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Miscibility studies on a poly (ether imide) and poly (methyl methacrylate) blends

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The miscibility criteria of a poly (ether imide) (Ultem) and poly (methyl methacrylate) (PMMA) was investigated at 25 °C in chloroform in dilute solutions by viscometric analysis. The intrinsic viscosity and viscometric parameters of these blend systems were determined for several Ultem/PMMA mixtures in compositions such as 80/20, 60/40, 40/60, 20/80 in chloroform solutions. The miscibility criteria on the basis of the sign of viscometry, Δb_m, $\Delta b'_m$, $\Delta b''_m$ and $\Delta[\eta]_m$ which are the difference between their experimental and ideal values were calculated by applying theoretical equations proposed by Krigbaum–Wall, Catsiff–Hewett and Garcia et al. The data obtained from the viscometry studies showed that the prepared blends were miscible in all the studied composition ranges at 25 °C. The miscibility of the polymers was confirmed by the results of differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy (FT/IR ATR) measurements.

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1. Introduction

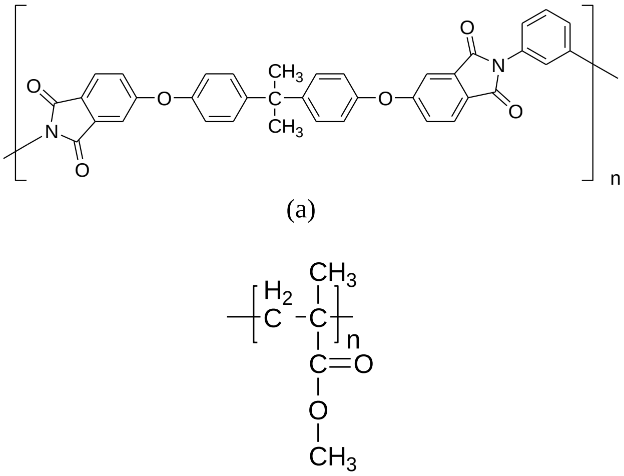
Commercial poly (ether imide) (Ultem) is an amorphous high performance thermoplastic with its repeat unit structure containing both the rigid aromatic imide units and the somewhat more flexible aromatic ether units. Owing to the unique structure of its backbone, Ultem exhibits high glass transition temperature (T_g = 215 °C), high mechanical strength and rigidity, yet has a good degree of ductility and melt processability. Its highly aromatic backbone structure also imparts an inherent flame retardancy and low smoke generation characteristics in the polymer. Because of these high performance characteristics, Ultem finds specialty niche applications in the automotive under the hood, aerospace, electronics and medical equipment markets. However, its relatively high cost has limited its market volume [1-3].

Poly (methyl methacrylate) (PMMA) was discovered in 1930. The resins have been used for the production of transparent plastic sheets, viz. Plexiglas™ or Perspex™ used for the military aircraft cockpit canopies, gunner's turrets and the like [4]. PMMA is used mainly in two forms, either as glazing materials with good abrasion resistance or as a part of variety of impact modifiers, forming either a rigid core or vice versa, a compatibilizing shell. Owing to the relatively high (for acrylic) glass transition temperature of common atactic PMMA, and its ability for free radical copolymerization as well as relatively frequent miscibility, PMMA has often been incorporated into acrylic formulations wherever higher rigidity was required. Since the 1930s either copolymerization and / or latex blending has been used to produce paint, adhesives or modifiers.

Modern technology thrusts challenging demands on the performance capabilities of materials, including polymers and their blends. A new approach to the science and technology of polymer blends has emerged recently, i.e., polymer blends by design, rather than by availability. These polymeric materials must perform under strenuous mechanical, chemical, thermal and electrical conditions imposed by the requirements of a specific application. Service in these applications usually involves several criteria to be fulfilled without a loss of economic advantage. Indeed, performance requirements of polymer blends are often at the limit of the properties that can be achieved. Moreover, these materials are expected to endure complex environmental conditions for extended time. All these factors stress the need for in-depth studies of the properties and performance of polymer blends [5-8].

While miscibility is limited to a specific set of conditions the immiscibility dominates most polymers form immiscible blend that require compatibilization. Alloys performance depends on the ingredients, their concentration, and morphology. The alloying process must result in stable and reproducible properties of the polymer blend. Thus, the morphology must either be stable, unchanged during the forming steps, or the changes must be well predicted. The alloying makes use of an appropriate dispersing method and compatibilization.

