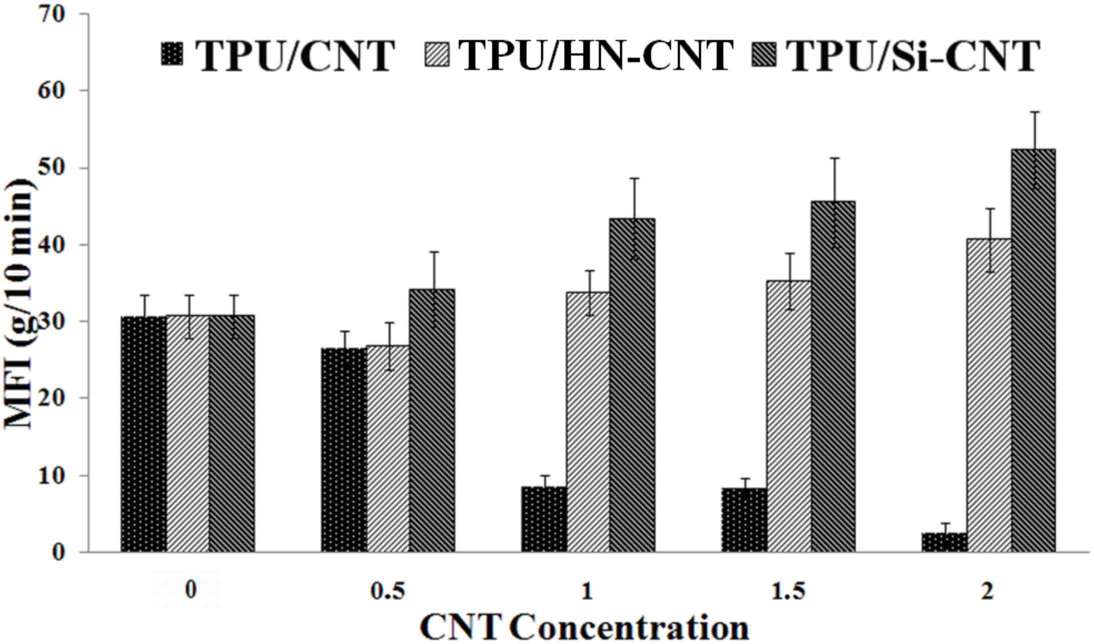


Figure 4.21 MFI values of TPU/CNT composites.

In contrast to unmodified CNT containing composites, nitric acid and silane treatments caused gradual increase in MFI values with increasing CNT content of composites. It is seen that there is a correlation between the adhesion and MFI values. Enhancement of surface interactions between phases leads to disperse carbon nanotubes more uniformly in matrix. Restriction effect of CNT bundles in polymer melt is overcomed by applying surface modifications.

4.2.2.4 SEM Analysis

Representative SEM micrographs of fracture surfaces of selected TPU/CNT composites are shown in Figure 4.22. Observations from the SEM micrographs of fracture surfaces of selected composites indicate that phase separation between CNT and TPU occurred and nanotubes remained bulky form for unmodified CNT loaded composites because of tendency of nanotubes to attract each other rather than polymeric matrix. It is clearly seen from SEM micrographs of HN-CNT and Si-CNT containing composites that is nitric acid and silane treatments improve the interfacial adhesion between CNT and TPU matrix. Surface functionalized CNT exhibits better dispersion in TPU composites. Formations of agglomeration gradually decrease for surface modified CNT containing composites due to excess charge of the modified CNT surface having high zeta potential [132]. These findings provide qualitative evidence for the mechanical and melt-flow properties of composites.

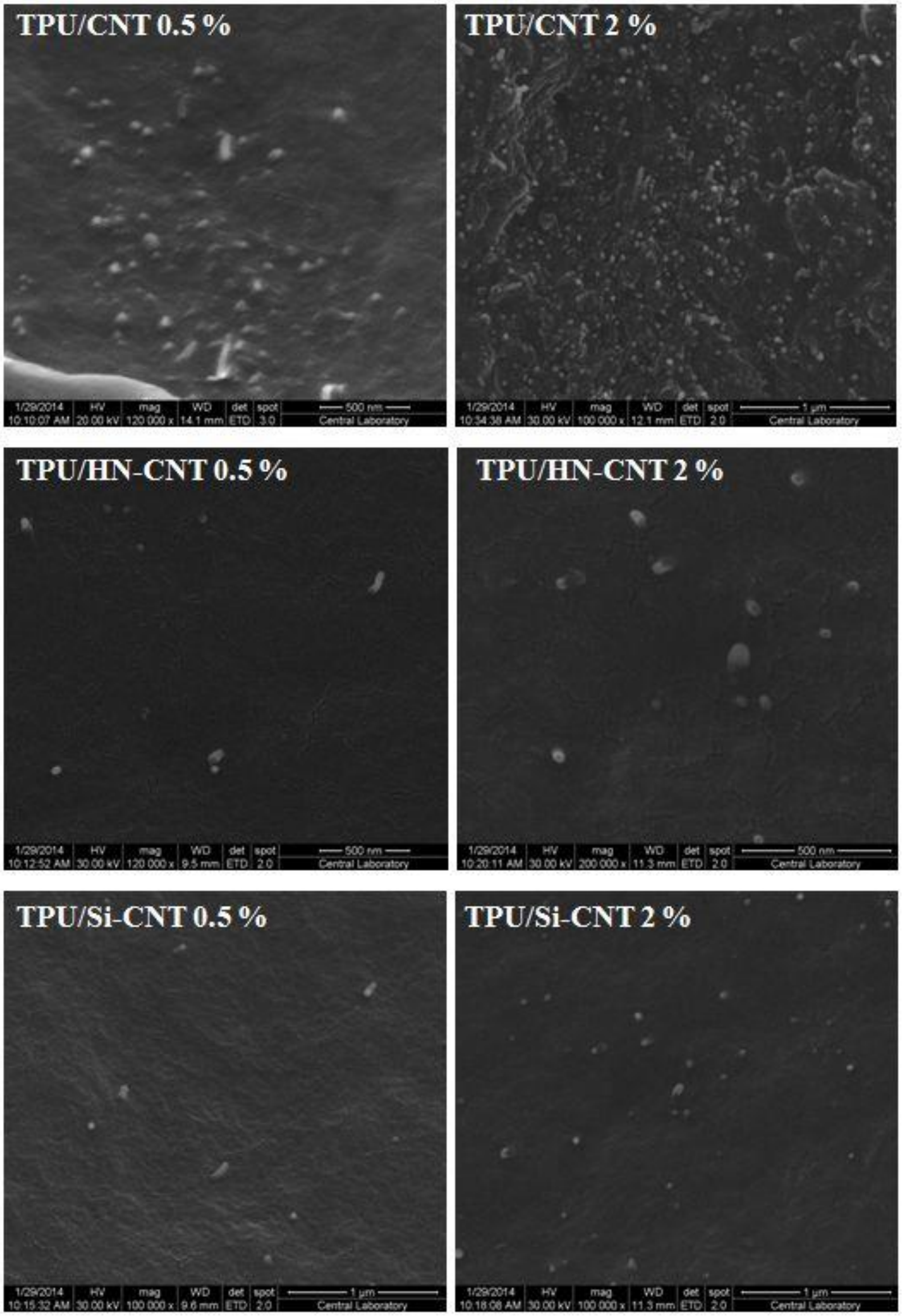


Figure 4.22 SEM micrographs of TPU/CNT composites.

4.2.3 Characterization of C_{60} Surface

4.2.3.1 FTIR Analysis

FTIR spectra of C_{60} and surface treated C_{60} samples are shown in Figure 4.23. The four intense peaks at 530, 580, 1180 and 1430 cm^{-1} are the characteristic C_{60} peaks that appear in all spectra [67, 133]. Absorption bands from 1000 to 1500 cm^{-1} range indicate the oxygen functionalities such as C–O stretching at broad peak from 1100 to 1200 cm^{-1} in which absorption increment of the peak for HN-C_{60} is clearly seen. Si–O–Si vibration band at 1050 cm^{-1} and Si–O–C vibration band at 1100 cm^{-1} present for Si-C_{60} only due to the formation of siloxane units after silane treatment [127, 134]. The absorption band at 875 cm^{-1} indicates the Si-OH bond which corresponds to hydrolyzed silane portion during silanization [135].

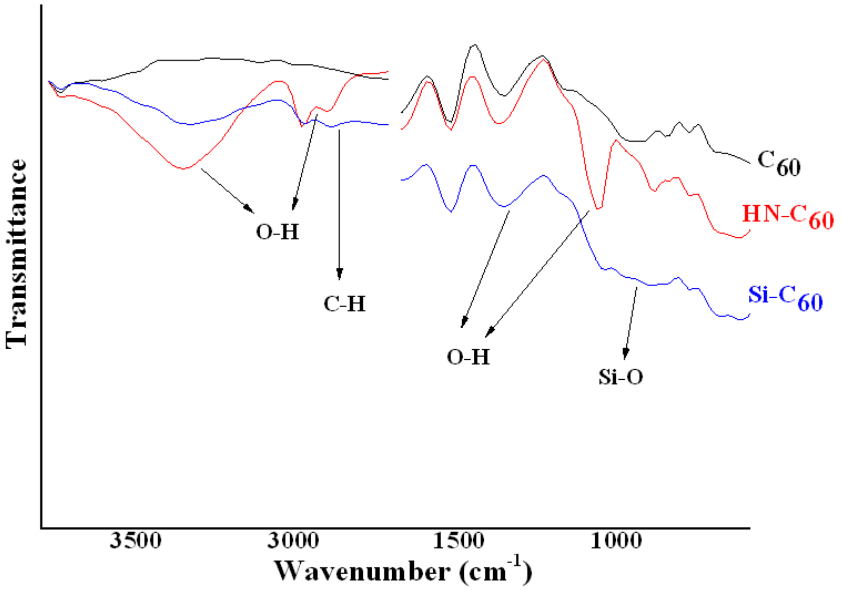


Figure 4.23 FTIR spectra of fullerene samples.

Broad band that centered at around 3400 cm^{-1} is the characteristic hydroxyl group stretching that is observed as more intense peak for HN-C_{60} than Si-C_{60}. Relatively low intensity band for Si-C_{60} assigns the chemical modification of surface hydroxyl groups with silane coupling agent. Appearance of another broad absorption band that in the range of 2800-3000 cm^{-1} is attributed to $–CH_2$ and $–CH_3$ stretching vibrations of methylene groups of APTES. These observations indicate that all the treatments resulted in increase of hydroxyl groups where silane modification causes slight decrease of these groups by chemical bond formation.

4.2.3.2 SEM/EDX Analysis

It is clearly observed from the elemental analysis on the Table 4.8 (see also Appendix A) that oxygen content raise by a factor of two times after nitric acid modification due to hydroxyl groups on fullerene surface and remarkable silicon percentage is observed after silanization which indicates the formation of siloxane units at the surface of fullerene after reaction of silane coupling agent surface hydroxyl groups. Oxygen content also increases somewhat possibly due to siloxane adsorption on fullerene surface.

Table 4.8 EDX results of fullerene and surface modified fullerenes.

SAMPLES	C Wt%/At%	O Wt%/At%	Si Wt%/At%
C_{60}	92.66/94.39	7.34/5.61	0/0
HN-C_{60}	88.55/91.15	11.45/8.85	0/0
Si-C_{60}	76.29/84.39	12.27/10.19	11.44/5.41

SEM images with 50,000 magnifications of pristine and surface treated C_{60} samples are shown in Figure 4.24. According to SEM images, HN-C_{60} and Si-C_{60} are seen in more bulky form relative to pristine C_{60} which may be arise from the increase in the intermolecular forces such as hydrogen bonding after nitric acid and silane treatments.

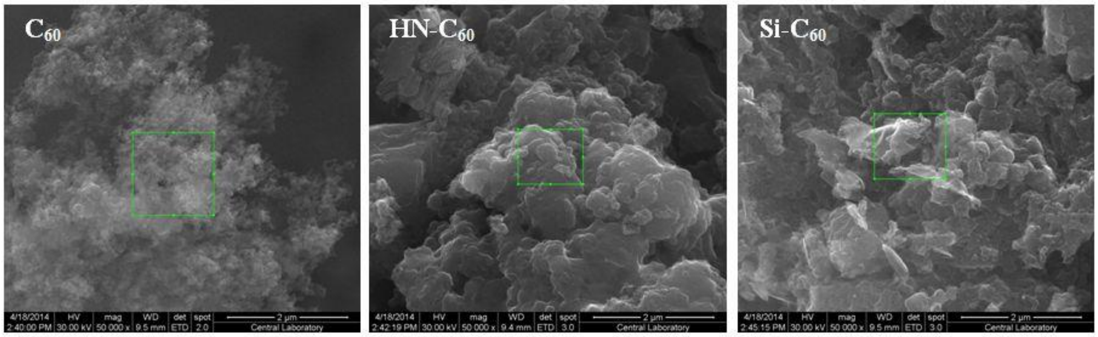


Figure 4.24 SEM micrographs of pristine and modified fullerenes.

4.2.4 Effect of Surface Modifications on Mechanical and Physical Properties of TPU/C_{60} Composites

4.2.4.1 Tensile Test

Tensile test data of TPU and its composites are listed in Table 4.9. It is seen from Table 4.9 that tensile strength and elongation at break values raise sharply with the addition of both modified and unmodified fullerene when compared with those of TPU. It is also observed from the table that tensile strength and percent elongation of HN-C_{60} and Si-C_{60} containing composites are improved with respect to unmodified fullerene containing composite. After nitric acid and silane treatment, surface hydroxyl and siloxane groups (Table 4.8) enhance the adhesion between fullerene and TPU matrix. Among these treatments, further modification of fullerene with silane causes slightly higher values in tensile strength and percent elongation values with respect to acid treatment. Tensile strength and percent elongation values exhibit a decreasing trend with increasing fullerene concentration for all cases. One reason of this decrease at high Si-C_{60} concentrations can be the formation of weak boundary layer with excess amount of siloxane. The best results are obtained in nitric acid and silane modified fullerene loaded composites at the lowest concentration (0.5 %). This may be due to fact that dispersion occurs more homogeneously at lower concentrations where composites exhibit the highest strength results. Both modified and pristine fullerene additions to TPU cause remarkable increase in Youngs' modulus values as seen in Table 4.9. The inclusion of fullerene at high concentrations slightly reduces the Youngs' modulus which may due to restriction of TPU chain motions after high filler loadings [136].

Table 4.9 Tensile test results of TPU and TPU/C_{60} composites.

SAMPLES	Tensile Strength (MPa)	Elongation at break (%)	Youngs' modulus (MPa)
TPU	24.8±1.7	331.8±4.3	33.4±3.0
TPU/0.5% C_{60}	38.9±2.4	574.0±5.5	65.3±2.8
TPU/1% C_{60}	35.7±2.0	573.3±6.9	65.1±3.2
TPU/1.5% C_{60}	32.4±1.9	419.7±5.8	64.1±3.5
TPU/2% C_{60}	30.9±2.0	347.8±5.4	54.2±3.1
TPU/0.5% HN-C_{60}	41.3±2.3	598.4±8.1	64.2±3.6
TPU/1% HN-C_{60}	38.6±2.1	554.3±7.2	65.8±3.2
TPU/1.5% HN-C_{60}	37.1±2.2	524.4±6.0	61.5±3.4
TPU/2% HN-C_{60}	34.0±2.2	445.3±5.8	61.4±2.9
TPU/0.5% Si-C_{60}	42.0±2.5	613.1±7.9	58.6±2.7
TPU/1% Si-C_{60}	40.3±2.0	579.8±6.6	59.9±3.3
TPU/1.5% Si-C_{60}	38.5±1.8	553.4±7.8	56.7±2.6
TPU/2% Si-C_{60}	35.2±2.3	559.8±8.2	63.0±2.8

4.2.4.2 Hardness Test

Hardness values of TPU and TPU/C_{60} composites are listed in Table 4.10. Hardness of TPU decreases with the inclusion of unmodified C_{60}. Pristine C_{60} particles do not disperse uniformly in polymer matrix due to their tendency to form agglomerates. Thus, unmodified C_{60} incorporation causes reduction in hardness of TPU. On the other hand, Shore hardness of TPU slightly increases with the addition of HN-C_{60} and Si-C_{60} at the lowest loading level (0.5 %). After that point, hardness values exhibit decreasing trend with further C_{60} additions. Si-C_{60} containing composites give higher hardness values than that of TPU/HN-C_{60} and TPU/C_{60} at the same concentrations.

