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Studies on Poly(Methyl Methacrylate) (PMMA) and Thermoplastic Polyurethane (TPU) Blends

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Blends of poly(methyl methacrylate) (PMMA) and thermoplastic polyurethane (TPU) in different compositions viz., 95/5, 90/10, 85/15 and 80/20 (by wt/wt, % of PMMA/TPU) were blended by melt mixing using a twin-screw extruder. All the PMMA/TPU blends have been characterized for physico-mechanical properties such as density, melt flow index, tensile behavior and izod impact strength. The impact strength of the PMMA/TPU blends were found to increase significantly with an increase in the percentage of TPU up to 20%, by retaining the tensile strength of PMMA. The effect of chemical aging on the performance of blends has been studied.

Keywords poly(methyl methacrylate), thermoplastic polyurethane, melt mixing, blends, physico-mechanical properties, chemical aging

Introduction

Polymer blends are a mixture of two or more components that make up a material with new properties, based on the properties of the components chosen. Polymer blends add a new dimension to both commodity and engineering plastics. Polymer blends are a potentially inexpensive route to the formulation of new products comparatively without the need for exhaustive research and development costs associated with the development of new base polymers (1). Interest has grown, as blends with improved physical properties, better processability and lower cost have been developed. Typically, polymers are blended to improve cost—performance profiles—tailoring the properties to suit given applications. The scientific and commercial progress in the area of polymer blends so far has been quite significant and was driven by the realizations that blending can usually be implemented more rapidly and economically than the development of new polymers. New technology has been developed which makes it possible to more easily modify polymers and enhance performance. Blending is the way of the present and future plastics.

The literature survey reveals that most of the investigations were carried-out through interpenetrating polymer network/solution process using a thermosetting type of polyurethane (PU) and different acrylic materials (2–7). However, thermoplastic polyurethane (TPU) may be mixed with poly(ethylene-co-methyl methacrylate) (8), polyolefins (9),

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polypropylene (PP) (10), styrene-acrylonitrile (SAN (11), polyacetal (12), poly (butylene-terephalate) (13), polycarbonate (PC) (14), acrylonitrile-butadiene-styrene (ABS) (15), polyamide-6 (16), etc., from the point of improving the mechanical properties particularly such as toughness and other properties. PMMA is a transparent polymer with good tensile properties and oil resistance, while TPU is a thermoplastic elastomer used extensively in the automotive and coating industries because of its easy processability with good elongation, excellent low temperature properties and high abrasion resistance. In this research article, the authors have reported on the melt blending of PMMA and TPU, with an objective of improving the toughness of PMMA by retaining its optical clarity.

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.

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Preparation of the Blends

The polymers were predried 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 weight % of PMMA/TPU) was carried out in Haake Rheocord [Model No.9000] system (Germany) CTW 100 with twin-screw granulator set up in the temperature range of 145–170°C at 20 rpm just after the physical pre-mixing by tumbling action. The resulting blends were subjected again to pre-drying conditions before molding into the appropriate test specimens as per standards specifications by injection molding in Engel, Austria [Type: ES330/80 HLS] computerized injection molding machine, set at 80 Tons for testing purpose.

Techniques

All the physico-mechanical properties of the PMMA/TPU blends were carried out as per ASTM standards specifications. Tensile behavior and impact strength were measured as per ASTM D 638 and ASTM D 256 using JJ Lloyds Universal Testing Machine (LR 100 K) (UK) and ATS Faar (Italy) impact tester, respectively. Density, surface hardness, vicat softening point and melt flow index of PMMA/TPU blends were studied as per ASTM D 792, ASTM D 2240, ASTM D 1525 and ASTM D 1238 methods, using a Mettler (Switzerland) balance, PSI Sales (India) Shore D Durometer hardness tester, ATS Faar (Italy) vicat softening point apparatus and a Davenport (UK) melt flow index tester, respectively. Chemical aging tests have been conducted as per ASTM D 543 at room temperature for 168 h in different chemical reagents. The effects of chemical aging on the tensile properties of blends have been reported Tables 2–4.

