Some Properties of Polymethylmethacrylate–Polyisobutylene Rubber Blends

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Polymethylmethacrylate (PMMA) was solution blended with medium and low molecular weight polyisobutylene rubber samples (PIB$_m$ and PIB$_l$) in toluene. The compatibility of the blends was assessed from density and viscometric methods at 2 per cent total solid content of solution. The experimental densities were observed to be lower than the theoretical values assuming additivity of volumes of the polymers and the solvent for both PIB samples. The plots of relative viscosities against composition were found to be non-linear. The experimental values for reduced viscosities were found to be lower than calculated values using Krigbaum-Wall equation for all blend solutions. A visual study of the blend films showed marked phase separation and impaired clarity. The tensile mechanical test on the blend films showed a higher yield stress and a larger area under the stress-strain curve compared to the pure PMMA, suggesting that blending with the PIB rubber toughened PMMA. The density and viscometric methods have again been proved to be an easy and reliable method for assessing polymer-polymer compatibility.

Introduction

The application of polymethylmethacrylate (PMMA) is principally concerned with its high transparency and good weathering resistance. Its principal limitation is its brittleness, which makes it crack easily when little stress is applied on it. Impact strength of brittle plastics has been improved by grafting with elastomers, modified with block copolymers or by blending with elastomers[1,2].

Blending of polymers is an easy method to obtain a wide spectrum of applications because of the change of physico-chemical properties by varying the blend composition[3]. It has been used commercially to improve flexibility, tensile and impact strength, chemical resistance and various other properties of polymers[4]. Blending imparts desired needs on the base polymer and synergistic effects have been reported in which one or more properties of the blend dominate those of any polymer in the blend[5]. Plastic-elastomer blend are often heterogeneous in nature but when there is good adhesion between the plastic and the elastomer, the energy propagates a crack when a stress is applied, which does not cause fracture but is absorbed by the elastomer particles[1]. Bucknall[6] has also postulated that the dispersed

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rubber particles lower crack formation when stress is applied by causing the applied stress to spread in different directions. This latter explanation, which describes toughening of plastics, is known as stress distribution and relief mechanism[6,7].

Blending of PMMA and PIB polymer were used to assess the suitability and PIB serve as impact modifiers for PMMA. The compatibility of PMMA with PIB rubber was also assessed in solution, using density and viscometric methods, which require inexpensive equipment and yet allow the blends to be classified as compatible or incompatible[8,9]. The study reports the effect of polyisobutylene rubber concentration and molecular weight on density and relative and intrinsic viscosities of PMMA/PIB blend solutions in toluene, as well as the morphology and tensile mechanical properties of some of the blend films.

Experimental Procedure

The polymethylmethacrylate (PMMA, $M_v = 3.7 \times 10^5$), the polyisobutylene samples (PIB, $M_v = 1.35 \times 10^6$, PIB$_l = 9.88 \times 10^5$) and toluene (used as solvent) are all reagent grade chemicals obtained from BDH, England. The polymer samples were used without further purification but the toluene (refractive index =1.49) was re-distilled before use.

Table 1 – Experimental and calculated densities for PMMA/PIB blend solutions in toluene

Blended composition PMMA/PIB	Calculated density (g cm^{-3})	Experimental density (g cm^{-3})	
		PMMA/PIB$_m$	PMMA/PIB$_l$
100:0	0.8520	0.8487	0.8460
90:10	0.8497	0.8472	0.8486
80:20	0.8493	0.8464	0.8520
70:30	0.8489	0.8460	0.8495
60:40	0.8485	0.8452	0.8477
50:50	0.8481	0.8444	0.8475
40:60	0.8477	0.8440	0.8472
30:70	0.8473	0.8420	0.8467
20:80	0.8469	0.8416	0.8461
10:90	0.8465	0.8408	0.8453
0:100	0.8460	0.8453	0.8453

A two-per cent stock solution was prepared for each of the polymer samples and appropriate volumes of the solutions were transferred into standard volumetric flasks to prepare PMMA/PIB blend of varying compositions from 100:0 to 0:100, all with a total solid content of 2 per cent. The densities of all blend solutions were measured using a standard specific gravity bottle at 25 ±1°C. The viscosity measurements were carried out in a thermostated water bath at 30 ±1°C. The relative viscosities were measured using an Oswald viscometer, while the reduced viscosity numbers were measured with a Ubbelohde dilution viscometer.

Film Casting and Mechanical Test

20 cm^3 of the polymer solutions were, in turn, poured into an open petri dish placed on a flat surface in a film cupboard and left for 24h for evaporation of the solvent. 10cm^3 distilled water was poured on the dry film in a petri dish. The dish with its content was left for 20 min, after which the film was removed and dried between filter papers. The very rubbery nature of the PIB film made it difficult to cast from solution using the above method. The mechanical properties were measured with the Instron Tensile Machine (model 1026) at strain rate of 50mm/min and chart crosshead speed ratio of 4:1 at room temperature. Sample films of dimensions 5:1:0.002cm were used.
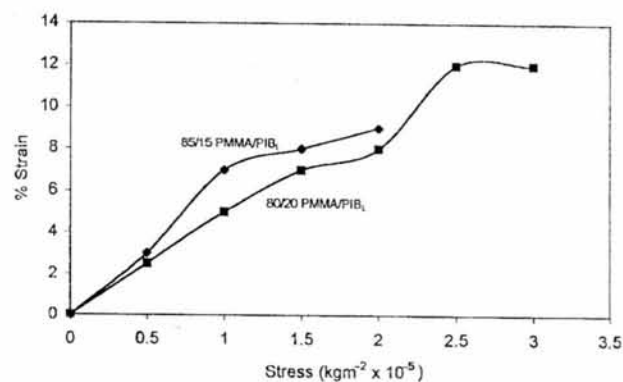

