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Thermal Degradation Kinetics of Polyurethane/Organically Modified Montmorillonite Clay Nanocomposites by TGA

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Polyurethane (PU) has been prepared by using polyether polyol (jagropol oil) and 1,6-hexamethylene diisocyanate (HMDI) as a cross-linker. The organically modified montmorillonite clay (MMT) is well-dispersed into urethane matrix by an *in situ* polymerization method. A series of PU/MMT nanocomposites have been prepared by incorporating varying amounts of nanoclay viz., 1, 3, 5 and 6 wt %. Thermogravimetric analysis (TGA) of the PU/MMT nanocomposites has been performed in order to establish the thermal stability and their mode of thermal degradation. The TGA thermograms exhibited the fact that nanocomposites have a higher decomposition temperature in comparison with the pristine PU. It was found that the thermal degradation of all PU nanocomposites takes place in three steps. All the nanocomposites were stable up to 205°C. Degradation kinetic parameters of the composites have been calculated for each step of the thermal degradation processes using three mathematical models namely, Horowitz–Metzger, Coats–Redfern and Broido's methods.

Keywords: Polyurethane, nanoclay, composites, thermo gravimetric analysis, thermal degradation behavior, kinetic parameters

1 Introduction

Polyurethane (PU) elastomers are derived from isocyanates and chain extenders (1). The hard segments form crystalline phase which serves at high temperature applications and offer stiffness to the resultant materials. Soft segments are amorphous and control low temperature properties. PU represents one of the most attractive polymers because they have the advantage, such as the best abrasion resistance, outstanding oil resistance and excellent low temperature flexibility. They also exhibit the widest variety of hardness and elastic moduli that just fill in the gap between plastics and rubbers.

The advent of polymer nanotechnology can be capitalized under these circumstances to obtain a variety of properties from the same set of organic raw materials through introduction of nanoscale particulate fillers, such as layered silicates. Carbon nanotubes (CNTs) and nanofibers, often hold the possibility of polymer chain-nanoparticle

interactions. The type of nanofillers and their state and degree of dispersion can be manipulated to obtain an array of properties so far not achievable from PUs or PUs filled with micrometer size inorganic filler particles (2, 3). Incidentally, small quantities of nanofillers, in the range 3–5 wt %, prove to be sufficient to reveal enormous enhancement in properties, thereby, reducing the cost and causing a drop in the weight of finished components in comparison to conventional microcomposites of silica or talc. The results reported to date on polymer nanocomposites, including PU nanocomposites, highlight dramatic increases in tensile modulus, often accompanied by increased tensile strength and reduced elongation at fracture. Wang and Pinnavaia (2) showed increased enhancement in tensile strength and modulus in intercalated composites of organically treated nanoclay in PUs. Subsequent studies (3, 4) on PU–nanoclay composites reported enhancement in tensile strength, modulus, and elongation at break except for one study (4), whereas a reduction in tensile modulus was noticed. Preparation, characterization and properties of PU/clay nanocomposites have been reported by many researchers (5–9).

The versatility of montmorillonite (MMT) based inorganic–organic hybrids offers polymers with improved properties such as durability, barrier properties (10), mechanical strength (11), stiffness and fatigue life (12), resistance towards the thermal (8, 13) and chemical stress (14);

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reduced flammability (15), improved corrosion resistance, gloss and color retention, as well as improved adhesive strength (16).

Many researchers have characterized the PU composites using thermogravimetric analyzer (TGA) techniques to be familiar with the thermal stability and kinetics of thermal degradation (17–19). Thermal decomposition and combustion reactions of polyether-PU and polyester-PU in air and nitrogen atmospheres investigated by Shufen et al. (20). Rein et al. reported the application of TGA to determine the kinetics of PU (21). Kuttu and coworkers (22) studied the thermal degradation of short kevlar fiber reinforced thermoplastic polyurethane (TPU) composites using TGA. They noticed that the incorporation of kevlar fiber enhanced the thermal stability of the TPU-kevlar composites.

The present research article deals with the thermal degradation kinetics of PU/organo clay (MMT) nanocomposites. Degradation kinetic parameters such as energy of activation (E_a) for different steps were calculated for the nanocomposites using three mathematical models namely; Horowitz–Metzger (HM) (23), Coats–Redfern (CR) (24) and Broido's (BR) (25) methods and the results are compared.

2 Experimental

2.1 Materials

The jagropol oil (Jagropol-115) (polyol) used in this study was supplied by Jayanth Agro-Organics Ltd., Mumbai. 1,6-hexamethylene diisocyanate (HMDI) was obtained from Sigma, Bangalore. Dibutyl tindilaurate (DBTL) ($C_{32}H_{64}O_4Sn$), trade name DABCO T120, Aldrich, USA was used as a catalyst to expedite the chain extension reactions. Organically modified montmorillonite (Nanomer I.31PS) was obtained from Sigma, Bangalore. It is a surface modified MMT clay: (Na)-modifiers-gamma-aminopropyl triethoxysilane, octadecylamine – (CEC ~145 meq/100 g), i.e., referred as MMT. All other chemicals used in this study are AR grades.

