The Effect of Coupling Agent on the Properties of Short Non-Woven Pet Microfiber Reinforced Polypropylene (PP) Composites

Prakash Mahanwar, and Pravin Gaikwad

***Abstract*—** Polyethylene Terephthalate (PET) fibers are now considered as the most important fibers for industrial application. The present work deals with the effect of concentration of PET short fibers and concentration of coupling agent on properties of Polypropylene (PP) composites. It is seen that tensile strength increases with increase in concentration of short PET microfibers when subjected to the surface treatment using vinyltrimethoxysilane (VTMO) as a coupling agent. Mechanical investigation manifested that treated fibers have strengthening effect (increase in tensile and flexural strength) on the performance of PP composites. Rheological behaviour of PP/PET microfiber composites was characterized by parallel plate rheometer system. The SEM morphology shows a good dispersion and strong interfacial adhesion between PP and modified PET fibers at 10 wt% concentration of fibers. Overall this study shows that surface treatment of PET fibers is one of the important factors influencing the mechanical and electrical properties of PP/PET microfiber composites.

***Keywords*—**PET microfibers, Polymer Composites, SEM, VTMO.

I. Introduction

As on today it is not a practical solution to synthesis or modifies a new polymer as per the properties required for specific application. Hence there is an increasing demand of reinforcement of virgin polymer with the fillers so as to achieve overall performance of the polymer which cannot be achieved as individual. Fiber reinforced polymer composite (FRPCs) are currently used for a wide variety of structural applications such as aerospace, automotive and chemical industries due to their high strength to weight ratio and stiffness to weight ratios [1]-[2]. Polyethylene Terephthalate (PET) is a thermoplastic polymer of the polyester family and is used in various applications. PET fibers are most important fibers for industrial production due its high performance, low cost and recyclability and are one of the most attractive candidates for high strength fibers [3]. Polypropylene (PP) is a commodity polymer and is also find varied applications. In general, the reinforcing agent can be fibrous, powdered, spherical, crystalline or whiskered and either an organic, inorganic, metal or ceramic materials. Fibers have been used for improving the strength and rigidity of numerous polymers. Numerous studies have been reported concerning the reinforcement of polypropylene (PP) using different types of fibers in order to achieve improvement in tensile modulus, thermal and interfacial properties [4]-[6]. Some of the fibers induce transcrystalline morphology in PP when melt crystallized in contact with carbon, aramid as well as polymeric fibers [7]-[13]. The studies on PET/PP microfibrillar composites for morphological development as well as for thermal and impact properties by using compatibiliser are reported [14]-[15].Effect of incorporation of PET fibers on the properties of PP/elastomer blends is reported by Lopez et al. [16]-[17]. Ke et al. studied ternary $CaCO_3$/PET fibers /PP composites: increased impact strength and reinforcing mechanism [18]. Fu et al. reported tensile strength and rupture energy of hybrid poly (methylvinylsiloxane) composites reinforced with short PET fibers and Wollastonite whiskers [19].The structural development and mechanical properties of PP/fiber composite with and without compatibiliser are reported by C.Saujanya, and S. Radhakrishnan [20]. John et al. reported the effect of amphiphilic coupling agent on surface properties of fibers and composites [21]. The effect of alkali-silane treatment on the tensile and flexural properties of short fiber of non-woven kenaf reinforced PP composites was investigated by O.Asumani et al. [22]. N.Chand and U.Dwivedi have studied the effect of coupling agent on abrasive wear behaviour of chopped jute fiber reinforced PP composites [23].

In the present study the properties of PP reinforced with short PET microfibers were studied to optimize the concentration of fibers treated with coupling agent (VTMO) for fiber reinforced PP composites.

II. Experimental

A. Materials

The polymer Polypropylene (PP) Repol, injection molding grade with MFI 11gm/10min, the continuous PET fiber of nominal denier 0.8 and tenacity 6.7 Gpd was obtained from Reliance Industries Ltd, Mumbai. Vinyltrimethyloxisilane (VTMO) was obtained from Degussa, Germany; Isopropyl Alcohol (IPA) was supplied by S.D.fine Chem Ltd was used.

