

## **PHYSICO-MECHANICAL, THERMAL AND ACTIVATION ENERGY STUDIES OF JUTE-MAT/POLYVINYLCHLORIDE SANDWICH COMPOSITES**

TAIMUR-AL-MOBARAK, MD. FORHAD MINA\* AND MD. ABDUL GAFUR<sup>1</sup>

*Department of Physics, Bangladesh University of Engineering & Technology (BUET), Dhaka-1000, Bangladesh*

### **ABSTRACT**

Polyvinylchloride sheets (PVCS) as well as sandwiched composites of untreated jute-mat (JM)/PVC (UJPC) and organic acid treated JM/PVC (TJPC) were prepared with various JM contents by compression molding method at 160°C. Mechanical, chemical textural, surface morphological, thermal and water intake (*WI*) properties of these samples were measured using a universal testing machine, a Fourier transform infrared (FTIR) spectrometer, a scanning electron microscope, a thermal analyzer and the gravimetric method, respectively. Young modulus (*Y*) and tangent modulus (*G*) of TJPC are found to increase from UJPC. FTIR spectra clearly exhibited distinct absorption peaks of UJPC and TJPC, indicating a modified texture of treated JM. The observed *WI* value was lower in TJPC than UJPC. Fiber-tearing of fractured surface micrographs observed for TJPC and fiber pull-out for UJPC suggested a good adhesion between JM and PVC in the former one. Most importantly, the activation energy ( $E_a$ ) analysis by Ozawa' method gives its value of 164 KJ/mol for TJPC and 135 KJ/mol for UJPC.

Key words: Jute-mat, Polyvinylchloride, Composites, Compression molding, Mechanical properties, Activation energy

### **INTRODUCTION**

Use of jute fiber (JF) as reinforcement in polymeric composites raised great interest and expectations among materials scientists and engineers in the last decades (Mohanty *et al.* 2000, Khan *et al.* 2008, Khan *et al.* 2010). The primary advantages of using this fiber as an additive for fabrication of polymer composites are that it has some attractive properties like biodegradability, low cost, low density, non-abrasive nature, high possibility of filling levels, low energy consumption, wide varieties, and above all it can generate an agriculture-based economy (Bogoeva *et al.* 2007). Despite its great advantages and scopes, JF has two major drawbacks that preclude its promising uses in composites fabrication. One of them is its hydrophilic nature, causing moisture absorption that reduces its durability. The other one is its poor wettability that deprives it from applying in engineering applications.

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\* Corresponding author: <mfmina@phy.buet.ac.bd>.

<sup>1</sup> Pilot Plant & Process Development Center, BCSIR, Dhaka, Bangladesh.

A number of research works have been carried out without surface modifications of JF by chemical treatments (Ray *et al.* 1997, Wang *et al.* 1997, Gowda *et al.* 1999), where a decrease of tensile strength, flexural strength, Young's modulus has been observed. These authors have claimed that the decrease in mechanical properties is most likely because of the poor adhesion between JF and polymer matrix. Thereafter, research interests on chemical treatments of fiber surface have been focused, because such treatments develop roughness of fiber surface, thereby increasing surface area available for a good contact with polymer matrix. Effect of alkali treatment of jute fiber on mechanical properties of jute-reinforced polymer composites has been studied by some researchers who have shown a modified fiber-surface texture and a considerable enhancement of mechanical properties (Ray *et al.* 2002, Kabir *et al.* 2010, Siregar *et al.* 2010, Al-Mobarak *et al.* 2013). Apart from alkali treatment, expensive compatibilizers or coupling agents like silane and maleic anhydride were also reportedly used for the improvement of adhesion between fiber and polymer (Khan *et al.* 2000, Mohanty *et al.* 2002, Sombatsompop *et al.* 2005). On the other hand, polyvinylchloride (PVC) is a widely used thermoplastic engineering material, possessing several advantageous properties and is known to exhibit a partially degradable-type composite when combined with jute (Khan *et al.* 2012).