2.2 Preparation of PU/MMT Nanocomposite

The synthesis of new organic–inorganic nanocomposite materials was achieved by the intercalation of PU onto organically modified MMT through an *in situ* polycondensation polymerization technique. Jagropol oil (0.001 mol) was initially dissolved in 50 ml of methyl ethyl ketone (MEK) and placed in a three-necked round bottomed flask. PU nanocomposites were prepared by solvation of the organo-clay (MMT) with the jagropol oil. The calculated amount of modified clay was swelled easily in the polyol at room temperature. The content was stirred for 10–20 min or until the uniform mixture was obtained. This solvation was followed by adding the HMDI ((0.002 mol) and 2 to 3

drops of DBTL as catalyst. The reaction mixture of the flask was stirred continuously for about 1 h under oxygen free nitrogen gas purge at 60–70°C. The nanocomposites were synthesized through the intercalation of polyols into organo-clay interlayers followed by the addition of HMDI to produce the intercalated PUs. The reaction mixture was poured into a cleaned and releasing agent coated glass mold and allowed to stand for 12 h at room temperature. Then the mold was kept in a preheated circulating hot air oven at 70°C for 8–10 h. The toughened CEPU composite sheet thus formed was cooled slowly and removed from the mold. The above procedure was repeated for different weight percent of MMT contents, viz., 0, 1, 3, 5 and 6%. The yields of the products ranged from 75% to 95%. It was found that the percentage of yield in the nanocomposites is higher than the yield percentage of linear PU, which may be attributed to a catalytic effect of the clay (26). The different ratios of organo-clay used during the polymerization do not appear as an important factor to affect the percent yield of the product.

2.3 Treatment of TGA Data

The thermal degradation parameter of PU nanocomposites was evaluated using a DuPont TA Instrument with a TGA-Q 50 module. The instrument was calibrated using a pure calcium oxalate sample before analysis. About 8–10 mg of sample was subjected to dynamic TGA scans at a heating rate of 20°C/min in the temperature range of ambient to 700°C in N_2 atmosphere. The TG curves were analyzed as percentage weight loss as a function of temperature. The oxidation index (OI) was calculated based on the weight of carbonaceous char (CR) as related by the empirical equation:

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

The thermal degradation kinetic parameters were determined for PU/MMT nanocomposites using Horowitz–Metzger (23), Coats–Redfern (24) and Broido's (25) methods which provide overall kinetic data. For the sake of calculations and to understand the nature of the decomposition, the complete thermogram was divided into distinct sections according to their degradation processes.

The Horowitz–Metzger (HM) (23) relation used to evaluate the degradation kinetics is;

$$\ln[\ln(W_0 - W_t^f)/(W - W_t^f)] = E_a\theta / RT_s^2 \quad (2)$$

where, W_0 is the initial weight of the sample, W_t^f is the final weight of the sample, W is the weight remaining at a given temperature, T , E_a is the activation energy, $\theta = T - T_s$, T_s is the DTG peak temperature and T is the temperature corresponding to weight loss. The plot of $\ln[-\ln(1-\alpha)]$ vs. θ should give a straight line whose slope is E_a/RT_s^2 . The Coats–Redfern (CR) (24) relation is as follows;

$$\log(-\log(1-\alpha)/T^2) = (\log(AR/\beta E_a)) - (E_a/2.303RT) \quad (3)$$

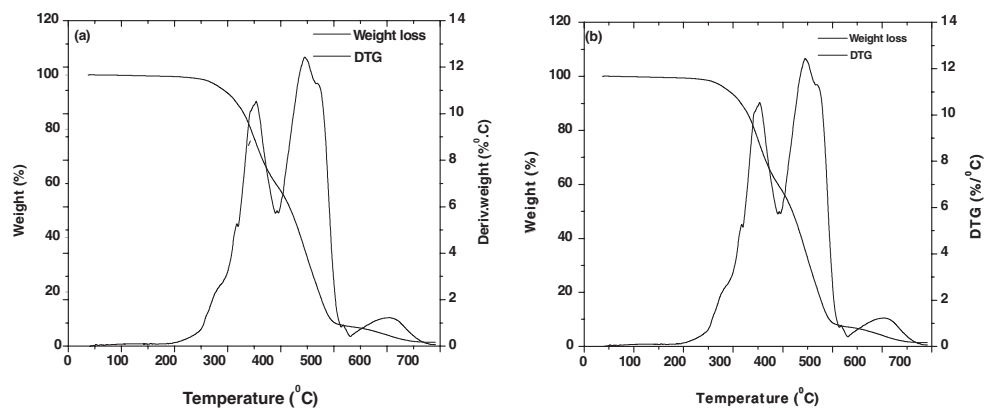


Fig. 1. TGA and derivative thermograms of, (a) 1% and (b) 3% MMT filled PU nanocomposites.

where, α is the fraction of sample decomposed at temperature T , T is the derivative peak temperature, A is the frequency factor, β is the heating rate, E_a is the activation energy, and R is the gas constant.