Table 4.10 Shore A hardness of TPU and TPU/C_{60} composites.

C_{60} Content (%)	TPU	TPU/C_{60}	TPU/HN-C_{60}	TPU/Si-C_{60}
0.5	84.8±0.2	83.7±0.3	84.9±0.2	85.3±0.2
1	84.8±0.2	82.0±0.2	84.1±0.1	84.5±0.2
1.5	84.8±0.2	79.5±0.1	83.0±0.3	83.4±0.2
2	84.8±0.2	77.3±0.2	81.6±0.1	81.8±0.1

4.2.4.3 MFI Test

MFI values of TPU and its composites are given in Figure 4.25. It is clear that melt flow index increses as unmodified fullerene amount in composites increase. MFI values of pristine fullerene containing composites are much lower than that of neat TPU. Fullerene particles tend to form agglomerates due to interparticle adhesion rather than fullerene-matrix adhesion. The formation of agglomerates causes increase in melt viscosity in contrary reduction in MFI values [136].

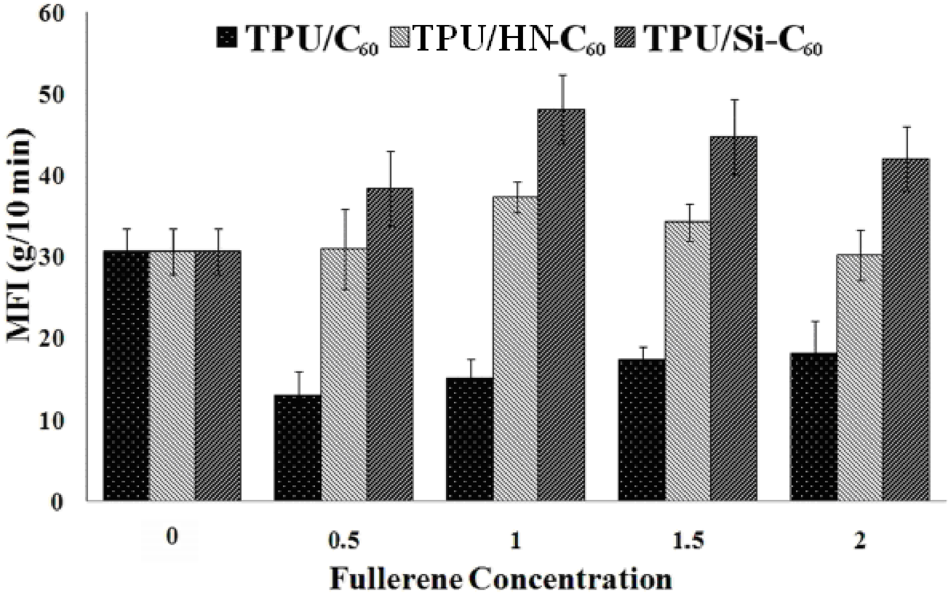


Figure 4.25 MFI values of TPU/C_{60} composites.

4.2.4.4 SEM Analysis

SEM micrographs of fracture surfaces of selected TPU/C_{60} composites are shown in Figure 4.26. Observations from the SEM micrographs indicate that surface functionalized fullerene exhibits better dispersion compared to pristine fullerene in their TPU composites. Agglomeration formations gradually decrease for surface modified fullerene loaded composites due to excess charge of the modified fullerene surface having high zeta potential [132].

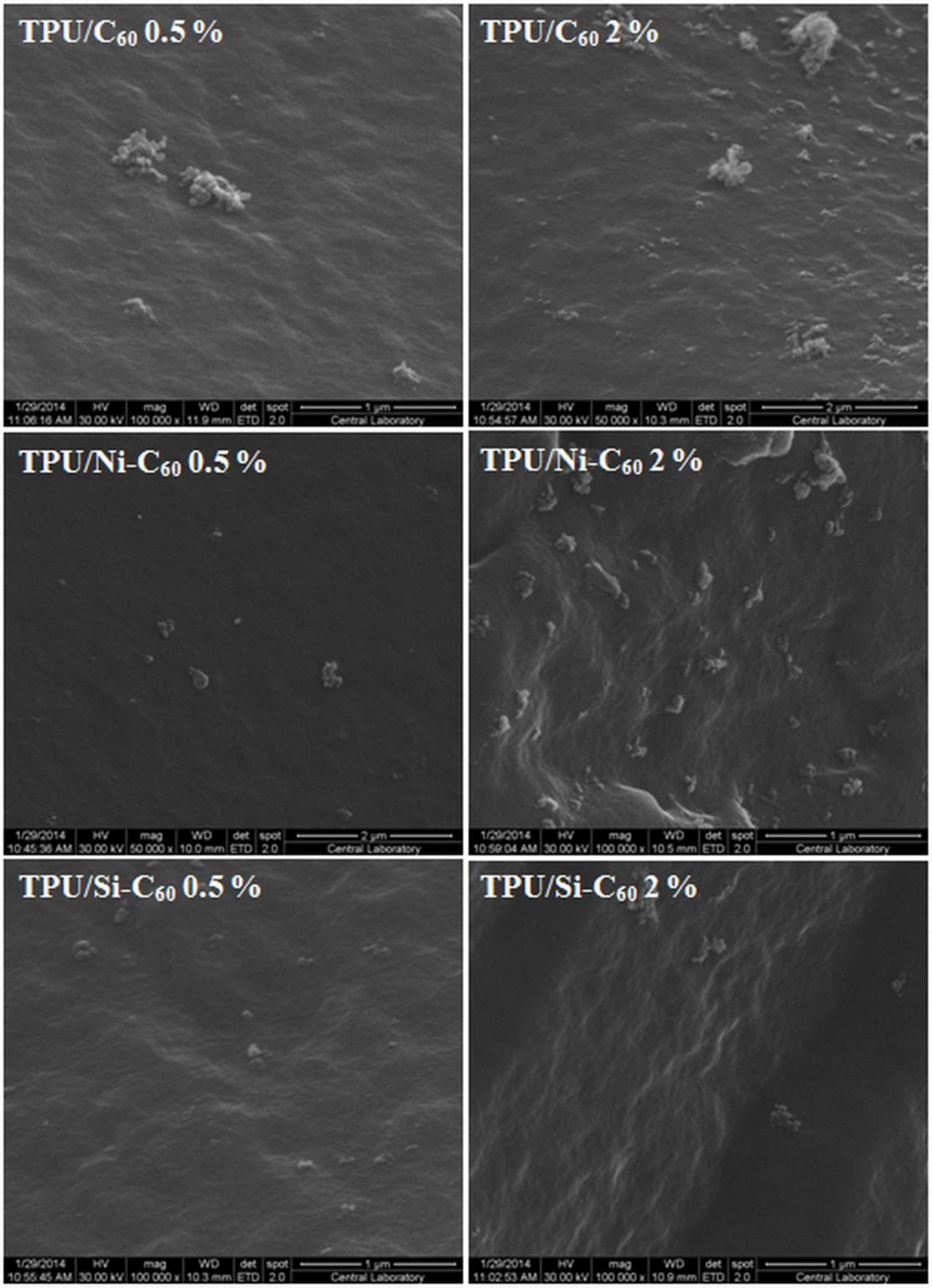


Figure 4.26 SEM micrographs of TPU/C_{60} composites.

4.2.5 Characterization of CF Surface

4.2.5.1 FTIR Analysis

The FTIR spectra of desized and sized CF samples are shown in Figure 4.27. Absorption peaks at 2850 cm^{-1} and 2930 cm^{-1} are due to –CH hydrocarbon groups of desized CF [137]. The Absorption band at 1720 cm^{-1} corresponds to C=O streching vibrations of carbonyl and carboxyl groups [138]. C–O vibrations of sized CF samples can be seen at 1050 cm^{-1} [139]. The peak at 1400 cm^{-1} results from–N=C=O stretching [140]. This characteristic nitrile peak appears for urethane containing surface of PU-CF, MD-CF and CM-CF samples and disappears for EP-CF. Characteristic hydroxyl group peaks at 700 cm^{-1} and around 3500 cm^{-1} present for sized CF samples which indicate O–H stretching and O–H bending, respectively [141].

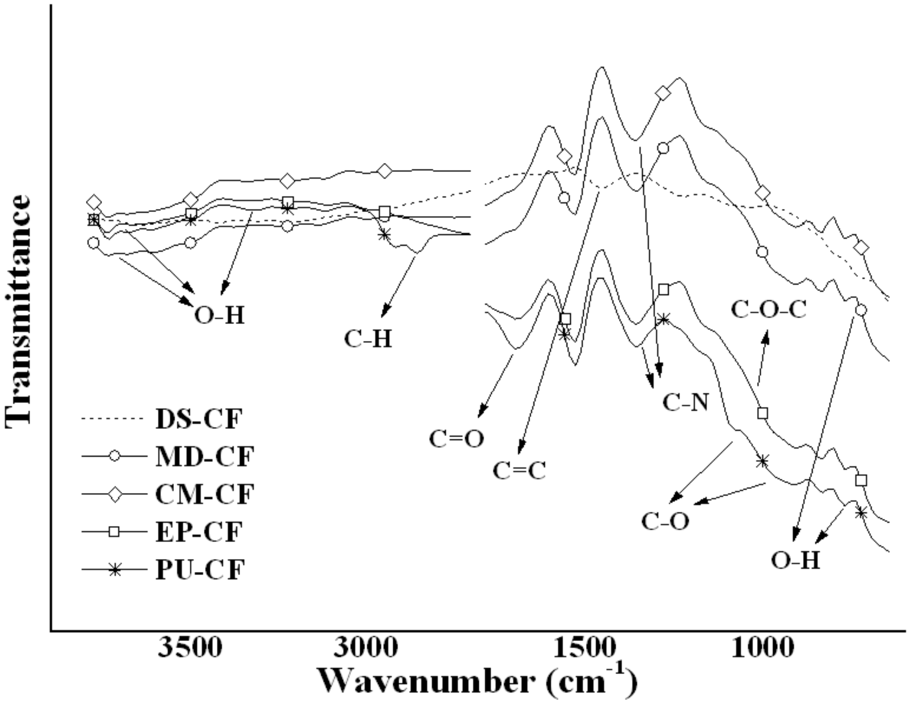


Figure 4.27 FTIR spectra of CF samples.

4.2.5.2 SEM/EDX Analysis

According to elemental analysis data form the Table 4.11 (see also Appendix A), it is clearly observed that oxygen content of desized CF raise by a factor of about 2.5 after isocyanate and cured isocyanate modifications. The highest oxygen content is seen for EP-CF sample due to epoxy unit existence at the fiber surface. Remarkable nitrogen percentages are also observed for commercially sized and isocyanate modified samples. Nitrogen content is slightly lower for CM-CF relative to MD-CF because of formation of carbon containing groups after curing process. Oxygen and nitrogen contents of commercially PU sized CF are seen as very close to that of isocyanate treated CF samples. These observations are attributed to formation of isocyanate units at the surface of CF after treatments.

Table 4.11 EDX results of dezised and sized CF samples.

SAMPLES	C Wt%/At%	O Wt%/At%	N Wt%/At%
DS-CF	96.93 /97.68	3.07 /2.32	0/0
EP-CF	88.26 /90.92	11.74 /9.08	0 /0
PU-CF	89.16 /91.39	8.31 /6.39	2.53 /2.22
MD-CF	90.11 /92.18	7.80 /5.99	2.09/1.83
CM-CF	90.86 /92.79	7.26 /5.56	1.88/1.65

SEM images with x1,000 and x10,000 magnifications of desized, commercially sized and sized CF samples are shown in Figure 4.28. It is clearly seen from SEM images that commercially sized CF surfaces are smoother relative to DS-CF. Isocyanate treated CF surfaces are also seen as smooth which indicates that fiber surfaces were covered by pMDI resin homogeneously.

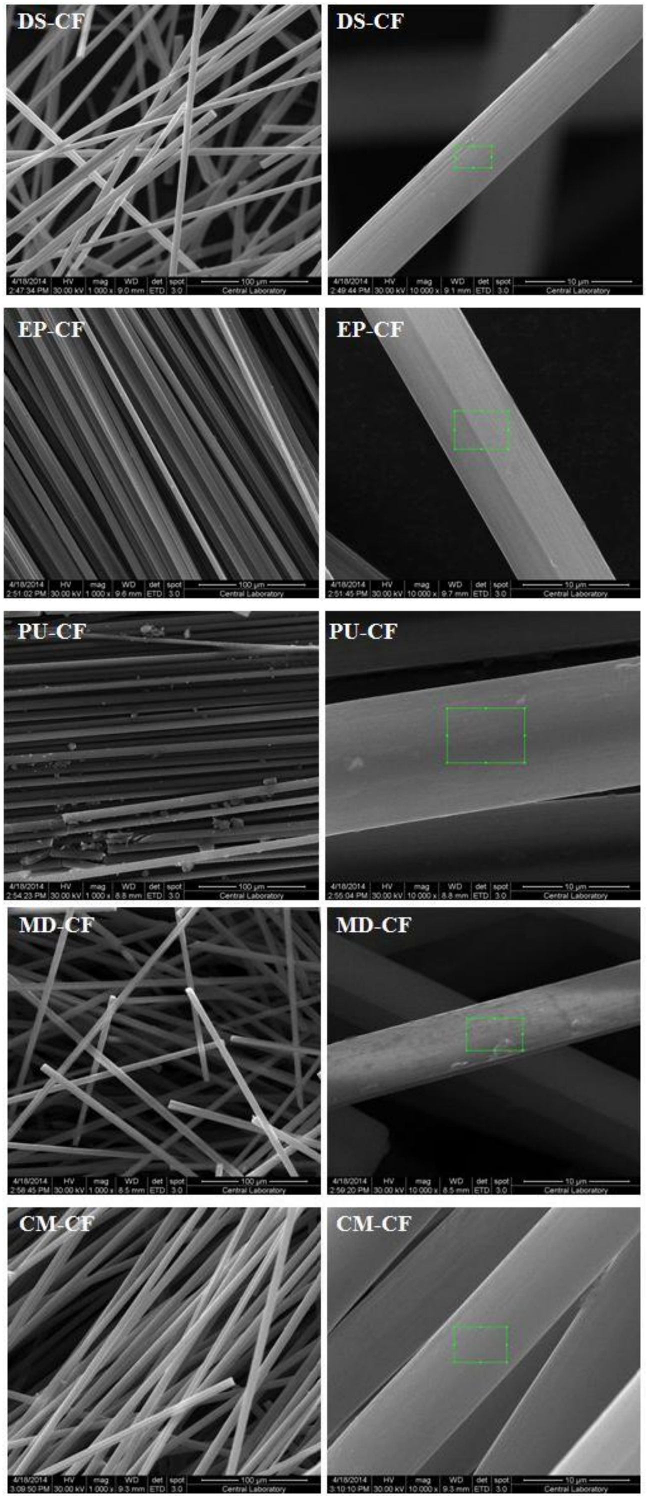


Figure 4.28 SEM micrographs of desized and sized CF samples.

