Studies on Polyethylene Oxide and Phenolic Resin Blends

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ABSTRACT: Blends of poly(ethylene oxide) (PEO) and novolac type phenolic resin were prepared by a solution cast method using acetonitrile as a solvent. In this work, we have investigated the PEO/phenolic blends having low phenolic content (0 to 30 wt %) with the objective in mind to design a crystallizable component for a shape memory polymer system having adjustable switching temperature. The blends were characterized by Fourier transform infrared (FTIR) spectroscopy, polarized optical microscopy (POM), and differential scanning calorimetry (DSC). The rate of crystallization and crystallinity (calculated from heat of crystallization value) decrease with increase in novolac content. FTIR analysis indicates the existence of H-bonding between hydroxyl groups of novolac and ether groups of PEO. POM studies indicate that size of Maltese cross section decreases with increase in novolac content and in the blends containing higher novolac content less regular leaf like texture was obtained. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2156–2162, 2008

Key words: poly(ethylene oxide); novolac; blends; optical microscopy; DSC

INTRODUCTION

Poly(ethylene oxide) (PEO) is a crystalline thermoplastic polymer with the general structure $H(-O-CH_2-CH_2)_n-OH$, where n is the number of repeat units, which finds a wide range of applications such as thougheners/flexibilizers for thermosets,[1,2] solid polymer electrolyte,[3–5] and crystallizable component of a shape memory polymer system.[6,7] The polyether chain of PEO provides flexibilizing effect when chemically attached to a rigid polymer chain.[8,9] The polyether chain of PEO can also strongly coordinate with alkali cations (Li^+, Na^+, Ca^{+2}, etc.) leading to the formation of a solid polymer electrolyte for use in battery, supercapacitor, and fuel cell applications.[10,11] Lot of works have been done to improve the conductivity of PEO-based electrolytes by blending with a nanofiller like organoclay[12–14] and carbon nanotube.[15–17] Nanofillers with high aspect ratio block the crystalline growth fronts and thereby reduce the cystallinity. This improves the conductivity as the amorphous part of PEO is only responsible for the coordination with metal ions.[18]

PEO has been envisaged also as a thermal storage material. Thermal energy transfer occurs when a material undergoes solid/liquid and liquid/solid transition accompanied with heat absorption or release respectively.[19,20] It offers good physical and chemical stability, reproducible thermal behavior without encapsulation problems, and adjustable transition zone unlike the conventional inorganic thermal storage material.[21,22] The area has become very important because of increasing awareness in energy management and efficient use of waste energy.[23]

Recently, PEO-based shape memory polymers have drawn considerable attention.[24,25] PEO acts as crystalizable switching segment and shows reversible shape memory effect because of melting and crystallization.[6,26] Shape memory polymers (SMPs) belong to a class of smart polymers, which are intensively explored in last few years because of their application[27–29] in microelectromechanical systems, and biomedical devices. A successful development of SMP requires the possibility to manipulate the recovery temperature upon the target applications (recovery temperature must lie below that of the system temperature). This has prompted us to study PEO/phenolic blend, which is expected to offer the possibility to set the switching temperature by changing the blend compositions.

PEO/phenolic and PEO-polycaprolactone block copolymer/phenolic blends have been investigated.[30–34] However, the published studies give particular attention to PEO/phenolic blends where
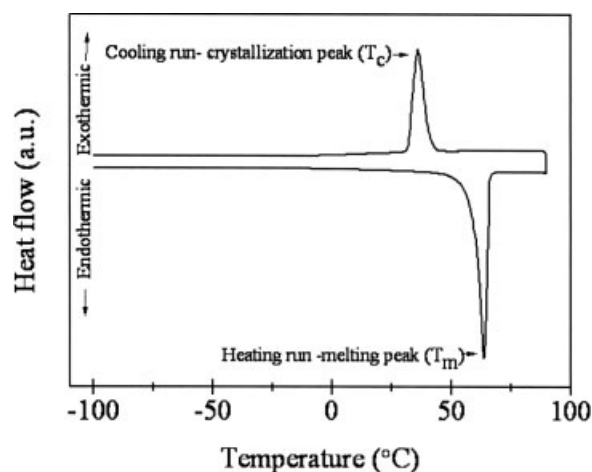
Figure 1 DSC heating and cooling scans of PEO showing melting and crystallization.