A plot of $\log\{-\log(1-\alpha)/T^2\}$ vs. $1/T$ gives the slope for evaluation of the activation energy most appropriately. The mathematical expression of Broido's (BR) (25) method is as follows;

$$\text{Log}(-\log(1-\alpha)) = - (E_a / 2.303R) ((1/T) + \text{const}) \quad (4)$$

where, $(1-\alpha)$ is the fraction of number of initial molecules not yet decomposed, T is the peak temperature of derivative curve of TGA, R is the gas constant and E_a is the activation energy and it can be calculated from the plot of $\log(-\log(1-\alpha))$ vs. $1/T$.

3 Results and Discussion

The TGA thermograms of 1%, and 3% nanoclay loaded PU composites are shown in Figures 1 (a and b), respectively along with derivative thermograms. TGA thermograms of all PU nanocomposites are shown in Figure 2. The different stages of thermal degradation were analyzed from the TGA

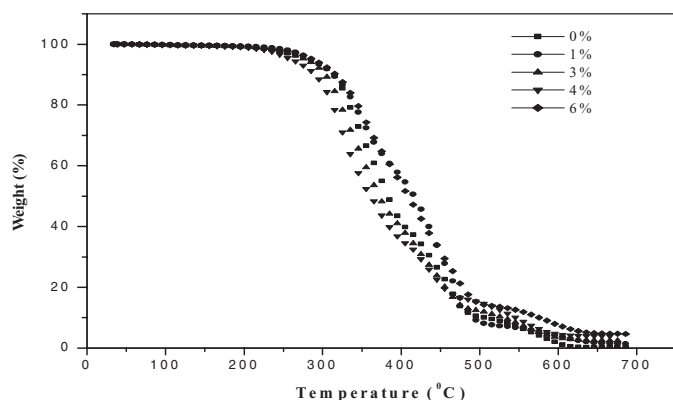


Fig. 2. TGA thermograms of PU/MMT nanocomposites.

thermograms and are given in Table 1. TGA thermograms of pristine PU indicates three stage thermal degradation processes. The first stage thermal degradation occurred in the temperature range 205–403°C with the major weight loss of 61.3%. The weight loss in the first step was due to the breaking of soft segment of PU and volatile impurities and main pyrolysis product could be carbon dioxide, alcohols, amines, aldehydes, CO, etc., (27–28). The second stage thermal degradation of PU occurred in the temperature range 409–500°C with the weight loss of 28.5%. The weight loss in the second stage may be due to the polyol decomposition. Since polyols used in this study are based on CO, the main chain may result in the formation of 10-undecanoic

Table 1. Temperature range obtained from derivative TGA curves of PU/MMT nanocomposites

MMT content in PU (wt%)	Degradation stage	Temperature ($^{\circ}\text{C} \pm 2$)			Weight loss (%)
		T_0	T_p	T_c	
0	1	205	330	403	61.3
	2	409	464	500	28.5
	3	500	579	639	10.0
	Ash	—	—	—	0.2
1	1	201	353	391	47.0
	2	391	449	531	42.3
	3	531	605	677	9.4
	Ash	—	—	—	1.3
3	1	198	337	403	58.0
	2	403	466	502	29.4
	3	502	571	662	9.9
	Ash	—	—	—	2.7
5	1	191	344	427	65.0
	2	427	465	504	18.8
	3	504	569	657	11.8
	Ash	—	—	—	4.4
6	1	190	345	435	64.8
	2	435	472	512	21.4
	3	512	583	670	8.8
	Ash	—	—	—	5.0

acid and heptanal as is evident by the thermal degradation of Ricinoleic acid, (29) which is the main constituent of CO. The third step weight loss occurs in the temperature range 500–639°C with a mass loss of 10 %. This could be

