Mechanical, Thermal and Morphological Behaviors of Castor Oil Based PU/PS Interpenetrating Polymer Network-Metakaolin Composites

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The meta kaolin (MK) clay particulate filler with different weight ratios viz., 0, 5, 10, 20 and 30 wt% were incorporated into castable polyurethane (PU)/polystyrene (PS) (90/10) interpenetrating polymer network (IPN). The effects of MK particulate filler loading on the mechanical and thermal properties of PU/PS (90/10) IPN composites have been studied. From the tensile behavior, it was noticed that a significant improvement in tensile strength and tensile modulus as an increase in MK filler content. Thermogravimetric analysis (TGA) data reveals the marginal improvement in thermal stability after incorporation of MK filler. TGA studies of the IPN composites have been performed in order to establish the thermal stability and their mode of thermal degradation. It was found that degradation of all composites takes place in two steps. Degradation kinetic parameters were obtained for the composites using three mathematical models. Tensile fractured composite specimens were used to analyze the morphology of the composites by scanning electron microscopic (SEM) technique.

Keywords: Meta kaolin, interpenetrating polymer network, polyurethane, mechanical properties, thermal behavior

1 Introduction

Interpenetrating polymer networks (IPNs), as a special sort of blend, refer to two or more than two kinds of polymer systems produced by interpenetration with each other, when at least one polymer is synthesized and/or crosslinked in the immediate presence of the other (1). IPNs have been made potential utilities as functional materials in many applied fields (2–3). Up to now, most reports on IPNs have focused on polyurethane (PU) based systems, the preparation methods, and the relationship between structure and property of the system formed. Many scientists reported on their applications (4–5).

PUs is a class of very useful and versatile material and widely used for various applications such as electrical/electronic potting and encapsulation, construction, water proofing membranes, asphalt extended membranes, highway sealants, sound and vibration damping, automotive and rubber parts etc., due to its unique property i.e., it offers the elasticity of rubber combined with the toughness and durability of metals (6–9). The physical properties of PUs are derived from their molecular structure,

as well as the supramolecular structure caused by interaction between the polymer chains. The segmental flexibility, the chain entanglement, the interchain forces, and the crosslinking are all factors that influence the properties and determine the use of the end products. The properties of the PUs can be adjusted mainly by two routes. The first route is based on the chemistry of PUs, formulating the PU based on different isocyanate/polyol ratio and using different amounts of chain extender. The second route is altering the properties of the PUs with different fillers and reinforcements (10). PUs have been reinforced with certain fillers such as talc, mica and glass fiber in the form of polymer matrix composite material (10). These fillers enhance the tensile strength but reduce the elongation at break and discolour the polymer (11).

The effect of thermal and mechanical properties of filled PU rubber has been studied by Salih Benli et al. (12). Wen Yen Chiu et al. have reported the effect of sodium chloride filler on thermal ageing and hygroscopic ageing of PU (13). Kendaganna Swamy and Siddaramaiah established the structure-property relationship of starch filled chain extended PUs (14). Many researchers have extensively studied on chain extended PUs and its IPN (15–18), but little attention has been paid to the filled IPNs. To overcome the disadvantages of PU such as low thermal stability and low mechanical strength, a great deal of effort has been devoted to the development of nanostructured PU and clay

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composites in recent years (19–20). However, reports on the preparation and properties of particulate filler filled with inorganic powders or fibers with IPNs are relatively few.

Kaolin is probably more widely known as the clay mineral, china clay. It is found in hydrothermal, residual and sedimentary deposits around the world. The kaolins are widely used in the refractory, rubber, paint, plastic, chemical, pharmaceutical and ceramic industries.

Thermogravimetric analysis (TGA) has proved to be a suitable method to investigate the thermal stability of polymeric systems (21). Thermal degradation and mode of decomposition under the influence of heat is highly recommended for the optimization of process. The threshold decomposition temperature gives an indication of the highest processing temperature that can be adopted, whereas the study of the kinetics of the different thermal degradation processes helps to probe the degradation mechanisms.

Many researchers have characterized the PU composites using TGA techniques to know the thermal stability and kinetics of thermal degradation (22). Agi et al. (23) estimated the kinetic parameters for thermal degradation of PU elastomers based on poly (ether polyol) soft segment and aromatic-type diisocyanates. The kinetic parameters studied by Mothe et al. (24) for PU/bagasse composites revealed that the incorporation of 5% by weight of bagasse increased the activation energy of the PU composites. Satheesh and Siddaramaiah (25) studied the thermal degradation of castor oil based PU–polyester nonwoven fabric composites using TGA. By reinforcing the polyester nonwoven fabric into PU matrix, a slight improvement in the thermal stability of the composites was noticed.