However, JF treatment using acetic acid (AA) was seldom reported in the literature and much data on low-cost organic-acid treated JM reinforced PVC composites are still rare. Moreover, considerable attention has been given on activation energy analysis to examine the fiber-matrix adhesion in composites through kinetic study using several methods and of these, the Ozawa's method (Ozawa 1970) is a popular one, whose detailed analytical procedure is of particular interest to be presented in this article for estimating the activation energy of the resulting composites.

## MATERIALS AND METHODS

The raw materials used in this investigation were jute-mat (JM) of Bangladesh Jute Research Institute and commercial PVC sheet (PVCS) (Zhanjiang Kingstar Building Material Co. Ltd., province: Guangdong, China) of 3 mm thick, purchased from local market. JM is a woven network like structure of JM bundles, which are basically rolled JFs. Acetic acid (CH<sub>3</sub>COOH) of Merck, Germany was procured for treatment of JMs, which were initially washed with water flow, dried under sunlight and then in an oven for 24 hours. About 2 wt% AA solutions in water were prepared for treating JM, where the liquor ratio of JM to AA solution was 1 : 20. JMs were immersed in this solution at 30°C for one hand occasionally shaken. They were removed from the solution, washed with water-flow and dried subsequently at room temperature (30°C) and then in an oven at 100°C for 24 hours.

A series of JM-reinforced PVC composites were prepared with and without untreated and treated JMs. For fabrication of composites, layers of PVCS and JM are embedded and heat-pressed at 160°C by a compression molding machine using a load of 100 kN. PVCS to JM ratios in the composites were maintained as 2 : 0, 2 : 1, 1 : 2, 2 : 2 and 3 : 2, which refer to the layers of corresponding materials. Thus, the samples fabricated were heat-pressed PVCS (2 : 0), untreated JM-PVCS composites (UJPC) and AA treated JM-PVCS composites (TJPC).

Tensile strength ( $TS$ ) and Young's modulus ( $Y$ ) of the PVCS and the composites were measured by a universal testing machine (Hounsfield UTM 10KN; ASTM D-638-98) at a crosshead speed of 2 mm/min, keeping a gauge length of 48 mm. Flexural strength ( $FS$ ) and tangent modulus ( $G$ ) were also measured by the same apparatus, keeping a distance of 48 mm between two supports on which the samples were placed to employ load. Five samples of each composition were used in mechanical testing.

Fourier-transform infrared (FTIR) spectra of the samples were recorded at room temperature by using a double beam IR spectrophotometer (SHIMADZU, FTIR-8900 spectrophotometer, JAPAN) in the wave number range of 400 - 4000  $\text{cm}^{-1}$ . For these measurements, the samples were crushed and then mixed with KBr for recording the FTIR spectra in the transmittance (%) mode.

Water intake ( $WI$ ) property of UJPC and TJPC with PVC to JM ratio of 2 : 2 was measured. The test specimen was cut in a size of 60 mm length, 20 mm width and varying thicknesses. The cut samples were kept in an oven at 80°C for 24 hours and immediately weighed by electric balance. Let this weight be considered as initial weight  $w_i$ . The sample was then immersed in distilled water of 23°C and kept for 24 hours, taken out from water, wiped by a cloth and then weighed. Let this weight be  $w_f$ . Then the amount of water intake was calculated by the following formula:

$$WI (\%) = \left[ \frac{w_f - w_i}{w_f} \right] \times 100 \quad (1)$$

The above procedures were repeated for 48, 72, 96 and 120 hours with other samples, and corresponding values of  $WI$  were measured.

Fractured surface of the PVCS, UJPC and TJPC were studied by a scanning electron microscope (SEM) [Philips XL 30, Netherlands]. Each sample was cut from the region of fracture and the surface was coated with a thin layer of gold by sputtering prior to the SEM measurement. The surface micrographs of the fractured samples were taken at the maximum operating voltage of 30 kV of the apparatus.