4.2.6 Effect of Surface Modifications on Mechanical and Physical Properties of TPU/CF Composites

4.2.6.1 Tensile Test

Tensile test data of TPU and its composites are represented in Figures 4.29, 4.30 and 4.31 which indicate tensile strength, Youngs' modulus and elongation at break as a function of CF concentration, respectively.

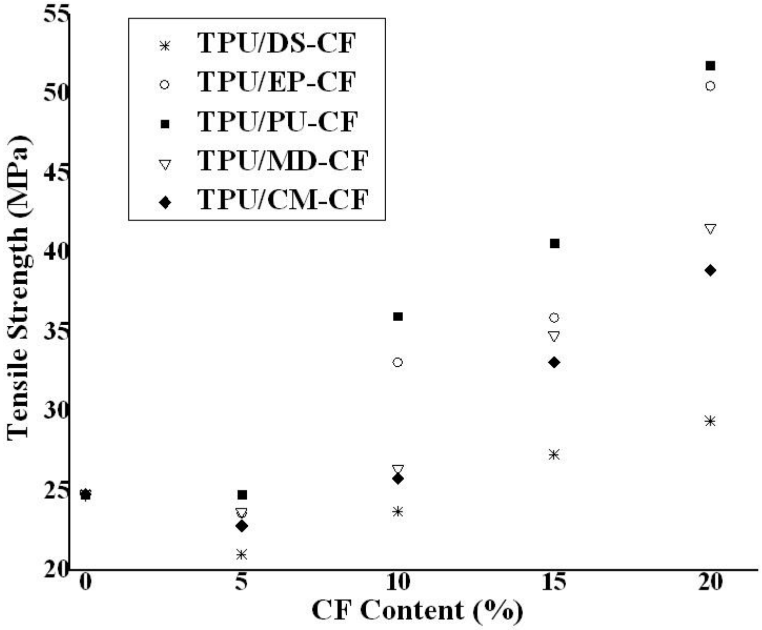


Figure 4.29 Tensile strength results of TPU/CF composites.

It is observed from the Figure 4.29 that tensile strength values were improved with increasing CF composition. MD-CF containing composites exhibit highest strength results at all concentrations except the lowest (5 wt %) composition. Additions of either sized or unsized CF with 5 wt % concentration result in slight decrease on tensile strength of neat TPU. It is obvious that further additions cause level up strength to higher values. Tensile strength improvement is about 68% for the composite that contains 20 wt % of MD-CF with respect to neat TPU.

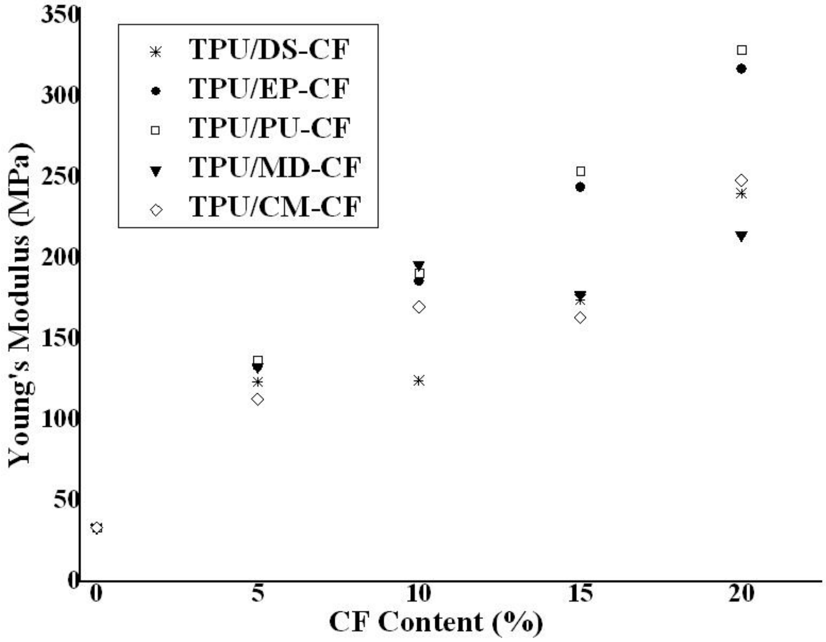


Figure 4.30 Youngs' modulus results of TPU/CF composites.

Youngs' modulus values were raised sharply with the addition of both modified and unmodified CF as compared with those of TPU as shown in Figure 4.30. The inclusion of CF even at lowest concentrations enhanced Youngs' modulus by a factor of about 3.5 times with respect to neat TPU due to restriction of motion of polyurethane chains after fiber loadings. This result is in agreement with theoretical predictions [142,143] in which increase in Youngs' modulus occurred nonlinearly with increase in short fiber amount in polymer composites.

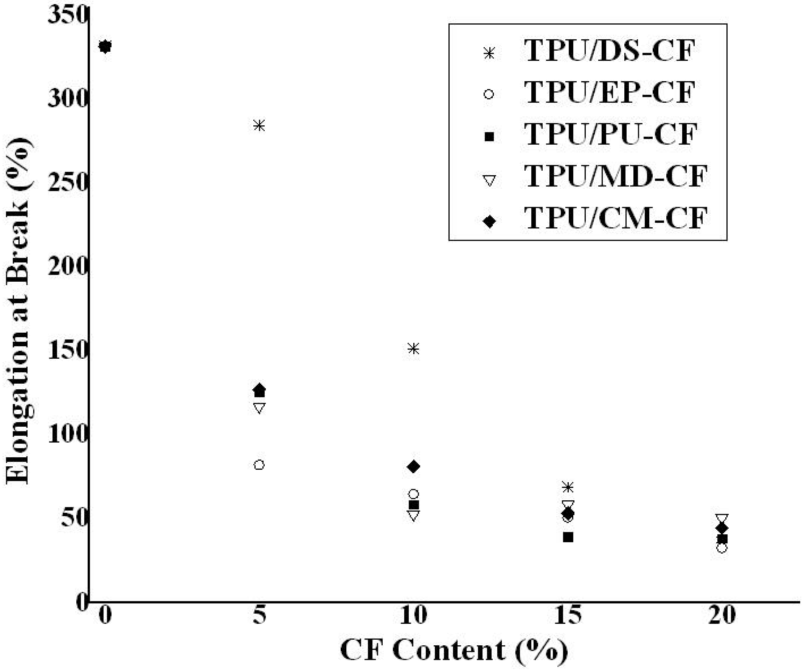


Figure 4.31 Elongation at break results of TPU/CF composites.

It can be seen from Figure 4.31 that both sized and desized CF additions to TPU cause remarkable decrease in percent elongation of composites. Reduction is more significant for MD-CF and CM-CF loaded composites as compared to those of DS-CF.

4.2.6.2 Hardness Test

Shore A hardness values of TPU and TPU/CF composites are listed in Table 4.12. It can be clearly seen from these values that hardness of TPU increases with both desized and modified CF additions. Among these modifications, PU sized CF give the highest value. Shore hardness values are improved with increase in CF concentration for all cases. Hardness values of MD-CF and CM-CF loaded composites are found as almost identical. EP-CF containing composite exhibits slightly lower hardness values than composites loaded CFs that applied other modications.

Table 4.12 Shore A hardness of TPU/CF composites.

CF Content (%)	TPU/ DS-CF	TPU/ EP-CF	TPU/ PU-CF	TPU/ MD-CF	TPU/ CM-CF
0	84.8±0.2	84.8±0.2	84.8±0.2	84.8±0.2	84.8±0.2
5	86.7±0.1	90.2±0.1	92.7±0.1	91.1±0.1	91.8±0.1
10	88.8±0.2	91.4±0.2	93.1±0.1	92.3±0.1	92.9±0.1
15	89.6±0.2	92.9±0.1	94.0±0.2	93.9±0.1	93.5±0.2
20	90.0±0.1	93.3±0.1	95.6±0.2	94.6±0.2	94.0±0.1

4.2.6.3 DMA

The storage modulus versus temperature graphs of TPU and 20 wt % CF containing composites are shown in Figure 4.32. It can be seen from these curves that storage modulus of all the samples exhibits the sharp reduction around -40 ^{0}C which corresponds to glass transition temperature of TPU. Storage modulus of MD-CF and CM-CF containing composites are seen as almost identical and they give higher storage modulus which also mean higher stiffness than that of TPU/DS-CF and pristine TPU. The enhancement of stiffness and storage modulus is related with the stress transfer at the interface between fibers and the matrix [144-146]. The highest and lowest storage modulus values are observed for PU-CF and EP-CF loaded composites, respectively. This may due to better compatibility of PU-CF with TPU matrix with respect to other CF samples.

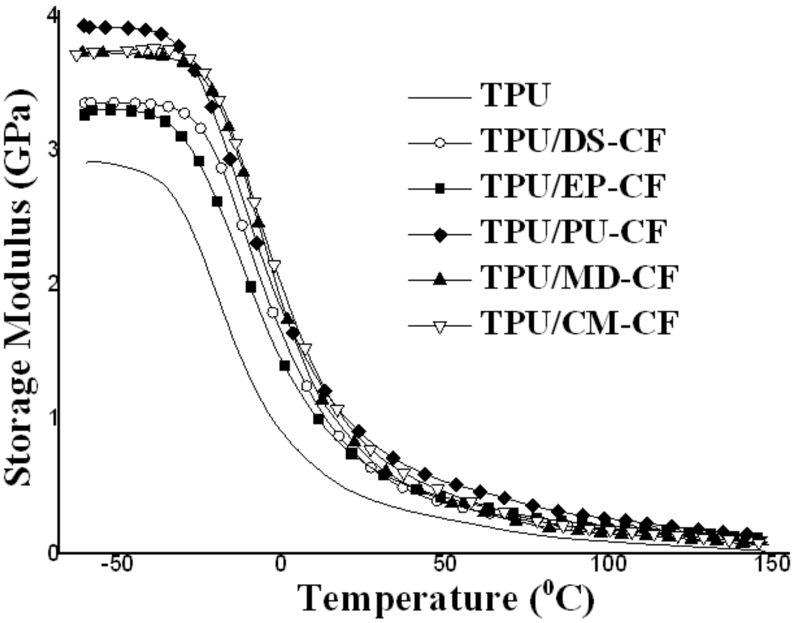


Figure 4.32 Storage modulus-temperature curves of TPU and TPU/CF composites.

Damping properties of composites are analyzed with their tan δ versus temperature curves which are shown in Figure 4.33. The peak of tan δ curve of TPU shifts to higher temperatures by the addition of both desized and sized CFs. This means that T_g of TPU increases by addition of CF. Isocyanate and cured isocyanate treatments cause significant increase on tan δ values of composites with respect to that of TPU/DS-CF and TPU. This observation may be arising from the hinderance of TPU chain motions due to improvement of interfacial interactions. The highest tan δ values are observed for MD-CF and CM-CF loaded composites, respectively. The peak value of tan δ curve of TPU is remained unchanged after EP-CF addition to TPU.

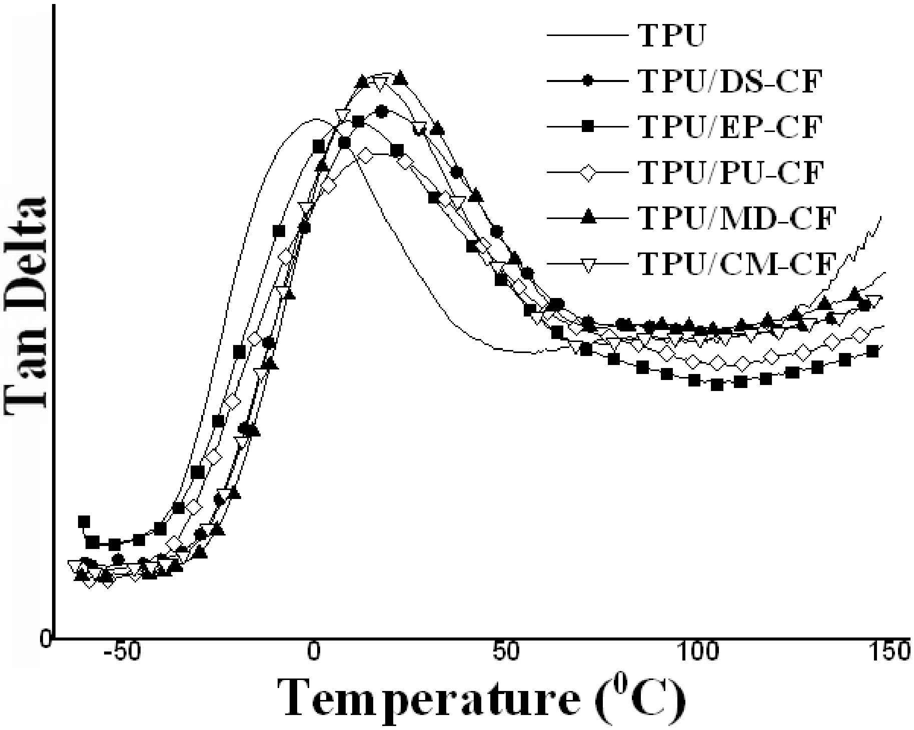


Figure 4.33 Tan δ-temperature curves of TPU and TPU/CF composites.

4.2.6.4 MFI Test

MFI values of commercially sized and isocyanate sized containing composites are given in Figures 4.34 and 4.35, respectively. MFI values of DS-CF containing composites are lower than that of neat TPU and they exhibit decreasing trend with increase in concentration by the exception of 10 wt% concentration. The unmodified fibers tend to form bundles due to poor adhesion to matrix. The formation of bundles causes increase in melt viscosity in contrary reduction in MFI values because of fiber-to-fiber separation creates a complicated flow in matrix [147,148]. On the other hand, MFI values of modified CF containing composites are slightly lower than neat TPU at the lowest loading level. Further additions of MD-CF and CM-CF cause slight increase in MFI. It is seen that there is a correlation between the adhesion and MFI values. MFI values of sized CF containing composites are slightly higher as compared with TPU/DS-CF for all concentrations. As an overall investigation, it can be said that incorporations of both desized and sized CFs give no remarkable change in MFI value of TPU at process temperature.

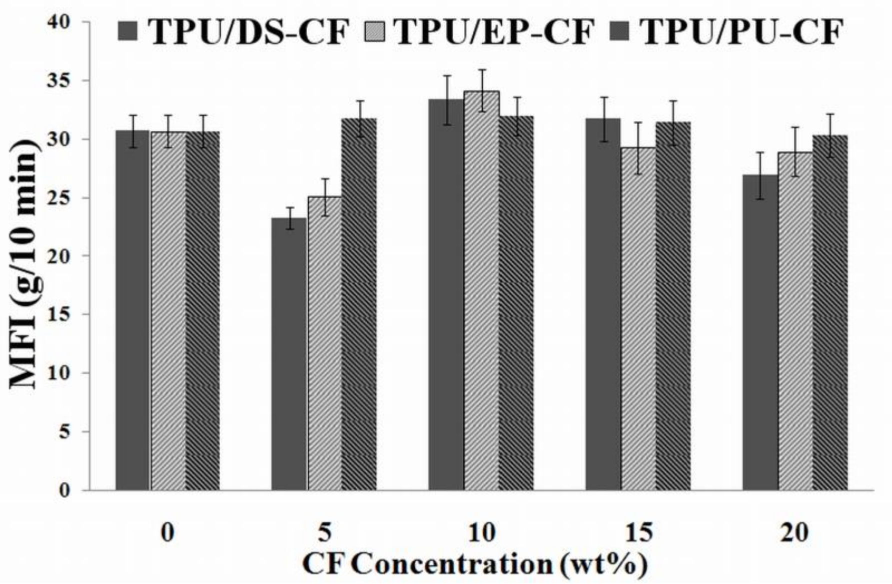


Figure 4.34 MFI values of commercially sized CF reinforced composites.