The objective of the present research article is to study the effect of MK filler content on the mechanical, thermal and morphological behaviours of PU/PS (90/10) IPN composites.

2 Experimental

2.1 Materials

Castor oil was obtained from S.D. Fine Chemicals Ltd., and it was dried overnight at 90°C before use. Toluene diisocyanate (TDI), styrene (monomer), benzoyl peroxide (initiator) and dibutyl tin dilaurate (DBTL) (catalyst) supplied by Fluka were used as received. Methyl ethyl ketone (MEK) AR grade was used after distillation. Meta kaolin (MK) was obtained from Speciality Minerals, Baroda, India. It was dried at 80°C for 8 h before mixing with PU/PS IPN.

2.2 Fabrication of IPN Composites

Castor oil (0.001 mole) was initially dissolved in 50 ml of MEK and placed in a three-necked reaction flask. Toluene

diisocyanate (0.0015 mol) was added followed by 2–3 drops of DBTL catalyst and the contents of the flask were stirred mechanically for about 30 min under oxygen-free nitrogen gas purge at 60–70°C to prepare pre-PU polymer. The calculated amount of styrene monomer and benzoyl peroxide (0.5 wt %) were added to the pre-PU and stirred again for 1 h at 60–70°C. Then, a calculated amount of MK was added and stirred for about 5 min. The solution was degassed under vacuum and poured into a releasing agent coated, cleaned glass mold. The mold was kept in preheated circulating hot air oven at 70°C for 8–10 h. The MK filled PU/PS (90/10) sheet thus formed, was cooled slowly and removed from the mold. The above procedure was repeated to obtain IPN composites with varying amounts of MK particulate filler content.

2.3 Techniques

2.3.1. *Mechanical Properties*

The prepared PU/PS/MK composites were characterized for surface hardness according to the ASTM D 2240 method. The mechanical properties such as tensile strength, percentage elongation at break and tensile modulus have been performed as per the ASTM D 638 method using a 4302 model Houns Field universal testing machine (UTM), UK. A minimum of six samples were tested at room temperature for each formulation and the average values are reported.

2.3.2. *Thermogravimetric Analysis (TGA)*

Thermogravimetric Analysis (TGA) has been carried out on a Universal V4.3A, TA Instrument, under nitrogen atmosphere at a heating rate of 20°C/min in the temperature range of 30–800°C. About 6–8 mg of the sample was used for analysis under a continuous nitrogen gas flow of 200 mL/min. The oxidation index (OI) was calculated based on the weight of carbonaceous char (CR) as related by the empirical equation:

$$OI \times 100 = 17.5 \times 0.4 \, CR \qquad (1)$$

The thermal degradation kinetic parameters were determined for MK loaded PU/PS IPN composites using Broido (BR) (26), Coats and Redfern (CR) (27), and Horowitz and Metzger (HM) (28) methods which provide overall kinetic data. For the sake of calculations and to know the nature of the decomposition, the complete thermogram was divided into distinct sections according to their degradation processes. The activation energy for the thermal degradation process was evaluated using the Broido equation:

$$\ln[-\ln(1 - \alpha)] = -(E_a/RT) + const \qquad (2)$$

where, α is the $(w_o\text{-}w_t)/(w_o\text{-}w_\infty)$ in which w_o, w_t, and w_∞ are the weights of the sample before degradation, at time t

and after total conversion, respectively. R is gas constant, T is the temperature (in K), and E_a is the energy of activation, can be obtained from the plot of $\ln[-\ln(1-\alpha)]$ vs. $1/T$. Coats–Redfern (CR) equation is as follows:

$$\ln[-\ln(1-\alpha)]/T^2] = \log ZR/\beta E(1-2RT/E) - E/RT \quad (3)$$

where, Z is the frequency factor, β is the heating rate and E_a is the activation energy. A plot of $\ln[-\ln(1-\alpha)]/T^2]$ vs. $1/T$ should give a straight line whose slope is E_a/R. Horowitz-Metzger (HM) suggested the following equation to calculate energy of activation:

$$\ln[-\ln(1-\alpha)] = E_a\theta/RT_m \quad (4)$$

where, θ is the variable auxiliary temperature defined as $\theta = T - T_m$ in which T_m is the temperature of maximum degradation. Plot of $\ln[-\ln(1-\alpha)]$ vs. θ should give a straight line whose slope is E_a/RT_m.

2.3.3. *Scanning Electron Microscopy*

Morphological studies were performed by using scanning electron microscopy (SEM). The samples were dipped in liquid nitrogen for a few minutes and cryo-fractured. The cryo-fractured samples were mounted on the periphery of an aluminum stub (1.5 inch diameter) using a double-sided copper tape, so that the cross-sections could be imaged. This stub was sputter-coated with gold (300 nm thickness). Imaging was done on an FEI-Quanta 400 ESEM, at appropriate magnifications.