Prakash Mahanwar is the Head of Department of Polymer and Surface Engineering ,Institute of Chemical Technology,Mumbai,MH 400 019,India (corresponding author's phone: +91-9324134190 ; fax: +91-22-33611020; e-mail:pmahanwar@yahoo.com).

Pravin Gaikwad, is with the Department of Polymer and Surface Engineering ,Institute of Chemical Technology,Mumbai,MH 400 019,India (e-mail:pravingaikwad69@gmail.com).

B. Surface Treatment of PET Microfibers

The PET fibers were chopped manually to 5-7mm in length and predried. The surface treatment of PET microfibers was carried out by soaking PET chopped fibers in solution of silane coupling agent and in isopropyl alcohol equal to the total wt of the fibers and then silane was added at 0.5% by wt of fibers. The treated chopped PET fibers were allowed to dry in an air circulating oven for 3 hours at temperature of 65 ± 2^0C.

C. Preparation of The Polymer Composites

The PP/PET fibers composites with and without silane treatment were prepared in varying concentration viz.1,3,5,8,10 and 20% by wt of virgin polymer by melt blending in a twin screw extruder (Model MP19 PC, M/SAPV BAKER, UK) having L/D ratio of 25:1.and 60 rpm for all the composition. The temperature profile for the melt blending was kept as Zone1-160 ^{0}C, Zone 2-190^{0}C, Zone 3-210^{0}C, Zone 4-220^{0}C and Die-230^{0}C for the PP/PET microfibers composites. The extrudates was cooled to room temperature and pelletized. The pellets were used for further study.

D. Injection Moulding

The granules of the extrudates were predried in an air circulated oven at 80^{0}C for 4 hours and then injection molded in a microprocessor based injection moulding machine (Boolani) fitted with a master mould containing the cavity for tensile, flexural and impact specimens. The temperature profile used for injection molding was as Zone1:170^{0}C, Zone2: 210^{0}C, Zone3:230^{0}C for PP/PET Microfiber composites.

III. Characterization

A. Mechanical Properties

The dumbbell shape tensile strength specimens were injection molded as per ASTM D638 M-91 and tested using Universal Testing machine LR50K [Lloyd Instrument Ltd., U. K.] The crosshead speed of 50mm/min was maintained for testing using a load cell of 50 KN. The flexural strength and flexural modulus was measured using universal testing machine [LR 50 K, LLOYD Instruments, and U.K.] according to ASTM D790 M-92 at Jaw speed of 2.8 mm/min with 3-point flexural strength and the span of 60 mm. The impact strength was determined as per ASTM D 256 using Avery Denison's pendulum Impact Strength Tester, [model 6709] with 2.7J striker. The results reported are the average values of at least 3 specimens for each test.

B. Electrical Properties

The Dielectric Strength was determined according to ASTM D 149 using Zaran Instruments (India) with a 2mm thick composite disc. The configurations of the instruments were as follows: voltage: 240 V, 50 Hz, 1 PH; output: 0-50 KV; capacity: 100mA; rating: 15 min.

C. Rheological properties

The melt Rheology of the matrix polymer and the PP/PET Microfiber composites (both treated and untreated) were studied using rotational parallel plate rheometer (Physica MCR 101, Anton Paar, Germany), with diameter 35mm at 230^{0}C. The samples were predried before analysis.

D. Morphological Properties

Scanning Electron Microscope (SEM) was used to study the morphology of the composites. SEM studies of tensile test fractured and liquid nitrogen fractured samples were carried out using JSM-6380LA analytical scanning microscope of Joel make, Japan. The accelerated voltage used was 15KV.The samples were sputter-coated with platinum to increase surface conductivity. The digitized images were recorded.

