

## Research Article

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# Enhancement of mechanical, thermal and water uptake performance of TPU/jute fiber green composites via chemical treatments on fiber surface

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**Abstract:** Chopped jute fiber (JF) surfaces were modified using alkaline, silane and eco-grade epoxy resin. Surface characteristics of jute fibers were confirmed by FTIR and EDX analyses. JF filled polyurethane elastomer (TPU) composites were prepared via extrusion process. The effect of surface modifications of JF on mechanical, thermo-mechanical, melt-flow, water uptake and morphological properties of TPU-based eco-composites were investigated by tensile and hardness tests, dynamic mechanical analysis (DMA), melt flow index (MFI) test, water absorption measurements and scanning electron microscopy (SEM) techniques, respectively. Mechanical test results showed that silane and epoxy treated JF additions led to increase in tensile strength, modulus and hardness of TPU. Glass transition temperature ( $T_g$ ) of TPU rose up to higher values after JF inclusions regardless of treatment type. Si-JF filled TPU exhibited the lowest water absorption among composites. Surface treated JFs displayed homogeneous dispersion into TPU and their surface were covered by TPU according to SEM micro-photographs.

**Keywords:** polyurethane elastomer; jute fiber; surface treatment; eco-composites; melt mixing

## 1 Introduction

Economic and environmental reasons force research efforts towards to development of natural fiber filled composites, namely environmentally friendly (green or eco-) composites,

because of their ability for replacing man-made fiber composites (1-3). Eco-composites have several advantages such as having low density, bio-degradability, recyclability, and low cost. These distinctive properties make green composites favorable in various application fields including packaging, textile, transportation and construction (4-7). However, these applications of eco-composites are limited since the existence of incompatibility between hydrophilic natural fiber and hydrophobic polymer phase (8). Several chemical treatment methods for natural fibers are performed in order to drawback this limitation which effects their application in wide range. The most commonly preferred method is the alkaline treatment in which roughness on fiber surface is improved physically (9). Silane treatment is another effective technique that reactive and compatible fiber surface can be achieved (10). These modifications increase compatibility of natural fiber with polymeric matrix by introducing adhesive layer between two phases (11,12).

Polyurethane elastomer (thermoplastic polyurethane-TPU) is a fully recyclable polymer which provides ease of processability thanks to its excellent flexibility and good stability against various environments. Eco-grade TPU is a new class of elastomer which is produced from renewable source with a content of 46% of total mass. The novel polyurethane based eco-composites can be fabricated using natural fibers with this new grade of polyurethane elastomer (13-16).

Jute fiber (JF) is traditionally produced by extraction of jute plant using retting process by steeping in water. Cementing materials in JF undergo bacterial decomposition during retting technique. The retted JF is composed of cellulose, hemicellulose, and lignin constituents. JF found wide range of application fields mainly in roof tiles, panels, containers and tanks due to it is one of the strongest agricultural fibers. JF shows remarkable changes in diameter along with length of individual fibers, which is similar with other lignocellusics. The quality of this natural fiber is related with the parameters such as size, density and maturity (17-21).

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There have been several research attempts towards to investigate the basic properties of JF reinforced polymer eco-composites. Rahman et al. prepared JF filled polypropylene (PP) composites using compression molding. They treated JF surface by various acrylic monomers for improvement of interfacial interactions between fiber and polymer matrix (22). Haydaruzzaman et al. also fabricated PP based composites containing hydroxyl ethylmethacrylate and starch treated JF fabrics. They investigated that treated JF filled PP gave higher mechanical parameters such as tensile strength, tensile modulus, bending strength, bending modulus, impact strength as compared to untreated JF (23). Bulut et al. performed several surface treatments for JF including potassium dichromate, potassium permanganate and sodium perborate trihydrate. They found that the highest compatibility with PP matrix was achieved by sodium perborate trihydrate treated JF (24). Cabral et al. investigated the water uptake, mechanical and dielectric properties of JF loaded PP composites. Their findings showed that tensile strength and modulus increased with filling ratio of JF where, water absorption and dielectric properties of composites were varied according to JF content (25). Khan et al. studied the effect of hydroxy ethylmethacrylate and 2-ethylhexylacrylate treatments of JF on their PP based composites and they found that treated JF samples exhibited higher tensile properties and bending modulus than untreated ones (26). Liu et al. tried to enhance performance of JF/PP composites by the treatments of alkaline and maleic anhydride-grafted polypropylene emulsion. They postulated that these treatments caused increments in interfacial shear, flexural and tensile strengthes, however reductions for impact strength were observed (27). Baykus et al. examined the influence of pre-impregnation of JF with maleated coupling agents on mechanical and water uptake properties of JF filled PP and polyethylene (PE) composites. They observed that tensile strength of untreated JF containing PP and PE composites enhanced at about 90% and 40%, respectively. They also found that the highest reduction in water absorption was reached as alkaline and pre-impregnation treatments were used together for both PE and PP (28). Karmaker and Hinrichsen performed to produce PE and PP films containing JF. They reported that mechanical properties of films decreased with higher molding temperature and pressure due to damage of JF took place (29). Das et al. used silane coupling agent for the treatment of waste JFs and they mixed them with recycled PP matrix. They investigated that thermal and mechanical properties were improved for silane treated JF containing PP composites (30). Dogan et al. postulated the new route to modify JF surfaces with fatty acids. They produced low density polyethylene (LDPE) based composites with these JF