3 Results and Discussion

3.1 Mechanical Performance

The measured tensile behaviors of unfilled and MK filled PU/PS (90/10) IPN composites are given in Table 1. The plot of stress vs. strain curves for all PU/PS/MK composites are shown in Figure 1. From the figure, it was noticed that the unfilled system has very low tensile properties as compared to MK filled PU/PS composites. From the stress–strain curves, the properties such as tensile strength, percentage elongation at break and tensile modulus have been calculated and the values are given in Table 1. The tensile strength of unfilled PU/PS is 5.0 MPa. The tensile strength of the composites increases from 5.4 to 16.8 MPa with an increase in MK filler content from 5 to 30%. The strength of the IPN/MK was increased by 236% as compared to neat IPN. This result indicates that the mechanical properties of composites were improved with an increase in MK filler content. The increase in the tensile strength was significant which strengthens the hypothesis that there is a good physical interaction between IPN and MK because both are hydrophilic in nature. Percentage elongation at break of unfilled PU/PS IPN is 26, but as the MK

Table 1. Mechanical properties of MK filled PU/PS (90/10) IPN composites

Properties	Composites (IPN/MK)				
	100/0	95/5	90/10	80/20	70/30
Tensile strength (MPa)	5.0	5.4	9.3	15.4	16.8
Tensile modulus (MPa)	0.08	0.09	0.12	0.31	0.32
Elongation at break (%)	27	71	150	133	141
Surface hardness (Shore A)	62	68	74	77	82

content increases, the percentage elongation at break also increases. Both the tensile strength and elongation at break of IPN/MK are improved to a certain degree with the addition of the fillers. It may be due to the fact that the particulate filler has a large specific surface area hence, MK has a large interface with PU/PS. A similar type of observation is reported for guar gum filled PU and polyacrylonitrile IPNs (29). As we pointed out, the interfacial interaction could be improved greatly with the good surface adhesion of IPN onto MK. When a load is imposed on the IPN, it will be effectively transmitted to the MK particles nearby, and then to the matrix around the particles even the rupture of some of the chains would not endanger the whole system. In this way, the load can be dissipated quickly and effectively, furthermore both the strength and toughness of IPN/MK enhanced.

The tensile modulus of PU/PS IPN is 0.08 MPa and after incorporation of MK filler, a drastic improvement in the modulus of the composites was noticed. The addition of 30 wt% MK filler in PU/PS matrix enhances the modulus value by more than 300%. This is because the matrix transfers load and stress onto the MK filler. This leads to effective and uniform stress distribution. Hence,
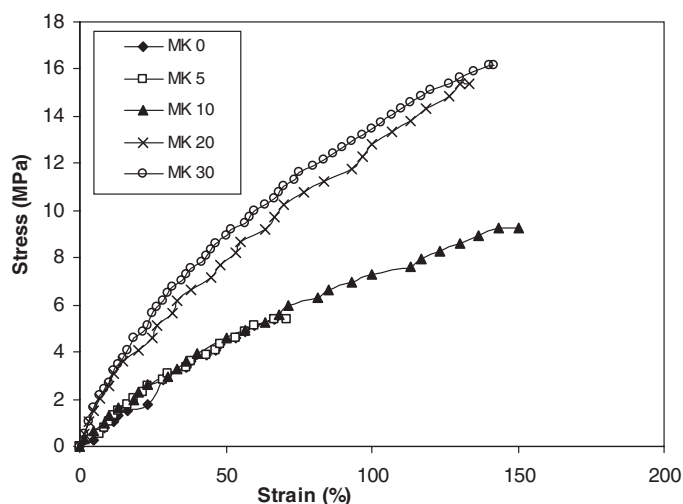

Fig. 1. The plot of stress vs. strain curves for PU/PS/MK composites.

