

# Effect of Cholesteryl Additive on Poly(ethyl Methacrylated)–Poly(vinyl Acetate) Blend

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## SYNOPSIS

Three different compositions (9 : 1, 7 : 3, and 1 : 1) of poly(ethyl methacrylate) (PEMA) and poly(vinyl acetate) (PVAc) are chosen to check the miscibility of a polymer pair. The 9 : 1 and 7 : 3 PEMA–PVAc blends are immiscible and have shown two distinct loss peaks in dynamic mechanical analysis (DMA) studies, while 1 : 1 PEMA–PVAc has shown a single loss peak. Immiscible composition 7 : 3 PEMA–PVAc is selected to study the effect of cholesteryl additives on the miscibility of the polymers. The additives chosen for the present studies are cholesteryl chloride, cholesteryl caprylate, and cholesteryl laurate. The DMA studies showed that all the additives caused a merging of the two loss peaks into one. X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) studies of the blend and blend with additive samples are utilized to get further information. The FTIR studies do not show any detectable change. The SEM micrographs of the blend and cholesteryl additive systems show a single-phase ordered structure, and XRD data studies indicate the presence of small crystallites.

## INTRODUCTION

Two or more polymers may be blended together to form a wide variety of random or structured morphologies. In general, most polymer pairs are thermodynamically immiscible, which precludes generating a truly homogeneous product. By grafting a functional group on one of the polymers, compatibilization of two normally immiscible polymers can be achieved.<sup>1</sup> The graft copolymer can preferentially locate at the interface between the two immiscible phases, causing reduction of interfacial energy and improved interfacial adhesion.<sup>2</sup> Therefore a more uniformly dispersed domain results. Another method used for compatibilization is to introduce electron donor and acceptor groups in the polymer backbones<sup>3</sup>; here specific interaction between the groups on the two different chains helps the miscibility at the molecular level. Lastly a molecule that can si-

multaneously interact with two different kinds of chains would be able to act as a compatibilizer for the two polymers. From our earlier studies, it has been found that several cholesteryl liquid crystals act as antiplasticizers for PVAc<sup>4</sup> and PEMA<sup>5</sup> through specific interactions. Hence this work is aimed at studying the effect of the same liquid crystals on the blends of these polymers.

## EXPERIMENTAL

Poly(ethyl methacrylate) ( $\bar{M}_v = 66,000$ ) and the additives cholesteryl chloride (ChCl), cholesteryl caprylate (ChCp), and cholesteryl laurate (ChL) were used for the present studies as received from the Aldrich Chemical Co. (United Kingdom) without further purification. Poly(vinyl acetate) was also used as received from BDH (research grade  $\bar{M}_n = 40,000$ ).

The films for the PEMA–PVAc blends (9 : 1, 7 : 3, and 1 : 1) are prepared by the solution casting technique using benzene as a solvent. The melt-blending method was not used to avoid degradation

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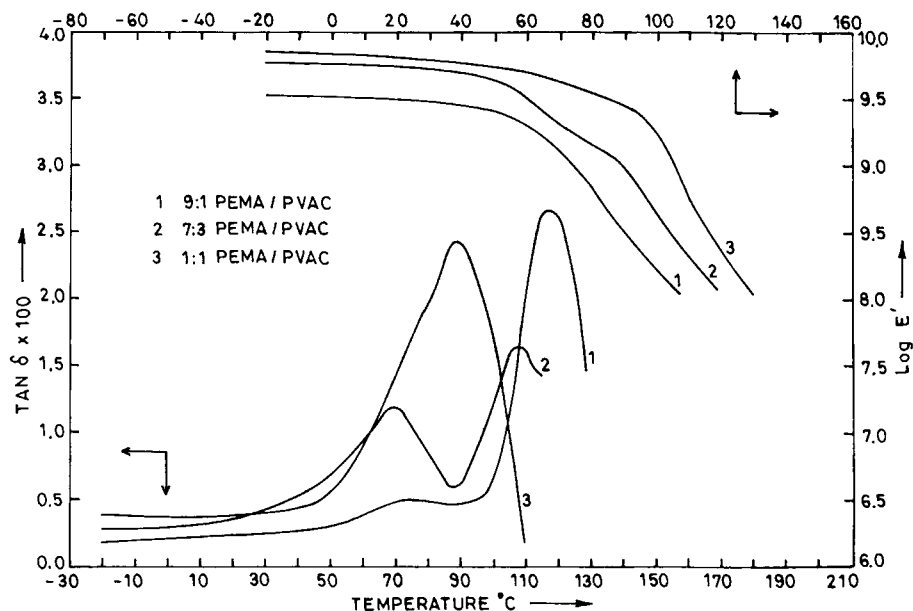