IV. Results and Discussion

A. Tensile Properties

Fig.1 enumerates the variation in tensile strength of the PP/PET microfiber composites as a function of PET microfiber in wt%. Tensile strength of composite was found to increase significantly with increase in the PET microfiber by wt% with and without coupling agent. The rate of increase of tensile strength is higher in the case of higher wt% loading of PET microfibers and found optimum at 10 wt% fibers content into the polymer matrix. Fig.2 shows the % elongation at break of PP/PET microfiber composites versus wt% PET microfiber loading. The percentage elongation at break decreased on addition of PET microfibers with and without coupling agent into the polymer matrix**.** This is due to the interference of fibers in the mobility or deformability of the matrix. This interference is created through the physical interaction and immobilization of the polymer matrix by the presence of mechanical restraints, thereby reducing the elongation at break.

Fig.3 and 4 although both the treated and untreated PET microfibers can imparts the high stiffness of the fiber to the matrix polymer as expected, the composites incorporated with surface treated silane coupling agent exhibits better strength and modulus over untreated PET microfibers. Accordingly, it is convinced that the denser and uniform distribution and less agglomeration of the fibers should play a more effective role in the enhancement of tensile properties. It is also observed that at 20wt% loading of PET microfibers the tensile strength of the composite decreased. This can be attributed to poor surface bonding of PET microfibers and there is a formation of fiber agglomeration leading to uneven stress transfer.

B.Flexural Properties

Fig. 5 and Fig. 6 depict the variation in flexural strength and flexural modulus of PP/PET microfiber composites with PET fibers wt% loading. The flexural strength of the composite increase with increase in wt% concentration of PET fibers for both of the treated and untreated composites. The flexural modulus of the composite also increases with

increase in wt% concentration of PET fibers for both of the treated and untreated composites. The increase in the flexural properties of the composites is due to increased interaction of fibers and matrix and this is mainly because of addition of coupling agent.

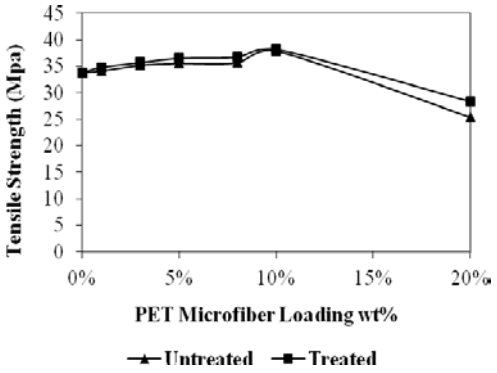


Fig. 1 Variation in tensile strength with PET microfiber loading by wt%.

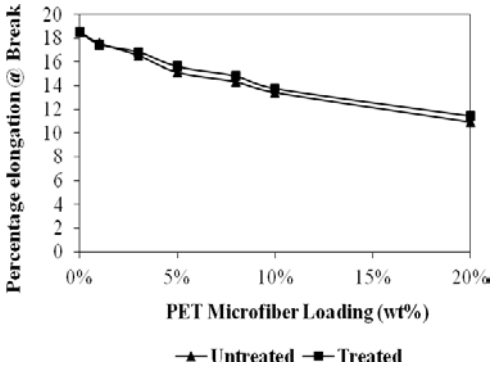


Fig. 2 Variation in percentage elongation at break with PET microfiber loading by wt%.

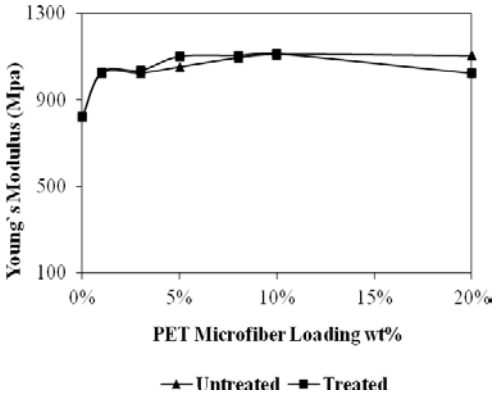


Fig.3 Variation in young's modulus with PET microfiber loading by wt%.