the composites showed a significant improvement in the mechanical performance (29–30). The probable reinforcing mechanisms may also be due to the formation of hydrogen bond between the hydroxyl impurities present in the filler with the urethane group of PU. These results clearly indicate a good physical interaction between IPN and filler. Similar observations are made by several researchers (31–33). In the earlier studies conducted on PUs and cellulose based fibers, all of them reported about the mechanical reinforcement (31–32). Rials and Wolcott (33) have investigated the composites by dynamic mechanical analyzer (DMA) and they reported the improvement in mechanical properties after incorporating wood fiber into PU matrix. Auad et al. (31) reported improved mechanical properties with the cellulose whiskers in PU matrix. In this study, the MK filler is acting as reinforcing filler.
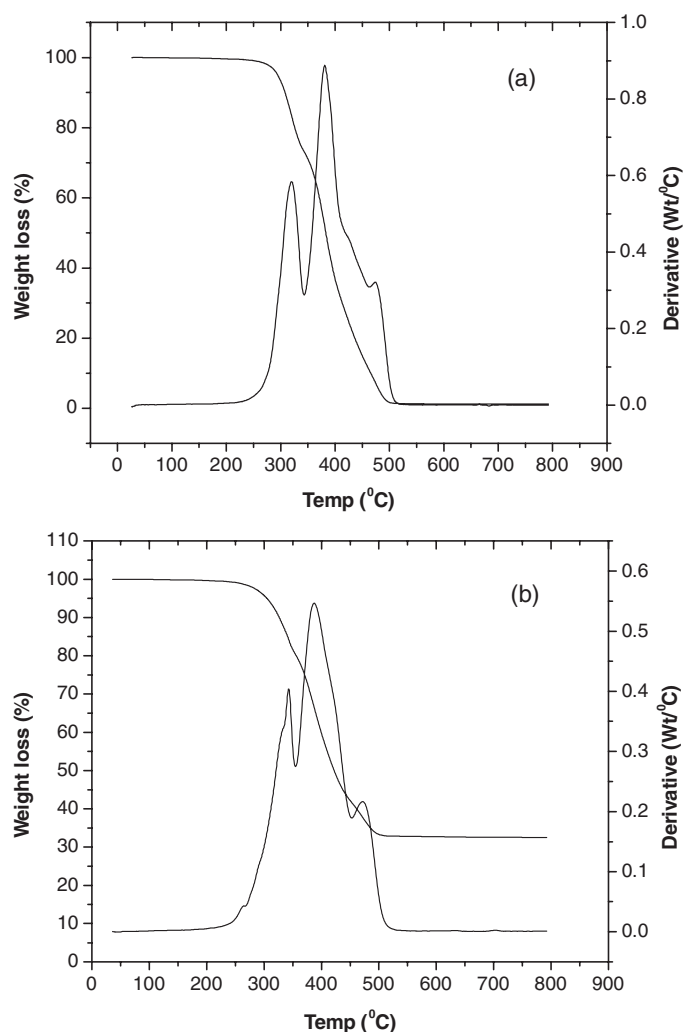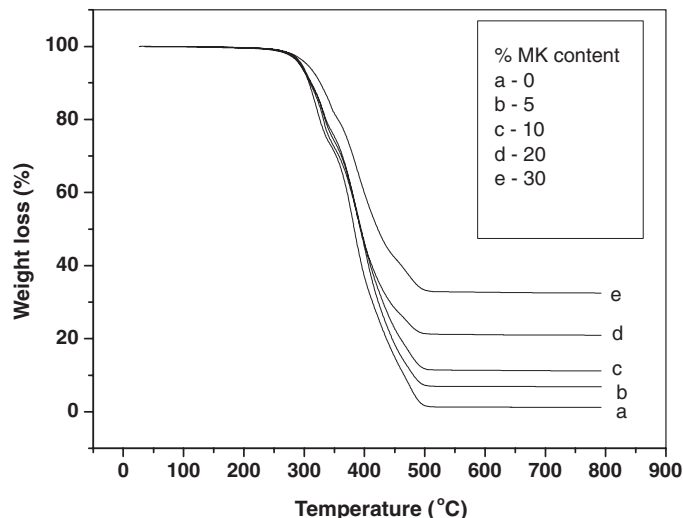

Fig. 3. TGA thermograms for all PU/PS/MK composites.

3.2 Thermogravimetric Analysis

The TGA thermograms of unfilled and MK filled (30%) PU/PS composites are shown in Figures 2 (a–b), respectively along with derivative thermograms. TGA thermograms of all IPN/MK composites are shown in Figure 3. The different stages of thermal degradation were analyzed from the TGA thermograms and are given in Table 2. TGA thermograms of composites indicate two stage thermal degradation processes. The first stage thermal degradation occurred in the temperature range 255–356°C with the weight loss of 27.5% for unfilled and 20.2% weight loss for 30% MK filled PU/PS composite. The weight loss in

Fig. 2. TGA and derivative thermograms for PU/PS IPN composites with (a) 0% and (b) 30% MK content.