The most commonly used techniques for investigation of polymer–polymer miscibility are thermal analysis, electron microscopy and spectroscopy [9-11]. These techniques are very powerful for such applications, but they are somewhat expensive for most of the researchers. Therefore, other methods on investigation of polymer–polymer miscibility were proposed either using alternative properties or low cost equipment. Among them, viscometry is a very promising technique. Several works on polymer–polymer miscibility via viscometry have been done in recent years [12-17]. This is no study in the literature on the miscibility of Ultem and PMMA. However their blends have some potential use in preparing transparent and thermal resistant strong composites. Chemical structures of Ultem (a) and PMMA (b) were given in Scheme 1.



(a)

(b)

Scheme 1. Chemical structure of (a) Ultem and (b) PMMA

In this study, the miscibility criteria of Ultem and PMMA were found by viscosity as suggested by several research groups such as Krigbaum–Wall, Catsiff–Hewett and Garcia et al., at 25 °C and differential scanning calorimetry (DSC) measurements.

2. Experimental

2.1. Materials and instrumentation

Ultem and PMMA were supplied by General Electric Plastics Division and Alfa Aesar, respectively. Both of the polymers were purified by dissolving in chloroform as a dilute solution and precipitated in a large amount of methanol.

All viscosity measurements were performed at 25 °C using a home-made modified Ubbelohde-type capillary viscometer in a constant temperature bath controlled with ± 0.02 °C by a Huber Type electronically controlled thermostat. Stock solutions of the binary and ternary systems were freshly prepared by dissolving appropriate amount of polymers in chloroform into a concentration of 0.5 g /100 cm^3 solutions. For each measurement, 5 cm^3 stock solution was loaded into the viscosimeter and diluted by adding 2 cm^3 chloroform to yield several lower concentrations. The elution time of each solution was taken as the average of four readings agreed to within ±0.5%.

Thermal parameters of the composites were characterized by DSC measurements on a differential scanning calorimeter (Perkin-Elmer Pyris-1 DSC 6) under a nitrogen flow at a rate of 20 mL/min with aluminum plate as sample container, and meantime, a blank aluminum plate was used as reference. Samples of the 5–9 mg mass were heated from 60 ^{o}C to 250 °C at a rate of 10 °C /min. Then, the samples were cooled to 60 °C at a rate of 10 °C/min and finally reheated to 240 °C also at a rate of 10 °C/min. The second scans were reported in the paper.

2.2. Theoretical background

For the ternary mixture of polymer (1), polymer (2) and a common solvent, at constant weight ratio of polymer 1 to 2 for a given composition, the well-known Huggins' equation is written as [18]

$$(\eta_{sp})_m / c_m = [\eta]_m + b_m c_m \tag{1}$$

where c, $(\eta_{sp})/c$, $[\eta]$ and b are concentration, reduced viscosity, intrinsic viscosity and viscometric interaction parameter of the polymer in the solution, respectively, while subscript "*m*" denotes "mixture". The miscibility of the polymer (1) and (2) is estimated by comparison of the experimental and ideal values of b_m and $[\eta]_m$.

Krigbaum and Wall [19] have defined the ideal value of the interaction parameter b_m^{id} as

$$b_m^{id} = b_{11} w_1^2 + b_{22} w_2^2 + 2 b_{12}^{id} w_1 w_2 \tag{2}$$

and the b_{12}^{id} as a geometric mean;

$$b_{12}^{id} = b_{11}^{1/2} b_{22}^{1/2} \tag{3}$$

Catsiff and Hewett [20] have defined the ideal value of the interaction parameter $b_{12}^{id'}$ as an arithmetic mean

$$b_{12}^{id'} = (b_{11} + b_{22}) / 2 \tag{4}$$

On the other hand, Garcia et al. [21] have stated that the Eq. (2) proposed by Krigbaum and Wall was mathematically erroneous and have defined the ideal value of the interaction parameter $b_{12}^{id''}$ as

$$b_{12}^{id''} = b_1 w_1^2 + b_2 w_2^2 \tag{5}$$

Furthermore, Garcia et al. have also proposed another miscibility criterion based on the difference between the experimental and ideal values of $[\eta]_m$ assuming that the intrinsic viscosity can be treated as an excess property. The value of $[\eta]_m^{id}$ has defined as

$$[\eta]_m^{id} = [\eta]_1 w_1 + [\eta]_2 w_2 \tag{6}$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities of corresponding polymers.

3. Results and discussion

The intrinsic viscosity and viscometric parameters of this system have been determined at 25 °C in chloroform. Fig. 1 show the plots of variation of reduced viscosity (η_{sp}/c) with total polymer concentration, c in the solution for the blends in the compositions of Ultem/PMMA: 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100 in chloroform by weight, respectively. The linear relationships are observed for pure polymers and all of the compositions studied.