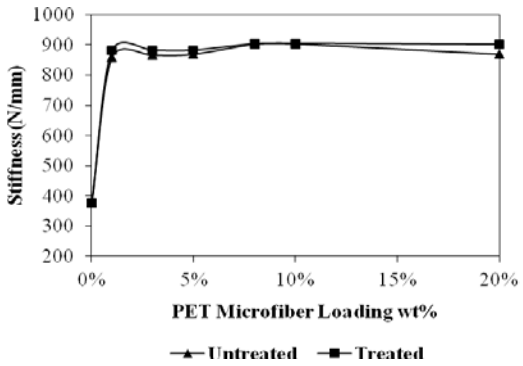


Fig. 4 Variation in stiffness with PET microfiber loading by wt%.

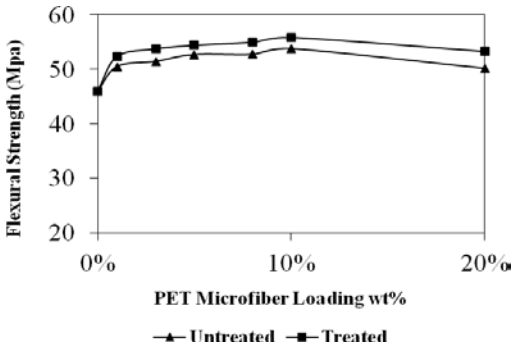


Fig.5 Variation in flexural strength with PET microfiber loading by wt%.

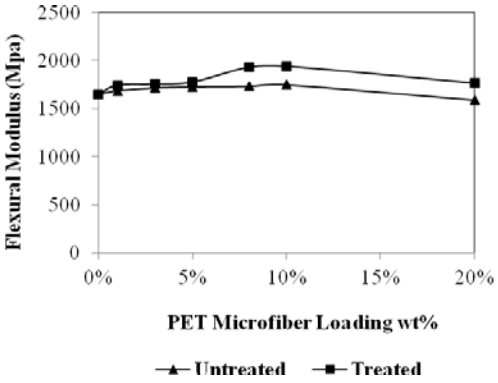


Fig. 6. Variation in flexural modulus with PET microfiber loading by wt%.

C. Impact Strength

Table I shows the results of the impact strength of the composite. It is found that with the increase in wt% loading of the PET fibers there is decrease in the impact strength of the composite. This is attributed to the reduction in the elasticity of the composite due to fiber addition and thereby reducing the deformability of the polymer matrix.

TABLE I
VARIATION IN IMPACT PROPERTIES OF POLYPROPYLENE (PP)/ PET MICROFIBER COMPOSITES.
COLUMN (A): IMPACT STRENGTH OF UNTREATED FIBERS.
COLUMN (B): IMPACT STRENGTH OF SILANE-TREATED FIBERS.

PET short fiber content (wt %)	Impact Strength (J/m)	
	a	**b**
0	27	27
1	24.66	25.10
3	20.82	23.28
5	18.12	20.42
8	18.50	19.68
10	17.28	18.23
20	16.25	17.89

D. Dielectric Strength

Table II shows the results of dielectric strength of the composite. It represents the variation in the dielectric strength of the PP/PET microfiber composites with wt % loading of PET fibers. It is observed that the dielectric strength of the composite increase as there is an increase in wt % concentration of PET fibers. The increase in dielectric strength is upto 10wt% loading of PET microfibers. The concentration wt% loading of synthetic fibers may have reached the threshold value at 10wt% and therefore the dielectric strength of the synthetic fiber filled PP composites remain constant after 10wt% concentration of microfibers.

TABLE II
VARIATION IN ELECTRICAL PROPERTIES OF POLYPROPYLENE (PP)/ PET MICROFIBER COMPOSITES.
COLUMN (A): DIELECTRIC STRENGTH OF UNTREATED FIBERS.
COLUMN (B): DIELECTRIC STRENGTH OF SILANE-TREATED FIBERS.