Figure 1 DMA:  $\log Y'$  and  $\tan \delta$  vs. temperature plot for PEMA-PVAc blends.

as no stabilizer was used. Since the previous work on homopolymer-cholesteryl additive systems was on solution-cast films, the blends for this study were also prepared by solution casting in order to have uniformity for comparison. The required amount of polymers and additives were weighed accurately, and the solutions were poured on a stainless steel plate kept on a mercury surface for initial drying. The films were kept in a vacuum oven at slightly elevated temperature ( $35^{\circ}\text{C}$ ) for removal of the last traces of solvent. The films thus prepared were used without further analysis.

The dynamic mechanical properties of the blends were studied by using the Du Pont model DMA 981 dynamic mechanical analyzer. The typical experimental conditions selected for the present studies were: sample dimensions were length 19 mm, width 10 mm, and thickness 0.01 mm; oscillation amplitude, 0.2 mm; sample mounting, vertical; heating

rate,  $10^{\circ}\text{C}/\text{min}$ ; and  $A/Z$  gain, 40%. The raw plots ( $X-Y-Y'$  recorder) obtained were millivolt signal of oscillating frequency (in hertz) and damping (millivolts) vs. sample temperature. The modulus and loss of all samples were obtained from the frequency and damping data using the equation

$$Y' = \frac{4\pi^2 f^2 J - K}{2W((L/2) + D)^2} \left(\frac{L}{T}\right)^3 \quad (1)$$

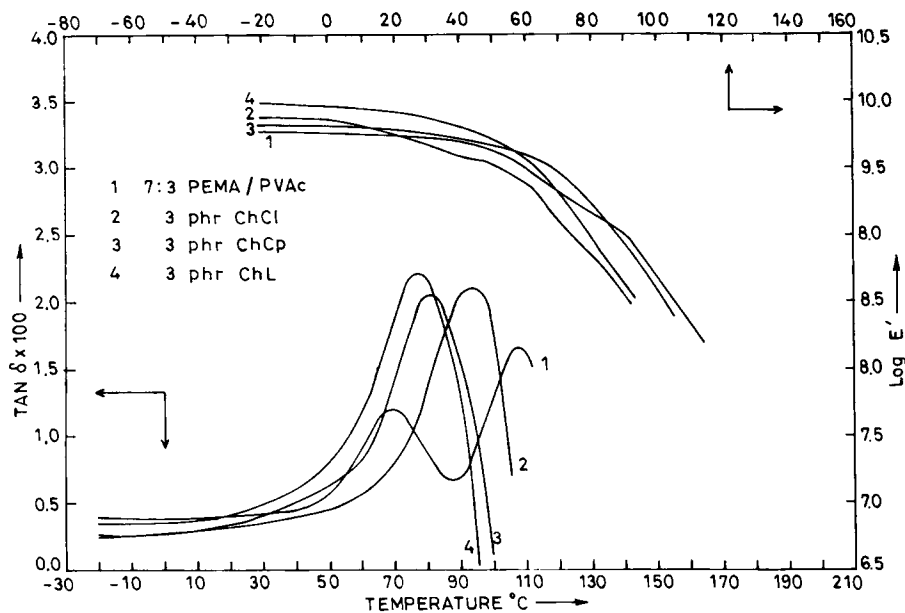
$$\tan \delta = CV/f^2 \quad (2)$$

where  $f$  is oscillation frequency,  $J$  moment of inertia,  $K$  the pivot spring constant,  $L$  sample length,  $T$  sample thickness,  $W$  sample width,  $D$  clamping distance,  $C$  the damping constant, and  $V$  measured damping voltage.

