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Degradation Kinetics of Poly(Ethylene Terephthalate) and Poly(Methyl Methacrylate) Blends

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Summary

Poly(ethylene terephthalate) PET and poly(methyl methacrylate) PMMA blends were made by melt mixing in a batch reactor. Three different weight ratios of PET : PMMA (25:75, 50:50 and 75:25) were chosen to study the effect of blend composition on the degradation kinetics. A relationship between the fractional volatiles evolved per unit time and the fraction of polymer degraded is established. The kinetic parameters for degradation were found using modified Avrami's non-isothermal equation. Parameters like degradation rate constant (k) and order of degradation (n), were evaluated for the virgin polymers and the blends.

Introduction

Poly(ethylene terephthalate) is a semicrystalline, polymeric material developed by many chemical companies for fiber and engineering applications [1-10]. Poly(methyl methacrylate) (PMMA) is an atactic polymer of high average molecular weight with a glass-transition temperature of 105 to 108°C, approximately.

Several studies have been conducted on the thermal degradation products of PET [11-13]. These studies indicate that the thermal degradation of PET is initiated by chain scission of the ester-linkage, yielding carboxyl and vinyl ester groups [13]. A maximum degradation with 80% weight loss is reported to occur for PET between 377-427°C due to random chain scission [14]. The thermal degradation of PET/poly(caprolatone) (PCL) blends showed that addition of PET to PCL increased the thermal stability of the latter and improved the biodegradability of PET [15]. The reaction mechanism and thermal stability of polyamide/poly(ethylene terephthalate) blends have also been investigated in detail [16].

Blends of PET and PMMA were commercially traded under the trade name Ropet [17]. These blends reinforced with fiberglass were used for electrical applications.

Mallette et al.[18] has reported the electro-conductive properties of the immiscible PET/PMMA system in which carbon black (CB) was used as a conductor. In this study the blends were made in a Brabender mixer chamber at 245°C at 30 rpm and varying weight percentages of PET, PMMA and CB.

The blends of PET/PMMA are of commercial importance and are being used in electrical and electronic applications because of property advantages and lower cost than PMMA and lower wrap and shrink compared to PET. When these blends are used in electrical applications, voltage overshoot and continuous usage of these parts over extended periods can cause degradation of the blends. Study of thermal degradation properties would be of great advantage to optimize the structure-property relationship of these blends. Also thermal stability of a blend is an important property for both processing and application.

No attention has been given in the past to characterization and degradation of PET/PMMA blends. In the present study three different compositions of the blends (PET 25/PMMA 75, PET 50/PMMA 50 and PET 75/PMMA 25 (weight/weight basis)) were made to study the degradation kinetics and to know the thermal stability.

Experimental

Materials

PET (bottle grade) was supplied in pellet form by Century Enka Pvt. Ltd., Pune, India. The intrinsic viscosity of the resin was 0.60 $(g/100ml)^{-1}$, measured at 25°C using Cannon Ubbelhode viscometer. The virgin PMMA used was injection moulded material in sheet form. The injection molding pressure was 12,000 psi, cylinder temperature 177 to 210°C and mould temperature 79°C. The moulded PMMA sheet had a specific gravity of 1.18, tensile strength 9000 psi and flexural strength 15,000 psi. The PMMA sheet was cut into small pellets before use.

Sample Preparation

PET and PMMA (PET/PMMA 25/75, 50/50, and 75/25 pellets (weight basis)) were dried in a vacuum oven at 100°C for 5 hours. The pre-blends were then melt-mixed in a reactor at 100 rpm for one hour at 275°C. No degradation was observed during sample preparation hence drying of the polymers at 100°C for 5 hours was fixed. The blended product was removed from the reactor and ground using a mixer grinder.