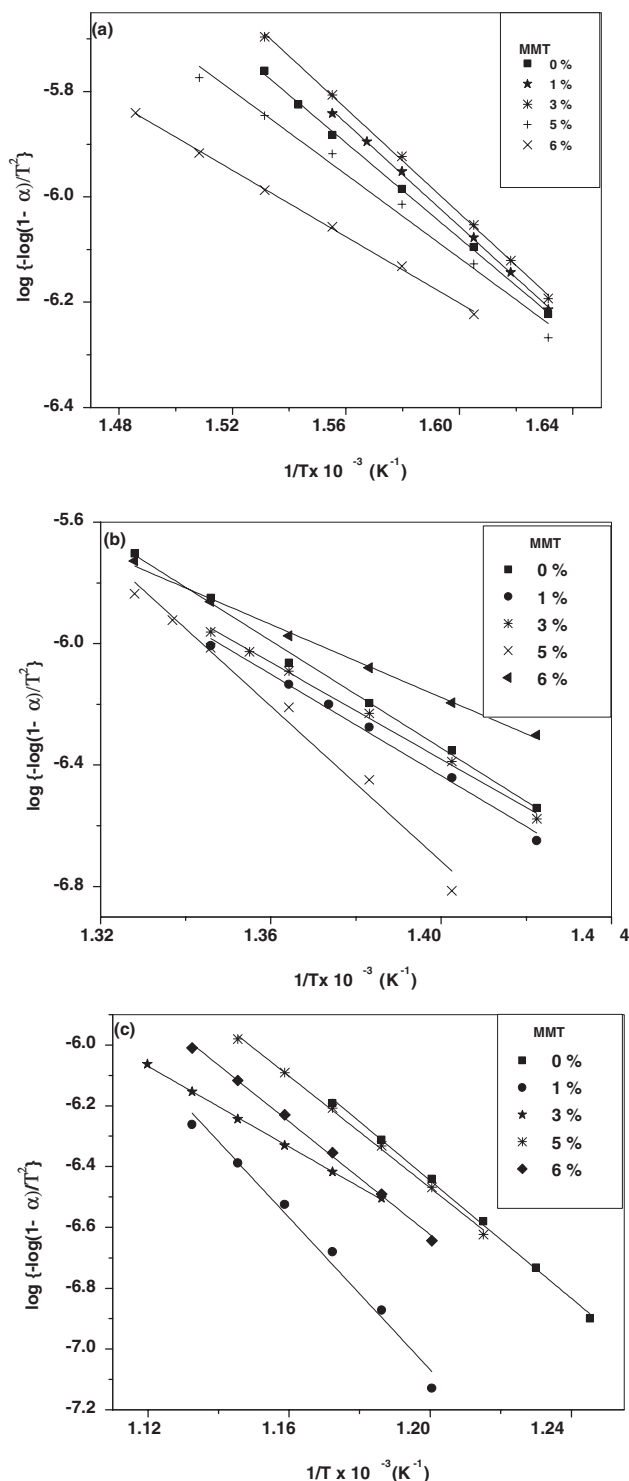


Fig. 3. Plots of $\log\{-\log(1-\alpha)\}$ vs. $1/T$ using the Coats-Redfern method for (a) first step, (b) second step and (c) third step thermal degradation for PU/MMT nanocomposites.

due to de-crosslinking of the rest of the PU. In this step, weight loss may be due to the liberation of HCN, nitriles of aromatics, carbon dioxide and ethers (27, 30).

The TGA curves for all nanocomposites indicate that there are three stages of thermal degradation. The major weight loss occurred in the first stage degradation process, which is due to the thermal decomposition of the intercalated PU, especially the polymers present on the surfaces of the clay. The decomposition temperature in this stage was started at 190°C and takes place up to 435°C, which corresponds to the weight loss ranging from 47.0% to 65.5%. In this stage, there is no clear difference between the samples. Also, it was found that the pure PU degrades slightly faster than the nanocomposites. This may be attributed to the degradation of the small molecules between the interlayers. The weight loss occurred in the second stage ranged from 18.5% to 42.3% in the temperature range 391–531°C. In this stage, the composites displayed higher thermal resistance