The FTIR spectra of blends and blends with additive samples were recorded on a Nicolet DX-50

Table I Dynamic Mechanical Properties of PEMA-PVAc Blends

Composition of System PEMA-PVAc	Modulus at $20^{\circ}\text{C}$ , $\times 10^{-9}$ (Pa)	Peak PVAc		Peak PEMA	
		$T_{\max}$ (K)	$\tan \delta$ ( $\times 100$ )	$T_{\max}$ (K)	$\tan \delta$ ( $\times 100$ )
9 : 1	6.3072	331.0	0.5043	365.0	2.6029
7 : 3	5.5305	325.0	1.2018	365.0	1.6406
1 : 1	3.2249		339.0		2.4332



**Figure 2** DMA:  $\log Y'$  and  $\tan \delta$  vs. temperature plot for PEMA-PVAc (7 : 3) blend and additive systems.

spectrophotometer using very thin films. A Siemens autoscan scanning electron microscope was used for the SEM studies of these blends. The coating used for the present SEM studies was gold-palladium carried out by sputtering technique. X-ray diffractograms were obtained on a Philips PW 1820 X-ray diffractometer. The target was Fe and the instrument was operated at 40 kV, 30 mA.

## RESULTS AND DISCUSSION

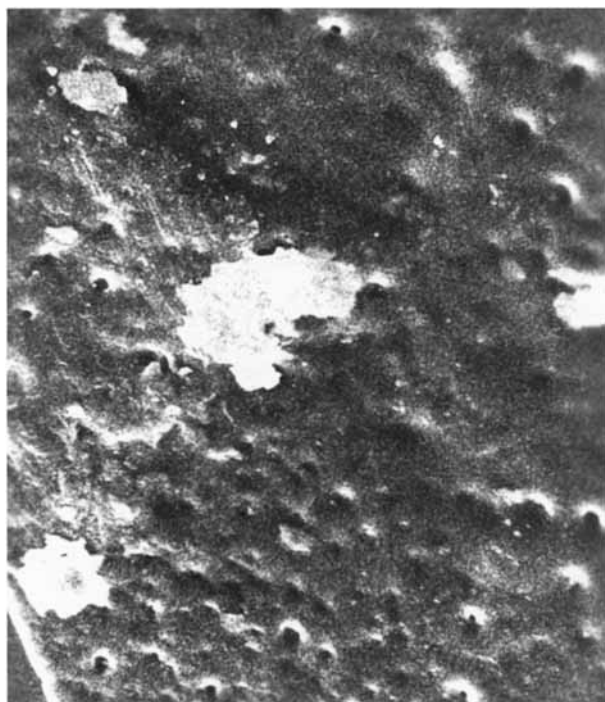
The method adopted in the present study to find compatibility is studying the viscoelastic behavior using the Du Pont DMA 981 dynamic mechanical analyzer. For the PEMA-PVAc blend it is found that the polymers are incompatible at the 9 : 1 and 7 : 3 compositions as they show well-separated loss

peaks, whereas a 1 : 1 composition shows only one loss peak intermediate between the two (Fig. 1, Table I). The peak temperature is shifted to a higher value compared to that of the pure homopolymers for both 7 : 3 and 9 : 1 PEMA/PVAc blends. Therefore, it can be said that the constituent polymers, although incompatible, affect each other's segmental motion through interchain interaction. Although one cannot quantitatively describe the extent of incompatibility of 9 : 1 and 7 : 3 blends, an approximate qualitative picture can be obtained from the difference in the two observed transition temperatures, 34 and 40°C, respectively, for 9 : 1 and 7 : 3 blends. The difference in the transition temperatures of the two homopolymers is 40°C.

The modulus of the blends is also highly composition dependent, and a steady increase in the modulus is observed with an increase in PEMA con-

**Table II** Dynamic Mechanical Properties of PEMA-PVAc Blend Containing Cholesteryl Additives

System PEMA/PVAc 7 : 3	Modulus at 20°C, $\times 10^{-9}$ (Pa)	Transition Temperature (K)	$\tan \delta$ (max) ( $\times 100$ )
—	5.5308	325.0, 365.0	1.20, 1.64
3% ChCl	5.9924	350.0	2.07
3% ChCp	5.5958	333.0	2.21
3% ChL	8.3240	335.0	1.98



**Figure 3** Microphotograph of SEM for 9 : 1 PEMA-PVAc blend (magnification 800).

tent. Olayemi and Ibiyeye<sup>6</sup> also reported an improvement of mechanical properties on blending. The improvement of properties was considered to be the result of the presence of favorable and strong (PVAc-PEMA) intermolecular interactions. Having known from earlier studies that ChL, ChCp, and ChCl act as antiplasticizers for pure PVAc and pure PEMA, the 7 : 3 composition of PEMA-PVAc is chosen to study the effect of cholesteryl additives on the behavior of the blends. In the homopolymer-additive systems, the concentration of cholesteryl additives was in the range of 2–6% w/w. The maximum concentration used in all our earlier studies was restricted to 6–8% due to limited solubilities of these cholesteryl compounds in various polymers. Since variation in concentration of additives does not show any profound difference, in this work, all three additives were added in 3% concentration only.