samples. They found that tensile strength and modulus were enhanced using stearic acid modified JF and stearyl azide treated JF showed decrease in the degree of crystallinity with respect to alkaline treated JF (31). Mohanty et al. studied the suitability of maleic anhydride grafted PE modified JF as an additive in high density polyethylene (HDPE) matrix. According to thermo-mechanical analysis they conducted, treated JF addition caused increments in storage modulus of HDPE (32). Islam et al. performed to fabricate JF reinforced polyvinyl chloride (PVC) and PP hybrid composites using compression molding. They showed that tensile strength and modulus, bending strength and modulus parameters of composites were varied with PP content (33). Hu et al. examined the hydrothermal aging behaviour of JF filled polylactide (PLA) composites and they investigated that tensile strength of composites showed reduction after aging process due to the formations of microcracks, pores and delamination in the microstructures (34). Huq et al. studied the effect of soil degradation on JF loaded polyethylene terephthalate (PET) based composites. Their findings exhibited that tensile strength and bending strength of composites decreased drastically after 6 weeks' period of soil degradation test (35). Sarkhel and Choudhury investigated the mechanical, thermal and viscoelastic properties of JF filled ternary composites based on ethylene-propylene-diene terpolymer (EPDM) blends of LDPE and HDPE. In their study, HDPE gave higher storage and loss modulus than LDPE and mechanical properties of composites increased with JF and compatibilizer contents (36). Khan and Hassan treated the JF surface with silane and they prepared JF reinforced polycarbonate (PC) composites. According to their test results, silane treated JF showed improvement for mechanical properties as well as increase in storage and loss modulus (37).

The novelty of this research work lies in the investigations of basic properties of JF reinforced TPU based eco-composites by increasing interfacial interactions between fiber and polymer matrix thanks to applied eco-friendly chemical treatments to JF surface. Enhancement of mechanical, physical and water resistance performance of green composites leads to potential use including outdoor applications with low cost and practical processing methods. For these reasons, short JF samples were surface treated using alkaline, silane and eco-grade epoxy resin. Surface characteristics of fibers were examined by infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Polyurethane elastomer-based composites were prepared via extrusion process. Eco-grade TPU was used in this study having biomass content of 46% of total mass. JF loadings were kept constant at 30% by weight in all composites. Test samples

were shaped by injection molding process. The influence of surface modification of JF on mechanical, thermo-mechanical, melt-flow, water ageing and morphological properties of TPU based eco-composites were investigated by tensile and Shore hardness tests, dynamic mechanical analysis (DMA), melt flow index test, water absorption test and SEM technique, respectively.

## 2 Materials and methods

### 2.1 Materials

The commercial thermoplastic polyurethane was purchased from FKA Merquinsa, Barcelona, Spain under a trade name of Pearlthane® ECO D12T85. This eco-grade TPU consists of biomass with 46% content and it has a density of 1.15 g/cm<sup>3</sup> according to producer. Bangladesh oriented jute fibers (JFs) used in this study and they were obtained from the local supplier in rowing form. JFs were chopped into 3-4 mm length before surface treatments and compounding steps. Reagent grade sodium hydroxide (NaOH) and ether solvent were supplied by Sigma Aldrich, Missouri, USA. Silane coupling agent was  $\gamma$ -aminopropyl triethoxy silane (APTES) and solvent was ethanol were purchased from Merck AG, Darmstadt, Germany. Eco-grade epoxy resin was supplied from Ferrer Dalmau SA, Barcelona, Spain under the trade name of Super Sap CPM. It has bio-content of 47.5% and a density of 1.09 g/cm<sup>3</sup> indicated by producer.

### 2.2 Surface treatments of JF

JF were washed to remove impurities and dried at 80°C for 24 h using vacuum oven (FN 055/120, Nuve AS, Ankara, Turkey). The neat JF sample was named as JF. Alkaline treatment was applied to JF by continuous mixing in 2 wt% water solution of NaOH for 2 h. The excess of NaOH was eliminated after washings 3 times with water. This portion was dried at 80°C in vacuum oven overnight and named as Na-JF. Silanization of JF was applied using similar modification routes in literature (38-40). During silane treatment, Na-JF was mixed in 2 wt% solution of APTES/ethanol for 2 h. The excess of silane contamination was removed by washing 3 times with ethanol. Silane modified JF was named as Si-JF. Another portion of Na-JF was subjected to epoxy modification via mixing in 4 wt% solution of epoxy/ether for 1 h. After washings 3 times with ether, sample was air-dried at room temperature. Epoxy treated portion was named as EP-JF.