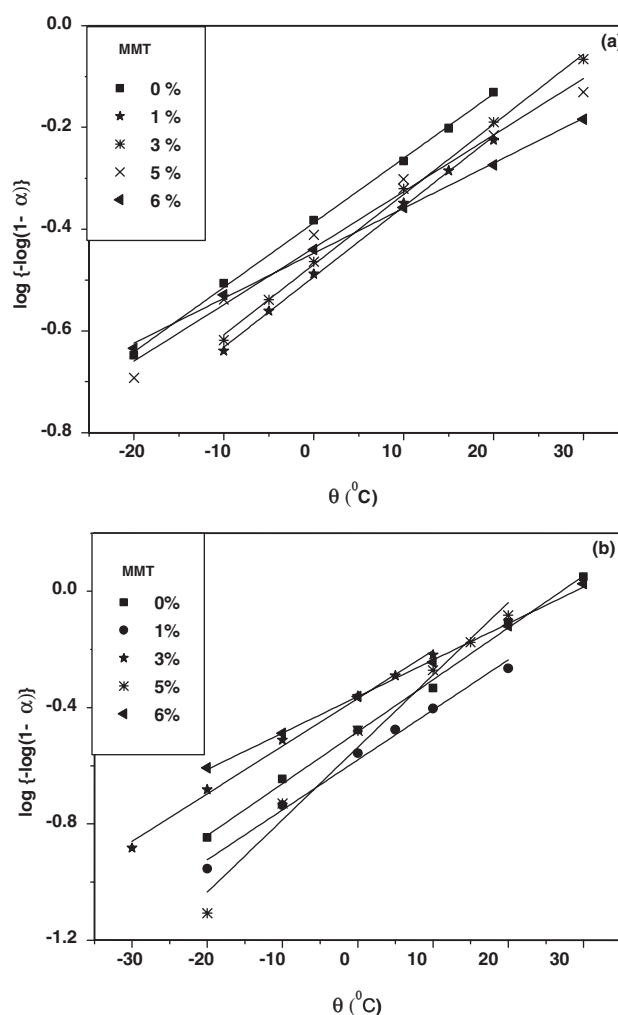


Fig. 4. Plots for the Horowitz-Metzger method to determine activation energies for PU/MMT composites for (a) first step and (b) second step thermal degradation.

than pure PU. The third and final step weight loss occurs in the temperature range 502–677°C with a weight loss ranging from 9.1% to 12%. The weight loss in the second and third steps can be attributed to further decomposition of the remaining intercalated polymers, especially the polymers present in the interlayers of the clay or some salts in the interlayer of the clay or the clay mineral loses -OH groups and the crystallographic structure collapsed (31).

The onset degradation of PU/MMT nanocomposites is higher than that of neat PUs (Table 1). This can be attributed to the presence of MMT, which has relatively higher thermal stability than PU. The obtained percentage ash content is higher in MMT (17%) as compared to neat PUs (0.2%) and their composites. The low ash content in the case of neat PUs could be due to the fact that, the

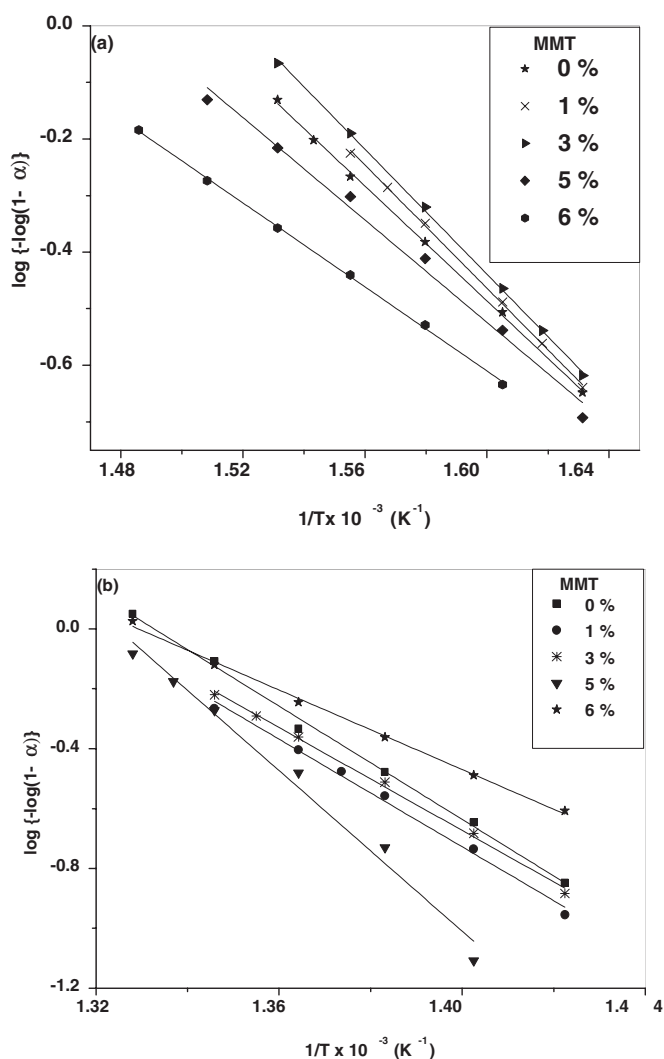


Fig. 5. Broido's plot for the determination of activation energies for (a) first step and (b) second step thermal degradation processes of PU/MMT nanocomposites.

