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Thermal and Morphological Studies on Poly(Methyl Methacrylate)/Thermoplastic Polyurethane Blends

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Poly(methyl methacrylate) (PMMA) and thermoplastic polyurethane (TPU) blends in different compositions viz., 95/05, 90/10, 85/15 and 80/20 (by wt/wt% of PMMA/TPU) have been prepared by melt mixing using a twin screw extruder. The thermal stability of these blends has been characterized by thermogravimetric (TG) analysis. All the blends are stable up to 381°C and complete degradation occurs at 488°C. A slight improvement in thermal stability was noticed with an increase in TPU content in the blends. Surface morphology of the blends has been studied by an optical microscope. Optical microphotographs revealed two-phase morphology for all the blends.

Keywords PMMA, TPU, blends, thermal behavior, morphology

Introduction

The largest commercial exploitation of polymer blending has been connected with the attempt to improve the impact strength of plastics by the inclusion of elastomeric materials (1). Among elastomers, thermoplastic polyurethane (TPU) is a promising candidate for its industrial importance due to its easy processability with good elongation, good optical properties, excellent low temperature properties and high abrasion resistance. TPUs are affected by exposure to elevated temperatures, softening and loss of their VC (virtually crosslinked) properties, which often hinder the potential applications. In order to overcome these disadvantages, attempts have been made to make blends/composites with conventional polymers, where the TPU exists as the dispersed phase. On the other hand, poly(methyl methacrylate) (PMMA) offers transparency, good tensile properties and oil resistance. Several researchers (2–7), have studied blending through an interpenetrating polymer network/solution process using a thermosetting type of polyurethane (PU) and different acrylic materials. To select the suitable material for a given application, polymer technologists require knowledge about their dimensional stability and thermal history (8).

In continuation of our previous communication (9), the PMMA/TPU blends have been analyzed for their thermal stability using thermogravimetric analyzer (TGA) and surface morphology by optical microscopy.

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Experimental

Materials

PMMA grade Gujpol-P 876-h-001 and TPU, grade Desmopan 385 S were obtained from M/s. Gujarat State Fertilizers Company Limited and M/s. Bayer Industries Private Limited, India, respectively. Specific gravity of PMMA is 1.19, whereas its flow temperature is 152°C.

Preparation of the Blends

The polymers were pre-dried in an air-circulating oven at 80°C for 4 h and mixed physically for 2 min prior to blending. Blending of the polymers in different proportions (95/5, 90/10, 85/15 and 80/20 by wt/wt% of PMMA/TPU) was carried out in Haake Rheocord Fison 9000 system (Germany) CTW 100 twin-screw extruder, (with twin-screw granulator set up) in the temperature range 145–170°C at 20 rpm just after the physical pre-mixing by tumbling action. Some of the typical properties of PMMA, PMMA/TPU blends and TPU are given (9) in Table 1.

Technique

The TGA thermograms were obtained using a TA Instruments Inc., TGA 2950 (USA) thermal analyzer at a heating rate of 20°C/min in nitrogen media. The TGA profiles were taken over a temperature range 30–800°C. The weight of the samples used for each analysis was 6–8 mg.

The TGA curves were analyzed to give percentage mass loss as a function of temperature. The oxidation index (OI) was calculated based upon the weight of carbonaceous char (CR) as related by the empirical equation:

$$\mathrm{OI} \times 100 = 17.5 \times 0.4\ \mathrm{CR} \tag{1}$$

Surface morphology of PMMA/TPU blends was analyzed on a Leica Microsystems optical microscope, Leica MeF4, Wetzlar (Germany).

Table 1
Typical physico-mechanical properties of PMMA, TPU and PMMA/TPU blends

Compositions of PMMA/TPU (%, wt/wt)	Density (g/cc)	Tensile strength (MPa)	% Elongation at break	Izod impact strength (J/m)
100/0	1.1827	80.4	10.6	19.1
95/05	1.1763	69.4	11.3	19.4
90/10	1.1787	66.7	29.2	24.4
85/15	1.1821	63.9	34.7	26.4
80/20	1.1835	50.9	36.3	29.3
0/100	1.1934	—	—	—

Results and Discussion

Thermogravimetric Studies

TGA and its derivative thermograms for PMMA and TPU homopolymers are given in Figures 1(a) and (b), respectively. Typical TGA thermograms for all PMMA/TPU blends, along with the homopolymers are shown in Figure 2.