phenolic resin is the main component. The blends have been investigated with the objective to modify the properties of phenolic or for academic interest to study the intercalations and miscibility of various blend systems. It was reported that amorphous phase of PEO is miscible with phenolic resin. In this work, we have investigated the PEO/phenolic blends having low phenolic content (from 0 to 30 wt %) with the objective in mind to design a crystallizable component for a shape memory polymer systems having adjustable switching temperature. Characterization of PEO/phenolic blends with differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, polarized optical microscopy (POM) are discussed in this article. Applications of the developed blends for shape memory applications will be presented in a later communication.

EXPERIMENTAL

Materials

The PEO with weight average molecular weight of 20,000 g mol^{-1} was purchased from Aldrich. Novolac type phenolic resin (Supraplast 1763, M_w: 989 g mol^{-1}) was supplied by Sud-West-Chemie GmbH, Germany and used as received. The solvents acetonitrile and tetrahydrofuran (AR grade) are procured from Merck, KgaA, Germany.

Preparation of blends

PEO/novolac blends of 2.5, 5, 10, 15, 20, and 30 wt % of novolac were prepared by solution casting using acetonitrile as a solvent. The solution containing 10 wt % polymer mixtures was stirred for 2–3 h using a magnetic stirrer and cast on an aluminum mold. The solvent was allowed to evaporate slowly at room temperature for 24 h. The blends were then dried at 60°C under vacuum for 24 h.

Characterization of blends

FTIR spectroscopy

FTIR Spectra of samples were collected on a Nicolet 510 FTIR Spectrometer, Germany, from 400 to 4000 cm^{-1} with a nominal resolution of 2 cm^{-1}. For each spectrum 64 runs were collected and averaged. The specimens were prepared by adding ∼ 1 wt % of the blend sample to dry KBr powder and pressed into a disc of 13 mm in diameter and 1.5–2 mm thickness.

DSC analysis

Thermal behavior of PEO and PEO/novolac blends were studied with DSC (Metler–Toledo DSC821 Instrument, Greifensee, Switzerland). About 10 mg of sample was placed in an aluminum pan and heated from −100 to 90°C at a heating rate of 5°C min^{-1}. The melted sample is then cooled to −20°C at a cooling rate of 3°C min^{-1}. A typical DSC curve showing melting and crystallization are shown in Figure 1. The reference was an empty aluminum pan. To study the effect of cooling rate on crystallization, the pure PEO sample was cooled at different cooling rate such as 1, 3, 5, 10, 15, and 20°C per min.

Melting point (T_m), crystallization temperature (T_c), and enthalpy of melting (ΔH_m) and crystallization (ΔH_c) were calculated from the DSC curves considering as the maximum position of the endothermic/exothermic peaks and the area of melting and crystallization curve under the DSC thermograms, respectively.