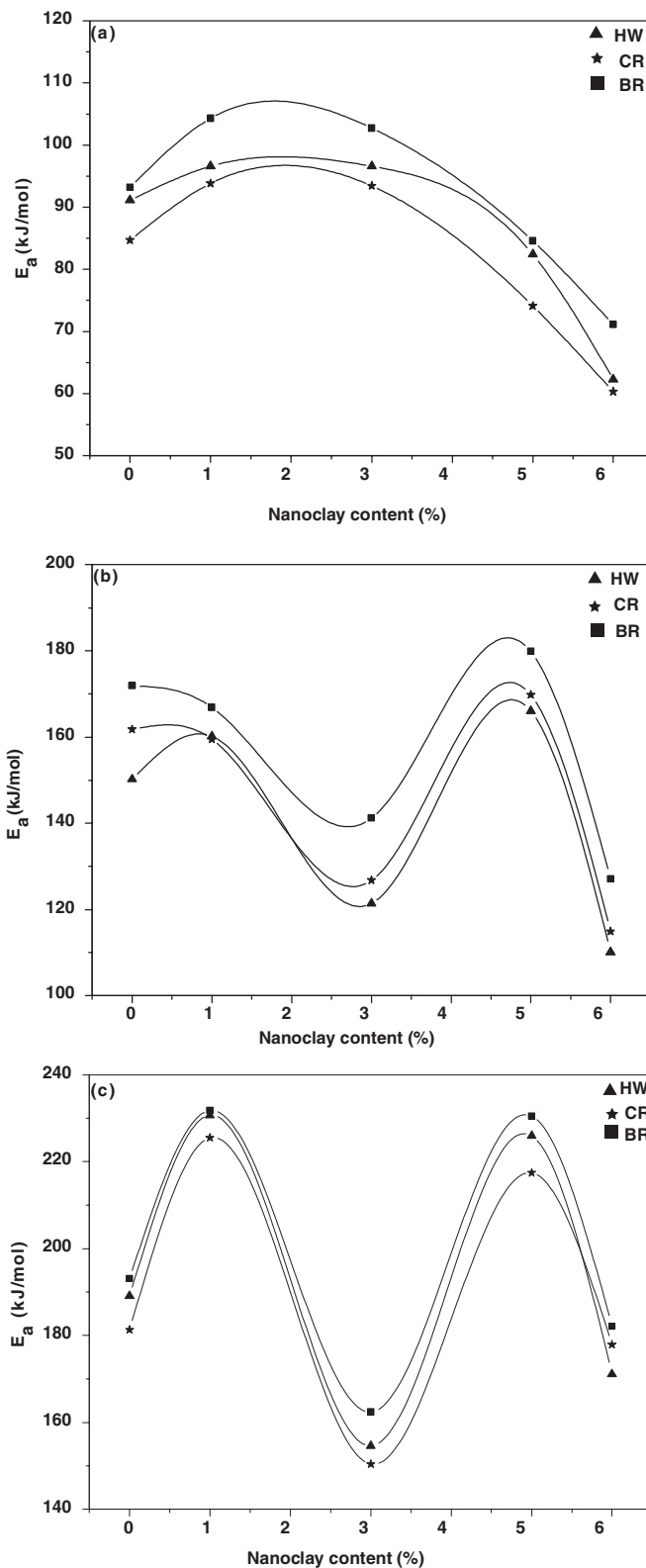


Fig. 6. Activation energy as a function of weight percent of MMT in PU/MMT obtained by different methods for different thermal degradation stages; (a) first step, (b) second step and (c) third step.

Table 2. Thermal data obtained from TGA thermograms of PU/MMT nanocomposites

MMT content in PU (wt %)	Temperature at different weight loss ($\pm 4^\circ\text{C}$)					Oxidation Index (OI)
	T ₀	T ₁₀	T ₂₀	T ₅₀	T _{max}	
0	205	309	334	383	495	0.014
1	217	313	343	419	496	0.091
3	226	314	334	383	492	0.189
5	250	314	333	381	604	0.308
6	259	316	339	403	628	0.350

polyol present in the PU contains more oxygen units and hence, PU undergoes combustion leaving less residue or ash. The ash content in composites increases with increase in nanoclay content as expected. Ash content of MMT filled PU composites lies in the range 1.3–5.0 %, which is slightly lower than the nanoclay filler loaded theoretically. This is due to the fact that MMT clay is organically modified. There is no systematic variation in weight loss in any step. However, the weight loss in first step degradation is greater for higher MMT clay loaded composites. It may be ascribed to the higher amount of small molecular weight PUs between the interlayers of clay, which degrade at lower temperature. Pielichowski et al. (32) noticed a similar trend for the thermal degradation of PU obtained from MDI and different polyols.