The TGA curves obtained under dynamic scans were analyzed in order to determine a thermal stability trend. The measured temperature characteristics such as, T_o (temperature of onset of decomposition), T_{10} (temperature for 10% mass loss), T_{20} (temperature for

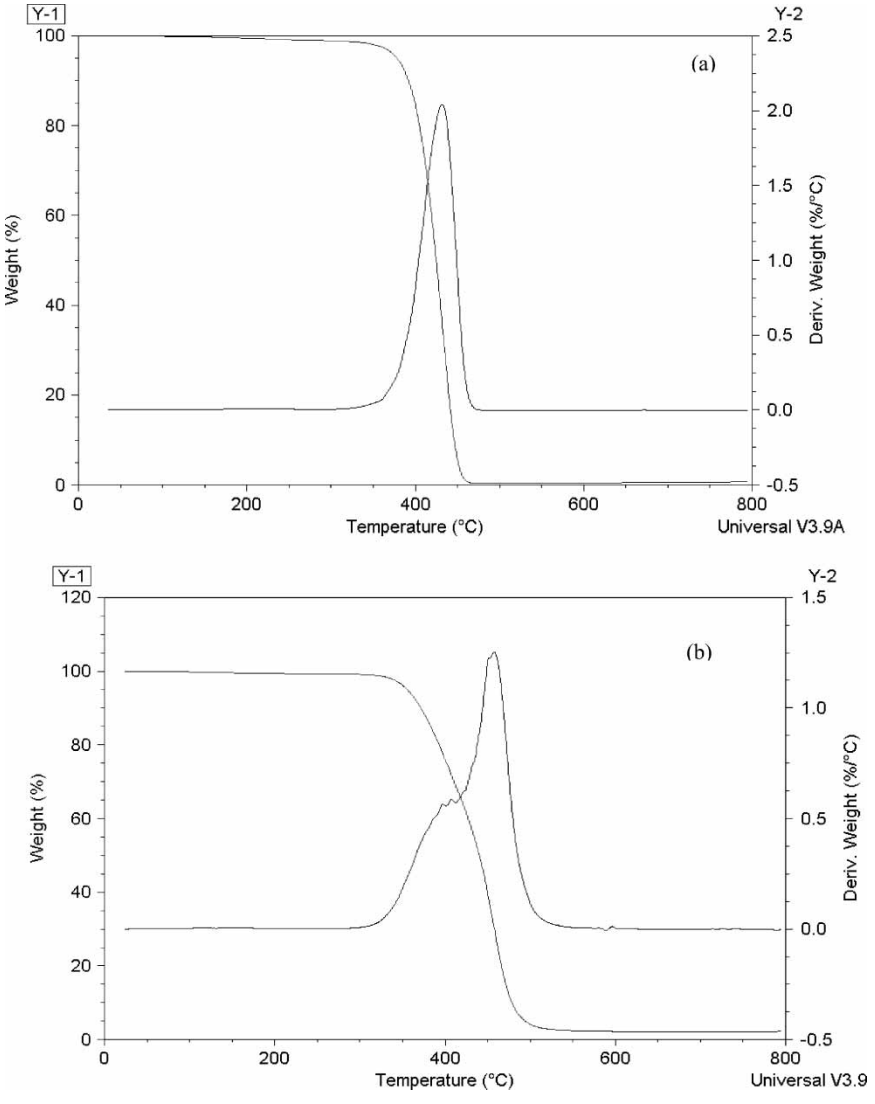

Figure 1. TGA and its derivative thermograms of: (a) PMMA and (b) TPU homopolymers.