Table 2. Thermal data obtained from TGA thermograms for MK filled PU/PS composites

Sample composition IPN/MK (wt/wt %)	Degradation stages	Temperature (°C) ± 2			Weight loss (%)
		T_i	T_{max}	T_f	
100/0	1	255	318	345	27.6
	2	345	380	511	71.2
	Ash	—	—	—	1.2
95/5	1	231	331	351	27.9
	2	351	402	511	65.3
	Ash	—	—	—	6.8
90/10	1	251	331	351	26.2
	2	351	391	512	62.6
	Ash	—	—	—	11.2
80/20	1	236	331	348	24.2
	2	348	383	513	54.8
	Ash	—	—	—	21.0
70/30	1	288	342	356	20.2
	2	356	388	519	47.4
	Ash	—	—	—	32.4

Table 3. Transition temperature data obtained from TGA curves for PU/PS/MK composites

Sample composition IPN/MK (wt/wt %)	Temperature at different weight loss (°C) ± 2						
	T_i	T_{10}	T_{20}	T_{30}	T_{50}	T_c	OI
100/0	251	308	325	353	383	511	0.082
95/5	231	309	331	357	393	511	0.473
90/10	251	311	334	361	394	512	0.780
80/20	236	310	336	363	393	513	1.456
70/30	288	326	356	380	422	519	2.259

the first step was due to the soft segment of PU and volatile impurities and main pyrolysis product could be carbon dioxide (34). The second stage thermal degradation of IPN occurred in the temperature range 345–511°C with the major weight loss of 71.2%. This could be due to de-cross linking of IPN composites. In this step, weight loss may be due to liberation of HCN, nitriles of aromatics, carbon dioxide and ethers (34, 35).

The effect of MK filler on thermal stability of all PU/PS composites is shown in Figure 3. From the figure, it can be clearly observed that the weight loss markedly decreases with an increase in MK content. The ash content increases with an increase in MK content. Ash content of MK filled PU/PS composites lies in the range 6.8–32.4% (Table 3), which is slightly higher than the MK filler loaded theoretically. These values lie in the expected line.

Some characteristics TGA data related to the temperature corresponding to weight loss of 10% (T_{10}), 20% (T_{20}), 30% (T_{30}), 50% (T_{50}), complete degradation (T_c), as well as oxidation index (OI) are tabulated in Table 3. The higher the values of T_{10}, T_{20}, T_{30}, T_{50} and T_c, the higher the thermal stability of the composites (36). From the table, it was

observed that, these values increase with an increase in MK content. This result indicates significant improvement in the thermal stability of the IPN after incorporation of a MK filler. The marked improvement in thermal stability of the composites may be due to the incorporation of highly thermal stable inorganic MK filler into the IPN matrix. The higher the values of oxidation index, the higher the thermal stability (36). From the table, it is observed that the oxidation index increases with an increase in MK content which reveals that the MK filled IPN composites are more thermally stable than that of unfilled PU/PS IPNs.

3.3 Kinetic Analysis of Thermal Degradation Process of Composites

The plots of $\ln[-\ln(1-\alpha)]$ vs. $1/T$ (BR), $\ln[-\ln(1-\alpha)]$ vs. θ (HM) and $\ln[-\ln(1-\alpha)]/T^2$ vs. $1/T$ (CR) for the first stage degradation process of MK filled PU/PS IPN composites are shown in Figures 4 (a–c), respectively. Regression analysis was carried out for all the plots. The mechanism of R^2 close to unity was chosen. The regression analysis gives the results of slopes, constants and R^2 values corresponding to thermal degradation for the selected temperature range. The R^2 values and calculated activation energy (E_a) for each thermal degradation process and for each method are given in Table 4. BR and CR methods have shown almost identical values of E_a. The values of E_a are less for the HM method compared to the other two methods, which supports the data presented by other authors (37). To understand the mechanism of thermal degradation, the variation in activation energy as a function of weight percent of MK content in IPNs for different steps are shown in Figure 5. From the figure, it can be noticed that there is a slight reduction in activation energy after the incorporation of MK filler. The lowest E_a values were observed for

Table 4. Activation energies calculated by Horowitz-Metzger (HM), Coats-Redfern (CR) and Broido (BR) methods with the respective concurrency value (R^2) for MK filled PU/PS IPN composites