Results and Discussion

The measured physico-mechanical properties such as density, melt flow index (MFI), tensile behavior and izod impact strength of the PMMA/TPU blends are shown in

Table 1
Physico-mechanical properties of PMMA/TPU blends

Properties	Compositions of PMMA/TPU in (wt/wt%)					
	100/0	95/5	90/10	85/15	80/20	0/100
Density (g/cc)	1.1827	1.1763	1.1787	1.1821	1.1835	1.1934
MFI (g/10 min.)						
230°C/1.2 kg	1.35	1.95	2.08	2.37	4.24	—
2300°C/3.8 kg	4.33	6.89	9.66	11.86	13.65	—
VSP (0°C at 10 N load)	95.0	93.55	93.20	92.60	92.50	92.30
Tensile strength (MPa)	80.4	69.4	66.7	63.9	50.9	—
Tensile modulus (MPa)	1156	900	880	851	746	—
Elongation at break (%)	10.6	11.3	29.2	34.7	36.3	—
Izod impact strength (J/m)	19.1	19.4	24.2	26.4	29.3	—
Surface hardness (Shore-D)	90	88	85	83	82	31

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Table 1. The density values for pure PMMA and TPU were found as 1.1827 and 1.1934 g/cc, respectively. The density values of blends were found to be in between that of the homopolymers. The theoretical densities of the blends were calculated by the volume additive principle, which states that ($\rho = W_1\rho_1 + W_2\rho_2$), where, ρ is the density of the blends. W_1 and W_2 are the weight fractions of the constituents 1 and 2 respectively and ρ_1 and ρ_2 are their corresponding densities. The variation of ρ of the blends with composition is shown in Figure 1. The figure indicates that there is no good physical and chemical interaction between PMMA and TPU. As the proportion of TPU content increases in the blends, the density values increased correspondingly, due to incorporation of high dense TPU in the PMMA matrix. MFI values were found to increase as the percentage of TPU increases in the blends. This might be ascribed to the highly viscous nature of TPU. The Vicat softening point at 10 N load of pure PMMA and TPU were 95.0 and 92.5°C, respectively, compared to that of the blends being in the range 92.5–95.0°C. The surface hardness value of all the blends lies between the corresponding

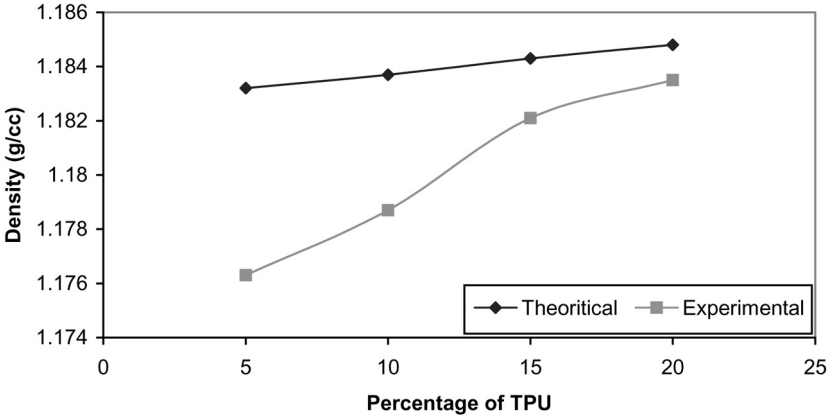

Figure 1. Variation of density with composition of TPU in blends.