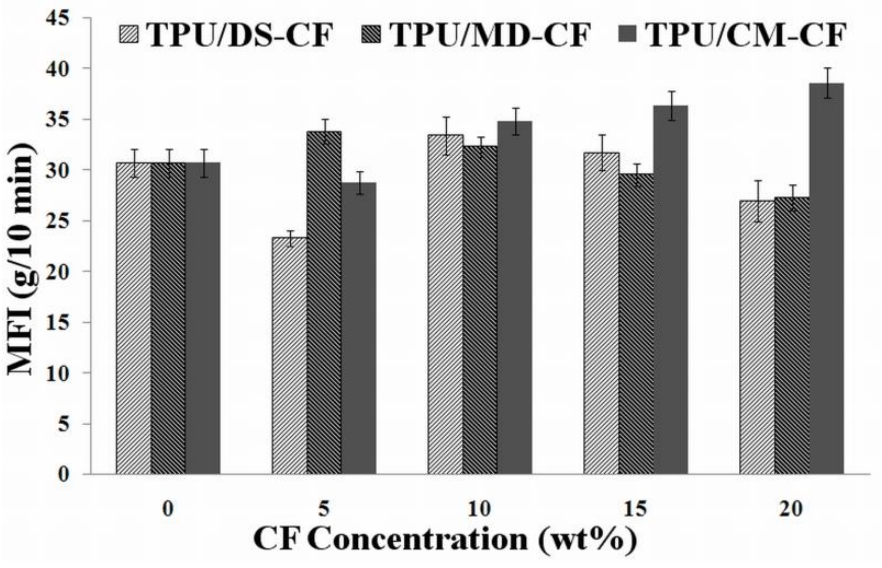


Figure 4.35 MFI values of isocyanate sized CF reinforced composites.

4.2.6.5 SEM Analysis

Representative SEM micrographs of fracture surfaces of selected TPU/CF composites are shown in Figure 4.36. Observations from the SEM micrographs indicate that modified CFs exhibit more homogeneous dispersion with respect to desized CF in their TPU composites. It is clearly observed from micrographs of TPU/DS-CF composites that fibers are tend to form bundles and debonding takes place between CF and TPU phases. On the other hand, modified surfaces of CF are covered by TPU matrix due to improved interfacial adhesion. Bundle and debonding formations are decreased for sized CF loaded composites. These findings are in accordance with the results explained previously and they provide qualitative evidence for the mechanical properties of composites.

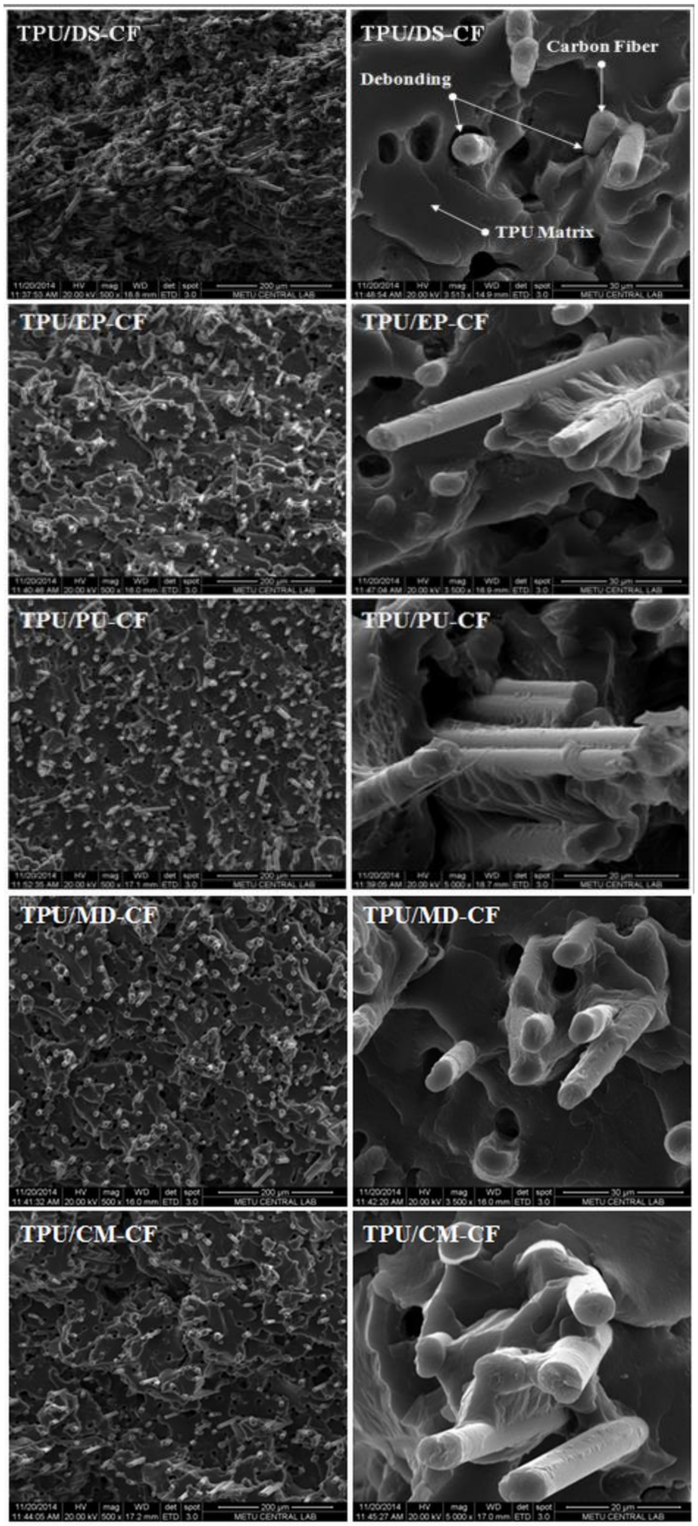


Figure 4.36 SEM micrographs of TPU/CF composites.

CHAPTER 5

CONCLUSIONS

In this thesis, influences of several surface modifications of different kinds of fillers to mechanical and physical properties of TPU based composites are investigated. Most of these modifications result in improvement of mechanical and physical properties of composites as compared to their untreated ones.

5.1 Effect of Surface Treatments on Mechanical, Physical and Water Uptake Properties of TPU/RS Green Composites

The five different surface modifications of RS on the mechanical, flow and water uptake properties of TPU based green composites are investigated. Hot water, alkaline and silane treatments of RS improve the tensile strength and Youngs' modulus of composites containing pure RS. Si-RS containing composite has the highest tensile strength and elastic modulus due to better dispersion and strong interfacial interactions between fiber surface and TPU matrix. The inclusions of BP-RS and PM-RS reduce the mechanical properties with respect to composite containing Na-RS. It is thought that the reduction in mechanical properties of composites arises from the loss of the mechanical strength of RS during treatments. All surface treatments decrease the water uptake capacity with respect to unmodified RS filled composite. Silane modified RS containing composite has the lowest water uptake values. This sample gives also the best mechanical properteis among TPU/RS composites investigated.

5.2 Effect of Surface Treatments on Mechanical, Physical and Water Uptake Properties of TPU/FF Green Composites

The effects of four different surface modifications of FF on the mechanical, flow and water uptake properties of TPU based green composites are investigated. All surface modifications enhance the tensile strength of composites with respect to composite containing untreated FF. Si-FF containing composite gives the highest tensile strength and storage modulus owing to better dispersion and stronger interfacial interactions between fiber surface and TPU matrix. Surface treatments cause fibrillation along the elementary fibers and bundle formation decreases the melt flow index of composites due to fiber-fiber adhesion rather than fiber-matrix adhesion. All surface treatments reduce the water uptake capacity with respect to TPU/FF composite. The lowest water uptake behavior is observed for Si-FF containing composite due to hydrophobic nature of silane-treated surface.

5.3 Comparations of RS and FF as Reinforcers for TPU Green Composites

In the first part of this study, green polymer composites are prepared by incorporating rice straw and flax fiber both as pure and surface modified. Observation of reductions of tensile strength values by inclusion of unmodified fillers into TPU are the common results for RS and FF. Surface modified FF containing composites exhibit slightly better mechanical properties than that of RS filled composites. This may be arising from the higher aspect raito of FF compared to RS. In the case of surface modifications, silanization gives the highest results for both of these fillers and silane modification can be considered to be most suitable among applied treatments for RS and FF reinforced TPU green composite applications.

5.4 Effect of Surface Modifications on Mechanical and Physical Properties of TPU/CNT Composites

Surface oxidation and silanization of CNT on the mechanical, melt flow properties and morphologies of TPU composites are investigated. Surface modifications of CNT improve the mechanical properties as a result of well dispersion. The best tensile strength values are observed for the lowest concentration of modified CNT filled composites. MFI values of modified CNT containing composites are found as much higher for all concentrations than that of neat CNT which attribute to better dispersion of surface modified CNT in TPU matrix. SEM analysis shows that bundle formations of agglomerates gradually decrease after surface modifications. Surface oxidation and silanization cause better dispersion due to improved interactions between CNT and TPU matrix. These interfacial interactions result in enhancements in mechanical properties of TPU/CNT nano-composites.

5.5 Effect of Surface Modifications on Mechanical and Physical Properties of TPU/C_{60} Composites

Surface oxidation and silanization of fullerene on the mechanical, flow properties and morphologies of TPU composites are investigated. Surface modifications of fullerene increase the tensile strength and percent elongation of composites with respect to TPU as a result of dispersion enhancements. Addition of functionalized fullerenes into TPU leads to almost two-fold increase in tensile strength, percent elongation and Youngs' modulus values compared to pristine fullerene. The highest results are obtained in nitric acid and silane treated C_{60} containing composites at the lowest concentration (0.5 %). Surface functionalized fullerenes exhibit higher MFI values because of their better dispersion in TPU matrix. These interfacial interactions result in enhancements in mechanical properties of TPU/fullerene composites.

5.6 Effect of Surface Modifications on Mechanical and Physical Properties of TPU/CF Composites

Short carbon fiber (CF) is used as commercially sized, desized and isocyanate sized in the study. Tensile strength and Youngs' modulus of the composites improves with incorporations of both sized and desized CF into TPU matrix. In the contrary, percent elongation values drop down with CF loadings in TPU. It is revealed from DMA results that, storage modulus of composites increases with the addition of surface modified CFs due to improvement of interfacial interactions. DMA results also show that glass transition temperature of the TPU shifts to higher temperatures with inclusion of both desized and sized CFs into TPU matrix. Higher MFI values are observed for isocyanate modified CF filled composites with respect to neat TPU. Formation of bundles and debonding between desized carbon fibers and TPU are observed from SEM micrographs. Debonding disappears for sized CF containing composites and fibers disperse in the matrix more homogeneously after surface modifications.

5.7 Comparations of Carbonaceous Reinforcers for TPU Composites

In the second part of study, carbonaceous fillers containing TPU composites are prepared by incorporating carbon nanotube, fullerene and carbon fiber as pristine and modified forms. CNT and C_{60} additions cause significant increase in tensile strength, percent alongation and Youngs' modulus values where CF additions result also increase in strength and modulus but sharp reduction is observed in percent elongation. Tensile values exhibit different trend with concentration of these fillers. The highest tensile strength and percent elongation values are observed at the lowest concentration (0.5 wt %) for CNT and C_{60} and these values decrease with increasing CNT and C_{60} content. This result is not suprising because of well-known agglomeration tendency of nanofillers as their higher loadings. On the other hand, CF reinforced composites exhibit increasing trend with increase in CF content. The greatest strength value is observed at the highest loading level (20 wt %) for TPU/CF composites. Surface modifications of CNT and C_{60} give higher MFI values than pristine ones. As a difference; MFI decreases as unmodified CNT content increases where pristine C_{60} addition result in increase in MFI values. Remarkable differences are observed in MFI values of TPU/CNT and TPU/C_{60} composites among their concentrations and their surface functionality. In the case of TPU/CF composites, no significant differences are obtained for MFI values. This means that reinforcement with CF results in better processability than that of CNT and C_{60} for their TPU composites.

5.8 Overall Evaluation of Surface Modifications on the Mechanical and Physical Properties of TPU Composites

In this study, two kinds of composites are prepared using two different grades of polyurethane elastomer. Rice straw and flax fiber filled cerenol-based TPU green composites exhibit lower mechanical properties as compared with carbon nanotube, fullerene and short carbon fiber reinforced polyester-based TPU. Carbonaceous fillers are stronger than natural fillers that may be the reasonable explanation for that result. Surface modifications mostly cause enhancements in mechanical characteristics of composites as well as improvements in their physical properties since the interfacial interactions between inorganic filler and polymeric matrix are enhanced. It is concluded from water absorption test results that, silane treatment of RS and FF open ways to several outdoor applications for their TPU composites besides having good mechanical properties. Dispersing problem of nano-fillers is overcomed after using proper surface treatments. Melt blending method has been rarely used for this type fillers in literature. Incorporating surface modified CNT and C_{60} into TPU give good mechanical results. Their additions result in two-fold increase in tensile strength and percentage strain at the same time. Therefore, it might be possible to obtain required materials as the production of TPU/CNT and TPU/C_{60} nano-composites would be taken place in large-scale. Surface modifications of chopped carbon fiber also improve mechanical properties of their composites. Although isocyanate treated CF do not reach to level that commercially sized CFs have, it can be said that isocyanate treatment can be an alternative sizing system for CF. CF additions even at high loading levels cause no remarkable change in MFI value of unfilled TPU which means that short CF is a suitable reinforcer for TPU along its processing window. The basic conclusion of this work is that proper surface treatments of fillers extended up the mechanical and physical properties of composites to required levels thank to enhance interfacial interactions between filler and polymer surfaces.

REFERENCES

[1] Akovali G. ‘Handbook of composite fabrication’ Rapra Technology, Shawbury, UK, 2001.

[2] Xanthos M. ‘Functional fillers for plastics’ Wiley VCH, Weinheim, 2005.

[3] Sabu T., Kuruvilla J., Malhotra S.K., Koichi G., Sreekala M. ‘Polymer composites’ Wiley VCH, Weinheim, 2012.

[4] Mazumdar S.K. ‘Composites manufacturing materials, product, and process engineering’ CRC Press LLC, Boca Raton, 2002.

[5] Pukanszky B. ‘Interfaces and interphases in multicomponent materials: past, present, future’ European Polymer Journal, 41, 645–662, 2005.

[6] Mohanty A.K., Misra M., Drzal L.T. ‘Natural fibers, biopolymers and biocomposites’ Taylor&Francis, Boca Raton, 2005.

[7] Fuqua M.A., Hou S., Ulven C.A. ‘Natural fiber reinforced composites’ Polymer Reviews, 52(3-4): 259, 2012.

[8] Faruk O., Bledzki A.K., Fink H.-P., Sain M. ‘Progress report on natural fiber reinforced composites’ Macromolecular Materials and Engineering, 299: 9–26, 2014.

[9] Mohanty A.K., Misra M., Drzal L.T. ‘Sustainable bio-composites from renewable resources opportunities and challenges in the green materials world’ Journal of Polymers and the Environment, 10(1-2): 19-26, 2002.

[10] El-Saied H., Basta A.H., Hassanen M.E., Korte H., Helal A. ‘Behaviour of rice-byproducts and optimizing the conditions for production of high performance natural fiber polymer composites’ Journal of Polymers and the Environment, 20(3): 838-847, 2012.

