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# Effect of casting solvent on the crystallization in PEO/PMMA blends

## S. Radhakrishnan* and P. D. Venkatachalapathy
*Polymer Science and Engineering, National Chemical Laboratory, Pune 411008, India*
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The crystallization in polyethylene oxide/polymethyl methacrylate (PEO/PMMA) blends was investigated with respect to composition and different casting solvents. Sharp changes in the intensities of the major reflections (120 and 112/004 from PEO) were observed in their X-ray diffraction scans when these blends were cast from different solvents. Large deviations were noted in the crystallinity values as well as the intensities of the peaks from those expected from simple rules of mixture or dilution law. The various results could be explained on the basis of restricted growth of the PEO crystallites along certain directions in the presence of PMMA. Copyright © 1996 Elsevier Science Ltd.

Polymer blends have attracted tremendous attention in recent years because of large improvements obtained in their physical properties, processibility and cost effectiveness[1–4]. The physical properties of these blends are very much dependent on the phase morphology, degree of mixing and interfacial interaction between the two components.

Amongst the various blends, the poly(methyl methacrylate) (PMMA) mixed with poly(ethylene oxide) (PEO) or poly(vinylidine fluoride) (PVF$_2$) have drawn considerable interest since these show partial/full miscibility or compatibility[5–9] in spite of the fact that one of the components has a strong tendency to crystallize out. These blends show a single glass transition temperature ($T_g$) and optical clarity which are taken as evidence for their compatibility. On the other hand PMMA is known to be amorphous and many authors contend that it inhibits the crystallization of PEO simply by the principle of dilution[8–11]. During our experiments on the solution cast films of PEO/PMMA blends it was noted that the quality and appearance of the films was very much dependent on the solvent used. This was felt to be associated with corresponding changes in either phase miscibility or morphology. Hence, the effect of casting solvent on the structure and morphology of these blends was studied and the results are described in this communication.

The PEO (Polyox WSR-N750, MW $3 \times 10^5$, BDH, England) and PMMA (acactic grade, Gujpol 932 HR, GSFC, Baroda India) were dissolved in the various solvents with slight warming (50°C) when necessary. A variety of solvents were used having solubility parameters ranging from 8.6 to 12.5 cal mol$^{-1}$ but the results of only three, viz. dichloromethane (DCM), tetrahydrofuran (THF) and toluene (TL), are reported here since these yielded better quality films. In all these cases clear solutions with no turbidity were obtained before and after mixing at all proportions of the component polymers. These films were cast in flat glass petri dishes

held at 27°C and dried over a period of 15 h. The resulting films were pealed off the substrate and part of them subjected to isothermal melt crystallization. The samples were first heated on microscopic glass slides to a temperature of 130°C and quickly transferred to the hot stage of a microscope preconditioned at 37°C and crystallized for more than 3 h. Structure and morphology of these films were investigated by X-ray diffraction and optical microscopy in the same manner as reported elsewhere[12,13].

The wide angle X-ray diffraction (WAXD) scans for the PEO/PMMA films cast from THF containing different concentration of PMMA are depicted in *Figure 1*. It is seen that in all cases there are mainly two strong peaks occurring at the diffraction angle ($2\theta$) of 19.1° and 23° corresponding to 120 and 112/004 reflections from the PEO crystallites. The intensities of both these peaks decrease monotonically with the increase of PMMA content and such observations seem to suggest a simple mechanism for decrease of crystallinity due to increase of the amorphous component (PMMA) and the dilution effect. However, more detailed analysis indicates that the relative intensities of these peaks and the crystallinity values deviate considerably from those expected from a simple law of mixtures which is discussed later in the paper. *Figure 2* shows the WAXD of toluene cast films subjected to a melt crystallization and in this case similar results are also observed as in *Figure 1*. On the other hand, dramatic changes in the intensities of these peaks were noted for samples cast from DCM and subsequently crystallized from melt. *Figure 3* and *Figure 4* show the WAXD scans for these samples and the extraordinarily high intensity of the peak at $2\theta$ of about 19° is quite evident. This peak usually has lower intensity than the peak at 23° (see *Figures 1* and *2*). It is interesting to note that there are two additional peaks in some cases occurring at $2\theta$ of 13.7° and 16.6° which are not normally observed for PEO whether it is solution cast or crystallized from the melt. The detailed analysis of these WAXD scans revealed that the various *d*-values could be matched