### 2.3 Preparation of composites

TPU and JF samples were dried at 100°C for a period of 8 h to avoid possible moisture before extrusion process. Composites were fabricated using lab-scale twin screw extruder (15 mL micro-compounder, DSM Xplore, Netherlands) at constant loading level of 30 wt%. Processing temperature, screw speed and mixing time parameters were 200°C, 100 rpm and 5 min, respectively. The unfilled TPU was also mixed under the same processing conditions. Test samples of composites were shaped using injection molding instrument (Micro-injector, Daga Instruments, UK) in which barrel temperature of 205°C and injection pressure of 5 bar were applied. Injection molded dog-bone shaped specimens with the dimensions of 7.4 × 2.1 × 80 mm<sup>3</sup> according to ASTM D-638 standard (41) were obtained from injection molding process.

### 2.4 Characterization methods

Fourier transformed infrared spectroscopy (FTIR) measurements in attenuated total reflectance (ATR) mode were performed using IR-spectrometer (Bruker VERTEX 70, Massachusetts, USA). The measurements were done at a resolution of 2 cm<sup>-1</sup> with 32 scans from 600 cm<sup>-1</sup> to 3800 cm<sup>-1</sup> wavenumbers. Elemental analysis was studied with energy dispersive X-ray spectroscopy (EDX) technique during examination of selected SEM microphotographs (JSM-6400 Electron Microscope, JEOL Ltd, Tokyo, Japan) of JF samples. Tensile test measurements of TPU and TPU/JF composites were performed by using Lloyd LR 30 K (West Sussex, UK) universal tensile testing machine in accordance with the ASTM D-638 standard. 5 kN load cell and 5 cm·min<sup>-1</sup> crosshead speed were applied during tensile test. Tensile strength, elongation at break and tensile modulus parameters were recorded as an average of five samples. Digital Shore hardness tester (Zwick R5LB041, Ulm, Germany) was utilized in order to evaluate A-type Shore hardness values of TPU and composites. Measurements were carried out according to ASTM D2240 standard (42). DMA analyses were done by conducting DMA 8000 (Perkin Elmer, Massachusetts, USA) dynamic mechanical thermal analyser at temperature range between -120°C and 120°C in dual cantilever bending mode at a constant frequency of 1 Hz and heating rate of 5°C·min<sup>-1</sup>. MFI values of TPU and its composites were measured by Coesfield Meltfixer LT, Dortmund, Germany. Test measurements



were conducted under the standard specified load of 2.16 kg at process temperature of 200°C. Melt flow rate results represent an average value of at least ten weighted samples with standard deviations. The characterization of water uptake values of TPU and composites was performed by immersing samples in a water bath at room temperature according to ASTM D570 procedure (43). Test samples were periodically taken out from the water, wiped with tissue paper to avoid their surface water, weighed and put back into the water repeatedly during 30 days period. Morphological characterizations of composites were examined by JSM-6400 field emission scanning electron microscope, JEOL Ltd, Tokyo, Japan. Surfaces of cyro-fractured samples were coated with a thin layer of gold in order to obtain conductive surface. SEM micrographs were taken at various magnifications from  $\times 250$  to  $\times 5000$ .