[11] Buzarovska A., Bogoeva-Gaceva G., Grozdanov A., Avella M., Gentile G., Errico M. ‘Potential use of rice straw as filler in eco-composite materials’ Australian Journal of Crop Science, 1(2): 37-42, 2008.

[12] Habibi Y., El-Zawawy W.K., Ibrahim M.M., Dufresne A. 'Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibers from Egyptian agro-industrial residues' Composites Science and Technology, 68, 1877, 2008.

[13] Yao F., Wu Q., Lei Y., Xu Y. 'Rice straw fiber-reinforced high-density polyethylene composite: Effect of fiber type and loading' Industrial Crops and Products, 28, 63, 2008.

[14] Chen G.H., Wang D.D. 'Mechanical properties of rice straw particle/HDPE composites' Applied Mechanics and Materials, 457-458, 227, 2014.

[15] Abdel-Hakim A.A., Sabah I.A.-S., Metwally M.S., El Begawy S., Elshafic E.S. 'Mechanical properties and morphology studies of nanocomposites based on RSF/Nanoclay modified/HDPE nanocomposites' Life Science Journal, 9, 134, 2012.

[16] Louis N.S.M., Thomas S. 'Effect of rice husk ash on mechanical properties of low density polyethylene' Journal of Scientific & Industrial Research, 72, 441, 2013.

[17] Rahman W.A.W.A., Adenan N., Ali R.R., Sulaiman H. 'Effect of silane crosslinker on the thermal properties of rice straw/HDPE biocomposite' Journal of Applied Science, 9, 3041, 2009.

[18] Ming-Zhu P., Chang-Tong M., Xu-Bing Z., Yun-Lei P. 'Effects of rice straw fiber morphology and content on the mechanical and thermal properties of rice straw fiber-high density polyethylene composites' Journal of Applied Polymer Science, 121, 2900, 2011.

[19] Ogah A.O., Afiukwa J.N. 'Characterization and comparison of mechanical behavior of agro fiber-filled high-density polyethylene bio-composites' Journal of Reinforced Plastics and Composites, 33, 37, 2014.

[20] Hassan M.M., Karim A., Shabram T., Bhuiyan A.H., Khan M.A. 'Effect of gamma radiation on the mechanical properties of urea-treated rice straw polypropylene composites' Polymer-Plastics Technology and Engineering, 51, 977, 2012.

[21] Bassyouni M., Taha I., Abdel-Hamid S.M.S., Steuernagel L. 'Physico-mechanical properties of chemically treated polypropylene rice straw bio-composites' Journal of Reinforced Plastics and Composites, 31, 303, 2012.

[22] Chen M., Ma Y., Xu Y., Chen X., Zhang X., Lu C. 'Isolation and characterization of cellulose fibers from rice straw and its application in

modified polypropylene composites' Polymer-Plastics Technology and Engineering, 52, 1566, 2013.

[23] Hassan M.M., Mueller M., Tartakowska D.J., Wagner M.H. 'Mechanical performance of hybrid rice straw/sea weed polypropylene composites' Journal of Applied Polymer Science, 120, 1843, 2011.

[24] Ashori A. 'Effects of nanoparticles on the mechanical properties of rice straw/polypropylene composites' Journal of Composite Materials, 47, 149, 2012.

[25] Kalagar M., Khademieslam H., Bazyar B., Hejazi S. 'Morphology and mechanical properties of alkali-treated rice straw flour-polypropylene composites' Bioresources, 6, 4238, 2011.

[26] Kamel S. 'Preparation and properties of composites made from rice straw and poly(vinyl chloride) (PVC)' Polymers for Advanced Technology, 15, 612, 2004.

[27] Petwattana N., Covavisaruch S. 'Effects of rice hull particle size and content on the mechanical properties and visual appearance of wood plastic composites prepared from poly(vinyl chloride)' Journal of Bionic Engineering, 10, 110, 2013.

[28] Xu Y., Wu Q., Lei Y., Yao F., Zhang Q. 'Natural fiber reinforced poly(vinyl chloride) composites: Effect of fiber type and impact modifier' Journal of Polymers and the Environment, 16, 250, 2008.

[29] Zhao Y., Qui J., Feng H., Zhing M., Lei L., Wu X. ‘Improvement of tensile and thermal properties of poly(lactic acid) composites with admicellar-treated rice straw fiber’ Chemical Engineering Journal, 173, 659, 2011.

[30] Wu C., Liao H., Jhang J., Yeh J., Huang C., Wang S. ‘Thermal properties and characterization of surface-treated RSF-reinforced polylactide composites’ Polymer Bulletin 70, 3221, 2013.

[31] Liao Z., Sang G., Shi F., Yin Z., Yang Y., Niu Z., Tang G. 'Preparation and characterization of PLA/Rice straw fiber composite' Applied Mechanincs and Materials, 71, 1154, 2011.

[32] Ismail M.R., Yassen A.M., Afify M.S. 'Mechanical properties of rice straw fiber-reinforced polymer composites' Fibers and Polymers, 12, 648, 2011.

[33] Wu C.S., Liao H.T. 'Polycaprolactone-based green renewable ecocomposites made from rice straw fiber: characterization and assessment of mechanical and thermal properties' Industrial & Engineering Chemistry Research, 51, 3329, 2012.

[34] Zhao Y., Qiu J., Feng H., Zhang M. 'The interfacial modification of rice straw fiber reinforced poly(butylene succinate) composites: Effect of aminosilane with different alkoxy groups' Journal of Applied Polymer Science, 125, 3211, 2012.

[35] Cooper P.A., Balatinecz J.J., Flannery S.J. ‘Agricultural waste materials for composites: a Canadian reality’ Centre for Management Technology Global Panel Based Conference, Kuala Lumpur, October, 1999.

[36] Sal’nikov V.V., Ageeva M.V., Yumashev V.N., Lozovaya V.V. 'The ultrastructure of bast fibers' Russian Plant Physiology, 40, 416, 1993.

[37] Faruk O., Bledzki A.K., Fink H.P., Sain M. ‘Biocomposites reinforced with natural fibers: 2000–2010’ Progress in Polymer Science, 37(11), 1552–1596, 2012.

[38] Yan, L., Chouw N., Jayaraman K. ‘Flax fibre and its composites – A review’ Composites Part B: Engineering, 56, 296–317, 2014.

[39] Li X., Panigrahi S., Tabil L.G. 'A study on flax fiber-reinforced polyethylene biocomposites' Applied Engineering in Agriculture, 25, 525, 2009.

[40] Wang B., Panigrahi S., Tabil L., Crerar W. 'Pre-treatment of flax fibers for use in rotationally molded biocomposites' Journal of Reinforced Plastics Composites, 26, 447, 2007.

[41] Arbelaiz A., Cantero G., Fernandez B., Mondragon I., Ganan P., Kenny J.M. 'Flax fiber surface modifications: effects on fiber physico mechanical and flax/polypropylene interface properties' Polymer Composites, 26, 324, 2005.

[42] Cantero G., Arbelaiz A., Llano-Ponte R., Mondragon I. 'Effects of fibre treatment on wettability and mechanical behavior of flax/polypropylene composites' Composite Science and Technology, 63, 1247, 2003.

[43] Soleimani M., Tabil L., Panigrahi S., Opoku A. 'The effect of fiber pretreatment and compatibilizer on mechanical and physical properties of flax fiber-polypropylene composites' Journal of Polymers and the Environment, 16, 74, 2008.

[44] Aydin M., Tozlu H., Kemaloglu S., Aytac A., Ozkoc G. 'Effects of alkali treatment on the properties of short flax fiber–poly (lactic acid) eco-composites' Journal of Polymers and the Environment, 19, 11, 2011

[45] Wong S., Shanks R., Hodzic A. 'Interfacial improvements in poly (3-hydroxybutyrate)-flax fibre composites with hydrogen bonding additives' Composite Science and Technology, 64, 1321, 2004.

[46] Baiardo M., Zini E., Scandola M. 'Flax fiber-polyester composites' Composites Part A: Applied Science, 35, 703, 2004.

[47] Cristaldi G., Latteri A., Recca G., Cicala G. In: Dubrovski Polona Dobnik, editor 'Composites based on natural fibre fabrics, Woven Fabric Engineering' InTech, 317–342, 2010.

[48] Kilbride B.E., Coleman J.N., Fraysse J., Fournet P., Cadek M., Drury A., Hutzler S., Roth S., Blau W.J. ‘Experimental observation of scaling laws for alternating current and direct current conductivity in polymer-carbon nanotube composite thin films’ Journal of Applied Physics, 92, 4024-4030, 2002.

[49] Burghard M, Balasubramanian K. ‘Chemically functionalized carbon nanotubes’ Small, 1 (2), 180-192, 2005.

[50] Ajayan P.M., Stephan O., Colliex C., Traut D. ‘Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite’ Science, 265, 1212-1214, 1994.

[51] Bokobza L. ‘Multiwall carbon nanotube elastomeric composites: A review’ Polymer, 48, 4907-4920, 2007.

[52] Coleman J.N., Khan U., Blau W.J., Gun'ko Y.K. 'Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites' Carbon, 44, 1624-1652, 2006.

[53] Ma P., Siddiqui N.A., Marom G., Kim J. 'Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review' Composites Part A: Applied Science, 41, 1345–1367, 2010.

[54] Moniruzzaman M., Winey K.I. 'Polymer nanocomposites containing carbon nanotubes' Macromolecules, 39, 5194–5205, 2006.

[55] Abdullah S.A., Iqbal A., Frormann L. 'Melt mixing of carbon fibers and carbon nanotubes incorporated polyurethanes' Journal of Applied Polymer Science, 110, 196-202, 2008.

[56] Benedito A., Buezas I., Gimenez E., Galindo B., Ortega A. 'Dispersion and characterization of thermoplastic polyurethane/multiwalled carbon nanotubes by melt mixing' Journal of Applied Polymer Science, 122, 3745-3750, 2011.

[57] Fernandez M., Landa M., Munoz M.E., Santamaria A. 'Tackiness of an electrically conducting polyurethane–nanotube nanocomposite' Journal of Adhesion and Adhesives, 30, 609-614, 2010.

[58] Zhang R., Dowden A., Deng H., Baxendale M., Peijs T. 'Conductive network formation in the melt of carbon nanotube/thermoplastic polyurethane composite' Composites Science and Technology, 69, 1499-1504, 2009.

[59] Pötschke P., Häußler L., Pegel S., Steinberger R., Scholz G. 'Thermoplastic polyurethane filled with carbon nanotubes for electrical dissipative and

conductive applications’ Kautschuk und Gummi Kunststoffe, 60, 432-437, 2007.

[60] Ma P., Siddiqui N.A., Marom G., Kim J. ‘Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review’ Composites Part A: Applied Science, 41, 1345–1367, 2010.

[61] Raja M., Shanmugharaj A.M., Ryu S.H. ‘Influence of surface functionalized carbon nanotubes on the properties of polyurethane nanocomposites’ Soft Materials, 6, 65-74, 2008.

[62] Barick A.K., Tripathy D.K. ‘Preparation, characterization, and properties of acid functionalized multi-walled carbon nanotube reinforced thermoplastic polyurethane nanocomposites’ Material Science and Engineering B, 176, 1435-1447, 2011.

[63] Brown R. ‘Handbook of polymer testing-Physical methods’ Rapra Technology, Shawbury, 1999.

[64] Langa F., François J. ‘Fullerenes: Principles and applications’ 2nd ed. Cambridge, RCS Publishing, 20, 2012.

[65] Nierengarten J-F. et al. ‘Fullerene-containing macromolecules for materials science applications’ Carbon, 42, 1077–1083, 2004.

[66] Wang C., Guob Z-X., Fua S., Wub W., Zhu D. ‘Polymers containing fullerene or carbon nanotube structures’ Progress in Polymer Science, 29, 1079–1141, 2004.

[67] Burchell T.D. ‘Carbon materials for advanced technologies’ Pergamon, Amsterdam, 1999.

[68] Badamshina E.R., Gafurova E.R. ‘Characteristics of fullerene C_{60}-doped polymers’ Polymer Science Series B, 50, 215-225, 2008.

[69] Liu H., Song P., Fang Z., Shen L., Peng M. ‘Thermal degradation and flammability properties of HDPE/EVA/C_{60} composites’ Thermochemica Acta, 506, 98-101, 2010.

[70] Zhao L., Guo Z., Cao Z., Zhang T., Fang Z., Peng M. ‘Thermal and thermo-oxidative degradation of high density polyethylene/fullerene composites’ Polymer Degradation Stability, 98, 1953-1962, 2013.

[71] Wan D., Wang Y., Wen X., Qiu J., Jiang Z., Tan H., Tang T. ‘The rheological, thermostable, and mechanical properties of polypropylene/fullerene C_{60} composites with improved interfacial interaction’ Polymer Engineering and Science, 52, 1457-1463, 2012.

[72] Fang Z., Song P., Tong L., Guo Z. ‘Thermal degradation and flame retardancy of polypropylene/C_{60} composites’ Thermochemica Acta, 473, 106-108, 2008.

[73] Gocek I., Keskin R., Ozkoc G., Yilmaz K., Kamac Y. ‘Mechanical and electrical properties of polyamide 66 nanocomposites reinforced with buckminster fullerene C_{60}’ Fiber Society, Fall Meeting, Boston, USA, 2012.

[74] Ouyang J., Goh S.H. ‘Crystallization, morphology, and dynamic mechanical behavior of supramolecular [60] fullerene-containing poly(ethylene-co-acrylic acid)’ Fullerenes Nanotubes Carbon Nanostructures, 10, 183-196, 2002.

[75] Dilsiz N., Erinc N.K., Bayramli E., Akovali G. ‘Surface energy and mechanical properties of plasma-modified carbon fibres’ Carbon, 33, 853–858, 1995.

[76] Muzzy J.D. ‘Thermoplastic-properties. In: Kelly A., Zweben C. editors ‘Comprehensive composite materials’ Amsterdam, Elsevier Science; 2000.

[77] Moon B.-Y., Kang G.-J., Kang B.-S., Kelly J.M. ‘Design and manufacturing of fibre reinforced elastomeric isolator for seismic isolation’ Journal of Materials Processing Technology, 130-131, 145–50, 2002.

[78] Kang G.J., Kang B.S. ‘Dynamic analysis of fiber-reinforced elastomeric isolation structures’ Journal of Mechanical Science Technology, 23, 1132–1141, 2009.

[79] Soutis C. ‘Carbon fibre reinforced plastics in aircraft structures’ Materials Science and Engineering A, 412 (1–2), 171–176, 2005.

[80] Mahieux C.A. ‘Cost effective manufacturing process of thermoplastic matrix composites for the traditional industry: the example of a carbon-fiber reinforced thermoplastic flywheel’ Composite Structures, 52 (3–4), 517–521, 2001.

[81] http://www.reinforcedplastics.com/view/39230/sgl-starts-production-of-thermoplastic-compatible-carbon-fibre/ (Last access: 30.04.2015)

[82] http://www.designnews.com/author.asp?doc_id=273312&dfpPParams=ind_183 (Last access: 30.04.2015)

[83] Bhowmick A.K., Stephens H.L. ‘Handbook of Elastomers’ second ed., Marcel Dekker, New York, 2001.

[84] Chen T.-K., Tien Y.-I., Wei K.-H. ‘Synthesis and characterization of novel segmented polyurethane/clay nanocomposites’ Polymer, 41, 1345–1353, 2000.

[85] Markarian J. ‘Thermoplastic elastomer compounds continue upward trend’ Plastics, Additives and Compounding, 10 (5), 38–40, 42–43, 2008.