Figure1—Stresss-strain data for 18/20 and 85/15 PMMA/PIB$_l$ blends

Results and Discussion

The results, in Table 1 and Figure 1 show that the experimental densities of blend solutions are lower than calculated assuming additivity of volumes of the polymers and solvent for both the low and medium molecular weight polyisobutylene samples. The experimental densities are closer to the calculated ones for the blend solutions with the low molecular weight PIB sample. The lower experimental densities, compared to the calculated, are attributed to less chain packing in solution, which is evidence of incompatibility. The closeness of experimental values to the calculated for the low molecular weight PIB suggests that the degree

Table 2 – Variation of reduced viscosity with blend

Composition PMMA/PIB blend composition	PMMA/PIB Limiting viscosity (dL/g)		PMMA/PIB Limiting viscosity (dL/g)	
	Calculated	Experimental	Calculated	Experimental
100/0	0.7400	0.7400	0.7400	0.7400
95/5	0.7655	0.7615	0.7810	0.7054
90/10	0.7910	0.7896	0.8220	0.8106
85/15	0.8125	0.8105	0.8531	0.8520
80/20	0.8420	0.8406	0.8600	0.8600
0/100	1.25	1.25	1.56	1.56

of incompatibility decrease, as the molecular weight of the second polymer decrease[12, 13]. The higher experimental densities for the 80/20 and 70/30 PMMA/PIB$_l$ blend solutions suggest special interaction at these compositions that can aid compatibility[10].

The plot of relative viscosity against composition is non-linear (Figure 2). This latter result also suggests incompatibility of PMMA with PIB, since for compatible blends the plot of relative viscosity against composition is linear[9, 10]. The results in Table 2 show that the experimental limiting viscosities are lower than calculated for the PMMA/PIB solutions. Compatible blend solutions give higher experimental values of limiting viscosities. The lower experimental values here suggest decreased molecular interactions between the polymers in solution, which again signifies incompatibility of the two polymers. Using the Krigbaun-Wall equation[14, 15], it was found that the experimental values are again closer to the calculated ones for blend solutions with the low molecular weight polyisobutylene. This collaborates the earlier observation that the degree of incompatibility is molecular weight dependent and decreases as the molecular weight of the second polymer decreases.

Film Morphology

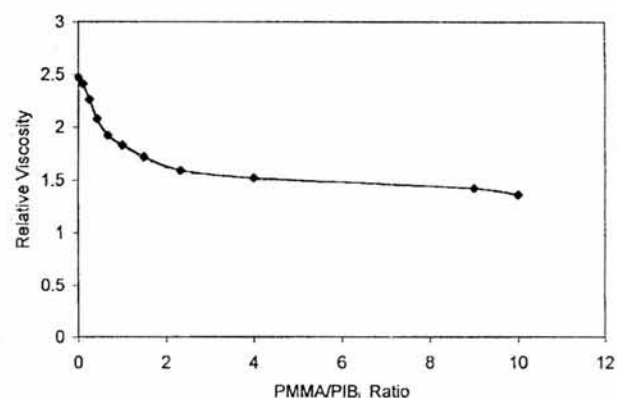Many techniques are used to determine whether a blend is single or multiphase[11, 12, 13, 16], however, a quick

Figure2— Variation of relative viscosity with composition for the PMMA/PIB$_l$ blends

but not totally reliable method is by film clarity. Compatible blends give transparent films but a translucent or opaque film is an evidence of incompatibility. Incompatible blends do give transparent films when the refractive indices of the polymers are very close or the films are very thin, but phase separation is a strong evidence of immiscibility of one polymer in another. Only the pure PMMA film was transparent. All blend films have impaired clarity when compared to PMMA. There was also phase separation observed for all blend films. At fairly low percentage PIB$_l$ (5 to 10 per cent) in the blend, the rubber phase appear evenly distributed in the PMMA phase. Clarity was impaired and phase separation observed for all PMMA/PIB$_m$ blend films examined.

Table 3 – Mechanical properties of some selected blends

Blend composition PMMA/PIBl	Initial modulus x 10^{-5} kg m^{-2}	Ultimate modulus x 10^{-5} kg m^{-2}	Stress at break x 10^{-5} kg m^{-2}	Strain at break per cent
85/15	1.67	2.22	2.0	9.0
80/20	2.0	3.33	3.0	12.0

Mechanical Property

For the selected blends with the low molecular weight PIB, the initial and ultimate modulus, stress at break increase with the PIB content of the blend (Table 3). The area under the stress-strain plots also increase with the rubber concentration (Figure 1). This is an evidence of toughening of PMMA by PIB rubber.

Conclusion

PMMA is incompatible with PIB rubber. The degree of incompatibility decreases with decreasing molecular weight of the PIB. PMMA was toughened when blended with the rubber at fairly low concentrations, but its clarity is impaired. Blending with a lower molecular weight PIB may give a toughened and more transparent product.

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