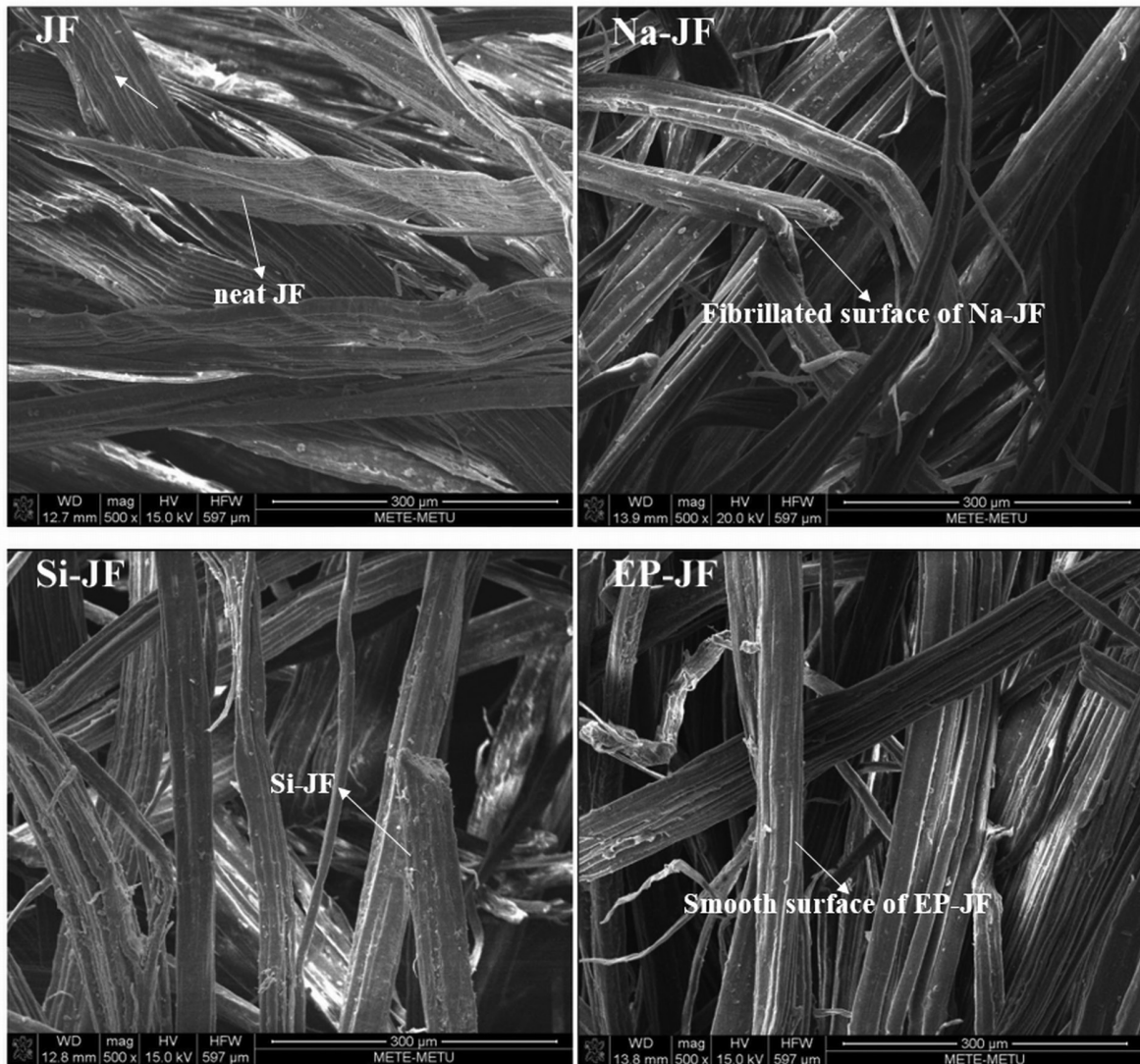
### 3 Results and discussion

#### 3.1 EDX and FTIR analyses of JF surface

The elemental analysis data and SEM micrographs of fibers obtained from the SEM/EDX analysis are represented in the Table 1 and Figure 1, respectively. It can be seen from

**Table 1:** SEM/EDX data of JF samples.

Samples	C wt%/at%	O wt%/at%	Si wt%/at%
JF	54.53/62.96	40.15/34.81	0.93/0.46
Na-JF	45.64/53.73	49.73/43.96	2.19/1.10
Si-JF	54.05/62.62	39.04/33.95	4.39/2.18
EP-JF	60.66/68.42	35.41/29.98	1.12/0.54



**Figure 1:** SEM images of JF samples.

the Table 1 that oxygen content of unmodified JF increased by 9.58% after alkaline treatment due to formation of hydroxyl groups on the surface of Na-JF. Silicon content also rose with 3.46% at the surface of Si-JF attributed to the silane coupling agent. Carbon concentration of EP-JF observed as 6.13% higher compared to JF which indicates the presence of epoxy groups on the fiber surface. As can be seen from Figure 1, alkaline treatment caused fibrillation for untreated JF. Surface of JF became smoother after epoxy treatment.

FTIR spectra of pristine JF and surface treated JF samples are given in Figure 2. The characteristic absorption bands from  $400\text{ cm}^{-1}$  to  $1800\text{ cm}^{-1}$  range display the oxygen functionalities, which owing to C–O stretching at broad peak between  $900\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$ , COO<sup>−</sup> asymmetric stretching and C=O stretching vibrations around  $1620\text{ cm}^{-1}$  and  $1730\text{ cm}^{-1}$ , respectively (44,45). Increments on absorption of these oxygen related peaks for Na-JF were clearly observed. Intensities of these peaks were relatively lower in the case Si-JF which indicates the chemical modification of silane coupling agent with the surface hydroxyl groups. The intensity of band at  $1420\text{ cm}^{-1}$  which stem from COO<sup>−</sup> group slightly increases after alkaline treatment. The band at  $1270\text{ cm}^{-1}$  assigned to C–O and COO<sup>−</sup> groups of hemicellulose which was observed as remarkably more intense for untreated JF (46,47). Broad band that centered at  $3300\text{ cm}^{-1}$  is attributed the stretching hydroxyl group (48).

Si-JF and EP-JF exhibited lower transmittance for that band due to the modification of hydroxyl groups of cellulose and lignin portions of JF with silane coupling agent and epoxy resin, respectively. The peak around  $870\text{ cm}^{-1}$  is stem from the characteristic Si–O vibration which is observed in the spectrum of Si-JF samples (49–51). These findings proved that chemical changes were taken place on the surface of JF during chemical treatments.