The most interesting and important observation is that in all three cases the systems show a single loss peak, viz., a single transition temperature, and the modulus of blend containing liquid crystalline additive is higher than the one without cholesteryl additive (Fig. 2, Table II). The antiplasticization behavior of cholesteryl additives toward PEMA and PVAc is due to the dipolar interactions of polymer

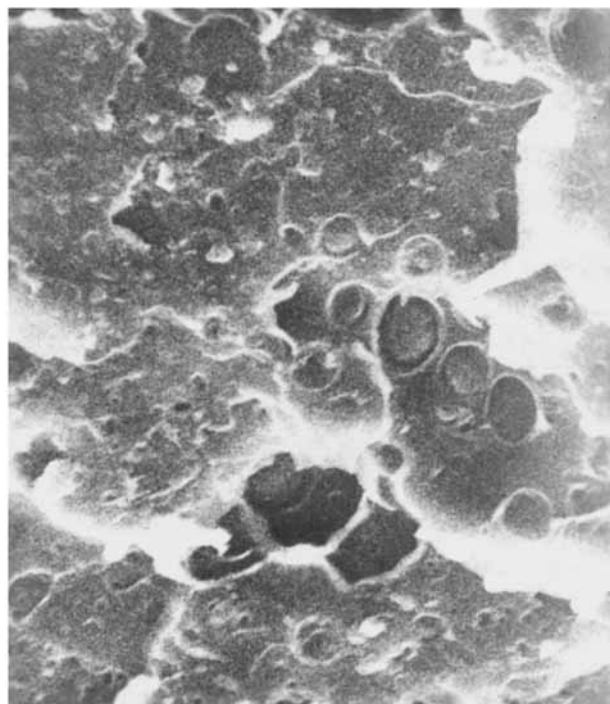
and additive. When such an additive is added to blend, the dipolar forces can cause the additive molecule to act as a bridge between the two polymer chains, which are otherwise incompatible. The dipolar interaction of polymer and additive is thus responsible for bringing the two polymer chains closer, which in turn leads to miscibility.

To get further evidence, FTIR and SEM studies of the blends and the blends with additives were undertaken. The FTIR spectra of blends with additives do not show any detectable shift in carbonyl band frequency. The SEM micrographs of blends are quite informative.

The SEM micrographs of 9 : 1 and 7 : 3 blends show the presence of two distinct phases (Figs. 3 and 4). Figure 5 is the SEM micrograph of a 1 : 1 PEMA-PVAc blend. The DMA study of the blend showed only one broad peak. However, in the SEM micrograph two phases seem to be present, but they are less distinct than that in the 9 : 1 or 7 : 3 blend (Figs. 3 and 4). The SEM micrographs of the blends with additives are quite interesting and important. The addition of liquid crystalline additives show increased order of the blend. The SEM micrograph of the blend now shows a single phase-ordered structure (Figs. 6–8).



**Figure 4** Microphotograph of SEM for 7 : 3 PEMA-PVAc blend (magnification 800).



**Figure 5** Microphotograph of SEM for 1 : 1 PEMA-PVAc blend (magnification 800).

X-ray diffractograms were taken for cholesteryl compounds and a blend of PEMA-PVAc (7 : 3) (Figs. 9 and 10) and for the same blend with 3% additives (Figs. 11-13). The homopolymers show only the diffused intensity pattern expected of amorphous polymers. The cholesteryl compounds



**Figure 7** Microphotograph of SEM for 7 : 3 PEMA-PVAc blend and 3% cholesteryl caprylate (magnification 800).

show sharp peaks in the interval of  $2\theta = 6^\circ, \dots, 22^\circ$ . The blend also gives XRD corresponding to amorphous polymer. However the X-ray data on all blend-additive systems show two prominent peaks at  $2\theta$  values of  $38^\circ$  and  $44^\circ$ . Concentration of additive