Thermal properties of the samples were monitored by a coupled differential thermal analyzer (DTA) and thermogravimetric analyzer (TGA) [Seiko-Ex-STAR-6300, Japan].

The measurements using this analyzer were carried out from 35 to 600°C at various heating rates such as 20, 30 and 50°C/min under nitrogen gas flow. The DTA traces provide the melting and degradation temperatures of the samples as determined from the exotherm versus temperature curves and the TGA runs exhibit the weight-loss of the sample with temperature.

In kinetic analysis of activation energy ( $E_a$ ) from TGA data, the following relation given by Ozawa (1970) was used:

$$\ln S = -0.4567 \frac{E_a}{RT} - 2.315 + \ln \left( \frac{AE_a}{Rg(\alpha)} \right) \quad (2)$$

where,  $\beta$  = heating rate (°C/min),  $R$  = gas constant (8.314 J/mol-K),  $T$  = temperature,  $A$  = frequency factor of the reaction,  $g(\alpha) = \int f(\alpha) / d\alpha$  is the integral form of  $f(\alpha)$ , which is a function of reaction and  $\alpha$  is defined by the relation below:

$$\alpha = \frac{m_i - m_T}{m_i - m_f} \quad (3)$$

where,  $m_i$ ,  $m_T$  and  $m_f$  are percentage of initial-weight, weight at  $T$  and final-weight, respectively. According to equation (2), it is obvious that a plot of  $\ln S$  versus  $\frac{1}{T}$  shows a

straight line, whose slope equals to  $0.4567 \frac{E_a}{R}$ . Thus, the value of  $E_a$  can be easily obtained from the known value of  $R$ . However, to calculate  $E_a$  using the TGA data, a straight line needs to be drawn, requiring more than one value of  $\alpha$ , and hence each category of samples is heated more than one heating rate.

In this study, the selected range of TGA data were divided into nine partitions, referred to as the percentage of reaction fraction (RF%), successively giving rise to values of 10, 20, 30, 40, 50, 60, 70, 80 and 90%, which indicate the maximum weight-loss of the sample in each partition. The average value of  $E_a$  from the range RF = 10 - 90% for each sample was also determined.

## RESULTS AND DISCUSSION

The  $TS$  for PVCS, UJM, TJM, UJPC and TJPC with various ratios of PVC and JM are plotted in Fig. 1. The  $TS$  values for PVCS, UJM and TJM are, respectively found to be 26, 89 and 93 MPa (Fig. 1a) and those for UJPC and TJPC increase with increasing JM content (Fig. 1b). For each PVCS to JM ratio, the  $TS$  value for TJPC is found to be higher than that for UJPC. The highest  $TS$  values of UJPC and TJPC obtained with PVC : JM = 3 : 2 are 38 and 40 MPa, respectively. Therefore, the  $TS$  increase of TJPC from PVCS and UJPC is 55 and 5%, respectively. This increase may be attributed to the fact that because of chemical treatment the swelling behavior of the fiber surface is expected

to increase, resulting in rough surface that helps develop better interfacial adhesion between the JM and PVC matrix.

