

Studies on microhardness, compatibility and thermal stability of poly(ethylmethacrylate) (PEMA) and poly(ethyleneoxide) (PEO) polyblends

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Received 29 October 2001, accepted 18 November 2002

Abstract . Microhardness study on polyblends of poly(ethylmethacrylate) (PEMA) and poly(ethyleneoxide) (PEO) is carried out by Vicker's microhardness testing. Thermal stability of this blend is investigated by Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA). The decrease in the value of surface microhardness with increasing content of PEO in the blend reveals plasticization effect. The variation in thermal stability with increasing content of PEO is observed by TGA. The variation in compatibility and crystallinity of blend with increasing content of PEO is observed by DTA. Attempts have been made to correlate the results of microhardness and TGA-DTA.

Keywords : Polyblend, microhardness, TGA, DTA, thermal stability, plasticization, compatibility, crystallinity

PACS Nos. 61.41.+e, 62.20.Fe, 81.40.Gh, 81.40.Lm

1. Introduction

Polymers are widely used in industry largely owing to their valuable mechanical properties. In recent years, attention has been focused on mixtures of polymers *i.e.* polymer blends. Polymer blends are formed by mixing two or more polymers in common solvent. Polymer blends have better mechanical properties than their constituent polymers. By correctly choosing the polymers having different mechanical properties and chemical structures, one can obtain required set of valuable properties.

Now a days, lot of attention has been devoted to the characterization of these polymer blends [1–5]. The characterization of polymer blend means investigation of mutual compatibility of constituent polymers, variation of miscibility with varying composition of constituent polymers, structural changes induced by blending, variation of mechanical properties, variation in thermal stability, change in crystallinity *etc.*

The blend system presented here, comprises of a amorphous polymer PEMA and a crystallizable polymer PEO. The blend system with one of the components as crystallizable, has interesting behaviour. The addition of an amorphous polymer to a crystallizable polymer can have remarkable effect on miscibility, plasticization and crystallization behaviour of such polymer blends [2].

Thermogravimetric analysis (TGA) is a versatile technique to study thermal degradation of polymers [6]. Knowledge gained from studies of polymer degradation may lead to more useful and stable polymers. TGA is a continuous process that involves the measurement of sample weight as the reaction temperature is changed by means of a programmed rate of heating [7]. To study the thermal stability of PEMA : PEO blends, TGA has been utilized.

Differential thermal analysis (DTA) is an important technique for understanding the structure, organization and properties of polymer blends. DTA has been used for the

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determination of compatibility and incompatibility of polymer blends [8–10]. In general, compatible system exhibits single glass transition temperature (T_g) that falls between the T_g 's of the blend constituents. Compatibility is a representation of how close a blend can approach the ultimate state of mixing. The lack of compatibility leads to phase separation of the components and ultimately poor mechanical properties. DTA curves have been also used to detect change in crystallinity of blends [11]. DTA involves measurement of temperature difference (ΔT) between a sample and an inert reference material as the two are being heated or cooled at a known (linear) rate [11]. In the present investigation, DTA has been used to detect the change in compatibility and variation in crystallinity of PEMA : PEO polyblend with varying composition of PEO.

Microhardness testing has proved to be very popular for studying mechanical properties of polymers because of its simplicity and non-destructive nature [12]. In the present study, Vicker's microhardness testing has been used to detect the plasticization effect on PEMA : PEO blend and to study the effect of load and composition ratio of the two polymers on Vicker's microhardness number.

2. Experimental details

2.1. Materials :

For the preparation of the blends, the commercially available polymers PEMA (Aldrich, USA) and PEO (BDH, UK) were used. Polymer granules were supplied by M/s Redox, Jabalpur. PEMA with very high molecular weight grade and PEO having molecular weight of 300000 were quoted by the manufacturer.

2.2. Preparation of polyblend :

The solution cast technique was utilized to prepare the blends of the two polymers PEMA and PEO. The known amounts of two polymers were dissolved in benzene at 40 °C with constant stirring. A known quantity of this homogeneous solution was poured in glass mould kept inside the oven whose temperature was controlled automatically. The solution was then allowed to evaporate at a drying temperature of 40 °C for four hours. This yielded blend specimens in the form of pellets of size 6 cm² and 0.4 cm thickness.