PET short fiber content (wt %)	Dielectric Strength (KV/mm)	
	a	**b**
0	15.4	15.4
1	15.5	15.8
3	15.7	16.3
5	15.9	17.1
8	16.3	17.9
10	17.8	18.5
20	17.8	18.5

E. Rheological Properties

Fig.7 shows the viscosities behaviour of PP reinforced PET microfiber untreated composite at 230^0C. The shear viscosities of untreated PET microfiber wt% loading are found to be at lower range than virgin PP at low shear rates. It is also observed that as there is an increment in wt % loading of synthetic microfibers into the polymer matrix shear viscosities increased at low shear rates. At 20wt% loading of PET microfibers into the matrix, shear viscosities found to be higher as compared to lower wt% loading concentration of synthetic fibers in case of untreated composites.Fig.8 represents the viscosities behaviour of PP reinforced PET microfiber treated composite at 230^0C. The shear viscosities of treated PET microfiber wt% loading are found to be at higher range than virgin PP at low shear rates. Again it is observed that as there is an increment in wt % loading of synthetic microfibers into the polymer matrix shear viscosities increased at low shear rates. At 20wt% loading of PET microfibers into the matrix, shear viscosities found to be higher as compared to lower wt% loading concentration of PET fibers also as in case of treated composites. This increase in the viscosity suggests the possibility of improved adhesion between synthetic fibers and polymer matrix. Very high viscosity at low shear rates and relatively low viscosities at high shear rates clearly indicates that onset of non-Newtonian flow bahaviour of this composite system.

Storage Modulus (G′) Fig.9 a and b shows ω the dependence of G′ for PP/PET microfiber composites with and without silane treatment and virgin PP at 230^0C. The increase in G′ is mainly owing to stiffness imparted by the fibers that allows efficient stress transfer. Accordingly, the results indicated that the surface treatment of fibers improved the interaction between PP and fibers over untreated PP/PET microfiber composites.

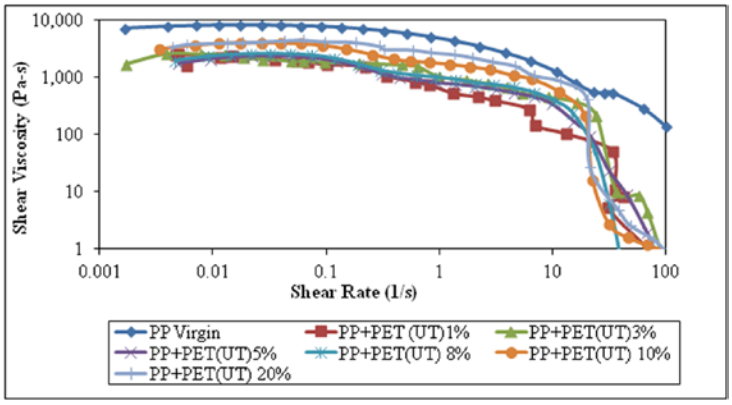


Fig.7 Shear viscosities of PP/PET microfiber (untreated) composites with wt% loading.

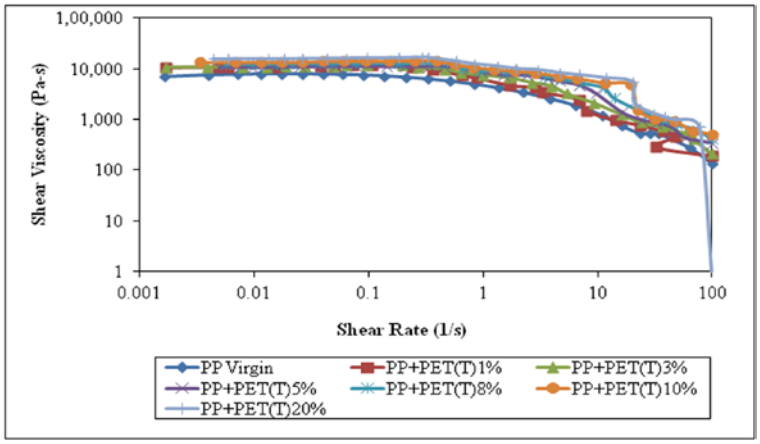


Fig.8 Shear viscosities of PP/PET microfiber (treated) composites with wt% loading.

