Microhardness and X-ray diffraction studies on polymer blends of poly (ethylmethacrylate) (PEMA) and poly (ethylene oxide) (PEO): Plasticization and crystallization aspects

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Polymers having different properties and chemical structures are usually mixed together to obtain polymer blends which have required set of valuable properties. A lot of attention has been devoted in recent years to the characterization of polymer blends. 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. The mechanical properties of blends are determined primarily by the mutual solubility or miscibility of the two polymers. For the amorphous/crystallizable polymer mixture, increased miscibility in amorphous phase was reported by Straka et al.

The crystallizable polymer often acts as a plasticizer for amorphous polymer. Plasticizers are low molecular weight materials which are added to rigid polymers to soften them and thus they induce plasticization in polymer blend.

In crystallization process a crystallizable substance crystallizes from its melt. The crystallization process of a polyblend with crystallizable and amorphous components is affected by the properties of constituent polymers.

Poly(ethylmethacrylate) (PEMA) is a non-crystallizable and poly(ethylene oxide) (PEO) is a crystallizable polymer. In the present study authors have utilized Vicker's Microhardness testing to study the mechanical behaviour of the PEMA:PEO polyblend. Vicker's Microhardness testing has been found to be a non-destructive method. This test 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.

The crystallization process of PEO is affected by blending with PEMA. X-ray diffraction (XRD) has been utilized to detect crystallinity changes in PEMA:PEO polyblend.

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 300,000 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. Known weight percentage of PEMA and PEO were dissolved in a common solvent benzene at a temperature of 40 °C with constant stirring. A known quantity of this homogeneous solution was poured in glass mould specially fabricated for this purpose. The solution was then allowed to evaporate by keeping the glass mould inside the oven whose temperature was controlled automatically. 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 (Hᵥ) was determined with mhp160 microhardness tester with a Vicker’s diamond pyramidal indenter, having a square base and 136° pyramidal angle attached to a Carl Zeiss NU2 universal research microscope. The Hᵥ was calculated using the relation:

\[ Hᵥ = \frac{1.854 \times L}{d^2} \text{ kg/mm}^2 \]

where \( L \) is the load in kg and \( d \) is diagonal of indentation in mm. Several indentations were obtained at each load and the average hardness number was calculated.

X-ray diffraction (XRD) studies — XRD patterns of polymer specimens have been recorded on Philips (Holland) automated X-ray powder diffractometer at RSIC, Nagpur University, Nagpur.

For XRD study polyblend pellet was packed in aluminium sample holder in such a way that upper surface is smooth and was exposed to X-rays in vertical goniometer assembly. The scan was taken between 5 to 70 degrees 2θ with scanning speed of 2.4 degrees 2θ per min. The operating target voltage is 35 kV, tube current is 20 mA and radiation used is FeKα alpha wavelength 1.93735 Å. The intensity versus 2θ scans were obtained for pure PEO, pure PEMA and PEMA:PEO polyblends.

For obtaining crystallinity index from XRD patterns of samples, the approach of Hermans and Weidinger has been utilized. This method can be successfully applied to polymers such as PEO having intense diffraction peaks. According to this method, the scan is resolved in crystalline peaks, amorphous peaks and the background. The following assumptions are made:

(a) The total scattering from the sample is divided between crystalline peaks from the crystallitles and amorphous peaks from the remaining amorphous regions.

(b) The total scattering from the sample is that included in the resolved crystalline and amorphous regions.

(c) The relative areas of the crystalline peak and the amorphous peak are respectively proportional to

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![Fig. 1 — Variation of Hᵥ with load for pure PEMA and PEMA:PEO polyblends](image-url)
the number of electrons (and thus mass) in the crystalline and the amorphous regions.

\[
X_c = \frac{A(C_r)}{A(C_r) + KA(A_{am})} = \frac{1}{1 + KR}
\]

where \(A(C_r)\) is the area of crystalline peak, \(A(A_{am})\) is the area of amorphous peak, \(R\) is the ratio of amorphous to crystalline peak areas and \(K\) is constant. For comparison, \(K\) is set to unity.

### 3 Results and Discussion

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

The increase in \(H_r\), with increasing load can be explained on the basis of the strain hardening phenomenon\(^{20,21}\). On applying load the polymer is subjected to some strain hardening. Finally, when \(H_r\) 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 \(H_r\) with increasing content of PEO suggests that PEO acts as a plasticizer or softner 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 \(H_r\).

The variation of \(X_c\), with the content of PEO in the samples is shown in Fig. 2. This figure shows that on mixing a PEMA (non-crystallizable) with PEO (crystallizable), crystallinity \((X_c)\) increases on increasing the content of PEO in the polyblend. Generally, for blends with 25 wt % of PEO, increased crystallinity is observed. For specimen with 50 wt % of PEO, the value of \(X_c\) is maximum and approaches that for pure PEO. This is also evident from XRD pattern for this sample (Fig. 3). The well-defined peaks in this figure suggests the presence of ordered crystalline phase in the blend specimen.

Thus in PEMA:PEO polyblend, crystallization of PEO occurs as revealed from XRD studies. However, the crystallization process of PEO is affected by wt % presence of PEMA. In the PEMA:PEO polyblend as PEO crystallizes the non-crystallizable component is rejected from the crystal region resulting in broad amorphous population,
which often affects the properties of polymers like glass transition temperature, crystal growth rate and bulk crystallization rate etc.

4 Conclusion

The microhardness and XRD studies enable to understand the issues related to the processing, structure and property relationship for PEMA:PEO blends. The increasing content of PEO in PEMA:PEO polyblend decreases the microhardness with added advantage of crystallizability. The ordered crystalline phase with lower values of microhardness is seen for polyblend having higher content of PEO. Thus by blending PEMA and PEO a plasticized material with ordered crystalline phase can be obtained.

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References