### 3.2 Tensile properties

Tensile test data of composites before and after water immersion including tensile strength, percentage strain and tensile modulus are listed in Table 2 and representative strength-strain curves of TPU and its composites are shown in Figure 3. Tensile test results of samples water absorption test applied are indicated with (WA) in Figure 3. According to Table 2, additions of JF and Na-JF caused reduction for tensile strength of neat TPU with the contents of 4.8% and 3.2%, respectively. On the other hand, Si-JF and EP-JF inclusions yield slight improvements in tensile strength values by displaying 0.3% and 0.6% increase, respectively. Percent elongations of composites were found to be much lower than that of TPU. Almost identical tensile modulus values were obtained for Na-JF and unmodified JF filled composites with modulus of

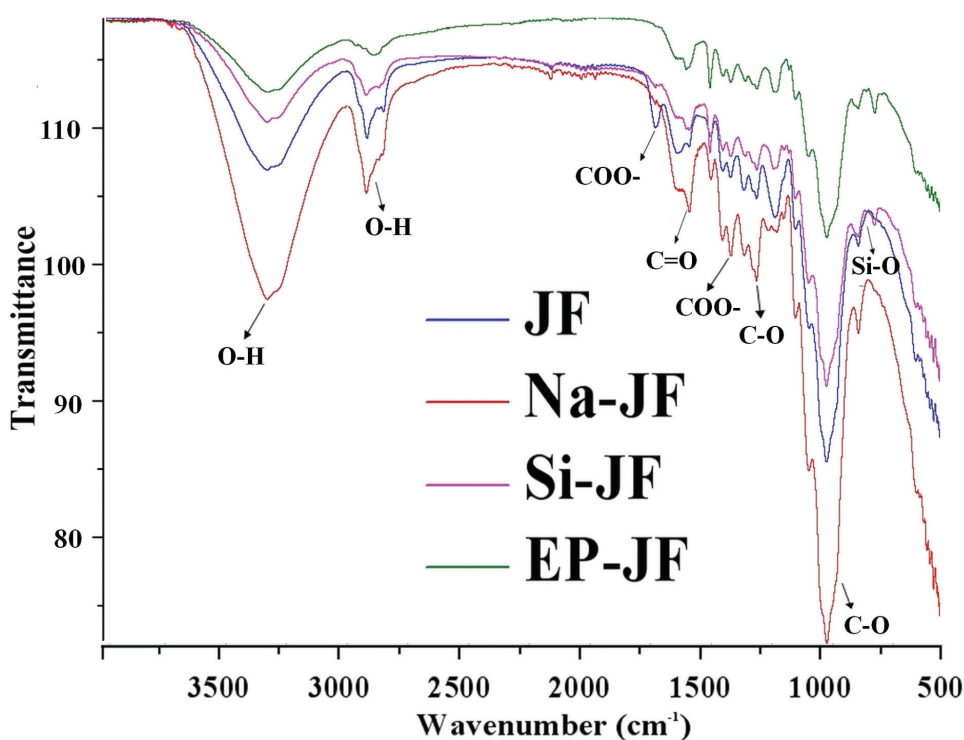


Figure 2: FTIR spectra of neat and modified JF samples.

**Table 2:** Tensile test data of composites before and after absorption test.

Samples	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
TPU	24.9 ± 1.4 / 24.8 ± 1.0*	333.7 ± 8.0 / 433.3 ± 8.7 *	57.8 ± 2.9 / 53.4 ± 4.1*
TPU/JF	20.1 ± 1.0 / 14.4 ± 1.9*	121.3 ± 6.4 / 263.2 ± 6.0*	62.9 ± 3.5 / 132.1 ± 5.3*
TPU/Na-JF	21.7 ± 1.2 / 15.8 ± 1.3*	144.3 ± 7.1 / 273.1 ± 5.6*	50.5 ± 3.2 / 119.7 ± 6.2*
TPU/Si-JF	25.2 ± 1.5 / 21.1 ± 1.8*	63.5 ± 5.3 / 90.2 ± 4.4*	231.0 ± 7.6 / 103.2 ± 5.7*
TPU/EP-JF	25.5 ± 1.1 / 20.1 ± 1.6*	61.3 ± 5.8 / 121.3 ± 6.3*	225.6 ± 6.3 / 106.9 ± 4.0*

\* Test results of samples water absorption test applied.

neat TPU. On the other hand, silane and epoxy treated JF containing composites showed remarkable increase in tensile modulus. Enhancements of tensile parameters by the inclusion of surface modified natural fiber to TPU matrix were also reported in the literature (38,40,52). It can be clearly seen from Figure 3 that, TPU/JF and TPU/Na-JF composites showed necking behavior.