| Composition (PU/PS)/MK	Degradation stage	Activation energy (E_a) (kJ/mol)					
		HW	R^2	CR	R^2	BR	R^2
100/0	I	76	0.9996	158	0.9995	167	0.9996
	II	108	0.9934	232	0.9944	242	0.9949
95/5	I	62	0.9958	124	0.9974	134	0.9978
	II	106	0.9745	215	0.9762	226	0.9785
90/10	I	59	0.9719	117	0.9738	127	0.9778
	II	126	0.9833	262	0.9847	272	0.9859
80/20	I	58	0.9996	116	0.9994	125	0.9950
	II	104	0.9750	222	0.9773	233	0.9794
70/30	I	55	0.9977	106	0.9936	116	0.9945
	II	79	0.9582	172	0.9606	183	0.9653
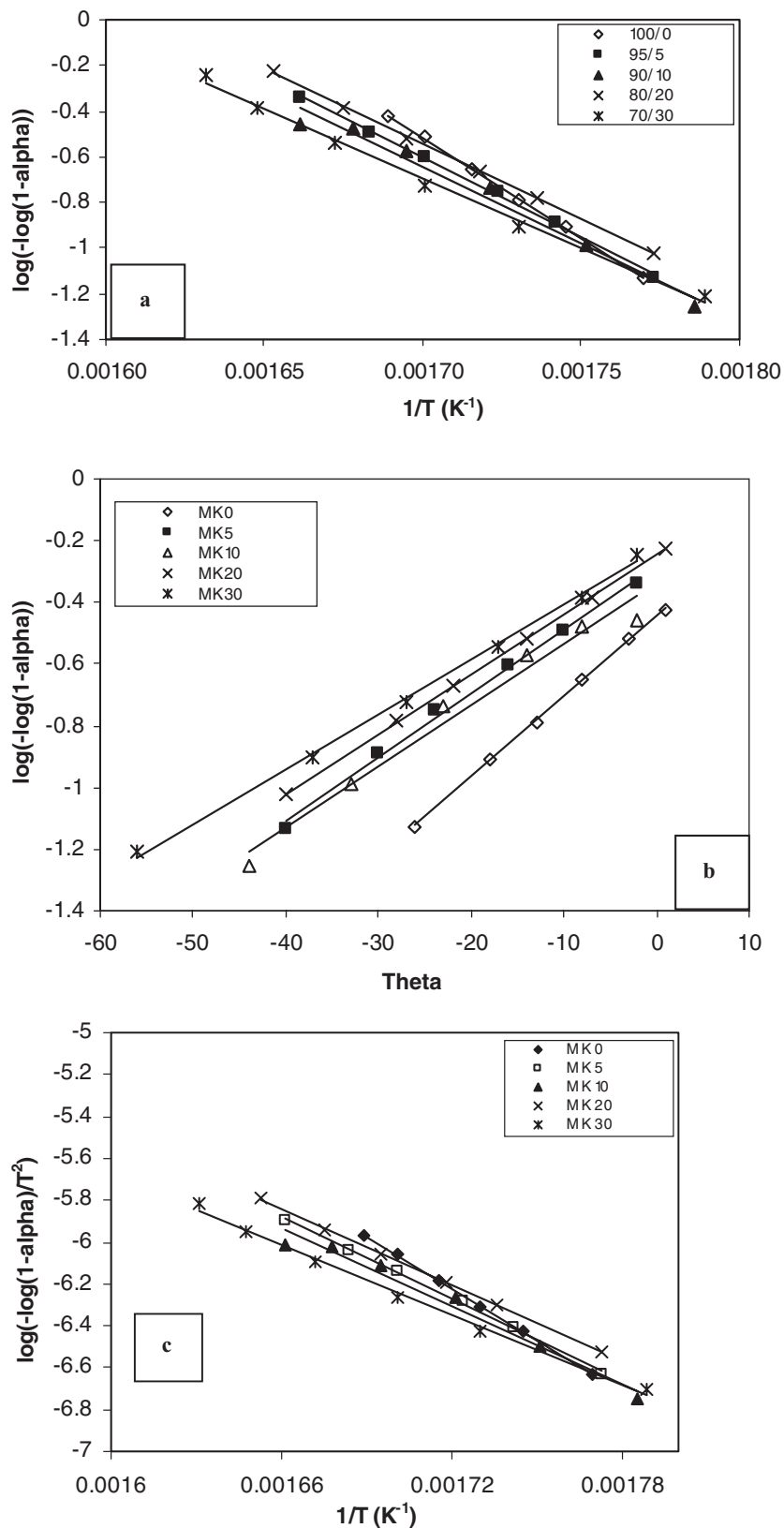
Fig. 4. Typical (a) Broido, (b) Horowitz–Metzger and (c) Coats-Redfern plots for the determination of activation energies for first step weight loss for MK filled IPN composites.
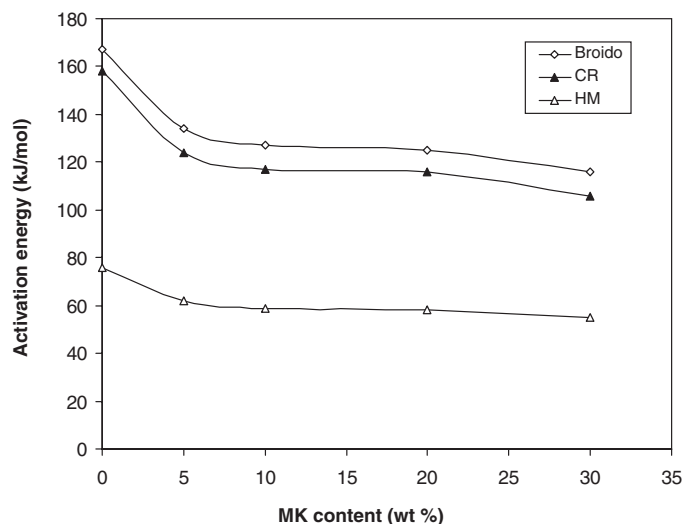
Fig. 5. Effect of MK content on activation energy of the IPN composites.