Thermal Analysis

Thermogravimetric analysis (TGA) was carried out for the virgin polymer and blends (9-10 mg) at heating rates of 5, 10, 15 and 20°C/min using TA instruments, SDT 2960, DSC- TGA unit. The unit has a temperature sensitivity of 0.1°C. A pure dry nitrogen purge of 20 ml/min was maintained for all the runs.

SEM Analysis

Scanning electron microscopy (SEM) was used to study the morphology of the virgin materials and the blends. The microscope used was Joel 6300 with eXL II energy dispersive spectroscope and WDX-400 spectroscope. The samples were gold coated before the SEM observations. The analysis was carried out at 1500 magnification.

Results and Discussion

A typical thermogravimetric curve for PET 25/PMMA 75, PET 50/PMMA 50, PET 75/PMMA 25, PET virgin and PMMA virgin is given in Figure 1. A single degradation curve is found for PMMA in the temperature range 280 to 410°C. 83% PET is found to degrade in the temperature range 375 to 461°C and 15 percent is found to degrade in the range 461 to 625°C. The shoulder observed in the range 461 to 625°C in virgin PET could be due to degradation of residual char. PET degrades by a series of reactions where parts of the PET structure are eliminated such as ethylene followed by decarboxylation of relevant units. Aromatic compounds normally form carbonaceous residue. The residual char will probably have some organic content that could gradually decompose at high temperatures.

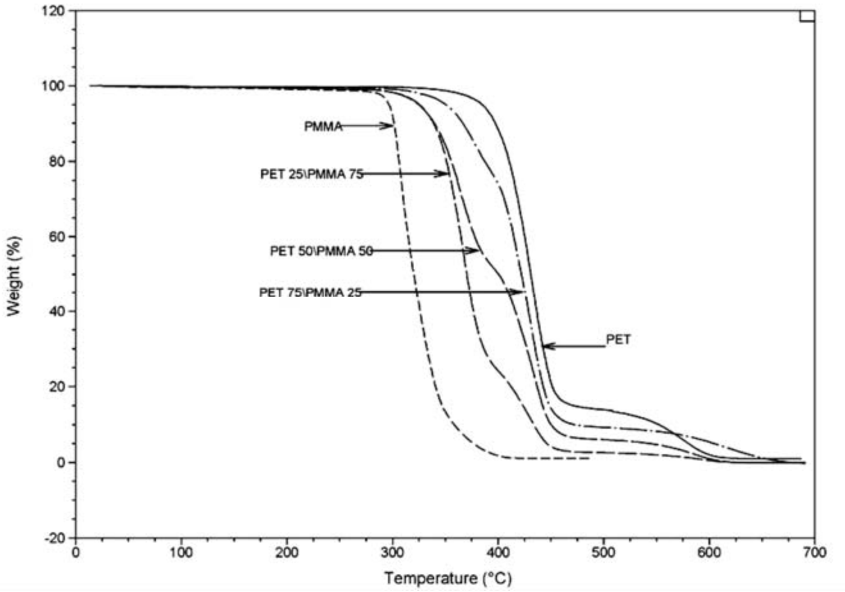

Figure 1: TGA curves for virgin polymers and blends obtained at a heating rate of 10°C/minute

The degradation behaviour of PET/PMMA blends are related to the variation in crystallinity in the blends. Shaban et al.[19] has reported the non-isothermal crystallization parameters for PET/PMMA blends. Four different compositions of PET and PMMA (25: 75, 50: 50, 75: 25 and 90: 10 wt%) were studied. Cooling rates of 1 and 2.5°C/min were used to obtain a proper crystal growth. For these rates it is noticed that as the PET content in the blend increases the enthalpy value (ΔH) increases with a maximum value noted for virgin PET. Table 1 indicates that as the PET content increases in the blend the degradation temperature range increases. This could be due to the increasing PET percentage, implying greater amount of crystallinity as is confirmed by kinetic studies conducted by Shaban et al.[19].