[86] Wongtimnoi K., Guiffard B., Van de Moortèle A.B., Seveyrat L., Cavaillé J.Y. ‘Electrostrictive thermoplastic polyurethane-based nanocomposites filled with carboxylfunctionalized multi-walled carbon nanotubes (MWCNT-COOH): Properties and improvement of electromechanical activity’ Composite Science and Technology, 85, 23-28, 2013.

[87] Zhao J-C., Du F-P., Zhou X-P., Cui W., Wang X-M., Zhu H. et al. ‘Thermal conductive and electrical properties of polyurethane/hyperbranched poly(urea-urethane)-grafted multi-walled carbon nanotube composites’ Composites Part B: Engineering, 42, 2111–2116, 2011.

[88] Korener H., Price G., Pearce N.A., Alexander M., Vaia R.A. ‘Remotely actuated polymer nanocomposites stress recovery of carbon nanotube filled thermoplastic elastomers’ Nature, 3, 115–120, 2004.

[89] Sedat G., Guillermo A.J., Sadhan C.J. ‘Carbonaceous fillers for shape memory actuation of polyurethane composites by resistive heating’ Carbon, 47, 981-997, 2009.

[90] Kabir M.M., Wang H., Lau K.T., Cardona F. ‘Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview’ Composites Part B: Engineering, 43, 2883-2892, 2012.

[91] Bledzki A.K., Gassan J. ‘Composites reinforced with cellulose based fibres’ Progress in Polymer Science, 24, 221–274, 1999.

[92] Li X., Tabil L.G., Panigrahi S. ‘Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review’ Journal of Polymer and the Environment, 15, 25, 2007.

[93] Baiardo M., Frisoni G., Scandola M., Licciardelo A. ‘Surface chemical modification of natural cellulose fibers’ Journal of Applied Polymer Science, 83 (1), 38, 2002.

[94] Kaila S., Kaith B.S., Kaur I. ‘Pretreatments of natural fibers and their application as reinforcing material in polymer composites: a review’ Polymer Engineering and Science, 49 (7), 1253, 2009.

[95] Mohanty A.K., Misra M., Drzal L.T. ‘Surface modifications of natural fibers and performance of the resulting biocomposites: an overview’ Composite Interfaces, 8 (5), 313, 2001.

[96] Liff S.M., Kumar N., McKinley G.H. ‘High-performance elastomeric nanocomposites via solvent-exchange processing’ Nature Materials, 6, 76-83, 2007.

[97] Roy N., Sengupta R., Bhowmick A.K. ‘Modifications of carbon for polymer composites and nanocomposites’ Progress in Polymer Science, 37, 781-819, 2012.

[98] Santos C.V., Hernández A.L.M., Castaño V.M. ‘Carbon nanotube-polymer nanocomposites: The role of interfaces’ Composite Interfaces, 11 (8-9), 567-586, 2005.

[99] Giles H.F., Wagner J.R., Mount E.M. ‘Extrusion The Definitive Processing Guide and Handbook’, William Andrew Publishing, New York, 2005.

[100] Strong A.B. ‘Plastics Materials and Processing’, Prentice Hall, New Jersey, 2006.

[101] Kanbur Y., Kucukyavuz Z. ‘Surface modification and characterization of multi-walled carbon nanotube’ Fullerenes Nanotubes and Carbon Nanostructures, 19, 497-504, 2011.

[102] Soylemez S., Kanik F.E., Uzum S.D., Hacioglu S.O., Toppare L. ‘Development of an efficient immobilization matrix based on a conducting polymer and functionalized multiwall carbon nanotubes: synthesis and its application to ethanol biosensors’ Journal of Material Chemistry B, 2, 511-521, 2014.

[103] Datsyuk V., Kalyva M., Papagelis K., Parthenios J., Tasis D., Siokou A., Kallitsis I., Galiotis C. ‘Chemical oxidation of multiwalled carbon nanotubes’ Carbon, 46, 833-840, 2008.

[104] Kanbur Y., Kucukyavuz Z. ‘Synthesis and characterization of surface modified fullerene’ Fullerenes Nanotubes and Carbon Nanostructures, 20(2), 119-126, 2012.

[105] Liu J., Huang C. ‘Biodegradable composites from rice straw and cornstarch adhesives’ Advance Journal of Food Science and Technology, 5(1), 41-45, 2013.

[106] Xiao B., Sun X.F., Sun R. ‘Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw’ Polymer Degradation and Stability, 74, 307, 2001.

[107] Herrera-Franco P.J., Gonzalez A.V. ‘A study of the mechanical properties of short natural-fiber reinforced composites’ Composites Part B: Engineering, 36, 597, 2005.

[108] Skrifvars B., Yrjas P., Kinni J., Siefen P., Hupa M. ‘The fouling behavior of rice husk ash in fluidized-bed combustion. 1. Fuel characteristics’ Energy Fuels, 19, 4, 1503, 2005.

[109] Pilla S., Gong S., O’Neill E., Yang L., Rowell R.M. ‘Polylactide-recycled wood fiber composites’ Journal of Applied Polymer Science, 111, 37, 2009.

[110] Marcovich N.E., Villar M.A. ‘Thermal and mechanical characterization of linear low-density polyethylene/wood flour composites’ Journal of Applied Polymer Science, 90, 2775, 2003.

[111] Petinakis E., Yu L., Edward G., Dean K., Liu H., Scully A.D. ‘Effect of Matrix–Particle Interfacial Adhesion on the mechanical properties of

poly(lactic acid)/wood-flour micro-composites' Journal of Polymers and the Environment, 17, 83. 2009.

[112] Bledzki A.K., Mamun A.A., Volk J. 'Physical, chemical and surface properties of wheat husk, rye husk and soft wood and their polypropylene composites' Composites Part A: Applied Science, 41(4), 480, 2010.

[113] Tayfun U., Dogan M., Bayramli E. 'Effect of surface modification of rice straw on mechanical and flow properties of TPU-based green composites' Polymer Composites, 2014. DOI: 10.1002/pc.23331

[114] Tayfun U., Dogan M., Bayramli E. 'Investigating agricultural waste-reinforced polyurethane elastomer green composites' SPE Plastics Research Online, 2015. DOI: 10.1002/spepro.005729

[115] Shakoor A., Muhammad R., Thomas N.L., Silberschmidt V.V. 'Mechanical and thermal characterisation of poly (l-lactide) composites reinforced with hemp fibres' Journal of Physics: Conference Series, 451, 2013.

[116] Bulut Y., Aksit A. 'A comparative study on chemical treatment of jute fiber: potassium dichromate, potassium permanganate and sodium perborate trihydrate' Cellulose, 20(6), 3155–3164, 2013.

[117] Sreekala M.S., Kumaran M.G., Joseph S., Jacob M., Thomas S. 'Oil palm fibre reinforced phenol formaldehyde composites: Influence of fibre surface modifications on the mechanical performance' Applied Composite Materials, 7 (5-6), 295–329, 2000.

[118] Madera-Santana T.J., Valdez H.S., Richardson M.O.W. ‘Influence of surface treatments on the physicochemical properties of short sisal fibers: Ethylene vinyl acetate composites’ Polymer Engineering and Science, 53 (1): 59–68, 2013.

[119] Titok V., Leontiev V., Yurenkova S., Nikitinskaya T., Barannikova T., Khotyleva L. ‘Infrared spectroscopy of fiber flax’ Journal of Natural Fibers, 7 (1): 61–69, 2010.

[120] Bos H.L., M.J.A.V.D.O., Peters O.C.J.J. ‘Tensile and compressive properties of flax fibres for natural fibre reinforced composites’ Journal of Materials Science, 37 (8) 1683–1692, 2002.

[121] Tayfun U., Dogan M., Bayramli E. ‘Influence of surface modifications of flax fiber on mechanical and flow properties of TPU based eco-composites’ Journal of Natural Fibers, 2016. DOI: 10.1080/15440478.2015.1029191

[122] Biagiotti J., M.A.L., Arroyo M., Kenny J.M. ‘Ternary composites based on PP-EPDM blends reinforced with flax fibers Part II: Mechanical properties/morphology relationship’ Polymer Engineering and Science, 43 (5), 1031–1043, 2003.

[123] Assarar M., Scida D., El Mahi A., Poilâne C., Ayad R. ‘Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: Flax-fibres and glass-fibres’ Materials and Design, 32 (2), 788–795, 2011.

[124] Arbelaiz A., Fernández B., Ramos J.A., Retegi A., Llano-Ponte R., Mondragon I. ‘Mechanical properties of short flax fibre bundle/polypropylene

composites: Influence of matrix/fibre modification, fibre content, water uptake and recycling’ Composites Science and Technology, 65 (10), 1582–1592, 2005.

[125] Wielage B., Lampke T., Utschick H., Soergel F. ‘Processing of natural-fibre reinforced polymers and the resulting dynamic–mechanical properties’ Journal of Materials Processing Technology, 139 (1-3), 140-146, 2003.

[126] Santos C.V., Hernández A.L.M., Castaño V.M. ‘Carbon nanotubes-polymer nanocomposites’ ed. S. Yellampalli, Chapter 13, 251, Intech, Rijeka, 2011.

[127] Scheibe B., Borowiak-Palen E., Kalenczuk R.J. ‘Effect of the silanization processes on the properties of oxidized multiwalled carbon nanotubes’ Acta Physica Polonica A, 116, 150-155, 2009.

[128] Kathi J., Rhee K.Y. ‘Surface modification of multi-walled carbon nanotubes using 3-aminopropyltriethoxysilane’ Journal of Material Science, 43, 33-37, 2008.

[129] Chena L., Pang X.-J., Yu Z.-L. ‘Study on polycarbonate/multi-walled carbon nanotubes composite produced by melt processing’ Materials Science and Engineering A, 457, 287–291, 2007.

[130] Yesil S., Bayram G. 'Effect of carbon nanotube surface treatment on the morphology, electrical, and mechanical properties of the microfiber-reinforced polyethylene/poly(ethylene terephthalate)/carbon nanotube composites' Journal of Applied Polymer Science, 127 (2), 982–991, 2013.

[131] Lee S.H., Kim M.W., Kim S.H., Youn J.R. 'Rheological and electrical properties of polypropylene/MWCNT composites prepared with MWCNT masterbatch chips' European Polymer Journal, 44, 1620-1630, 2008.

[132] Kanbur Y. 'Conductive Polymer Nanocomposites of Polypropylene and Organic Field Effect Transistors with Polyethylene Gate Dielectric' Ph D. Thesis, Polymer Science and Technology, METU, 2011.

[133] Scharff P. et al. 'Structure of C_{60} fullerene in water: spectroscopic data' Carbon, 42, 1203–1206, 2004.

[134] Yuen S.M., Ma C.C.M., Chiang C.L., Chang J.A, Huang S.W., Chen S.C., Chuang C.Y., Yang C.C., Wei M.H. 'Silane-modified MWCNT/PMMA composites-Preparation, electrical resistivity, thermal conductivity and thermal stability' Composites Part A: Applied Science, 38 (12): 2527–2535, 2007.

[135] Avilés F., Cauich-Rodríguez J.V., Rodríguez-González J.A., May-Pat A. 'Oxidation and silanization of MWCNTs for MWCNT/vinyl ester composites' Express Polymer Letters, 5, 766–776, 2011.

[136] Tayfun U., Kanbur Y., Abaci U., Guney H.Y., Bayramli E. 'Mechanical, flow and electrical properties of thermoplastic polyurethane/fullerene composites: Effect of surface modification of fullerene' Composites Part B: Engineering, 80, 101-107, 2015. DOI: 10.1016/j.compositesb.2015.05.013

[137] S.-J. Park, B.-J. Kim. 'Roles of acidic functional groups of carbon fiber surfaces in enhancing interfacial adhesion behavior' Materials Science and Engineering A, 408, 269–273, 2005.

[138] Zawadzki J. ‘IR spectroscopy investigations of acidic character of carbonaceous films oxidized with HNO solution’ Carbon, 19 (1), 19–25, 1991.

[139] Severini F., Formaro L., Pegoraro M., Posca L. ‘Chemical modification of carbon fiber surfaces’ Carbon, 40, 735–741, 2002.

[140] Mangun C.L., Benak K.R., Economy J., Foster K.L. ‘Surface chemistry, pore sizes and adsorption properties of activated carbon fibers and precursors treated with ammonia’ Carbon, 39, 1809–1820, 2001.

[141] Silverstein R., Webster F. ‘Spectrometric identification of organic compounds’ Wiley, New York, 2006.

[142] Liang J.Z. ‘Predictions of Youngs’ modulus of short inorganic fiber reinforced polymer composites’ Composites Part B: Engineering, 43 (4), 1763–1766, 2012.

[143] Fu S.-Y., Lauke B., Mader E., Yue C.-Y., Hu X. ‘Tensile properties of short-glass-fiber and short carbon fiber reinforced polypropylene composites’ Composites Part A: Applied Science, 31, 1117–1125, 2000.

[144] Karsli N.G., Aytac A. ‘Tensile and thermomechanical properties of short carbon fiber reinforced polyamide 6 composites’ Composites Part B: Engineering, 51, 270–275, 2013.

[145] Theberge J., Arkles B., Robinson R. ‘Carbon fiber reinforced thermoplastics’ Industrial and Engineering Chemistry Product Research and Development, 15, 100, 1976.

[146] Bakis C.E. et al. 'Fiber-reinforced polymer composites for construction-state-of-the-art review' Journal of Composites for Construstion, 6, 73-87, 2002.

[147] Bayramli E., Powell R.L. ‘Experimental investigation of the axial impregnation of oriented fiber bundles by capillary forces’ Journal of Colloids and Surfaces, 56, 83-100, 1991.

[148] Ozkoc G. ‘ABS/Polyamide-6 Blends, Their Short Glass Fiber Composites and Organoclay Based Nanocomposites: Processing and Characterization’ Ph D. Thesis, Polymer Science and Technology, METU, 2007.

APPENDIX

A.1 EDX Spectrum of CNT, C_{60} and CF Samples

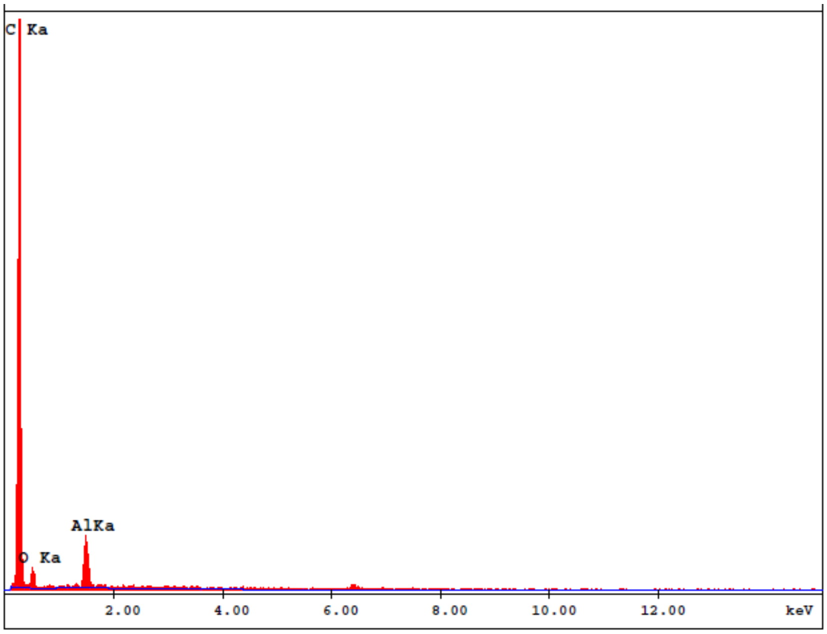


Figure A. 1 EDX Spectra of CNT.