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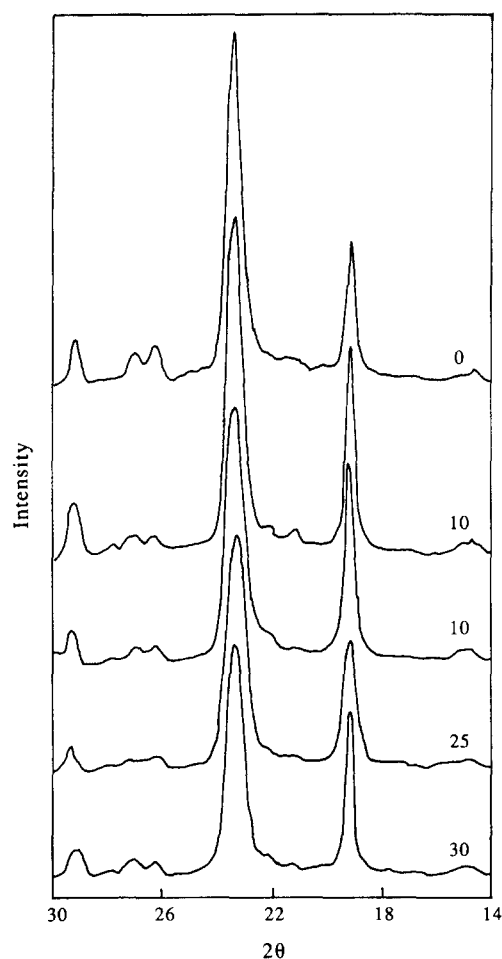* To whom correspondence should be addressed

**Figure 1** Wide angle X-ray diffraction scans for PEO/PMMA films cast from tetrahydrofuran. The numbers adjacent to the curves correspond to the PMMA content in wt%
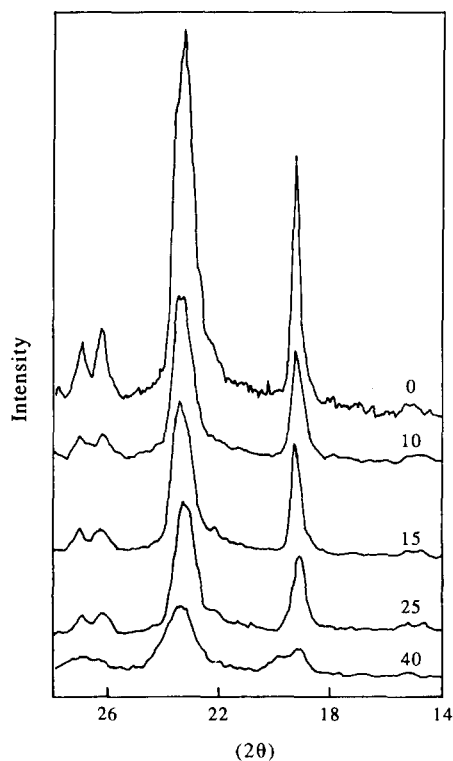


**Figure 2** WAXD of PEO/PMMA films cast from tetrahydrofuran and subjected to isothermal melt crystallization at 37°C. The PMMA content is indicated next to the corresponding curve
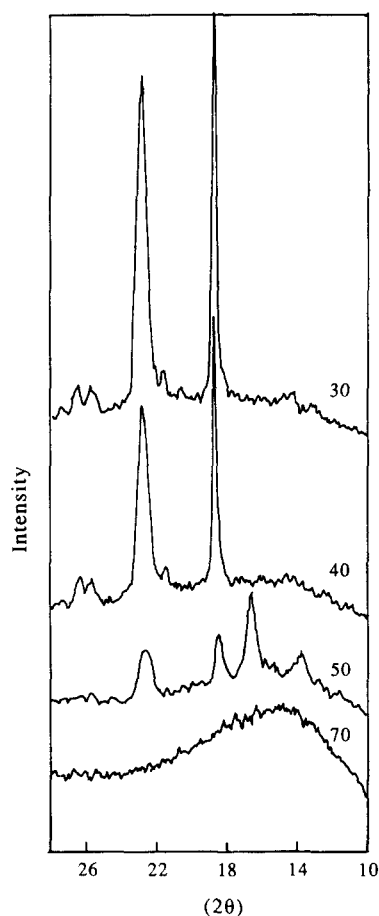


**Figure 3** WAXD for PEO/PMMA films cast from dichloromethane and subjected to the isothermal melt crystallization as in Figure 2

with those obtained from the monoclinic structure reported for PEO with lattice parameters of $a = 8.49\,\text{Å}$, $b = 13.57\,\text{Å}$, $c = 19.2\,\text{Å}$ and $\tau = 126°$, respectively[14,15]. These two new peaks correspond to reflections from the 111 and 003 planes.

The crystallization studies on PEO/PMMA blends reported in the past have been carried out mostly for films cast using chloroform as solvent or freeze dried samples using benzene solutions[8–10,16–18]. Some authors have briefly mentioned the crystallinity determined from X-ray diffraction methods but details of the patterns are not available for the same. In the present case many other solvents have been used by us in which the polymers could be dissolved individually. However, only a few yielded clear solutions after mixing and amongst these some gave transparent flexible films. The clarity and quality of the films suggested a high degree of mixing but as discussed above, there are differences in the crystalline nature/morphology of these films which depend on the casting solvent. The crystallinity ($Ci$) was determined experimentally as the ratio of the area under the crystalline peaks to the total area under amorphous halo including that due to PMMA. The $Ci$ value was also estimated for each composition following the simple rule of mixtures with non-interacting components viz.[4,12]