Time, temperature and weight loss data for all the systems were obtained from the TGA equipment. Figures 2 to 6 show the fraction volatiles evolved per unit time as a function of fractional amount of polymer degraded. The fraction of volatiles evolved per unit time (y-axis) was calculated using the formula;

$$r_{n+1} = \frac{C_{n+2} - C_n}{t_{n+2} - t_n} \tag{1}$$

where n, C_{n+2}, C_n, t_{n+2} and t_n indicate the volatiles evolved per unit time at any given point of calculation, conversion (gas evolved) in the succeeding stage relative to the point n, conversion (gas evolved) in the preceding stage relative to the point n, time corresponding to the C_{n+2} stage and time corresponding to the C_n stage.

Table 1: Degradation parameters obtained for PET, PMMA and PET/PMMA blends

Sample Name	**ϕ (°C/min)**	**k**	**n**	**Average SSE***	**Percentage degraded**	**Temperature range (°C)**
PET Virgin, Curve 1	5	5.51	2.61	0.00062	83%	375 to 461
	10	4.97	2.59	0.00070		
	15	4.74	2.58	0.00064		
	20	4.85	2.43	0.00065		
PET Virgin, Curve 2	5	4.20	2.47	0.00072	15%	461 to 625
	10	3.73	2.42	0.00058		
	15	7.61	2.22	0.00027		
	20	3.27	2.46	0.00058		
PMMA Virgin	5	3.80	2.28	0.00015	98%	280 to 410
	10	3.70	1.86	0.00034		
	15	3.55	2.49	0.00035		
	20	3.18	2.57	0.00055		
PET 25/ PMMA 75 Curve 1	5	7.16	2.63	0.00052	74%	300 to 400
	10	7.62	2.57	0.00046		
	15	8.39	2.29	0.00039		
	20	6.76	2.49	0.00044		
PET 25/ PMMA 75 Curve 2	5	4.23	3.17	0.00041	24%	400 to 612
	10	5.03	2.91	0.00061		
	15	5.91	3.49	0.00025		
	20	4.81	2.96	0.00070		
PET 50/ PMMA 50 Curve 1	5	24.49	2.13	0.00018	44%	284 to 374
	10	23.31	2.10	0.00020		
	15	27.53	2.41	0.00039		
	20	19.95	2.46	0.00045		
PET 50/ PMMA 50 Curve 2	5	5.59	2.59	0.00053	48% 7%	374 to 477 477 to 599
	10	4.83	2.65	0.00064		
	15	4.40	2.50	0.00076		
	20	4.41	2.54	0.00071		
PET 75/ PMMA 25 Curve 1	5	5.32	2.68	0.00052	90%	300 to 519
	10	4.71	2.57	0.00061		
	15	4.77	2.46	0.00066		
	20	4.34	2.36	0.00087		
PET 75/ PMMA 25 Curve 2	5	5.95	2.65	0.00040	9%	519 to 690
	10	3.58	2.47	0.00035		
	15	2.60	2.78	0.00042		
	20	3.23	2.31	0.00027		

*sum of square of errors

A sixth order polynomial was fitted to each curve shown in Figures 2 to 6 and based on a program developed using mathematica the area under each curve was estimated. Figure 2 indicates the fraction volatiles evolved per unit time as a function of fraction of the polymer degraded for PET virgin. The Figure indicates a large peak and a small peak for each heating curve. The large curve corresponds to the volatilization of hydrocarbons and the small curve indicates the volatilization of carbonaceous residues.