The thermograms obtained during the TGA scans were analyzed to give the percentage weight loss as a function of temperature. From TGA curves, it can be clearly observed that the weight loss markedly decreases with an increase in nanoclay content. Some characteristics of TGA data related to the temperature corresponding to weight loss such

as T₀ (temperature of onset decomposition), T₁₀ (temperature for 10% weight loss), T₂₀ (temperature for 20% weight loss), T₅₀ (temperature for 50% weight loss) and T_{max} (temperature for maximum weight loss) are the main criteria to indicate their thermal stability of the composites. The relative thermal stability of PU nanocomposites have been evaluated by comparing the decomposition temperatures at different percentage weight loss (Table 2). Higher the values of T₁₀, T₂₀, T₅₀ and T_{max}, higher will be the thermal stability of the composites (33). From the table it was observed that, these values increases with an increase in nanoclay content. From Table 2 it can be observed that, the MMT loaded PU composites showed increased onset degradation values as compared to that of neat PUs. This can be attributed to the synergistic effect of MMT and matrix present in the composite. The higher the values of oxidation index (OI), the higher will be the thermal stability (33, 34). From the table it was observed that the oxidation index values increases with an increase in MMT content and it lies in the 0.014–0.35 range. This data indicates that the MMT filled PU composites are more thermally stable than that of pristine PU. PU composites under investigation do not break down in a simpler manner, there may be a change in chemical composition and morphological structure of PUs at each and every degradation step of pyrolysis that affects the rate of decomposition.

3.1 Kinetic Analysis of Thermal Degradation

Kinetic parameters were evaluated from the TGA curves using Horowitz–Metzger, Coats–Redfern and Broido's methods. The plots of $\ln[-\ln(1-\alpha)]$ vs. θ (HM), $\ln[-\ln(1-\alpha)]/T^2$ vs. $1/T$ (CR) and $\ln[-\ln(1-\alpha)]$ vs. $1/T$ (BR) for PU/MMT nanocomposites are shown in Figures 3–5,

Table 3. Activation energies calculated by Horowitz-Metzger (HM), Coats-Redfern (CR) and Broido's (BR) methods along with the respective concurrency values (R^2) for PU/MMT nanocomposites

MMT content in PU (wt%)	Degradation stage	Activation energy (E_a) (KJ/mol) $\pm 4\%$					
		HW	R^2	CR	R^2	BR	R^2
0	I	91.1	0.998	84.7	0.998	93.2	0.999
	II	150.2	0.997	161.8	0.996	171.9	0.996
	III	189.1	0.996	181.3	0.998	193.1	0.998
1	I	96.6	0.998	93.8	0.999	104.3	0.999
	II	160.2	0.990	159.5	0.992	166.9	0.993
	III	230.7	0.982	225.5	0.985	231.8	0.986
3	I	96.6	0.998	93.4	0.999	102.7	0.999
	II	121.4	1.0	126.8	0.999	141.2	0.999
	III	154.6	0.995	150.4	0.995	162.4	0.997
5	I	82.4	0.985	74.1	0.987	84.6	0.990
	II	166.1	0.996	169.8	0.997	179.9	0.998
	III	225.9	0.981	217.4	0.983	230.5	0.985
6	I	62.3	0.998	60.3	0.998	71.1	0.999
	II	110.1	0.998	114.9	0.997	127.1	0.997
	III	171.1	0.996	177.9	0.997	182.1	0.997

respectively. The regression analysis gives the slopes, constants and R^2 for each degradation process. The linear plot with concurrency value (R^2) closer to one was chosen for all methods. The R^2 values and calculated activation energy (E_a) for each thermal degradation process and for each method are tabulated in Table 3.

The E_a values of the first, second and third steps lies in the range 60.3–104.3, 110.1–179.9 and 150.4–230.7 kJ/mol, respectively. The lowest E_a values were observed for the first step thermal degradation process as compared to the other two steps degradation processes for all the methods and for all nanocomposites. This is due to the lower energy required to remove volatile components and low molecular weight materials present in PU nanocomposites. Higher E_a values were observed for second and third step thermal degradation processes, because higher energies are required for bond scission and unzipping of crosslinked PU chains. Lower E_a values were observed for higher nano filler loaded PU composites. This is due to at higher dosage of MMT, formation of a greater amount of low molecular weight PUs between interlayers of nanoclay, for which less energy is sufficient for degradation. To understand the mechanism of thermal degradation, the variation of E_a as a function of MMT clay content for different steps is shown in Figure 6.

4 Conclusions

The thermal stability and degradation kinetics of PU/MMT nanocomposites have been reported in this research investigation. TGA thermograms indicates that all PU nanocomposites are stable up to 217°C and undergo three-step thermal degradation in the temperature ranges 205–403°C, 409–500°C, and 500–639°C for the first, second and third steps, respectively. It can be observed that the thermal stability of the nanoclay loaded PU composites is high compared to neat PUs. Kinetic parameters of degradation were evaluated by using Horowitz-Metzger, Coats-Redfern and Broido methods. Introduction of the nanoclay (inorganic) phase into PU matrix increases the thermal stability, and affects the total heat of degradation, which suggests a change in the degradation reaction mechanism. Kinetic studies reveal that the activation energy values calculated by all three methods are comparable. Lowest activation energy values were observed for all PU nanocomposites for first-step thermal degradation process as compared to second and third step degradation processes. This may be due to the fact that, less energy is sufficient to remove the soft segments of PU chains and volatile impurities. The kinetic analysis suggests that an enhanced thermal stability of nanocomposites is associated with the increase of the effective activation energy of their degradation.