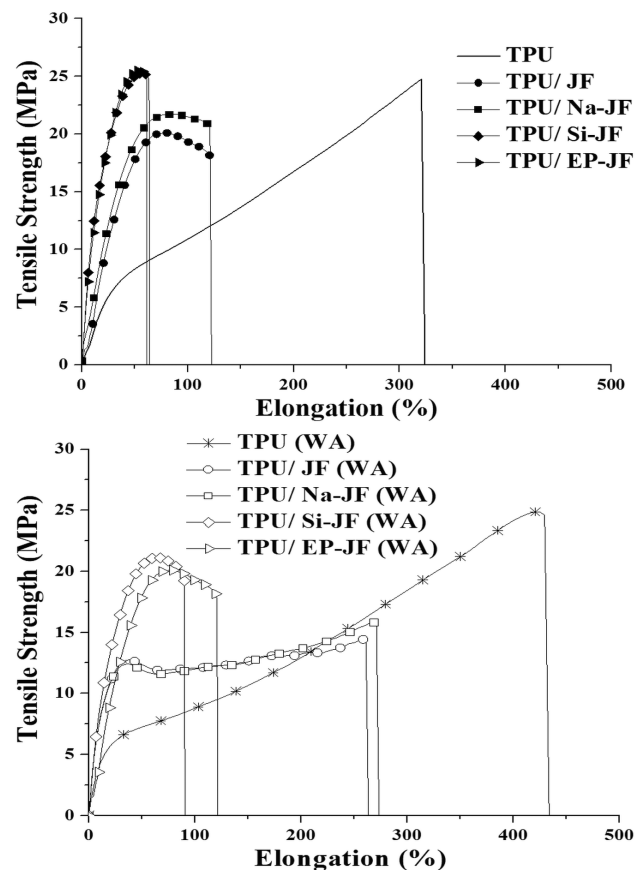
In the case of tensile test data obtained after water uptake test, the immersion of unfilled TPU into water caused no remarkable change in its mechanical properties. On the other hand, relatively lower strength values were observed for composites after water immersion. This reduction trend may due to the hydrophilic nature of JF which is common for all of the natural fibers (53,54). Percentage strain of composites displayed increase by water immersion which indicates the plasticizing effect. Based on the comparison of tensile test parameters before and after water ageing, silane treated JF containing composite exhibited the lowest changes thanks to JF gained hydrophobic character after silanization process (55).

### 3.3 Shore hardness test

Shore hardness is a characteristic parameter for elastomers and related composites. According to the A-type Shore hardness values displayed in Table 3, all of the composites gave around 10 points higher values than that of unfilled TPU. Si-JF addition led to the maximum improvement for shore hardness values among all of the composites by exhibiting 12 points higher value. The similar finding was obtained from the recent study in the literature that surface modification of natural additive led to increase in Shore hardness of TPU (56).

### 3.4 Thermo-mechanical performance

Storage modulus and Tan  $\delta$  curves as a function of temperature were shown in Figures 4a and 4b,

**Figure 3:** Stress-strain curves of TPU and composites.**Table 3:** Shore A hardness values of TPU and composites.

TPU	TPU/JF	TPU/Na-JF	TPU/Si-JF	TPU/EP-JF
83	91	94	95	94

respectively. Storage modulus curve of TPU became broadened after Si-JF and EP-JF additions. Relatively lower storage modulus values were observed for Na-JF and JF containing composites. Silane treated JF containing composite gave the highest storage modulus stem from the restriction of chain motions

after inclusion of Si-JF into polymer phase (57-60). The peak point of  $\tan \delta$  curve corresponds to glass transition temperature ( $T_g$ ) of polymer. According to Figure 4b, incorporations of JF caused increase in the peak value of  $\tan \delta$  regardless of treatment types. As a

similar with previous results, silane and epoxy treated JF containing composites exhibited enhancement of  $T_g$  values. As indicated in Figure 4b,  $T_g$  of unfilled TPU shifted to 17°C higher after Si-JF inclusion.

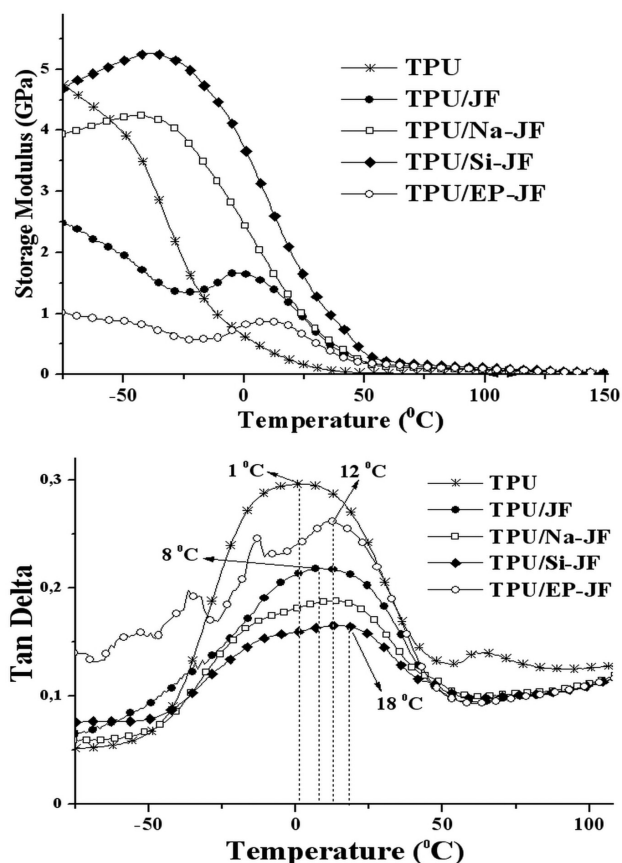


Figure 4: DMA curves of TPU and composites.