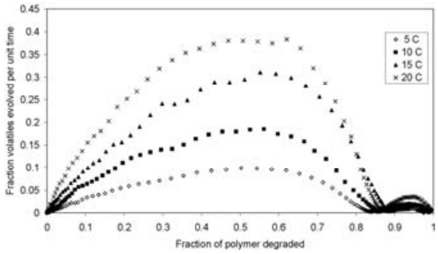

Figure 2: Fraction volatiles evolved per unit time versus fraction of polymer degraded for virgin PET at varying heating rates

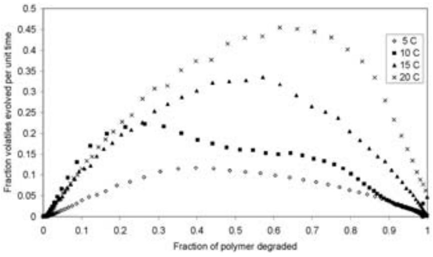

Figure 3: Fraction volatiles evolved per unit time versus fraction of polymer degraded for virgin PMMA at varying heating rates

Figure 3 indicates the fraction volatiles evolved per unit time as a function of fraction of polymer degraded for virgin PMMA. The Figure indicates one curve for all heating rates and an additional shoulder for 10°C/ min.

Figure 4 indicates the fraction volatiles evolved per unit time versus fraction of polymer degraded for PET 25/PMMA 75. The Figure clearly indicates a large peak ranging from 0 to 0.8 and small peak ranging from 0.8 to 1. As the heating rate is increased the volatile degradation rate was also found to increase.

Figure 5 indicates the fraction volatiles evolved per unit time versus fraction of polymer degraded for PET 50/PMMA 50. The Figure indicates three different peaks, the first large peak ranges from 0 to 0.5, the second peak ranges from 0.5 to 0.9 and third peak ranges from 0.9 to 1.0. Figure 6 indicates the fraction volatiles evolved per unit time versus fraction of polymer degraded for PET 75/PMMA 25. The first large peak ranges between 0 and 0.85 and the second small peak lies between 0.85 and 1.

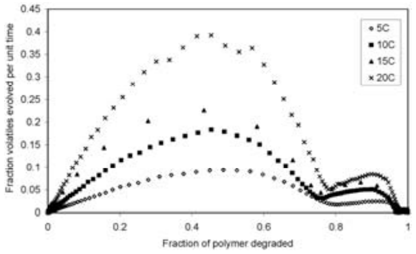

Figure 4: Fraction volatiles evolved per unit time versus fraction of polymer degraded for PET 25/PMMA 75 (wt %) at varying heating rates

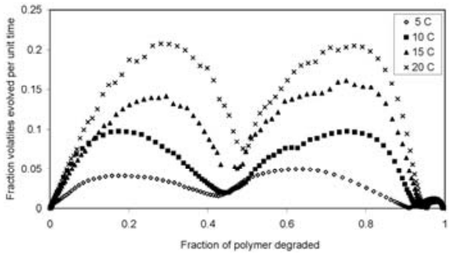

Figure 5: Fraction volatiles evolved per unit time versus fraction of polymer degraded for PET 50/PMMA 50 (wt %) at varying heating rates

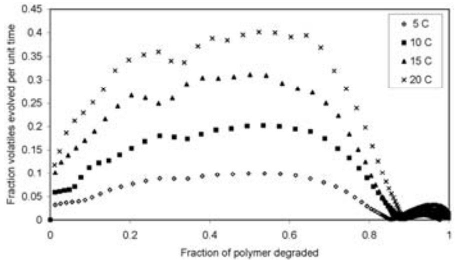

Figure 6: Fraction volatiles evolved per unit time versus fraction of polymer degraded for PET 75/PMMA 25 (wt %) for different heating rates

The kinetics of thermal degradation of PET/PMMA blends, virgin PET and PMMA was studied using an approximation that the mechanism of the degradation process has a variable order.

If n is assumed to be the order of the degradation mechanism and k is assumed as a degradation constant which takes into account inherent process during degradation like, splitting of individual monomers, oligomers or polymeric chains the modified Avrami's equation [20] given below was applied to the experimental data.

$$M = 1 - \exp(-kp^n) \qquad (\mathbf{2})$$

where M, k, p and n indicate the dimensionless experimental data obtained using Mathematica, degradation rate constant (dimensionless), fraction of polymer degraded (dimensionless) and order of degradation (dimensionless).