POM analysis

The spherulite formation during crystallization of PEO and PEO/novolac blends was observed using a POM (Leica, Wild Leitz gmbh, Germany) equipped with a hot-stage facility (TMS 91, Linkam Scientificinstruments, Waterfield, England). The specimens (layer of ∼ 40 μm thickness) were made on glass slides by solution cast. Crystals formation were observed while the samples were exposed to following temperature scans: heating at a rate of 10°C min^{-1} to 100°C, holding for 5 min to erase the thermal history effects and then cooling to 35°C at a slow cooling rate of 2°C min^{-1}, during which the crystallization takes place. The spherulites were photographed between crossed polarizers.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of PEO, novolac, and the blend (20 wt % novolac) are shown in Figure 2. PEO shows a large broad band at 2900 cm^{-1} and two narrow bands at 2740 and 2690 cm^{-1} due to asymmetric
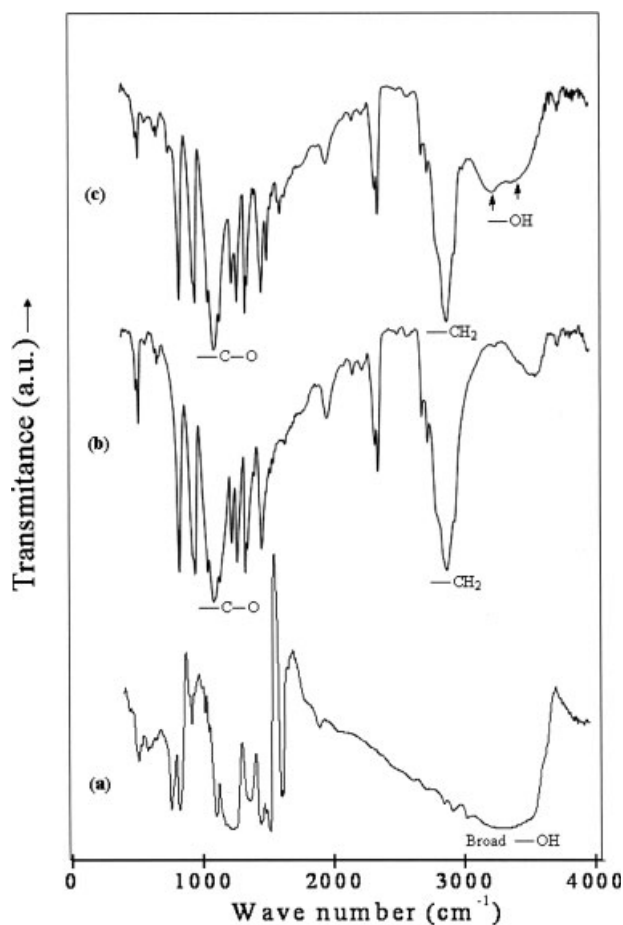
Figure 2 FTIR spectra of (a) novolac, (b) PEO, and (c) PEO/novolac blend (80/20 w/w).

—CH$_2$ stretching. In the blend the peaks at 2740 and 2690 cm^{-1} remain unchanged but peak at 2900 shifted to 2890 cm^{-1}. The peak at 843 cm^{-1} is assigned to the CH$_2$ rocking vibrations of methylene groups in the gauche conformation required for the helical conformation.[35,36] The absence of the characteristic PEO peak at 1320 cm^{-1} assigned to CH$_2$ vibrations of the ethylene group in the trans conformation as referred to Papke et al.[37] also confirms the helical structure of PEO. The peak at 962 cm^{-1} is also related to helical structure of PEO. No change in position of the peaks in the blend indicates that blending caused no perturbation of the helical structure of PEO as has been reported for the blend with higher concentration novolac studied earlier.

It may be noted that peaks in the region 1050 to 1150 cm^{-1} (asymmetric stretching of the C—O—C groups) get broadened in case of blend. The peak at 1080 cm^{-1} in PEO is shifted to 1060 cm^{-1} in the blend. Novolac shows as a broad peak consisting of two peaks at 3500 and 3300 cm^{-1}, which are assigned to the nonassociated free hydroxyl groups and self associated hydroxyl groups, respectively.

The blend shows two peaks at 3415 and 3250 cm^{-1}. The above observation clearly indicates the intermolecular association due to H-bonding of —OH groups of phenolic with oxygen atom of ether chain of PEO as shown in Figure 3. Blending of PEO with phenolic and other hydroxyl-containing polymers like poly (p-vinyl phenol), poly(vinyl alcohol), carboxylated poly (phenylene oxide), poly (hydroxylether of bisphenol A) (phenoxy) have been investigated and the existence of H-bonding between the ether oxygen of PEO and hydroxyl groups of other polymer have been proved.[38–41] The interassociation equilibrium constant between phenolic hydroxyl groups and PEO ether group is calculated from model compounds by using the classical Coggeshell and Saier (C&S) methodology.[42] However, the interassociation equilibrium constant obtained from model compounds differs from the same as that from the true polymer blend the intermolecular screening and functional group accessibility effects as well as the chain stiffness and connectivity in miscible polymer blend. Kuo et al.[33] determined equilibrium constant indirectly from a least square fitting procedure in ternary blends of PEO, phenolic, and polycaprolactam.