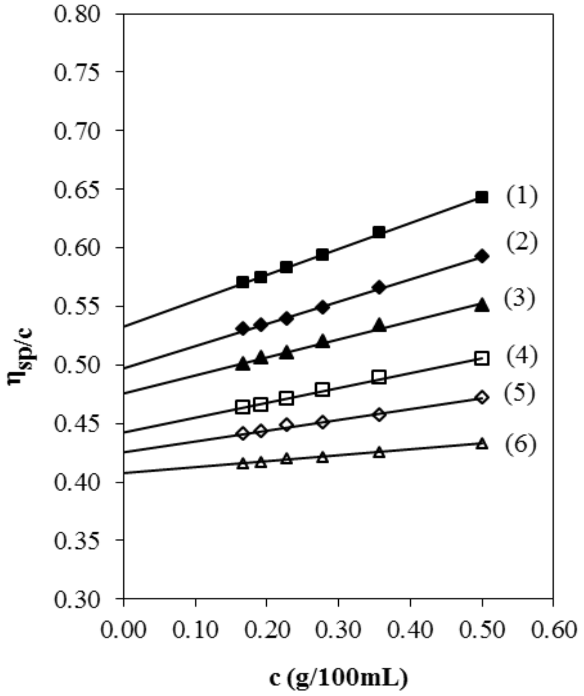


Fig. 1. Reduced viscosity values (η_{sp}/c) against total concentrations of the pure polymers of Ultem, PMMA and their mixtures at 25 °C in chloroform the following compositions of Ultem/PMMA: 100/0(6), 80/20(5), 60/40(4), 40/60(3), 20/80(2) and 0/100(1) by weight

The values of b_m^{exp} and $[\eta]_m^{exp}$ are determined from the slope and intercept of the linear straight line plotted according to Eq. (1) for solutions containing one of the polymer in binary mixtures or both of them at a given ratio in ternary mixtures. The data were collected in Table 1.

Table 1. Experimental dilute solution viscosity data of the blends and constituent polymers at 25 °C in chloroform

Ultem/PMMA 25 °C in chloroform	b_m^{exp} (cm^6/g^2)	$[\eta]_m^{exp}$ (cm^3/g)	r^2
100/0	0.0507	0.4072	0.9924
80/20	0.0923	0.4257	0.9921
60/40	0.1264	0.4424	0.9961
40/60	0.1538	0.4761	0.9921
20/80	0.1896	0.4972	0.9986
0/100	0.2203	0.5328	0.9994

The miscibility criteria Δb_m was described by Krigbaum and Wall. The polymer blend is miscible if $\Delta b_m = b_m^{exp} - b_m^{id} > 0$ and attractive molecular interactions are present or immiscible if $\Delta b_m = b_m^{exp} - b_m^{id} < 0$ and repulsive molecular interactions are considered. In the case of $\Delta b_m = 0$, neither attractive nor repulsive molecular interactions are present between polymers. The other miscibility criteria of a blend, $\Delta b'_m$ was found from Eq. (4). Catsiff and Hewett were proposed that $\Delta b'_m = b_m^{exp} - b_m^{id} > 0$ shows miscibility and $\Delta b'_m = b_m^{exp} - b_m^{id} < 0$ shows immicibility. The miscibility criteria of $\Delta b''_m$ and $\Delta[\eta]$ was described by Garcia et al. and found from Eq. (5) and (6). According to Garcia et. al, if $\Delta b''_m = b_m^{exp} - b_m^{id} > 0$ and $\Delta[\eta]_m = [\eta]_m^{exp} - [\eta]_m^{id} < 0$, the system is miscible, and if $\Delta b''_m = b_m^{exp} - b_m^{id} < 0$ and $\Delta[\eta]_m = [\eta]_m^{exp} - [\eta]_m^{id} > 0$, the system is immiscible.

The all miscibility criteria of Ultem/PMMA blends obtained using viscosity measurements were given in Table 2.

Table 2. Numerical values of polymer-polymer interaction coefficient for Ultem/PMMA blends

Ultem/PMMA 25 °C in chloroform	Δb_m (cm^6/g^2)	$\Delta b'_m$ (cm^6/g^2)	$\Delta b''_m$ (cm^6/g^2)	$-\Delta[\eta]_m$ (cm^3/g)
80/20	0.017	0.008	0.051	0.007
60/40	0.022	0.008	0.073	0.015
40/60	0.016	0.001	0.066	0.006
20/80	0.013	0.003	0.046	0.010

According to the values of miscibility criteria of Ultem/PMMA blends, $\Delta b_m > 0$, $\Delta b'_m > 0$, $\Delta b''_m > 0$ and $\Delta[\eta]_m < 0$ shows that Ultem/PMMA blends are miscible in all prepared compositions at 25 °C.