2.3. Characterization and testing :

Microhardness :

The Vicker's hardness number (H_V) was determined with mhp160 microhardness tester with a Vicker's diamond pyramidal indenter, having a square base and 136° pyramidal angle attached to an Carl Zeiss NU2 universal research microscope. H_V was calculated using the relation :

$$H_V = \frac{1.854 \times L}{d^2} \text{ kg/mm}^2,$$

where L is the load in kg and d is diagonal of indentation in mm. The load ranging from 10 to 100 g was applied gently at a steady rate. The time of application of load was 30 seconds in each case. Several indentations were obtained at each load and the average hardness number was calculated

TGA and DTA :

TGA and DTA studies of the samples have been carried out with Mettler Toledo Instrument, Switzerland at RSIC Nagpur University, Nagpur. The instrument here has a thermoanalyser which simultaneously record temperature and sample weight loss along with DTA curves. Simultaneous TGA and DTA patterns of pure PEMA and polymer blends having 5 wt% of PEO, 25 wt% of PEO and 50 wt% of PEO have been obtained.

3. Results and discussion

The variation of H_V with load ranging from 10 to 100 g for both the pure PEMA and PEO polyblend samples is illustrated in Figure 1. It is evident from this figure that the H_V value increases with load upto 40 and 50 g for pure PEMA and PEMA : PEO polyblends respectively. Beyond these loads, H_V tends to saturate. Further, the figure reveals that the microhardness of specimens decreases with increasing content of PEO in the polyblend.

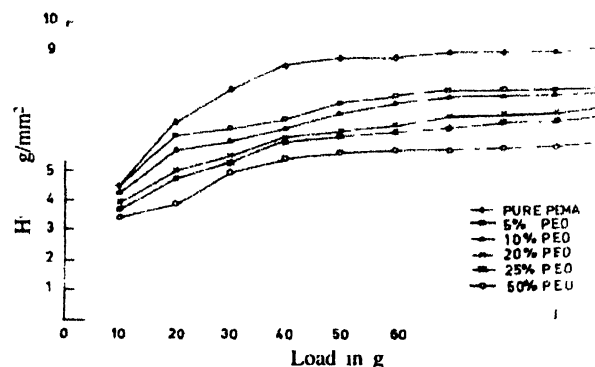


Figure 1. Variation of H_V with load for pure PEMA and PEMA : PEO polyblends.

The increase in H_V with increasing load can be explained on the basis of the strain hardening phenomenon [3,13,14]. On applying load, the polymer is subjected to some strain hardening. Finally, when H_V value tends to become constant, the polymer is completely strain-hardened. The rate of strain-hardening is greater at low loads and decreases at higher loads. Also it is evident that rate of strain-hardening decreases with increasing content of PEO. The decrease in the value of H_V with increasing content of PEO suggests that PEO acts as a plasticizer or softener for PEMA

The addition of PEO leads to the reduction of steric hindrance between PEMA chain molecules, thus resulting in the decrease in the value of H_V .

TGA-DTA traces for pure PEMA and the polyblend samples are given in Figures 2-5. In the case of pure PEMA (Figure 2), thermal degradation starts at about 167°C and

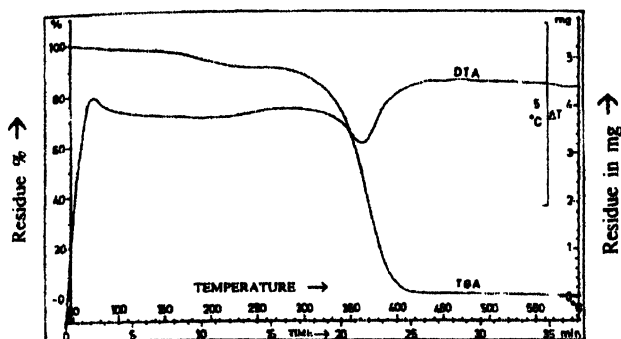


Figure 2. TGA-DTA pattern for pure PEMA.

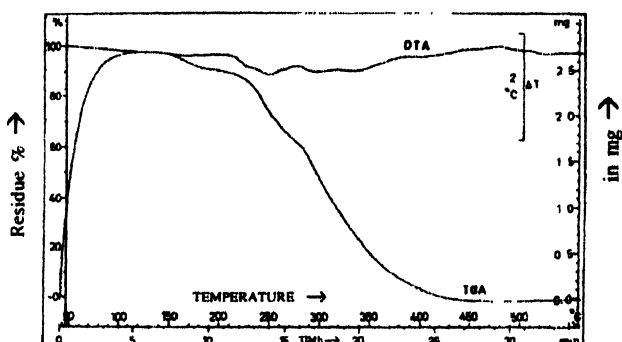


Figure 3. TGA-DTA pattern for specimen having 5 weight % of PEO.