**Figure 6** Microphotograph of SEM for 7 : 3 PEMA-PVAc blend and 3% cholesteryl chloride (magnification 800).



**Figure 8** Microphotograph of SEM for 7 : 3 PEMA-PVAc blend and 3% cholesteryl laurate (magnification 800).

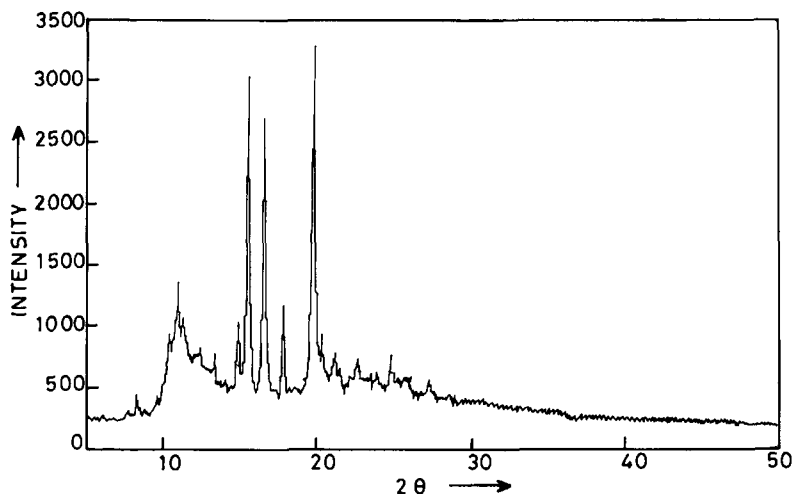


Figure 9 X-ray diffractogram of cholesteryl chloride.

being very small, peaks due to pure cholesteryl compounds are not observable. The presence of these new peaks is indicative of formation of crystallites very small in size. This behavior seems to be similar to local aggregations observed in ionomers.<sup>7</sup> Thus the cholesteryl compounds used here do help in the ordering and alignment of two polymer chains with respect to each other.

## CONCLUSIONS

The DMA studies of blends show that 1 : 1 PEMA-PVAc blend is compatible whereas 7 : 3 and 9 : 1 PEMA-PVAc blends are incompatible. The DMA data on the blend with cholesteryl additive show a single loss peak, and the modulus of blends con-

taining liquid crystalline additives is higher than that of one without additive. The FTIR spectra of the blend and the blend with additive do not show any detectable shift in carbonyl band frequency. The SEM micrographs of blends show the presence of two distinct phases. The SEM micrographs of blend with additive systems show a single phase-ordered structure. The X-ray diffractogram of the blend shows only a diffused intensity pattern similar to that of an amorphous polymer. The diffractograms of the blend with all cholesteryl additives show two new peaks at  $2\theta$  values of  $38^\circ$  and  $44^\circ$ . Based on all these observations, it can be concluded that the cholesteryl compounds used here, namely cholesteryl laurate, cholesteryl caprylate, and cholesteryl chloride, are responsible for bringing two polymer chains closer, leading to compatibility and increased order.