The area between each consecutive point for each typical curve shown in Figures 2 to 6 was divided by the total area of each curve to obtain the experimental value of M in equation (2). A program based on Mathematica was used to generate the theoretical value of M. The value of p in equation (2) is similar to the x-axis value in Figures 2 to 6.

Solver an optimization function in Excel was used to optimize the parameters k and n. The solver minimized the sum of squares of errors between the experimentally predicted M values and those obtained theoretically as seen in Table 1.

Figures 7 and 9 to 14 indicate fraction of polymer degraded as a function of volatiles evolved per unit time. Table 1 indicates the degradation data obtained for virgin polymers and polymer blends at different heating rates. The k values obtained from Figure 7 corresponds to the experimental data for the first curve in Figure 2. The k values are found to vary between 4.74 to 5.51, while for the second curve the values vary from 3.72 to 4.2. The values of n, which represent the order of degradation varies between 2.43 to 2.61 and 2.22 to 2.47. Degradation curve for PMMA at different heating rates is shown in Figure 8. This Figure indicates a systematic increase in degradation with increasing heating rates.

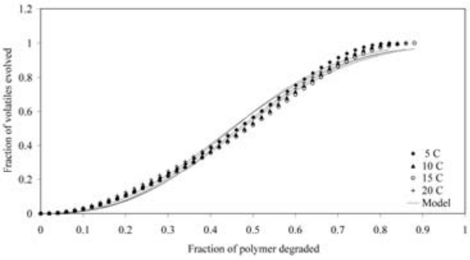

Figure 7: Fraction of volatiles evolved as a function of fraction of polymer degraded for virgin PET (curve 1)

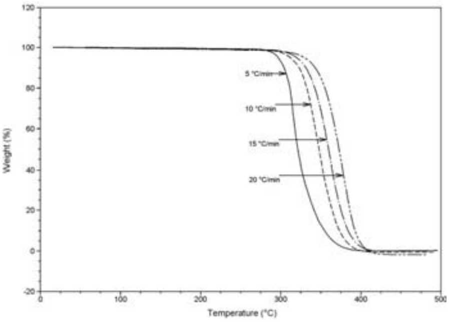

Figure 8: TGA curves for virgin PMMA

Figure 9 indicates fraction of polymer degraded as a function of volatiles evolved per unit time. A good match is obtained between theoretical and experimental data. The values of k lie between 3.18 to 3.80 and that of n lies between 1.86 and 2.7. Figure 10 is the first curve found in Figure 4 for PET 25/PMMA 75. A good match is obtained between experimental data and theoretical data. The values of k lie between 6.76 to 8.4 and the values of n lie between 2.29 to 2.63. Figure 11 is the second small curve found in Figure 4. A good match is obtained between experimental and theoretical data. The values of k lie between 4.23 to 5.91 and the values of n lie between 2.91 to 3.49.

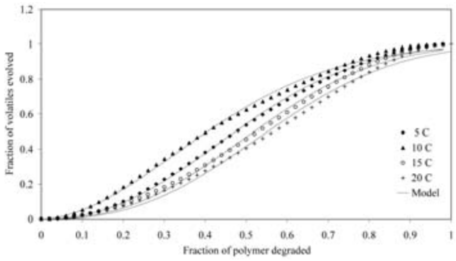

Figure 9: Fraction of volatiles evolved as a function of fraction of polymer degraded for virgin PMMA

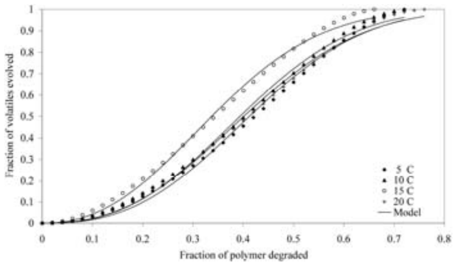

Figure 10: Fraction of volatiles evolved as a function of fraction of polymer degraded for PET 25/PMMA 75 (curve 1)

Figure 12 and 13 are representative curves drawn for obtaining the kinetic parameters for the first two curves given in Figure 5 for PET 50/PMMA 50. The area of the two large curves in Figure 5 are almost identical. The values of k and n (Table 1) for curve 1 are found to be higher than curve 2. The k values ranges from 19.95 to 27.5 while that of curve 2 range between 4.4 to 5.6. The values for n for curve 1 range from 2.1 to 2.46 while for curves 2 and 3 range from 2.5 to 2.65.