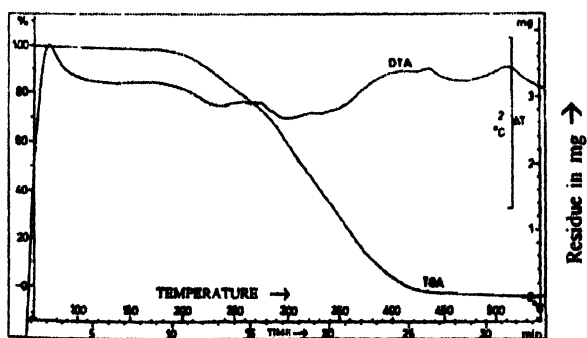


Figure 4. TGA-DTA pattern for specimen having 25 weight % of PEO.

about 5.2% weight loss occurs at 208°C. While in the case of polyblend having 5 wt% of PEO (Figure 3), thermal degradation begins little earlier around 153°C and only about 4.5% weight loss occurs at 175°C. For polyblend with 25 wt% of PEO (Figure 4), first decomposition begins at highest temperature of about 205°C while little higher weight loss of about 8% takes place at about 237°C. The first decomposition data for polyblend having 50 wt% of PEO

(Figure 5) is almost similar to that of polyblend with 5 wt% of PEO sample, although here the % weight loss is about 5% which is slightly higher.

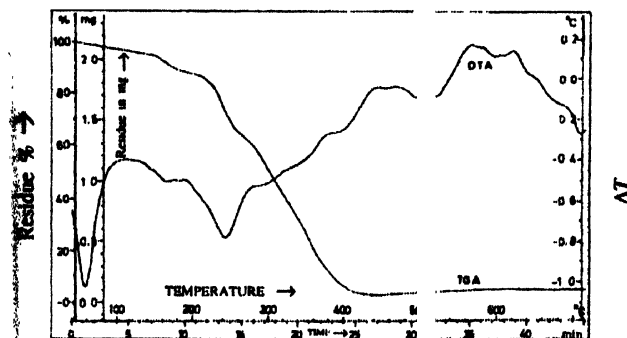


Figure 5. TGA-DTA pattern for specimen having 50 weight % of PEO.

The second decomposition in pure PEMA begins at about 338°C and almost complete decomposition (weight loss is about 89%) takes place at 387°C. For polyblend having 5 wt% of PEO, second decomposition begins at lower temperature of about 227°C; however, with lesser weight loss of about 65% takes place around 252°C. In the case of sample with 25 wt% of PEO, the second decomposition starts at higher temperature of about 282°C and about 72% weight loss occurs at 391°C. For sample with 50 wt% of PEO, second decomposition initiates at lowest temperature of about 222°C while lowest weight loss of about 20% takes place up to 253°C.

The samples with 5 wt% of PEO and that with 50 wt% of PEO, exhibits third decomposition also. In 5 wt% of PEO sample, it begins around 279°C and about 59% weight loss occurs at 361°C place, while for sample with 50 wt% of PEO, third decomposition starts at higher temperature of 298°C and ends around 387°C with about 53% weight loss.

The decomposition data obtained from the TGA patterns reveal that thermal stability of polyblend samples depend upon the concentration of PEO. Increased thermal stability is seen for blend specimens upto 25 wt% of PEO. For the blend having 50 wt% of PEO, thermal stability decreases. It is also evident from the TGA pattern of pure PEMA that thermal stability is somewhat more than that of polyblend samples having 5 and 50 wt% of PEO. The polyblends with 5 and 50 wt% of PEO show third decomposition, although their first and second decompositions begin at lower temperatures but the weight loss associated with first and second decompositions is lower than the pure PEMA. Although the polyblend samples having 5 and 50 wt% of PEO thermally degrade at lower temperatures but their decomposition phenomenon is expanded over wide range of temperature in comparison to that of pure PEMA which exhibits sharper decomposition pattern.

The DTA patterns for various blend specimens with 5, 25 and 50 wt% of PEO give the values of T_g as 110°C, 120°C, 130°C respectively. An increase in T_g with increasing crystallinity has been reported in the literature [15–17]. Thus, the crystallinity of PEMA : PEO polyblend increases with increasing concentration of PEO in polyblend. It is also evident from the DTA patterns that there is a single value of T_g , thus the constituents PEMA and PEO form compatible blends in the studied weight proportions of the two polymers. Also the occurrence of single T_g indicates the phase homogeneity and existence of single phase in the blend system.

4. Conclusion

The microhardness and TGA-DTA studies provide effective tools for the characterization of PEMA : PEO polyblend.

The increasing content of PEO in PEMA : PEO polyblend decreases the microhardness with added advantage of crystallizability and increased thermal stability. Increased crystallinity and better thermal stability with lower values of microhardness have been seen for polyblends having higher content of PEO. Thus PEMA : PEO forms compatible blend with a single phase system.

Acknowledgment

Authors are thankful to Regional Sophisticated Instrumentation Centre (RSIC), Nagpur University, Nagpur for providing TGA-DTA facilities.

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