the first step thermal degradation process as compared to final step degradation for all the methods. This is due to the lower energy required to remove volatile components and low molecular weight materials present in IPN composites. Higher E_a values were observed for the second step degradation process, because higher energies are required for bond scission and zipping of IPN chains.

3.4 Morphological Behavior

The properties of MK filled IPNs are strongly influenced by the morphology. The state of dispersion of MK particles in IPN matrix was analyzed using SEM. The SEM photomicrographs of fractured surfaces of unfilled and 30 wt% MK filled PU/PS IPNs is shown in Figures 6 (a) and (b),

respectively. From the SEM photomicrographs of unfilled PU/PS (Fig. 6(a)), it is clear that, the surface is smooth and homogeneous. From the photomicrograph (Fig. 6(b)), it was also noticed that the minor phase (MK) is dispersed in the major continuous PU/PS phase. The white areas reflect MK and the gray areas indicate PU/PS IPN matrix. The figures indicate the finer dispersion of MK in the PU/PS matrix. From SEM photomicrographs, it was concluded that all systems showed two phase morphology and uniform distribution of MK in PU/PS matrix.

4 Conclusions

From the aforesaid study, a significant improvement of mechanical properties such as surface hardness, tensile strength, percentage elongation at break and tensile modulus after incorporation of MK filler into PU/PS (90/10) IPN was noticed. Both the tensile strength and elongation at break of IPN/MK are improved to a certain degree with the addition of the fillers. The increase in the tensile strength was significant, which strengthens the hypothesis that IPN and MK have good interaction due to the hydrophilic nature of both components. The imposed load on IPN can be dissipated quickly and effectively on MK filler and by enhancing both the strength and toughness of the composites. TGA data reveals marginal improvement in thermal stability after incorporation of MK filler. Kinetic studies reveal that the activation energy calculated by the Horowitz-Metzger and Broido methods are comparable, whereas, the Coats-Redfern method gave relatively lower value. Lowest activation energy values were observed for all the IPN composites for the first-step thermal degradation process as compared to second step degradation process. This may be due to the fact that less energy is sufficient to remove the low molecular weight impurities.
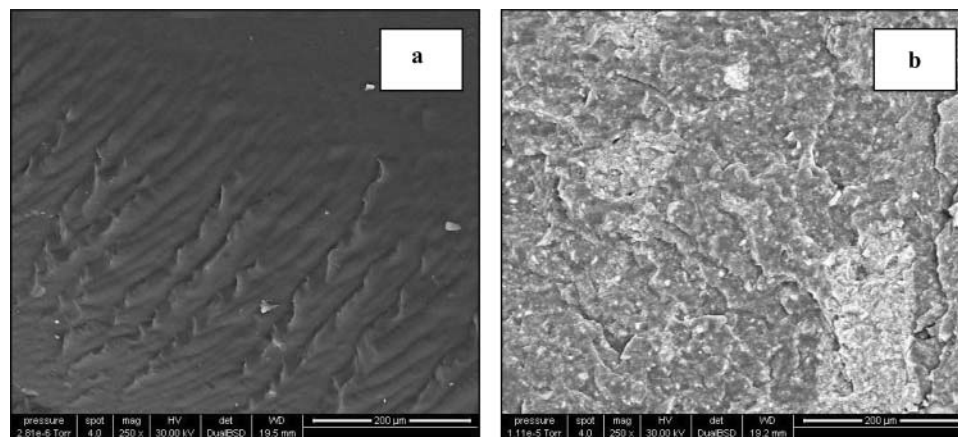

Fig. 6. SEM micrographs of (a) unfilled and (b) 30% MK filled PU/PS IPN composites.