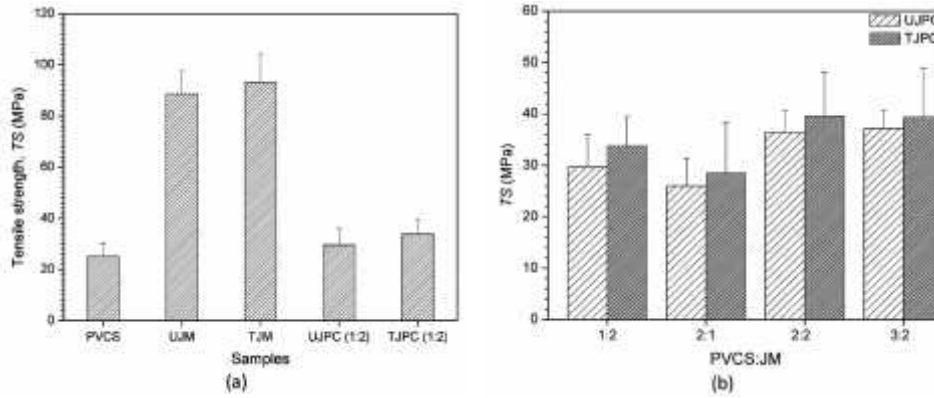


Fig. 1. Tensile strength of (a) PVCS, UJM, TJM, UJPC and TJPC (b) composites with various PVCS : JM.

Fig. 2(a) shows the  $Y$  values for the PVCS, UJM, TJM, UJPC and TJPC, while Fig. 2(b) compares the  $Y$  values of composites with increasing JM contents. The UJM and TJM show the highest  $Y$  value, which for TJPC is higher than those for PVCS and UJPC. A larger  $Y$  value for UJPC than that for PVCS may arise from higher  $Y$  value of JM than PVCS. Thus, the addition of fibers increases the stiffness of the resulting composite and fiber-surface treatment enhances this stiffness. While the maximum  $Y$  for PVCS is about 1.3 GPa, it is about 2.2 GPa for UJPC and even higher 2.5 GPa for TJPC. The respective  $Y$  increase of TJPC from PVCS and UJPC is 67 and 15%, suggesting better performance of the composites due to chemical treatment.

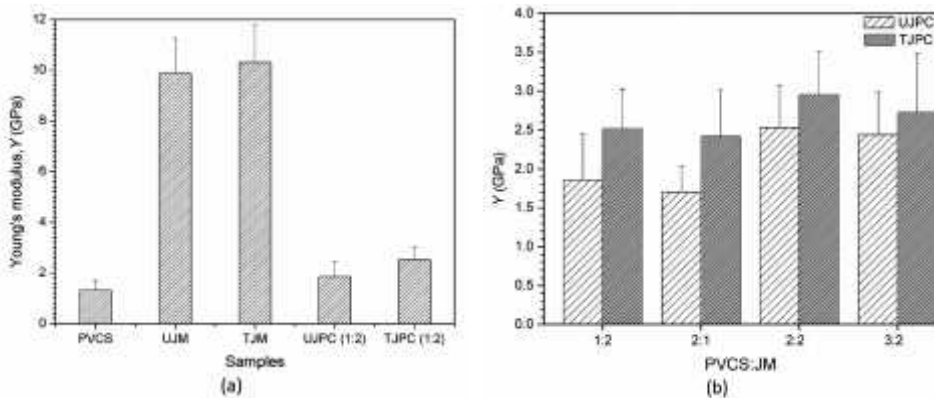


Fig. 2. Young's modulus of (a) PVCS, UJM, TJM, UJPC and TJPC (b) composites with various PVCS : JM.

Fig. 3 represents a comparison of (a)  $FS$  and (b)  $G$  values for various samples. The maximum  $G$  values for PVCS, UJPC and TJPC are 1.35, 2.0 and 2.25 GPa, respectively. The trend of changes of  $FS$  and  $G$  for the samples is similar to that of  $TS$  and  $Y$ .