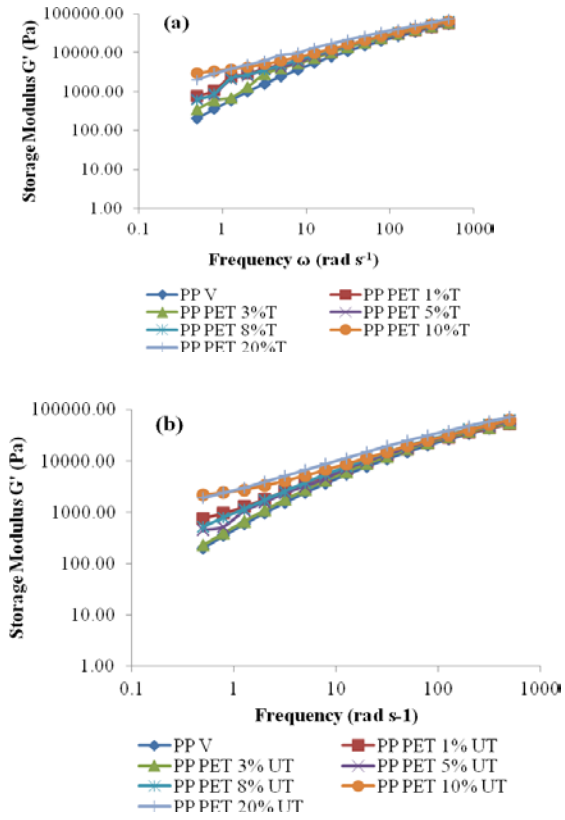
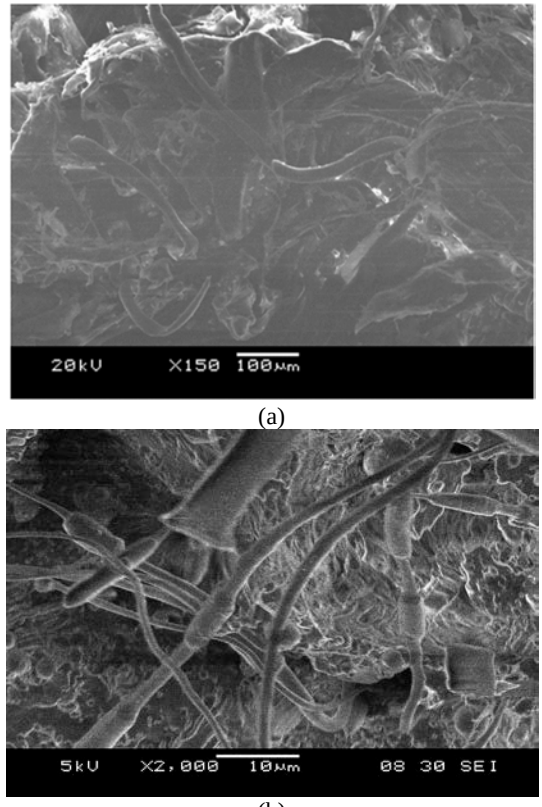


Fig.9 Relationship between storage modulus and frequency (ω) for matrix polymer and composites containing different wt% PET microfiber loading (a) VTMO treated (b) Untreated.