### 3.5 Melt-flow behaviors

MFI parameter provide processing related information of polymeric material in the case of melt blending technique. MFI values of TPU and relevant composites shown in Figure 5. All of treatments resulted in increase for MFI value of neat TPU. The highest improvement was observed on TPU/Si-JF composites with 8.42 points increase since enhanced surface interactions between silane covered surface of JF and TPU were established by the help of the treatment process (61-63).

### 3.6 Water absorption measurements

The water absorption test was conducted for composite samples in time interval of 30 days in order to evaluate their potential use for out-door applications. Water uptake values of TPU and composites can be seen in Figure 6. Nearly 1% water uptake was achieved for unfilled TPU within a few days and it remained constant throughout the test. This result is found to be in accordance with the single phase diffusion model described by Fick's law since the diffusion of water yield weight gain of material (64,65). The pristine JF loaded composite sample reached nearly 7% water absorption value at the end of the test. Additions of

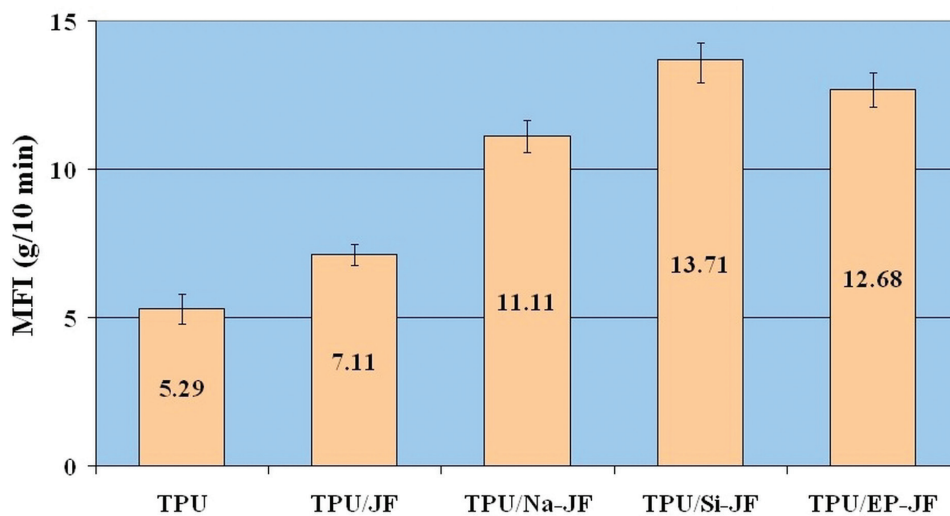


Figure 5: MFI values of TPU and composites.



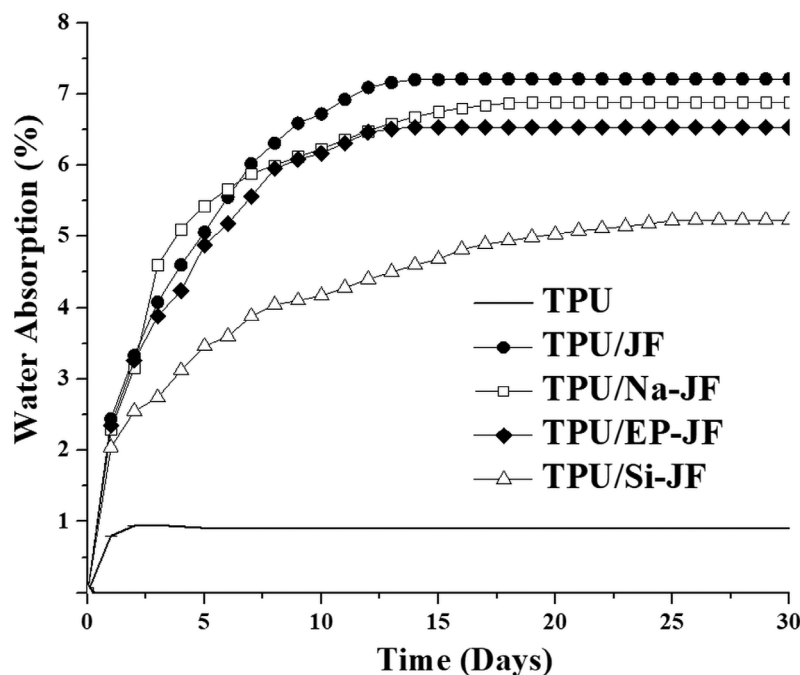


Figure 6: Water uptake curves of TPU and composites.

alkaline and epoxy treated JF yield slightly lower water uptake values compared to unmodified JF. On the other hand, the reduction of water uptake for silane modified JF containing sample was found to be the most distinctive among composites. Silane layer donated the hydrophobic character on the JF surface (66,67). For this reason, higher water repellency was obtained for TPU/Si-JF with respect to other composites.

### 3.7 Morphological characterization

Morphological properties of composites were examined by representative SEM micrographs of selected samples which are shown in Figure 7. According to SEM micrograph of neat JF filled composite, large gaps were formed between JF and TPU phase due to their incompatibility. Alkaline treated JF showed fibrillation and relatively better adhesion to polymer matrix. It can be clearly seen from Figure 7 that silane and epoxy treated JF surfaces were covered by TPU because of the improved adhesion. Si-JF displayed excellent adhesion to polymer matrix thanks to the increase of interfacial interaction between two phases after treatment process. Improvement adhesion between natural fiber and polymer matrix after surface treatments have

been indicated in similar studies in the literature (37,52,60,67,68). These findings proved the enhancement for related properties of composites described in earlier sections.