The T_g s of the blends were determined with the cast films by means of DSC. DSC thermograms of the polymers and their blends are shown in Fig. 2.

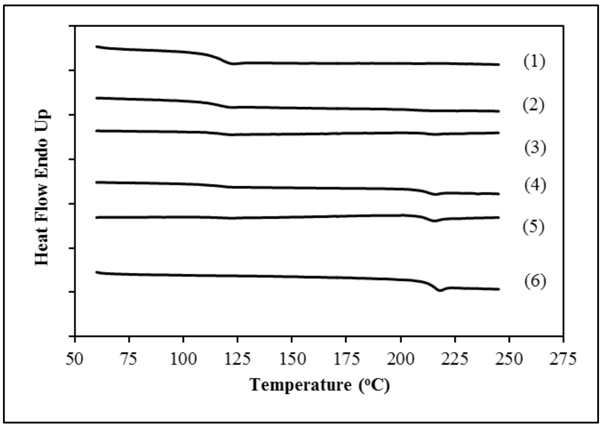


Fig. 2. DSC thermograms of PMMA (1), Ultem (6) and Ultem/PMMA blend in compositions at 20/80 (2), 40/60 (3), 60/40 (4) and 80/20 (5)

Table 3. Glass transition temperatures of Ultem, PMMA and their blends in the compositions of 80/20, 60/40, 40/60 and 20/80

Ultem/PMMA	T_g (°C)	
0/100 (1)	116	-
20/80 (2)	116	211
40/60 (3)	114	211
60/40 (4)	116	212
80/20 (5)	115	205
100/0 (6)	-	213

It can be seen that curves obtained for blends show two separate peaks (Fig. 2 and Table 3). The first peak is observed around 114-116 °C and is related to the T_g relaxation process of PMMA. The upper peak at 205-212 °C is related to the T_g relaxation of Ultem. The presence of two separate peaks confirms phase separation. While the position of the upper peak seems more or less stable, the upper peak shifts continuously down from 213 °C in plain Ultem to slightly 205 °C in the Ultem/PMMA 80/20 blend. Such shift must be related to partial miscibility, similarly to changes in T_g observed by DSC. It was observed in the peak position of T_g of the Ultem by increasing Ultem ratio.

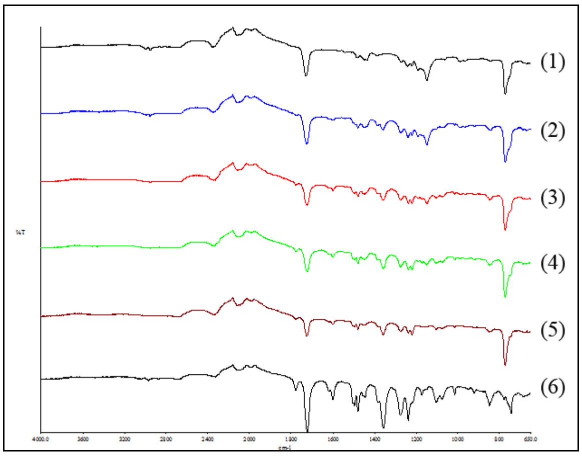


Fig. 3. FT/IR ATR spectra of PMMA (1), Ultem (6) and Ultem/PMMA blend in compositions at 20/80 (2), 40/60 (3), 60/40 (4) and 80/20 (5)

As can be seen from Fig. 3, the typical peaks of FTIR/ATR spectra of the films are centered at about 1724 cm^{-1} and 1721 cm^{-1} ($\nu_{C=O}$), 1600 cm^{-1}, 1496 cm^{-1} and 1478 cm^{-1} ($\nu_{C=C}$ aromatic) for Ultem; 1728 cm^{-1} ($\nu_{C=O}$), 771 cm^{-1} can be attributed to the α-methyl group vibrations and 988 cm^{-1} is the characteristic absorption vibration for PMMA. It is to detect the changes in carbonyl absorption band of Ultem and PMMA. This suggests that attractive forces are present between constituents of the blend.

4. Conclusions

The miscibility of Ultem/PMMA blends was investigated by viscometry, FT/IR ATR and DSC. According to the results, the miscibility criteria proposed by Krigbaum and Wall (Δb_m), Catsiff and Hewett ($\Delta b'_m$) and Garcia et al. ($\Delta b''_m$ and $\Delta[\eta]_m$) are in agreement in determination of the miscibility of polymers. All miscibility criteria which is close the zero obtained by viscosity experiments in this study exhibit partially miscibility property. The agreement on the results of FT/IR ATR, DSC and viscosity measurements for these polymer blends support the validity of this simple viscometric study.

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