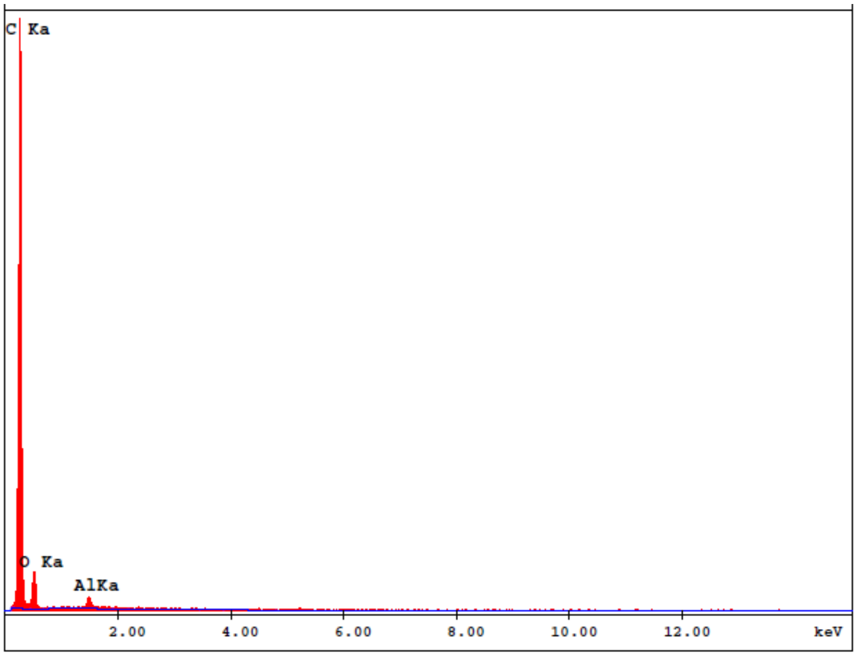


Figure A. 2 EDX Spectra of HN-CNT.

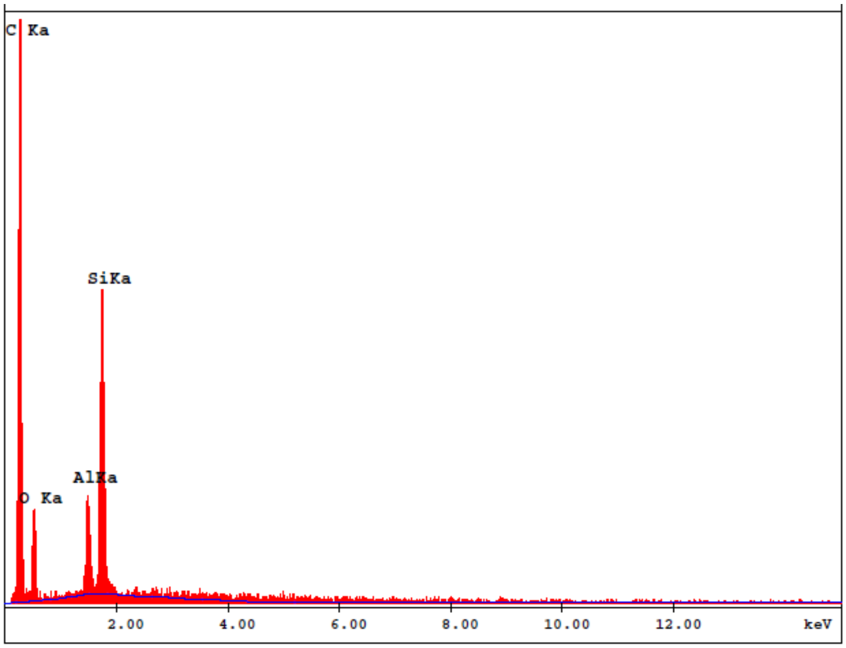


Figure A. 3 EDX Spectra of Si-CNT.

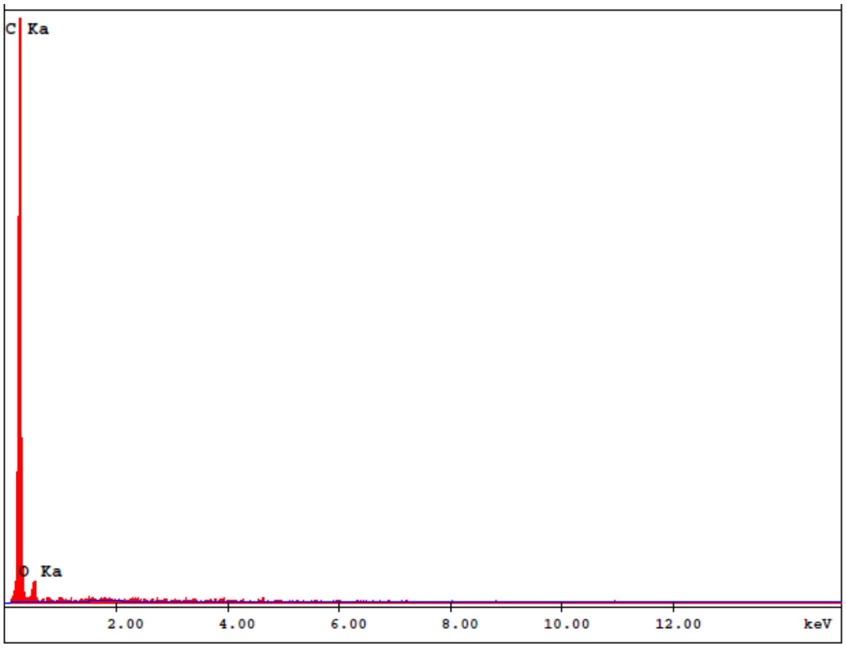


Figure A. 4 EDX Spectra of C_{60}.

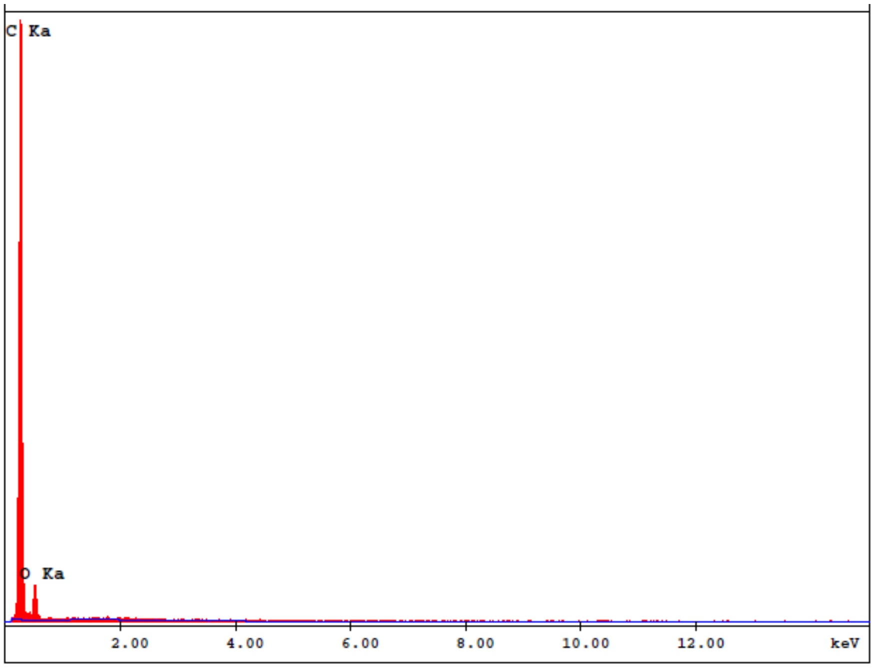


Figure A. 5 EDX Spectra of HN-C_{60}.

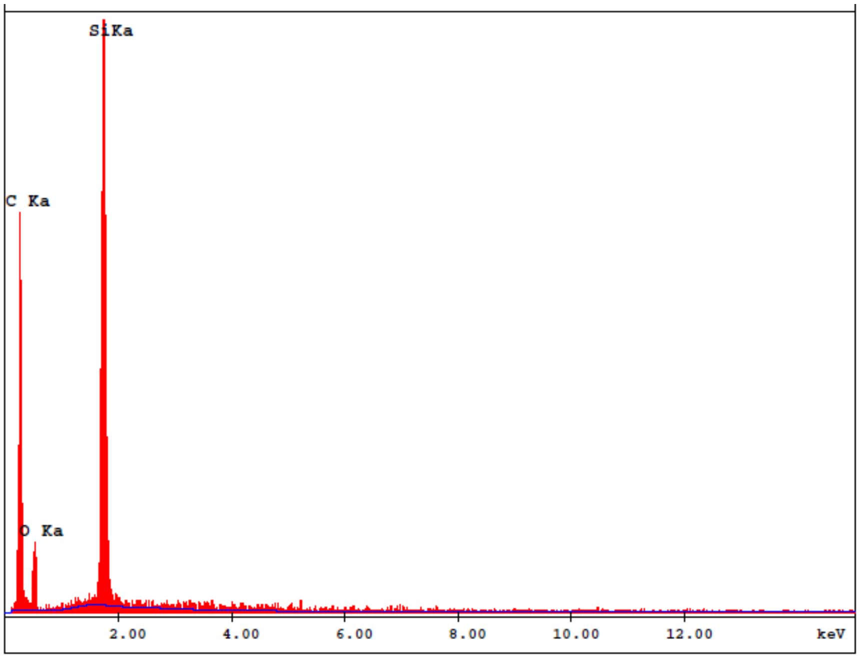


Figure A. 6 EDX Spectra of Si-C_{60}.

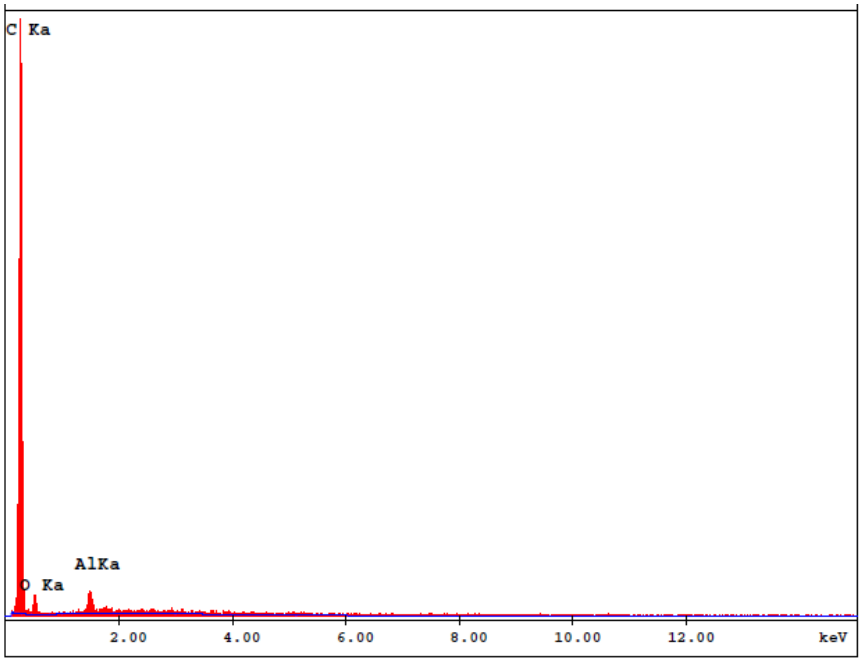


Figure A. 7 EDX Spectra of DS-CF.

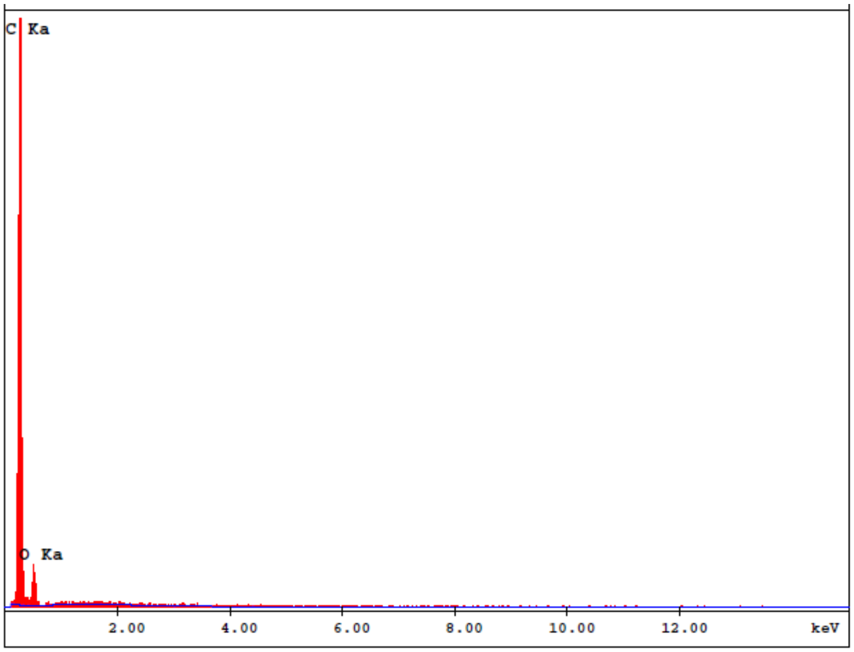


Figure A. 8 EDX Spectra of EP-CF.

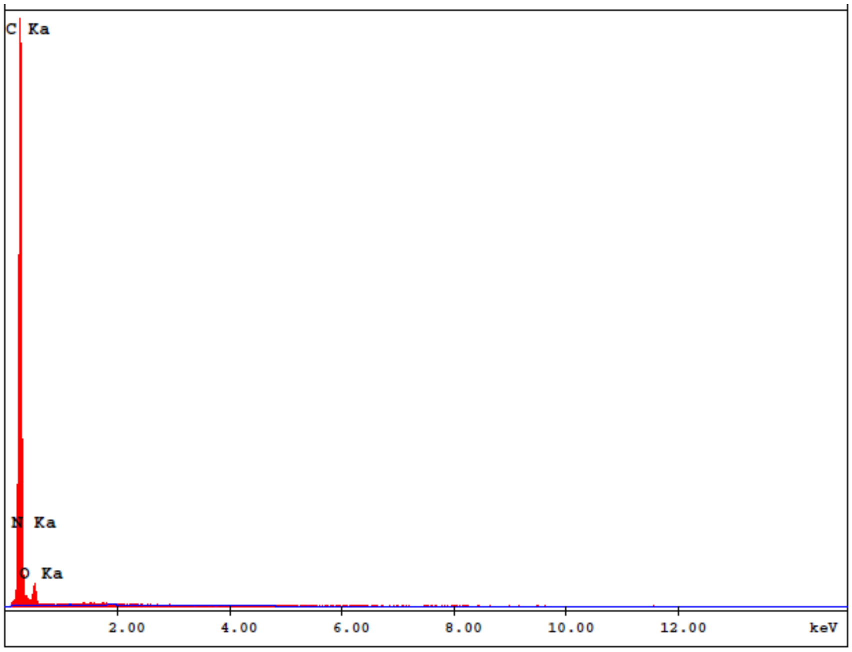


Figure A. 9 EDX Spectra of PU-CF.