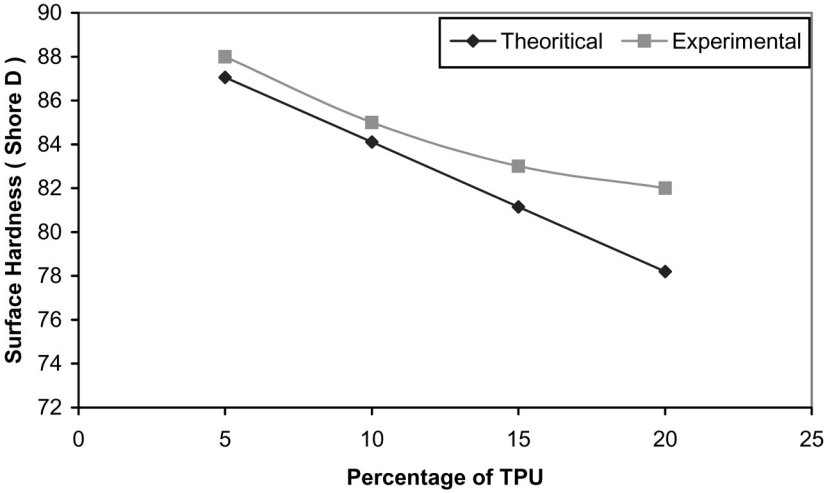

Figure 2. Effect of TPU addition on Surface hardness of blends.

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homopolymers. The surface hardness values of the blends lie in the range 82–88 Shore D, while that of 100% PMMA and TPU were found to be 90 and 31 Shore D, respectively. A reduction of about 2 to 9% in the surface hardness is observed as the TPU content increases from 5 to 20%. The reason for decreasing the surface hardness value is due to incorporation of amorphous, soft segments of TPU into the PMMA matrix. The calculated and experimentally obtained surface hardness values of the blends are shown in Figure 2. From this result (Figure 2), it is revealed that the dimensional stability of PMMA/TPU blends has been retained.

The stress verses strain curves for PMMA, TPU and their blends are shown in Figure 3. From Figure 3, it was noticed that the stress-strain curves of blends lies

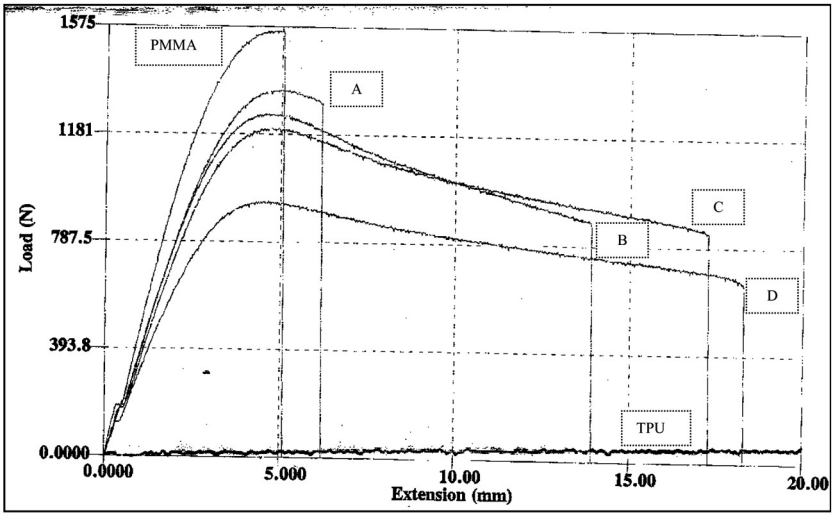

Figure 3. Stress-strain curves for PMMA, TPU and their blends for A: 95/05, B: 90/10, C: 85/15 and D: 80/20.