$$Ci(T) = m_1 Ci(1) + m_2 Ci(2)$$

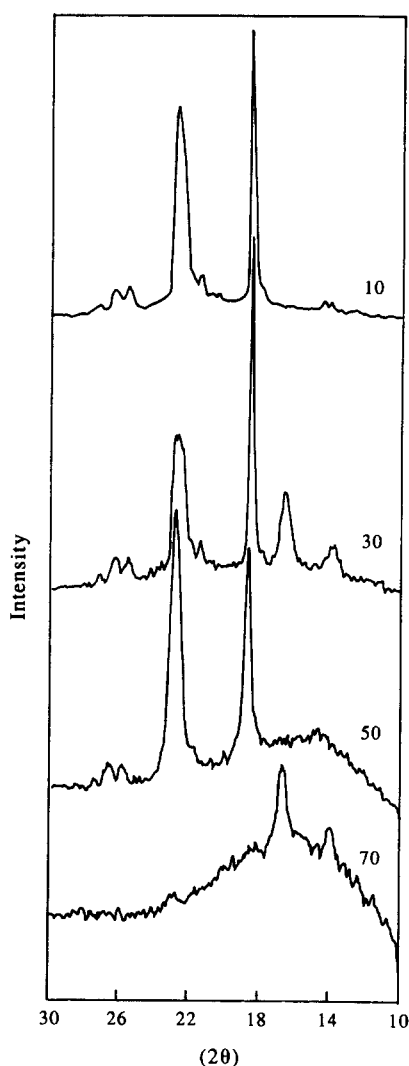where $m_1$ and $m_2$ are the mass fractions of components 1 and 2 and symbols in the brackets correspond to the total

**Figure 4** WAXD for PEO/PMMA films cast from toluene and subjected to the isothermal melt crystallization as in *Figure 2*
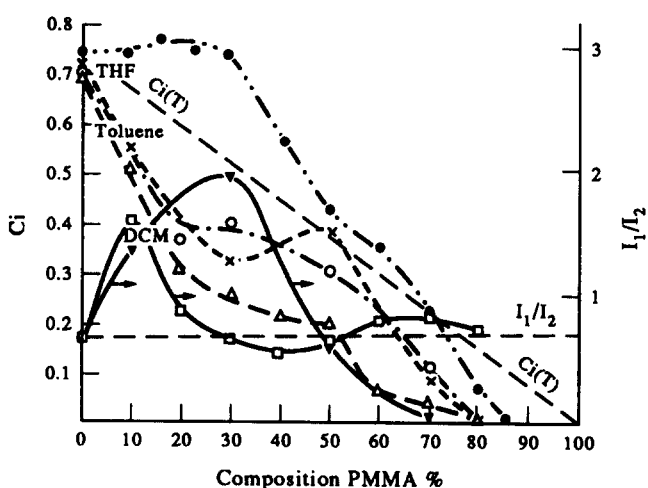


**Figure 5** The effect of casting solvent on the crystallinity and intensity ratio of major peaks in WAXD of PEO/PMMA blends. The curves with the symbols (- - o -), (- x -) and (- ● -) are for $Ci$ in samples cast from THF, toluene and DCM respectively and then subjected to melt crystallization. (- -▲ -) corresponds to $Ci$ for DCM cast film prior to melt crystallization. Solid curves represent $I_1/I_2$ ratio and dashed curves without legends are expected variations as per simple rule of mixtures

value of $Ci$ and its value for components 1 and 2 before mixing. Since $Ci(2)$ in the present case of PMMA is zero, $Ci(T)$ becomes essentially proportional to the mass fraction of PEO in the blend. *Figure 5* shows the variation of $Ci$ (experimental) as well as the intensity ratio of the two major peaks of WAXD $(I_1/I_2)$ with composition for the blend cast from different solvents and subsequently melt crystallized. The values expected for $Ci(T)$ from the above relation are also indicated for comparison. It is interesting to observe that in all cases large deviations are obtained from the expected values, especially for blends with PMMA content ranging from 20 to 50%.

These various results suggest that either (a) phase segregation is occurring or (b) PMMA inhibits the growth of PEO crystals preferentially in certain directions and not by simple dilution process. Considering the following facts that a number of authors have reported in the past the miscibility of PEO/PMMA blends which exhibit a single $T_g$, the solutions of the polymers in blend state were also clear without turbidity and the films cast from them were quite uniform and transparent, the possibility of phase segregation appears to be remote. On the other hand, the variation of intensity of certain reflection in comparison with others can be due to the inhibition of growth of the crystallites along particular directions. Additionally, the occurrence of two new reflections clearly suggests a different growth pattern of the crystallites of PEO in the blends than the usual one found in the homopolymer. The role of solvent could be that of providing diffusional paths for the polymer molecules in the host matrix and create the constrained morphology giving rise to the above noted changes in the WAXD. The most interesting part of the present observations is that the growth pattern induced during solution casting has an influence on the subsequent melt crystallization process as well. The exact origin for these changes is not yet fully understood and further work is being carried out on the role of hydrogen bonding and the dipolar contribution to the interaction parameter of the solvent in the formation of PEO/PMMA blends from solutions.

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