## 4 Conclusion

In this current study, the effect of surface modifications of JF on the mechanical, thermo-mechanical, melt-flow, water absorption and morphological properties of TPU-based eco-composites were reported. Comparisons were made based on effect of surface treatments of JF. According to test results silane and epoxy treatments led to higher mechanical performance due to increase for interfacial interactions between fiber surfaces and TPU matrix. Silane treated JF containing sample exhibited the lowest water absorption among composites thanks to hydrophobic character of silane layer. Enhanced adhesion between Si-JF and TPU matrix as well as EP-JF was confirmed by SEM investigations. It was concluded that silane and epoxy modifications were suitable for TPU/JF composite system. TPU-based composites filled with silane treated JF can be considered for out-door applications since they displayed the highest water uptake performance among composites.



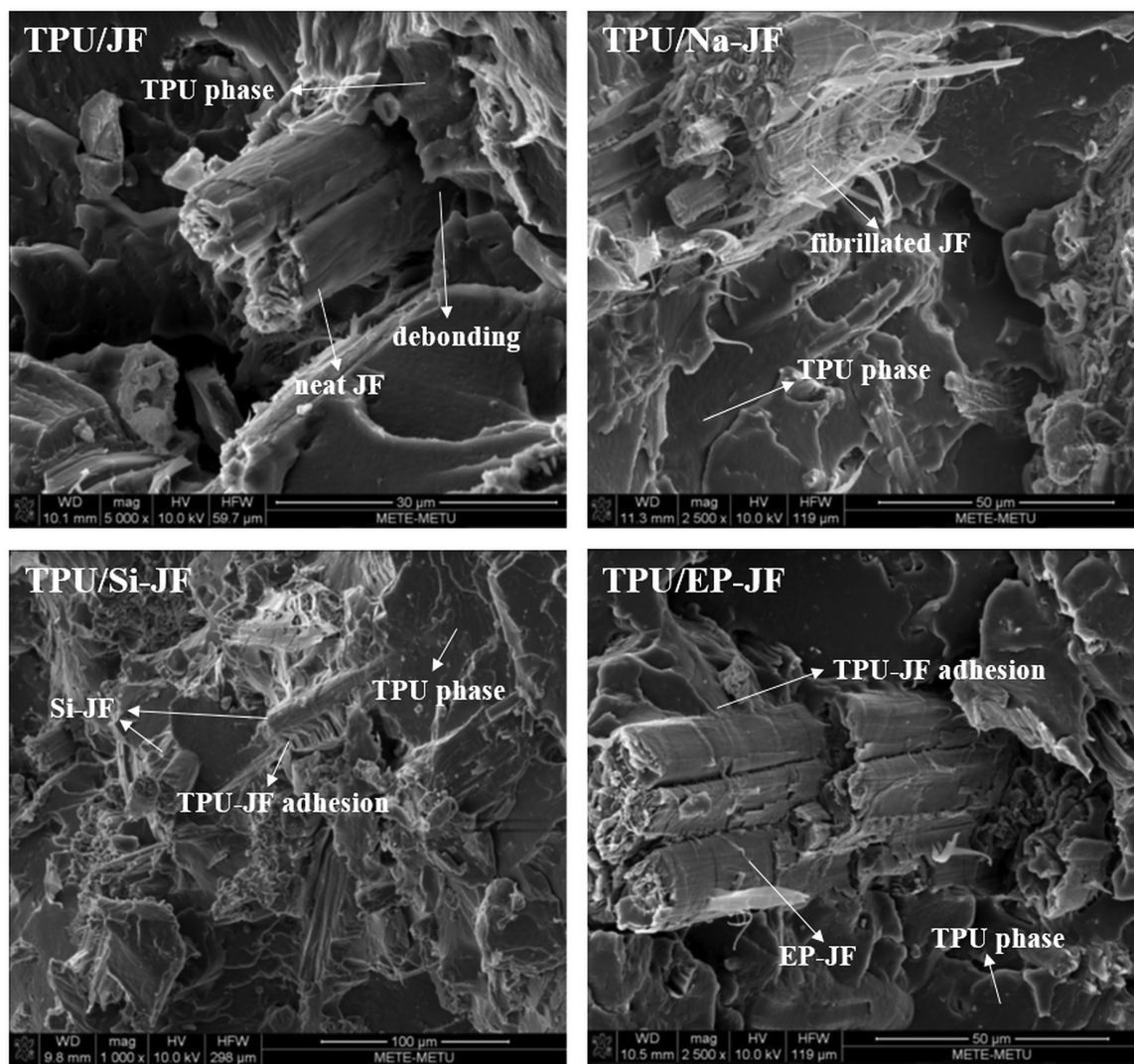


Figure 7: SEM micro-images of composites.

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