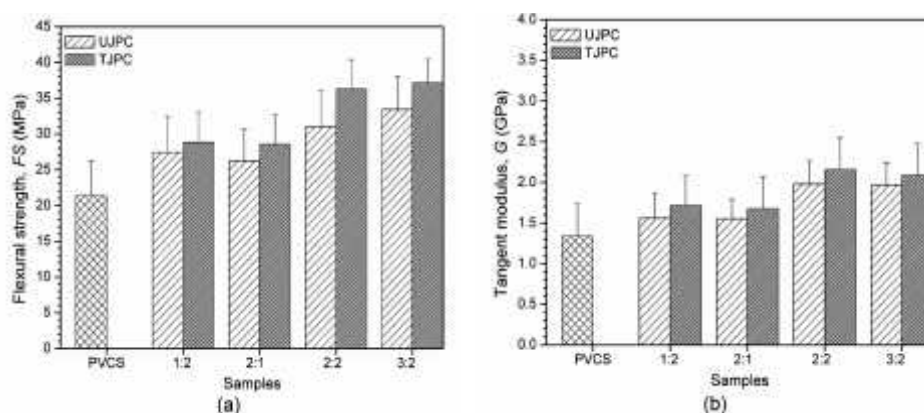


Fig. 3. (a) Flexural strength and (b) tangent modulus of PVCS, UJPC and TJPC with various PVCS : JM.

Fig. 4 shows the FTIR spectra of UJM and TJM, recorded as a transmittance versus wave number. The spectrum of UJM shows absorption bands of chemical group from the fabric molecules such as cellulose, hemicellulose, lignin etc., which are originated from aliphatic, aromatic and oxygen containing functional groups. The S-glucosidic linkage between sugar units of hemicelluloses appears at a wave number  $896\text{ cm}^{-1}$ . The C-O stretching and the O-H deformation vibrations are appearing at  $1077$  and  $1030\text{ cm}^{-1}$  are characteristics of cellulose and lignin, respectively. The band due to the C-O-C asymmetric stretching vibration for cellulose and hemicelluloses is observed at  $1244\text{ cm}^{-1}$ . The bands near  $1370$  and  $1320\text{ cm}^{-1}$  are assigned to  $\text{CH}_3$  bending and  $\text{CH}_2$  wagging in lignin. The peaks at  $1589$  and  $1500\text{ cm}^{-1}$  are due to benzene ring stretching in lignin.

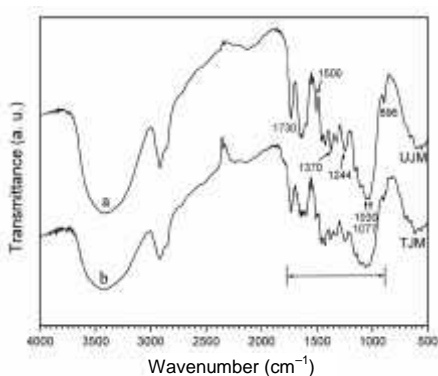


Fig. 4. FTIR spectra of (a) UJM and (b) TJM with PVCS to JM ratio of 2 : 2.

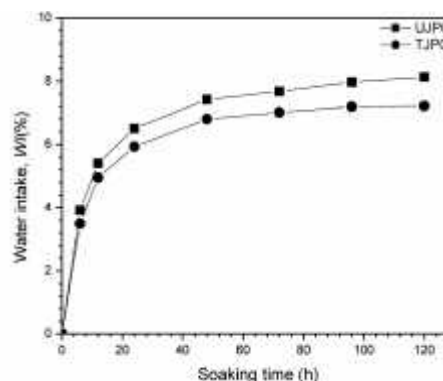


Fig. 5. Variation of water absorption with soaking time for UJPC and TJPC with PVCS to JM ratio of 2 : 2.

The peak at about  $1730\text{ cm}^{-1}$  is due to the stretching vibration of carbonyl group  $\text{C}=\text{O}$ , which is a characteristic bond of cellulose and hemicellulose. A very strong and broad band in the range of  $3200\text{-}3600\text{ cm}^{-1}$  is due to the stretching vibration of the O-H group

of cellulose. The observed spectral peaks of UJM are found to comply with those reported elsewhere (Liu and Dai 2007, Roy *et al.* 2011). A comparison between the spectra UJM and TJM at the above mentioned bands, within the marked region, shows a reduction in intensities in the treated fibers.