F. Microstructure Characterizations

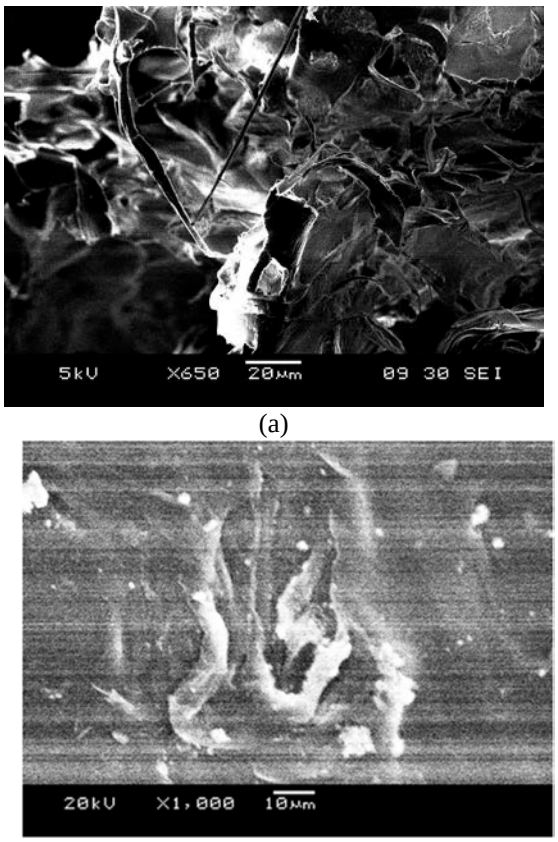
SEM micrographs were used to examine the morphologies of PP reinforced PET microfibers with VTMO silane treated and untreated. Fig. 10(a) shows the SEM micrographs of PP/PET microfiber at 10wt% composite with 0.5wt % concentration of silane coupling agent. It shows better dispersion of PET microfibers into the PP matrix. Fig. 10(b) shows the SEM micrographs of PP/PET microfiber at 10wt% composite without coupling agent. Debonding at the interface and subsequent fiber pullout are seen in the 20wt% fiber loading into the polymer matrix both in case of treated and untreated PET fibers as shown in Figure11 (a) and (b). As well as it can be seen that there is a formation of agglomeration of fibers into the PP matrix. This supports the decrement in the mechanical properties due to poor surface bonding.



(a)

(b)

Fig.10 SEM micrographs of Polypropylene (PP) composites with 10% PET microfiber content (a) VTMO treated (b) Untreated.



(a)

(b)

Fig.11 SEM micrographs of Polypropylene (PP) composites with 20% PET Microfiber content (a) VTMO treated (b) Untreated.

V. CONCLUSION

The surface treated PET microfibers filled PP composites shows better interfacial adhesion at 10wt% fiber concentration than untreated fiber composites. Through careful analysis of properties, the following conclusions can be drawn for PP-PET microfibers (treated and untreated).

a) Treatment with silane mainly results in increase of tensile, flexural, and dielectric strength of the composites.
b) The mechanical properties are enhanced when the content of silane treated fibers were at 10%.
c) An enhancement in tensile modulus, stiffness and flexural modulus were observed when fibers were treated with silane coupling agent.
d) Impact strength of the treated and untreated PP/PET microfiber composites reduced with increase in fiber content.
e) The percentage elongation at break of PP/PET microfiber composites is found to be decreased with an increase in wt% concentration of synthetic fibers into the matrix in both cases of treated and untreated composite
f) The change shear viscosity (η) and deflection angle (tanδ) of the composite and PP matrix, especially those for systems treated with silane, which was attributed to the interfacial adhesion enhancement.
g) In overall performance, treated synthetic microfibers in PP matrix outrate that of untreated PP/PET microfibers composite system.

REFERENCES

[1] ASM handbook, "Friction, lubrication and Wear Technology," *American Society for Metals*, Metals Park, Ohio, USA, vol. 18, 1992.

[2] Y. Yamaguchi, "*Tribology of Plastic Materials*," Tribology Series 16, Elsevier: New York, pp.143-155, 1990.

[3] T. Hobbs, and A.J. Lesser, "Preparation of high performance polyethylene terephthalate fibers: two stage drawing using high pressure CO_2," *Polymer*, vol.41, pp.6223-6230, 2000.

[4] J.A. Khan, M.A. Khan, R. Islam, and A. Gafur, "Mechanical, Thermal and Interfacial properties of jute fabric reinforced PP composites: Effect of potassium dichromate," *Material Science & Applications*, vol.1, pp.350-357, 2010.

[5] X. Luo, R.S. Benson, K.M. Kit, and M. M. Dever, "Kudzu fiber reinforced PP composites," *Journal of Applied Polymer Science*, vol.85, no.9, pp.1961-1966, 2002.

[6] P. Santos, and S.H. Pezzin, "Mechanical properties of PP reinforced with recycled PET fibers," *Journal of Material Processing Technology*, vol.143-144, pp.517-520, 2013.

[7] J.L. Thomason, and A.A. Rooyen, "Investigation of the transcrystallised interphases in fiber reinforced thermoplastic composites," *Journal of Material Science*, vol.27, no.5, 1992.