References

1. Das, S.K. and Lenka Y.S. (2000) *J. Appl. Polym. Sci.,* 75, 1487.
2. Chakrabarty, D., Das, B. and Roy, S. (1998) *J. Appl. Polym. Sci.*, 67, 1051.
3. Jo, W.H., Jun-Myoung Song and Ko, M.B. (2000) *J. Appl. Polym. Sci.*, 38, 1005.
4. Zhang, Y., Heath, R.J. and Hourston, D.J. (2000) *J. Appl. Polym. Sci.*, 75, 406.
5. Tang, D., Qin, C., Cai, W. and Zhao, L. (2003) *Materials Chem. and Phys.*, 82, 73–77.
6. Kim, S.C. and Spherling, L.H. IPNs Around the World: Science and Engg., John Wiley & Sons: NY., 75–102/155–202,1997.
7. Krol, P. (2007) *Progress in Materials Scienc*e 52, 91–1015.
8. Klempner, D. and Frisch, K.C. Advances in Interpenetrating Polymer Networks, Technomic Pub. Co.: Lancaster, PA, 4, 109–140/243–286, 1994.
9. Njuguna, J. and Pielichowski, K. (2004) *J. Matl. Sci.*, 39, 4081–4094.
10. Zhang, X., Xu, R., Wu, Z. and Zhou, C. (2003) *Polym. In*t., 52(5), 790–4.
11. Sternitzke, M., Derby, B. and Brook, R.J. (1998) *J. Am. Ceram. So*c., 81(1), 4–48
12. Benli, S., Yelzimer, U., Pekel, F. and Ozkar, S. (1998) *J. Appl. Polym. Sci.*, 1057.
13. Chin, W.Y., Ding, D.K. and Chen, C-C. (2003) *J. Appl. Polym. Sci.*, 43, 2175 –2185.
14. Kendaganna Swamy, B.K. and Siddaramaiah (2003) *J. Appl. Polym. Sci.*, 90(11), 2945–2954.
15. Alekseeva, T.T., Lipatov, Y.S., Babkina, N.V., Grishchuk, S.I. and Yarovaya, N.V. (2005) *Polymer*, 46, 419–428.
16. Basak, P., Manorama, S.V., Singh, R.K. and Prakash, O. (2005) *J. Phys. Chem. B*, 109, 1174–1182.
17. Sco, J.W. and Kim, B.K. (2005) *Polym. Bulletin*, 54, 123–128.
18. Mark, J., Jean, C. and Widmaier, M. (2005) *Polymer*, 46, 671–675.
19. Chang, J.H. and An, Y.U. (2002) *J. Polym. Sci. Part B, Polym. Phys.,* 40(7), 670
20. Tien, Y.I. and Wei, K.H. (2001) Macromolecules 34(26), 9045
21. Hatkeyama, T. and Quinn, F.X. Thermal Analysis, Fundamentals and Applications to Polymer Science, Wiley: Cichester, 1994.
22. Suhara, F., Kutty, S.K.N. and Nando, G.B. (1997) *Polym. Plast. Tech. Eng.*, 36, 399.
23. Agi, A., Govor, E. and Rek, V. (2006) *J. Elastomers Plast.*, 32, 105.
24. Mothe, C.G., de Araujo, C.R., de Oliveira, M.A. and Yoshida, M.I. (2006) *J. Thermal Anal. Calorim.*, 67, 305.
25. Satheesh Kumar, M.N. and Siddaramaiah (2007) *J. Appl. Polym. Sci.*, 106, 3521–3528.
26. Broido, A. (1969) *J. Polym. Sci. Part A*, 27, 1761.
27. Coats, A.W. and Redfern, J.P. (1964) *Nature*, 68, 201.
28. Horowitz, H.H. and Metzger, G. (1963) *Fuel*, 42, 418.
29. Kumar, H., Radha, J.C., Ranganathaiah, C. and Siddaramaiah (2007) *Eur. Polym. J.*, 43, 1580–1587
30. Jacob, M., Thomas, S. and Vergheese, K.T. (2004) *Comp. Sci. Tech.*, 64, 955.
31. Auad, M.L., Contos, V.S., Nutt S Aranguren, M.I. and Marcovich, N.E. (2005) Intl. Conf. on Sci. & Tech. of Composite Materials: Argentina, p. 3–36
32. Samir Masa Alloin, F., Sanchez, J.Y. and Dufresne, A. (2004) *Polyme*r, 45(12), 4149–4157
33. Rials, T.G. and Wolcott, M.P. (1998) *J. Mater. Sci. Let.*, 17 (4), 317–319.
34. Herrera, M., Matuschek, G. and Kettrup, A., (2003) *Polym. Degrad. & Stability*, 78, 323.
35. Chambers, J., Jircny, J. and Reese, C. (1981) *Fire Mater.*, 5, 133.
36. Jeevananda T. and Siddaramaiah (2001) *Thermochemica Acta*, 51, 376.
37. Gabriela, L., Avram, E., Paduraru, G., Irimia, M., Hurduc, N. and Aelenei, N. (2003) *Polym. Deg. Stab.*, 82, 73.