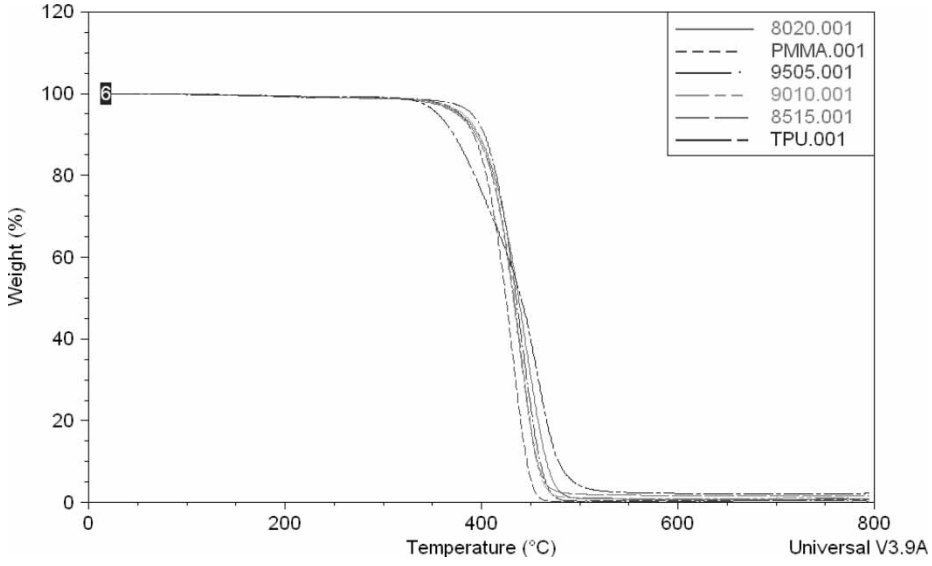

Figure 2. TGA thermograms for all PMMA/TPU blends along with the homopolymers.

20% mass loss), T_{50} (temperature for 50% mass loss) and T_{max} (temperature for maximum mass loss) were presented in Table 2.

T_o, T_{10}, T_{20}, T_{50} and T_{max} are the main criteria of the thermal stability of blends and signal features of the TG curves. The higher the values of T_o, T_{10}, T_{20}, T_{50} and T_{max}, the higher the blends heat stability will be (10). The temperature range of the degradation of PMMA and TPU are 333–475°C and 302–551°C, respectively. The rate of thermal degradation of TPU is slower than PMMA. The wider range of thermal degradation behaviour of TPU may be due to the presence of nitrogen and the presence of both hard and soft segments in TPU. The thermal degradation temperature range of the PMMA/TPU blends lies in between that of the homopolymers. From Table 2, it was noticed that there was no systematic variation in the characteristic temperature with compositions of blends. This is due to the complicated chemical structure and morphology of the blends.

A slight improvement in the thermal stability was noticed after incorporation of TPU in the matrix of PMMA. After incorporation of TPU, the presence of a urethane linkage inhibits/retards the rate of degradation of the blends. A similar observation was made by Goswami and Chakrabarty i.e., with an increasing proportion of PMMA, the onset of degradation of the interpenetrating polymer networks (IPNs) is shifted towards a lower temperature zone (11).

The ash content of PMMA is very low compared to TPU. The ash content increases with an increase in the TPU content. The carbonaceous char (CR) data reveals that there is slight improvement in the thermal stability of the blends, OI values of the blends lie in the 0.0107–0.0347 range. Hence, it is concluded that PMMA/TPU blends are good flame retardants as evidenced by their low OI values.

The temperature range of thermal degradation of the PMMA/TPU blends obtained from derivative TGA curves are given in Table 3. From Figure 1(b) and Table 3, it was noticed that the two-step thermal degradation process occurs for TPU in the temperature range of 302–414°C and 414–551°C for the first and second step, respectively. This behavior is associated with the weight loss of hard and soft segments present in TPU (12).

Table 2
Thermal data obtained from TGA scans for PMMA/TPU blends

Blend composition PMMA/TPU (%, wt/wt)	Temperature at different weight loss[a] ± 2°C					Ash content (mg)	Oxidation index (OI)
	T_o	T_{10}	T_{20}	T_{50}	T_{max}		
100/0	373	392	407	425	458	0.0792	0.0055
95/05	392	407	418	436	483	0.1540	0.0107
90/10	386	395	410	432	477	0.2883	0.0201
85/15	381	395	410	432	473	0.3970	0.0347
80/20	383	395	414	440	488	0.4954	0.0206
0/100	352	370	395	447	503	0.5580	0.0390

[a] T_o(temperature of onset of decomposition), T_{10}(temperature for 10% mass loss), T_{20}(temperature for 20% mass loss), T_{50}(temperature for 50% mass loss) and T_{max}(temperature for maximum mass loss).

Table 3
Temperature range of thermal degradation of blends obtained from the derivative curve of TGA

Blend composition PMMA/TPU (%, wt/wt)	Transition temperature range $\pm 2^{\circ}C$[a]		
	T_i	T_p	T_c
100/0	333	434	475
95/05	357	441	494
90/10	336	440	486
85/15	325	441	491
80/20	324	446	506
0/100	302	398	414
	414	458	551

[a]T_i: temperature at which decomposition starts; T_p: temperature at which the decomposition rate is maximum and T_c: temperature at which decomposition is completed.