References

- Iwata, K. (1987) Handbook of Polyurethane Resins, The Nikkan Kogyo Shinbun Ltd., Tokyo, Japan, (in Japanese, Chapters 1 and 2).
- Wang, Z. and Pinnavaia, T.J. (1998) *Chem. Mater.*, 10(71), 3769.
- Osman, M.A., Mittal, V., Morbidelli, M. and Suter, U.W. (2003) *Macromolecules*, 36, 9851–8.
- Zilg, C., Thomann, R., Muelhaupt, R. and Finter, J. (1999) *Adv. Mater.*, 11, 49–52.
- Cao, X., Lee, L.J., Widya, T. and Macosko, C. (2005) *Polymer*, 46, 775.
- Song, M. and Yao, K.J. (2004) *Mater. Sci. Technol.*, 20, 989.
- Xiong, J.W., Liu, Y.H., Yang, X.H. and Wang, X.L. (2004) *Polym. Degrad. Stab.*, 86, 549.
- Choi, W.J., Kim, S.H., Kim, Y.J. and Kim, S.C. (2004) *Polymer*, 45, 6045.
- Han, B., Cheng, A.M., Ji, G.D., Wu, S.S. and Shen, J. (2004) *J. Appl. Polym. Sci.*, 91, 2536.
- Lan, T., Kaviratna, P.D. and Pinnavaia, T.J. (1994) *Chem. Mater.*, 6, 573.
- Ma, J., Zhang, S. and Qi, Z. (2001) *J. Appl. Polym. Sci.*, 82, 1444.
- Song, M., Hourston, D.J., Yao, K.J. and Luo, D.Z. (2003) *J. Appl. Polym. Sci.*, 90, 3239.
- Ni, P., Li, J., Suo, J. and Li, S. (2004) *J. Appl. Polym. Sci.*, 94, 534.
- Burnside, S.D. and Giannelis, E.P. (1995) *Chem. Mater.*, 7, 1597.
- Yang, C.Y.W., Yang, H.C., Li, G.J. and Li, Y.K. (2004) *J. Polym. Res.*, 11, 275.
- Huang, H.H., Wilkes, G.L. and Carlson, J.G. (1989) *Polymer*, 30, 2001.
- Suhara, F., Kutty, S.K.N. and Nando, G.B. (1995) *Plast. Rubber Compos., Process Appl.*, 24, 37.
- Suhara, F., Kutty, S.K.N. and Nando, G.B. (1997) *Polym Plast Tech Eng.*, 36, 399.
- Satheesh Kumar, M.N. and Siddaramaiah (2007) *J. Appl. Polym. Sci.*, 106, 3521–3528.
- Shufen, J.Z., Yuan, K., Yu, S. and Chow, W.K. (2006) *Polym, Plast, Technol. Eng.*, 45, 95.
- Rein, G., Lautenberger, C., Carlos Fernandez-Pello, A., Jose, L.T. and David, L. (2006) *Urban Combust Flame*, 146, 95.
- Sunil, K.N., Kutty, T.K. and Nando, G.B. (1992) *Polym. Deg. Stab.*, 38, 187.
- Horowitz, H., Metzger, G. (1964) *Anal. Chem.*, 35, 68.
- Coats, A.W. and Redfern, J.P. (1964) *Nature*, 201, 68.
- Broido, A. (1969) *J. Polym. Sci.*, A2, 1761.
- Rehab, A. and Salahuddin, N. (2005) *Mater. Sci. and Engg. A*, 399, 368–376.
- Herrera, M., Matuschek G. and Kettrup, A. (2003) *Polym. Degrad. & Stability*, 78, 323.
- David, D.J. and Staley, M.P. Analytical Chemistry of Polyurethane, Part III: High Polymers; Wiley Interscience: New York, Vol. 16, p. 365, 1974.
- Saunders, J.H. and Frisch, K.C. Polyurethane Chemistry and Technology, Part I; Wiley Interscience: New York, Vol. 16, p. 51, 1963.
- Chambers, J., Jirny and J., Reese, C. (1981) *Fire Mater.*, 5, 133.
- Salahuddin, N. and Rehab, A. (2003) *Polym. Intl.*, 52, 241.
- Pielichowski, K., Pielischowski, J., Altenburg, H. and Ballof, H. (1996) *J. Thermochim. Acta*, 284, 419.
- Jeevananda, T. and Siddaramaiah (2001) *Thermochemica Acta*, 51, 376.
- Kumar, H., Anilkumar, A. and Siddaramaiah (2006) *Polym. Degrad. & Stability*, 91, 1097–1104.