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Table 2
Percent deviation of the tensile strength from corresponding composition after chemical aging

Composition PMMA/TPU	5% CH_3COOH	5% HCl	5% H_2SO_4	5% NaOH	5% Na_2CO_3	5% NH_4OH	C_6H_{14}	Distilled water
100/0	−6.6	−7.0	−5.8	−6.4	−9.7	−5.8	−9.1	−8.9
95/05	−0.2	+0.5	−3.7	−7.2	−9.7	−0.5	−0.4	−4.6
90/10	−1.7	−4.6	−3.8	−2.3	−7.9	−7.8	−7.9	−6.4
85/15	−5.6	−8.8	−9.0	−8.2	−10.3	−8.5	−7.7	−7.6
80/20	+1.0	+6.0	+1.6	−2.2	−1.9	−2.3	−5.0	−1.4

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Table 3
Percent deviation of the tensile modulus from corresponding composition after chemical aging

Composition PMMA/TPU	5% CH_3COOH	5% HCl	5% H_2SO_4	5% NaOH	5% Na_2CO_3	5% NH_4OH	C_6H_{14}	Distilled water
100/0	−5.1	−1.1	−1.3	+0.1	−19.0	−3.8	−0.5	−2.5
95/05	+13.7	+17.2	+15.2	+17.5	+0.5	+16.3	+17.2	+3.2
90/10	+5.5	+1.3	+5.2	+10.0	−3.9	+8.1	+0.4	−2.6
85/15	+13.5	−7.5	−13.1	−14.6	−12.5	+6.2	−8.86	−4.0
80/20	−27.6	−21.0	−24.5	−25.1	+2.2	+11.4	−1.0	+0.3

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Table 4
Percent deviation of the % elongation at break from corresponding composition after chemical aging

Composition PMMA/TPU	5% CH_3COOH	5% HCl	5% H_2SO_4	5% NaOH	5% Na_2CO_3	5% NH_4OH	C_6H_{14}	Distilled water
100/0	+56.9	+0.5	+20.8	+51.7	+0.8	−1.6	−12.9	+4.8
95/05	−20.7	+7.5	−28.0	−31.7	+17.0	−16.2	−8.8	+8.3
90/10	+29.9	−3.9	+27.6	+25.8	+22.4	+9.1	−2.3	+1.3
85/15	−19.7	−12.0	+17.9	−3.8	−1.7	−11.5	−7.9	−2.4
80/20	−7.85	−1.6	+16.0	+2.1	+8.2	+15.3	+5.4	−1.2

between the corresponding homopolymers. A significant reduction in tensile strength and tensile modulus was noticed an increase of the TPU content in the blend formulation. Tensile modulus decreased from 22 to 36% with an increase in TPU content from 5 to 20%. This is due to an increase in flexible TPU content in the blends. A drastic improvement in percentage elongation at break of the blends was noticed with increase in the TPU with content, i.e., about 6–242% improvement.

A significant improvement in impact strength of the blends was noticed after incorporation of TPU in the PMMA matrix. The percentage improvement in impact strength of the blends lies in the range 2–53%.

The blend specimens were exposed to different chemical reagents at room temperature for 168 h, as per ASTM standard (22). The effect of chemical aging on the tensile behavior of the blends has been evaluated. The percent deviation of the tensile behavior, such as tensile strength, tensile modulus and percent elongation at break, from the corresponding composition after chemical aging, was calculated and shown in Tables (2–4), respectively. A slight reduction or retention of tensile strength was noticed for all the blends, after exposure in different chemical reagents. However, reduction in tensile modulus and percent elongation at break of all the blends were observed.

Tables 2–4 also reveal that there was no systematic variation in the tensile behavior of the blends. A marginal change in tensile modulus and % elongation at break, is due to the plasticization effect of chemicals on the blends.

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Conclusions

A series of PMMA/TPU blends have been prepared by a melt blending method. A marginal reduction in tensile strength and tensile modulus was noticed with an increase in TPU content from 5 to 20% by weight ratio in the blends. A significant improvement in percentage elongation at break and impact strength was noticed with an increase in the TPU content in the blends. From the chemical aging behavior, it can be concluded that the percent elongation behavior is sensitive towards chemical aging. A drastic reduction in percentage elongation at break and tensile modulus of the blends were observed after exposure in different chemical reagents. This is due to the plasticization effect of chemical reagents in the blends.

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