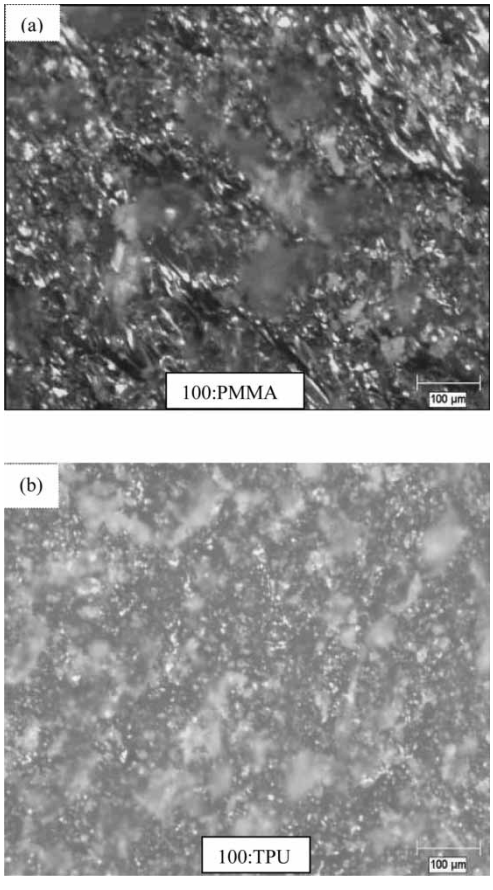

Figure 3. Optical micrographs of: (a) pure PMMA and (b) pure TPU.

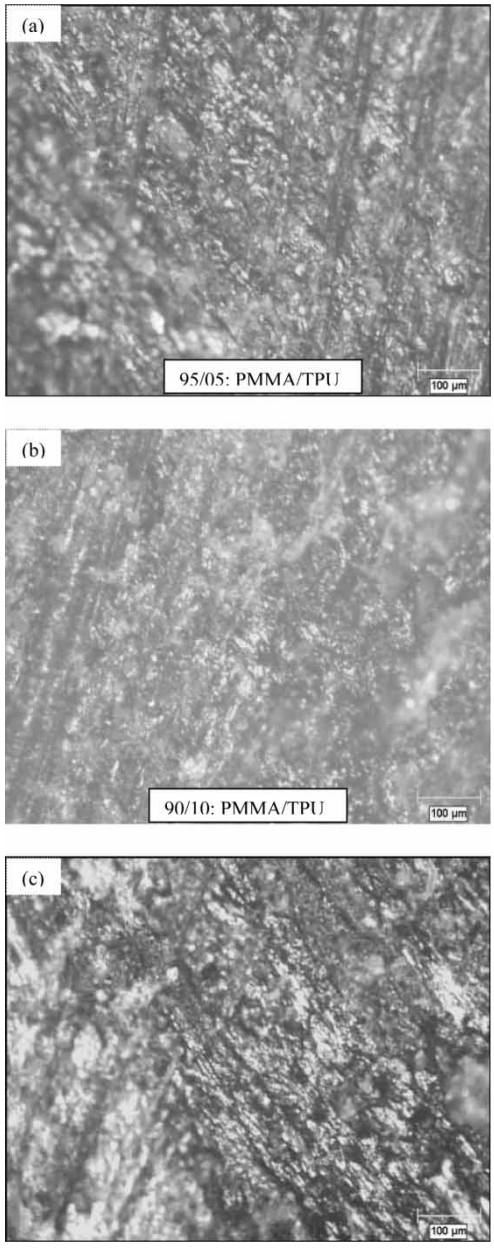

Figure 4. Optical microphotographs of: (a) 95/05, (b) 90/10, and (c) 80/20 PMMA/TPU blends.

Surface Morphology

Surface morphology of the system strongly influences the properties of the polymer blends (8). The optical microphotographs of PMMA and TPU are given in Figures 3(a) and (b), respectively. These figures revealed a two-phase morphology, for both PMMA and TPU. The two-phase morphology of PMMA is due to the coexistence of the amorphous and crystalline phase. The two-phase morphology in the case of TPU is due to the presence

of hard and soft segments. The microphotographs of the blends are shown in Figures 4 (a)–(c). From these figures, it is noticed that the dispersed TPU phase is distributed uniformly in the continuous phase of PMMA. Optical microphotographs of the 80/20 PMMA/TPU blend reveals the layered like structure. The domain size of the second phase is finer for 95/05 and 90/10, which results in high mechanical properties.

Conclusions

All the PMMA/TPU blends are stable up to 381°C. A slight improvement in the thermal stability of the PMMA was noticed after the incorporation of TPU. This result indicates, some kind of interaction between the carbonyl group of acrylate and urethane linkage of TPU. Optical microphotographs revealed the two-phase morphology for all the blends. TPU is uniformly distributed in the continuous phase of PMMA and the domain size of the second (TPU) phase increased, with an increase in the TPU content. A layered like structure was noticed for 80/20 blend.

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