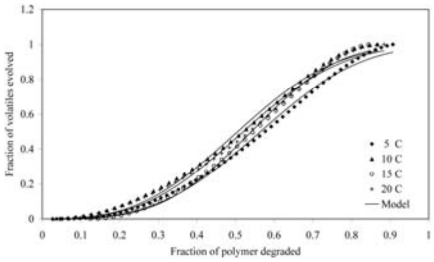

Figure 11: Fraction of volatiles evolved as a function of fraction of polymer degraded for PET 25/PMMA 75 (curve 2)

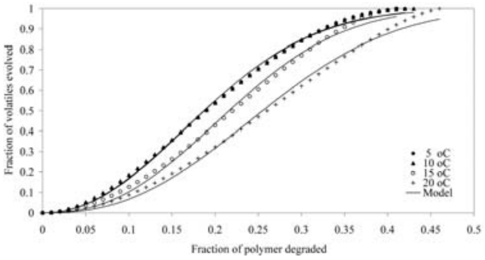

Figure 12: Fraction of volatiles evolved as a function of fraction of polymer degraded for PET 50/PMMA 50 (curve 1)

Figure 14 is the curve 1 for degradation of PET 75/PMMA 25. This Figure indicates the first large portion of the area seen in Figure 6. Values of k for curve 1 are greater than that of curve 2 indicating that different degradation mechanism occur in the blend. The n values are found to be almost similar.

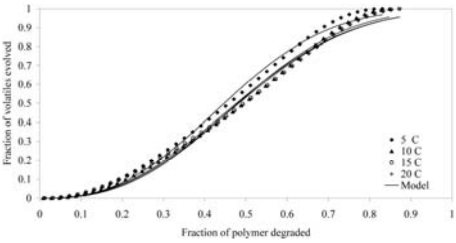

Figure 13: Fraction of volatiles evolved as a function of fraction of polymer degraded for PET 50/PMMA 50 (curve 2)

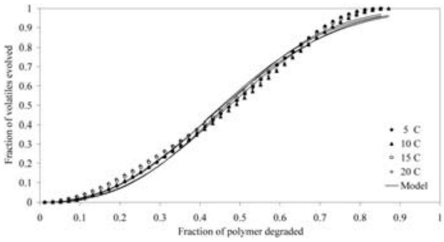

Figure 14: Fraction of volatiles evolved as a function of fraction of polymer degraded for PET 75/PMMA 25 (curve 1)

SEM Analysis

SEM analysis of the cryoscopically fractured virgin polymers and three blends are indicated in Figures 15 to 19 respectively. PET shows a disrupted fracture surface indicating semicrystalline nature while PMMA indicates a glassy nature. TGA curves indicate that 98% virgin PMMA degrades between 280-400°C while 83% virgin PET degrades between 375 to 461°C. This could possibly be due to the crystalline nature of