Fig. 5 shows the dependence of  $WI$  (%) on soaking time for UJPC and TJPC with PVC : JM ratio of 2 : 2. The  $WI$  (%) increases rapidly with time and tends to level off at about 120 h for both samples. AA treatment probably reduces its binding or cementing components such as lignin, pectin, etc. from the fibers, thereby decreasing the amount of hydrophilic groups. That is why the  $WI$  value in UJPC at a particular time is always higher than that in TJPC (Rashdi *et al.* 2009).

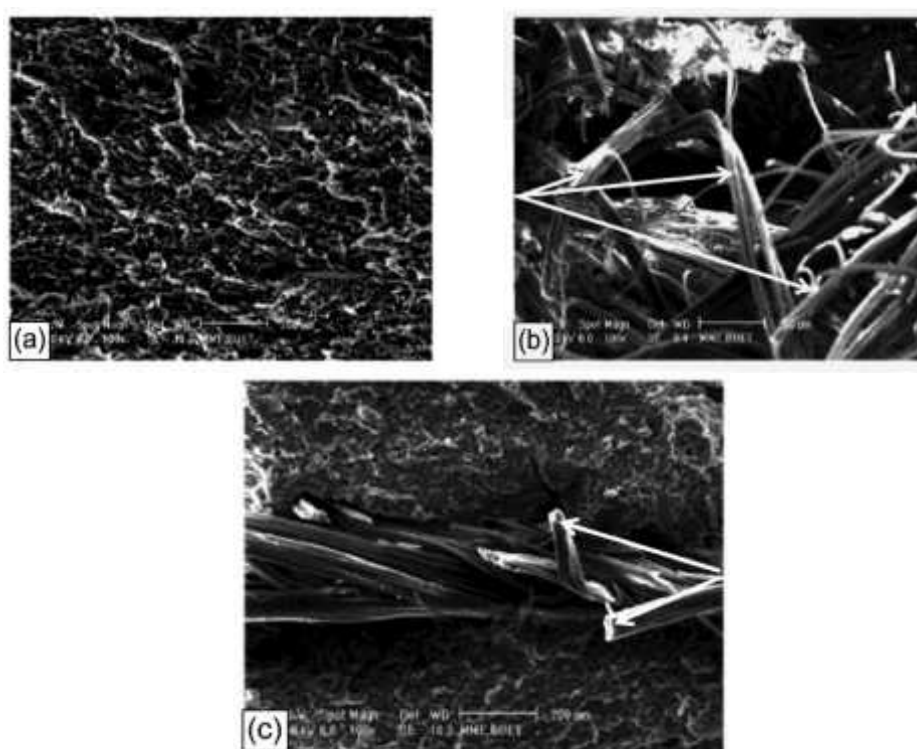


Fig. 6. SEM micrographs of the fractured surface for (a) PVCS, (b) UJPC (PVCS : JM = 2 : 2) and (c) TJPC (PVCS : JM = 2 : 2).

Fig. 6 illustrates the SEM micrographs of the fractured surface of PVCS, UJPC and TJPC. For PVCS (Fig. 6a), the surface structure is unsmooth and contains huge flaws. The micrograph of UJPC, however, shows that JM fibers are found to be pulled out from the PVC matrix (Fig. 6b), indicating a poor adhesion between these two components. In contrast, the TJPC micrograph shows that comparatively fewer fibers are observed to be pulled out from the matrix of PVC (Fig. 6c), where some fibers are seen to be fractured.