[8] D. Campbell, and M.M. Qayyum, "Melt crystallization of polypropylene: Effect of contact with fiber substrates," *Journal of Polymer Science Polymer Physics*, vol.18**,** pp.83-93, 1980.

[9] A.L. DiSalvo, "The thermal degradation of poly [ethylene methylene bis (4-phenyl carbamate)] by hexamethyldisilazine," *J Polym Sci Polym Lett*, vol.12, no.2, pp.65-67, 1974.

[10] A.M. Chatterjee, F.P. Price, and S. Newman, "Heterogeneous nucleation of crystallization of high polymers from the melt. I Substrate-induced morphologies," *Journal of Polymer Science Polymer Physics*, vol. 13, pp.2369-2383, 1975.

[11] A.M. Chatterjee, F.P. Price, and S. Newman, "Heterogeneous nucleation of crystallization of high polymers from the melt. II Aspects of transcrystallinity and nucleation density," *Journal of Polymer Science Polymer Physics*, vol.13, pp.2385-2390, 1975.

[12] A.M. Chatterjee, F.P. Price, and S. Newman, "Heterogeneous nucleation of crystallization of high polymers from the melt. III Nucleation kinetics and interfacial energies," *Journal of Polymer Science Polymer Physics*, vol. 13, pp.2391- 2400, 1975.

[13] C. Saujanya, and S. Radhakrishnan, "Development of a transcrystalline phase in poly (propylene) at the PET interface, *Macromolecular Material Engineering*, vol.286, pp.1-4, 2000.

[14] M. Asgari, and M. Masoomi, "Thermal and Impact study of PP/PET fiber composite compatibilized with Glycidyl Methacrylate and Maleic Anhydride," *Composites Part B: Engineering* vol.43, no.3, pp.1164-1170, 2012.

[15] X.D. Lin, and, W.L. Cheung, "Study on PET/PP microfibrillar composites: Morphological development in melt extrusion," *Journal of Applied Polymer Science*, vol.88, no.14, pp.3100-3109, 2003.

[16] M. A. Lopez, and M. Arroyo, "Optimization of composites based on PP/Elastomer blends and short PET fibers," *Rubber Chemistry and Technology*, vol.74, no2, pp.189-197. 2001,

[17] M. A. Lopez, and M. Arroyo, "Effect of incorporation of PET fibers on the properties of thermoplastic elastomer based on PP/elastomer blends," *Polymer*, vol.42, no.15, pp.6557-6563, 2001.

[18] F. Ke, X.W. Jiang, H. Xu,Y. Su, and J. Ji, "Ternary nano $CaCo_3$/Pet fiber/PP composites: Increased impact strength and reinforcing mechanism," *Composites Science and Technology*, vol.72,no**.**5,pp.574-579,2012.

[19] S. Fu, P. Wu, and Z. Han, "Tensile strength and rupture energy of hybrid poly (methylvinylsiloxane) composites reinforced with short PET fibers and Wollastonite whisker," *Composites Science and Technology* vol.62, no.1, pp.3-8, 2002.

[20] C. Saujanya, and S. Radhakrishnan, "Structure development and properties of PET fiber filled composites," *Polymer*, vol.42, no.10, pp. 4537-4548, 2001.

[21] M. John, C. Bellman, and R. Anandjiwala, "Kenaf-polypropylene composites: Effect of amphiphilic coupling agent on surface properties of fibers and composites," *Carbohydrate Polymers*, vol.82**,** no.3, pp.549-554, 2010.

[22] O. Asumani, R. Reid, and R. Paskaramoorthy, "Effect of alkali-silane treatment on the tensile and flexural properties of short fiber non-woven kenaf reinforced PP composites," *Composites Part A: Applied Science and Manufacturing*, vol.43**,** no.9, pp.1431-1440, 2012.

[23] N. Chand, and U. Dwivedi, "Effect of coupling agent on abrasive wear behaviour of chopped jute fiber reinforced PP composites," *Wear*, vol.26 pp.1057-1063, 2006.