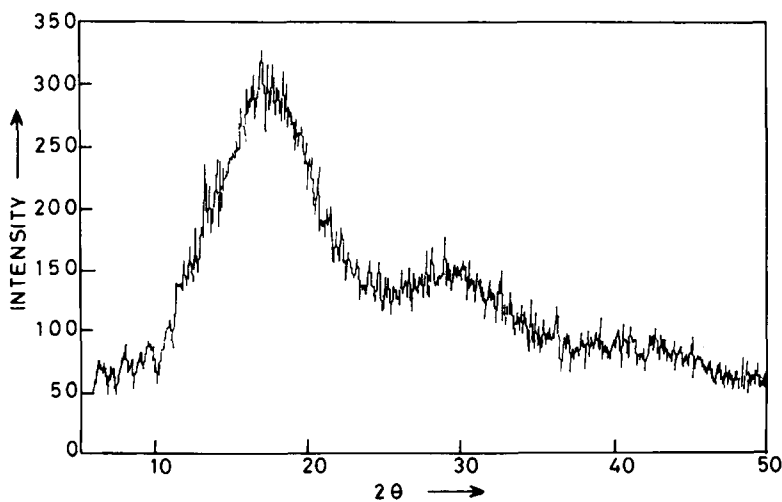
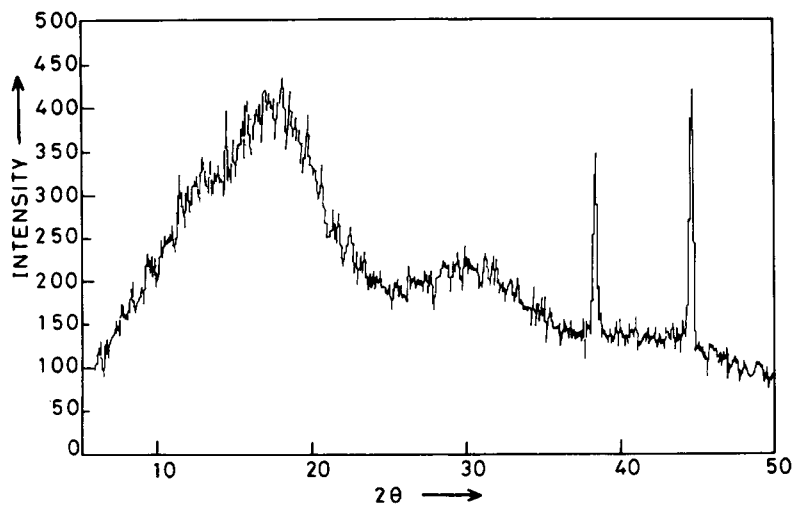
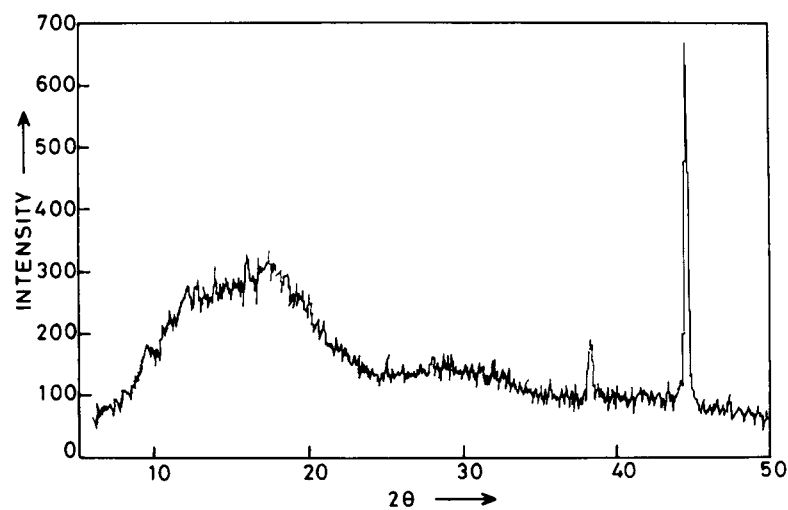


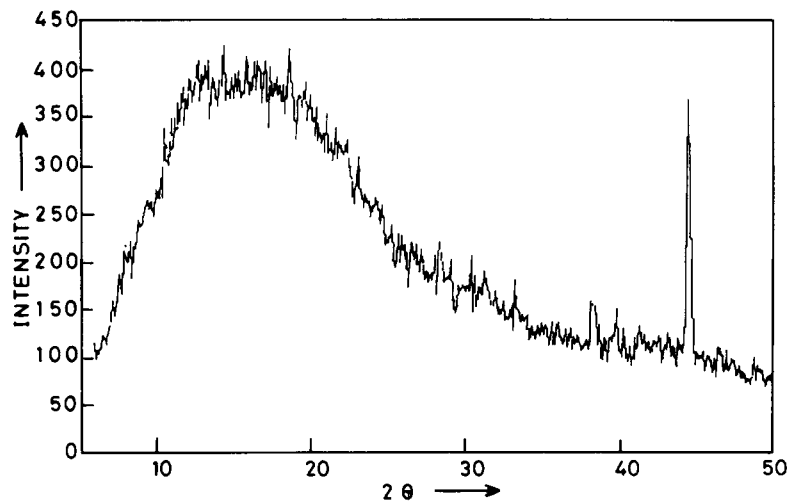
Figure 10 X-ray diffractogram of 7 : 3 PEMA-PVAc blend.



**Figure 11** X-ray diffractogram of 7 : 3 PEMA-PVAc blend and 3% cholesteryl chloride.



**Figure 12** X-ray diffractogram of 7 : 3 PEMA-PVAc blend and 3% cholesteryl caprylate.



**Figure 13** X-ray diffractogram of 7 : 3 PEMA-PVAc blend and 3% cholesteryl laurate.

Hence these additives can be described as compatibilizers for poly(ethyl methacrylate) and poly(vinyl acetate).

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