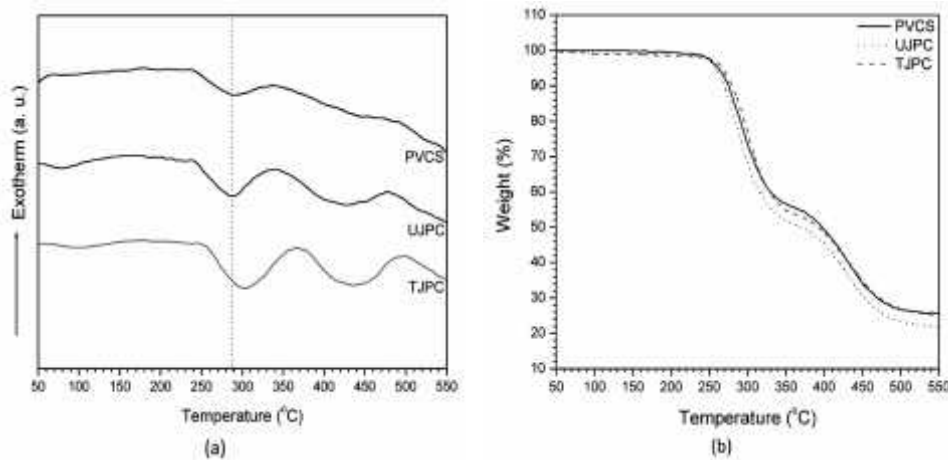


Fig. 7. A comparison of (a) DTA and (b) TGA curves for PVCS, UJPC and TJPC with PVC : JM ratio of 2 : 2 in the composites.

Thus, the SEM images clarify a better fiber-matrix adhesion in TJPC as compared to UJPC. Acid treatment may lead to dissolve binding materials from fibers, making fibers surface increasingly rough and increasing the effective surface area available for matrix wetting. The number of free hydroxyl groups on the fibers surface is also expected to increase by removal of binding components, thereby providing a greater number of active sites on the fibers surface to improve adhesion with PVCS (Suradi *et al.* 2011).

Fig. 7(a) represents a comparison of DTA curves for PVCS, UJPC and TJPC with PVC to JM ratio of 2 : 2. The PVCS shows a diffused endothermic peak at 288°C, indicating the degradation temperature  $T_d^{PVC}$  of PVC molecules. For composites, the peak at 100 °C can be assigned to  $T_d^C$  corresponding to the release of water molecules, and two endothermic peaks appearing near 300 and 430°C can be denoted by degradation temperatures  $T_d^{PVC}$  and  $T_d^{JM}$  of the components' (PVC or JM) molecules, respectively. Clearly,  $T_d^{PVC}$  and  $T_d^{JM}$  are different from that of UJPC and TJPC. A slight increase in degradation temperature of TJPC from UJPC may be attributed to a good adhesion between JM and PVC in the treated JM reinforced composites. Similar results were also reported in the case of jute fiber reinforced shellac composites (Khan *et al.* 2008).

Thermal degradation of PVCS, UJPC and TJPC in a temperature range of 50 - 550°C as observed by TGA runs is shown in Fig. 7(b). It exhibits the weight loss of the samples with increasing temperature. Analysis shows that degradation of UJPC and TJPC at 50% weight loss occurs at ~370 and 390°C, respectively. This difference in decomposition temperature may be connected to the kinetic parameters of thermal reaction. Of these parameters, activation energy is an important one, which can suggest the mechanism of distinct thermal degradation reaction for different samples.