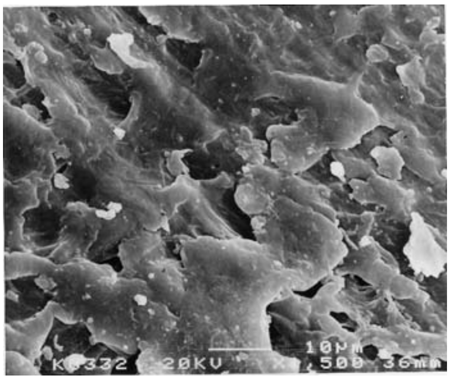

Figure 15: SEM micrograph for virgin PET

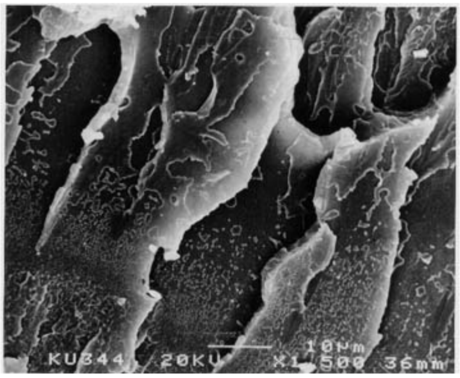

Figure 16: SEM micrograph for virgin PMMA

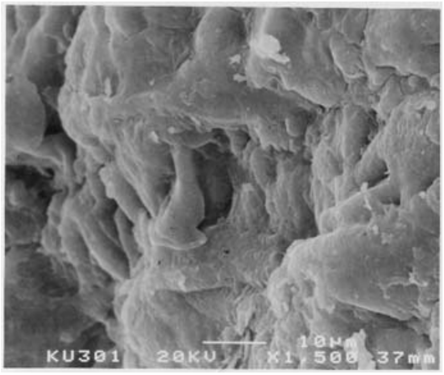

Figure 17: SEM micrograph for PET 25/ PMMA 75

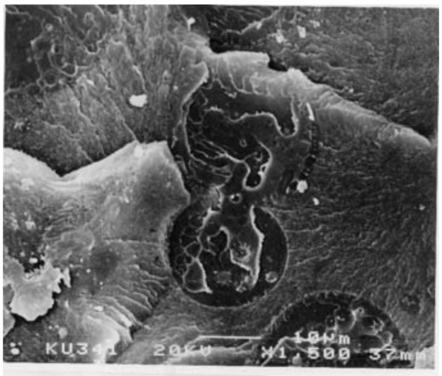

Figure 18: SEM micrograph for PET 50/ PMMA 50

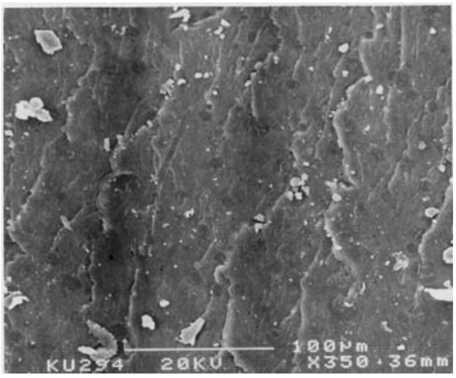

Figure 19: SEM micrograph for PET 75/ PMMA 25

PET. As seen in Figure 5 the fraction of volatiles evolved per unit time for PET 50/ PMMA 50 at different heating rates show an immiscible nature of the blend. The blend with 50 wt% PET exhibits a heterogenous morphology (Figure 18) in which the amorphous phase (PMMA) forms spherical particles distributed in the PET matrix.

Conclusion

Three different compositions of blends (PET 25/PMMA 75, PET 50/PMMA 50, and PET 75/PMMA 25) were synthesized using melt mixing method in a 500 ml batch reactor. Fraction volatiles evolved per unit time was estimated and plotted against fraction of polymer degraded. It was observed that virgin PET contained two degradation curves while virgin PMMA contained only one curve. PET 25/ PMMA 75 and PET 75/PMMA 25 blends also contain two curves while PET 50/PMMA 50 contains three curves. These curves signify that different reaction mechanisms occur on heating the blends. Maximum volatilization is found to occur at the highest heating rate.

Modified Avrami equation was used to study the degradation kinetics of virgin PET, PMMA and PET/PMMA blends. The equation is found to fit the experimental data. The degradation rate constant k and the order of degradation n was evaluated.

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