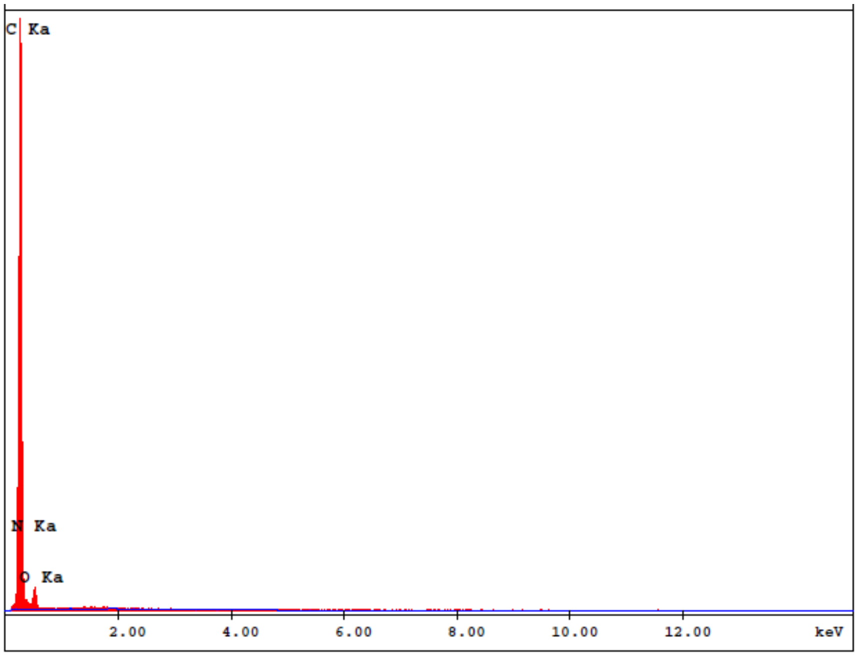


Figure A.10 EDX Spectra of CM-CF.

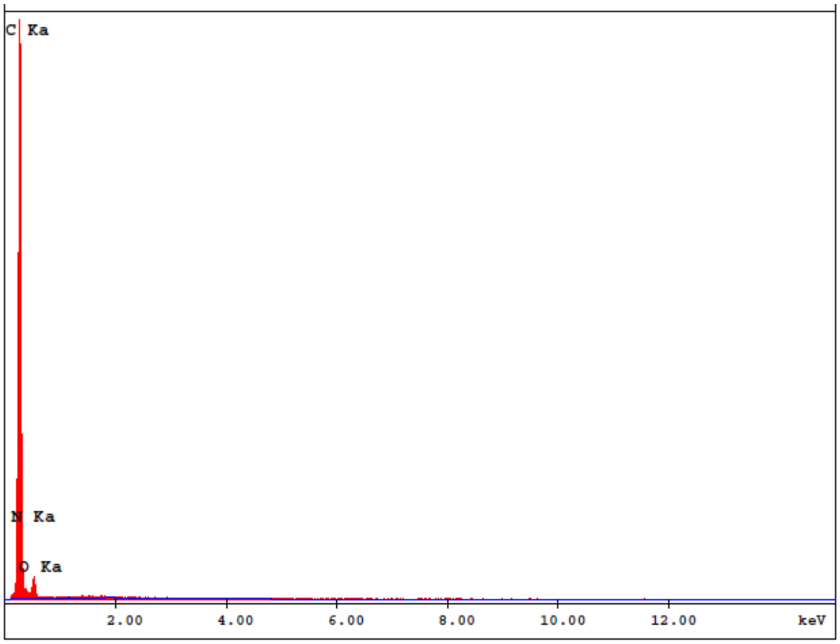


Figure A. 12 EDX Spectra of MD-CF.

A.2 Tensile Test Data of TPU and TPU/CF Composites

Table A.1 Tensile test results of TPU and TPU/CF composites.

SAMPLES	**Tensile Strength** (MPa)	**Elongation at break** (%)	**Youngs' modulus** (MPa)
TPU	24.8±1.7	331.8±4.3	33.4±3.0
TPU/DS-CF 5%	21.0±1.2	284.6±6.7	123.5±4.2
TPU/DS-CF 10%	23.7±2.1	151.5±4.2	124.4±5.2
TPU/DS-CF 15%	27.3±1.5	68.8±5.3	174.4±4.8
TPU/DS-CF 20%	29.4±1.8	36.1±4.4	240.2±7.3
TPU/EP-CF 5%	23.6±1.5	82.1±3.8	133.3±4.9
TPU/EP-CF 10%	33.1±1.9	64.8±2.8	186.1±5.5
TPU/EP-CF 15%	35.9±1.7	50.8±2.3	244.2±5.4
TPU/EP-CF 20%	50.5±2.6	32.7±3.2	317.4±6.8
TPU/PU-CF 5%	24.8±2.2	125.6±5.2	137.4±4.0
TPU/PU-CF 10%	36.0±2.4	58.6±4.7	191.2±4.6
TPU/PU-CF 15%	40.6±2.0	39.6±3.3	254.4±6.1
TPU/PU-CF 20%	51.8±3.2	38.4±2.7	329.3±7.2
TPU/MD-CF 5%	23.7±1.4	117.1±4.6	133.1±4.8
TPU/MD-CF 10%	26.4±2.7	52.9±3.0	196.2±5.6
TPU/MD-CF 15%	34.8±2.5	58.6±3.1	177.6±5.0
TPU/MD-CF 20%	41.6±3.1	50.7±2.8	214.4±6.4
TPU/CM-CF 5%	22.8±1.3	127.2±6.4	112.9±3.8
TPU/CM-CF 10%	25.8±1.8	81.1±5.1	170.1±4.7
TPU/CM-CF 15%	33.1±2.9	53.4±3.6	163.5±5.8
TPU/CM-CF 20%	38.9±2.4	44.4±4.5	248.5±7.6

CIRRICULUM VITAE

PERSONAL INFORMATION:

Name and Surname: Ümit TAYFUN

Date and Place of Birth: 28/02/1980, Ankara (TURKEY)
Sex: Male
Marital Status: Single
Nationality: Republic of Turkey
Correspondence Address
Work Address: Antiflam Kim. Dan. Ar. Ge. Dan. San. Tic. Ltd. Şti.
Üniversiteler Mah. İhsan Doğramacı Cd. Kosgeb
Tekmer Binası No: 219 ODTÜ Teknokent
Ankara / TURKEY

Home Address: Öveçler Mah. Hürriyet Cd. No: 4, Çankaya
Ankara/TURKEY

Phone: +90 542 670 1740 (Mobile)
+90 312 210 13 00-219 (Work)

E-mail: **tayfun.umit@metu.edu.tr, zenziyan@yahoo.com**

EDUCATIONAL BACKGROUND:

Ph.D.: METU Polymer Science and Technology Department, Ankara (3.21/4.00)
Date of Graduation: December, 2015

M.S.: METU Polymer Science and Technology Department, Ankara (3.00/4.00)
Date of Graduation: December, 2006

B.S.: Hacettepe University Department of Chemistry, Ankara (2.46/4.00)
Date of Graduation: August, 2003

High School: Incesu High School, Ankara (3.50/5.00)
Date of Graduation: January, 1997

RELEVANT SKILLS

- Four years of experience of working in three TUBİTAK-Teydeb projects.
- One year of experience of working in a San-Tez project.
- One year of experience of working in a Kosgeb project.
- Working knowledge of
    - Fourier Transform Infrared Radiation (FTIR) Spectroscopy
    - Differential Scanning Calorimetry (DSC)
    - Dynamic Mechanical Analysis (DMA)
    - Thermal Gravimetric Analysis (TGA)
    - Contact Angle Measurements with Optical Microscopy
    - Extruder (micro-compounder)
    - Injection Molding Machine
    - Tensile Testing
    - Shore Hardness Test
    - Melt Flow Index Instrument
    - Limiting Oxygen Index Instrument (LOI)
    - UL-94 Vertical Burning Test
    - Mass Loss Callorimetry Test
    - Crip 5 Test (BS 5852)

WORK EXPERIENCE:

November 2014-present: R&D Specialist at Antiflam Kim. Ar. Ge. Dan. Ltd. Şti. (METU TECHNOPOLIS-ANKARA)

August 2010-May 2012: R&D Specialist of the Building Group at Seranit A.Ş. (BEŞİKTAŞ-İSTANBUL)

April 2008-April 2009: Laboratory Officer of Food Quallity-Control Command at Turkish Army Forces (EĞİRDİR-ISPARTA)

September 2006-March 2008: R&D Specialist at Tarel Teknoloji Geliştirme A.Ş. (METU TECHNOPOLIS-ANKARA)

July 2002-September 2002: Internship at Aselsan A.Ş. (MACUNKÖY-ANKARA)

FOREIGN LANGUAGES:

- English-advanced
- German-beginner

PUBLICATIONS:

- **Tayfun U.**, Dogan M., Bayramli E.; Effect of surface modification of rice straw on mechanical and flow properties of TPU-based green composites, *Polym Compos*, **2014**. DOI: 10.1002/pc.23331
- **Tayfun U.**, Dogan M., Bayramli E.; Investigating agricultural waste-reinforced polyurethane elastomer green composites, *SPE Plast Res Online*, **2015**. DOI: 10.1002/spepro.005729
- **Tayfun U.**, Kanbur Y., Abaci U., Guney H.Y., Bayramli E.; Mechanical, flow and electrical properties of thermoplastic polyurethane/fullerene composites: Effect of surface modification of fullerene, *Compos Part B Eng*, 80, 101-107, **2015**. DOI: 10.1016/j.compositesb.2015.05.013
- Dogan S.D., **Tayfun U**., Dogan M.; New route for modifying cellulosic fibers with fatty acids and its application to polyethylene/jute fiber composites: *J Compos Mater*, **2015**. DOI: 10.1177/0021998315604706
- **Tayfun U.**, Dogan M.; Improvement the dyeability of poly(lactic acid) fiber using organoclay during melt spinning, *Polym Bull*, **2015**. DOI: 10.1007/s00289-015-1564-4
- **Tayfun U.**, Dogan M., Bayramli E.; Investigations of the flax fiber/Thermoplastic polyurethane eco-composites: Influence of isocyanate modification of flax fiber surface, *Polym Compos*, **2015**. DOI: 10.1002/pc.23889
- **Tayfun U.**, Dogan M., Bayramli E.; Improvement properties of flax fiber reinforced TPU bio-composites, *SPE Plast Res Online*, **2016**. DOI:10.1002/spepro.006290
- **Tayfun U.**, Dogan M., Bayramli E.; Influence of surface modifications of flax fiber on mechanical and flow properties of TPU based eco-composites, *J Nat Fibers*, **2016**. DOI: 10.1080/15440478.2015.1029191

PROFESSIONAL MEETINGS AND ACTIVITIES:

- Polimer katkılı bitüm bazlı kompozitlerin hazırlanması ve karakterizasyonu, Mehmet Doğan, **Ümit Tayfun**, Erdal Bayramlı, *I. Ulusal Polimer Bilim ve Teknoloji Kongresi ve Sergisi*, 2006, Ankara-Türkiye

- Effects of fillers on morpholical, mechanical, flow and thermal properties of bituminous composites, Mehmet Dogan, **Umit Tayfun**, Erdal Bayramli, *Polymer Processing Society 24th Annual Meeting*, 2008, Salerno-Italy

- Mechanical, rheological and electrical properties of TPU/fullerene nano-composites: Effect of surface modification of fullerene, **Umit Tayfun**, Yasin Kanbur, Ufuk Abaci, Hasan Yuksel Guney, Erdal Bayramli, *10th Nanoscience and Nanotechnology Conference*, 2014, Istanbul- Turkey

- Keten lifine çeşitli yüzey modifikasyonları uygulanmasının TPU/keten lifi eko-kompozitlerin mekanik ve reolojik özelliklerine etkileri, **Ümit Tayfun**, Mehmet Doğan, Erdal Bayramlı, *5. Ulusal Polimer Bilim ve Teknoloji Kongresi ve Sergisi*, 2014, Tokat-Türkiye

- Yüzey modifikasyonları uygulanmış karbon nanotüp içeren TPU nano-kompozitlerin mekanik, reolojik ve elektriksel özellikleri, **Ümit Tayfun**, Yasin Kanbur, Ufuk Abaci, Hasan Yuksel Guney, Erdal Bayramlı, *5. Ulusal Polimer Bilim ve Teknoloji Kongresi ve Sergisi*, 2014, Tokat-Türkiye

- Investigations on the short carbon fiber reinforced polyurethane elastomer composites, **Umit Tayfun**, Mehmet Dogan, Erdal Bayramli, *4th International Polymeric Composites Symposium*, 2015, Izmir-Turkey

- Mechanical, flow and water uptake properties of rice straw/TPU eco-composites: Influence of surface modification of rice straw, **Umit Tayfun**, Mehmet Dogan, Erdal Bayramli, *4th International Polymeric Composites Symposium*, 2015, Izmir-Turkey

- Keten lifine isosiyanat modifikasyonu uygulanmasının poliüretan elastomer/keten lifi eko-kompozitlerin mekanik, akış ve su emme özelliklerine etkileri, **Ümit Tayfun**, Mehmet Doğan, Erdal Bayramlı, *15. Tekstil Teknolojisi ve Kimyasındaki Son Gelişmeler Sempozyumu*, 2015, Bursa-Türkiye

- The effect of nanoclay on tensile, thermal and dyeing properties of poly (lactic acid) fiber, **Umit Tayfun**, Burhan Fuat Cnkaya, Mehmet Dogan, *11st Nanoscience and Nanotechnology Conference*, 2015, Ankara-Turkey

- Improving the dyeability of poly (lactic acid) fiber using N-Phenylaminopropyl POSS nanoparticle during melt spinning, Onur Baykus, Asim Davulcu, **Umit Tayfun**, Mehmet Dogan, *11st Nanoscience and Nanotechnology Conference*, 2015, Ankara-Turkey

PROJECTS INVOLVED:

- Bulaşık Makinesinde Kullanılmak Üzere Bütümlü Kompozit İzolasyon Malzemesi Geliştirme Projesi, TÜBİTAK Teydeb, ARÇELİK A.Ş. Bulaşık Mak.İşl.-ODTÜ Teknokent, Haziran 2004-Şubat 2006

- Seramik Parça Üretimi İçin Düşük Basınçta Çalışan Polimerik Kalıp Geliştirme Projesi, TÜBİTAK Teydeb, TAREL A.Ş.-SEREL A.Ş., Eylül 2006-Mart 2008

- Elektrik İletkenliğine Sahip Boya ve Isıtıcı Sistemin Oluşturulması, Üretilmesi ve Bunun Yeni Nesil Seramik Üzerine Uygulanması, Sanayi Bakanlığı San-Tez, Seranit Granit Seramik AŞ. Yapı Grubu, Temmuz 2011-Mayıs 2012

- Güç Tutuşur Polietilen, Polipropilen, Poliamid ve Poliester Kompozit Malzeme Geliştirme, Kosgeb Ar-Ge İnovasyon, Antiflam Ltd. Şti., Kasım 2014-Nisan 2016

- Koltuk Üretimine Yönelik, Yanmazlık Özelliğine Sahip, Kalıp Yöntemi ile Üretilmesi Tasarlanan Yüksek Performanslı Poliüretan Sünger Formülasyonu Geliştirilmesi ve Pilot Üretiminin Gerçekleştirilmesi, TÜBİTAK Teydeb, Rapido A.Ş.-Antiflam Ltd.Şti., Ocak 2015-Ocak 2016

- Karbon Elyaf Takviyeli Polipropilen Kompozitlerin Güç Tutuşurluk Özelliklerinin İyileştirilmesi, Erciyes Ünv. BAP, Ekim 2015-Ekim 2017

- Mikro Giyilebilir Solunum İzleme Cihazı, Sanayi Bakanlığı TGSD, İmge Sensör Teknolojileri, Eylül 2015-Eylül 2016

- Doğal Hidromagnezit Huntit Mineral Karışımının Sinerjik Etki Çalışmaları ile Güç Tutuşurluk Etkisinin Artırılması, Erciyes Ünv. BAP, Kasım 2015-Mayıs 2017

PERSONAL INTERESTS:

Playing football and tennis, reading books, playing bass guitar, composing miniature diorama, paintings and design, railway travel, taking photographs, web-design.