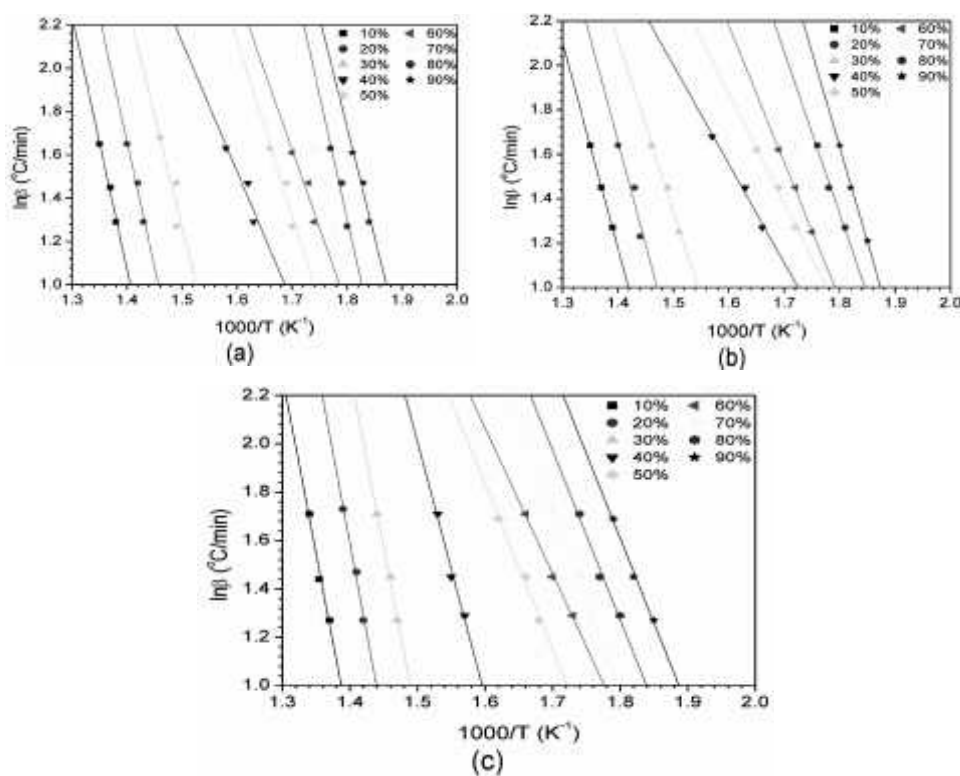


Fig. 8. Plots of the logarithm of heating rate versus the reciprocal absolute temperature of (a) PVCS, (b) UJPC and (c) TJPC with PVC to JM ratio of 2 : 2 for various RF%.

**Table 1. A comparison of activation energy for PVCS, UJPC and TJPC with PVC: JM of 2 : 2.**

No.	RF%	$E_a$ (KJ/mol)		
		PVCS	UJPC	TJPC
1	10	151.48	149.99	175.07
2	20	137.50	145.66	176.29
3	30	126.03	129.90	167.54
4	40	122.25	113.37	145.19
5	50	20.62	97.63	132.77
6	60	206.87	77.36	119.94
7	70	247.14	125.65	167.92
8	80	243.66	176.23	188.54
9	90	224.21	201.47	191.19

To study the degradation mechanism, the samples were been subjected to three heating rates. The plots of the logarithm of the heating rate versus the reciprocal absolute temperature at various RF (%) for PVCS, UJPC and TJPC are shown in Fig. 8(a), (b) and (c) respectively, from which the  $E_a$  for each sample has been evaluated. The values of  $E_a$  corresponding to various RF% are introduced in Table 1.

Evidently, the calculated average  $E_a$  for PVCS, UJPC and TJPC are about 175, 135 and 164 KJ/mol, respectively. Even, the  $E_a$  for TJPC at RF% = 10 is higher than those of other two samples. Since  $E_a$  is related to the energy barrier preventing polymer chain movement from one location to another, the observed higher  $E_a$  for TJPC than UJPC reveals a delayed degradation of PVC molecules because of the presence of cellulosic JFs and improved interfacial adhesion.

## CONCLUSIONS

The mechanical properties such as  $TS$ ,  $FS$ ,  $Y$  and  $G$  of the TJPC were observed to be higher than those of UJPC and PVCS, suggesting better performance due to acetic acid treatments of JM. FTIR analyses confirmed the surface modification of JM by treatment, which reduced the cementing components from fibers. The UJPC exhibits higher water-intake than the TJPC, indicating that untreated JM is more hydrophilic in nature than treated JM. Surface micrographs indicate a better fiber-matrix adhesion in TJPC than UJPC. The melting and decomposing temperatures of the TJPC are observed to be higher from that of UJPC. Finally, activation energy analysis of Ozawa' shows an improved fiber-matrix adhesion in TJPC.

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