DSC analysis

The DSC heating scan of PEO as shown in Figure 1 shows an intense crystalline melting peak. T_g is not discernible for PEO and blends containing up to 20 wt % of novolac probably because of high crystallinity. However, T_g can be detected in blends containing higher concentration of novolac as evident from DSC plot of 30 wt % novolac containing blend in Figure 4. The blend displays a single T_g (ca. −20°C) in between the T_g of novolac 55°C (Fig. 4) and the reported T_g of PEO (−62°C).[41] This indicates that the
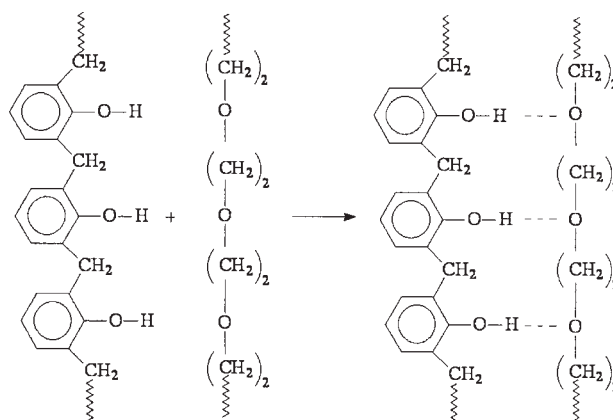

Figure 3 Schematic representation of inter-association H-bonding between PEO and novolac.
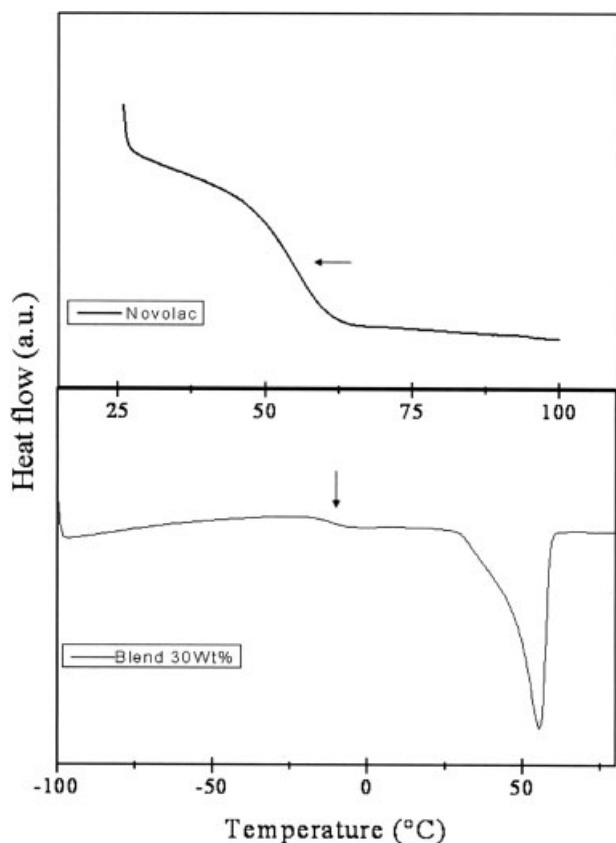
Figure 4 DSC scan of novolac and 30 wt % novolac containing blend.

amorphous phase of PEO is compatible with novolac and crystalline phase remains as a separate one as evident from the melting peak. The theoretical T_g value for the blend was calculated by using Fox equation as given below:

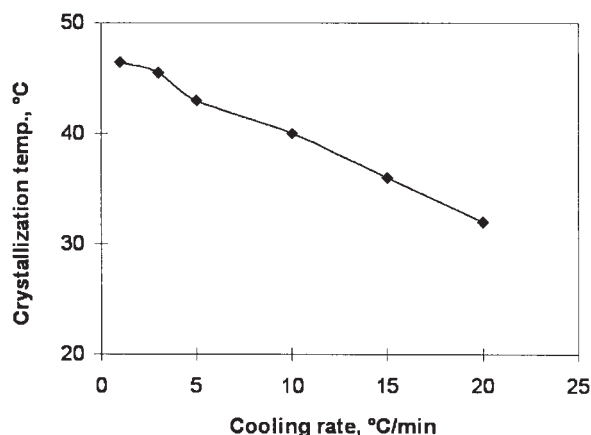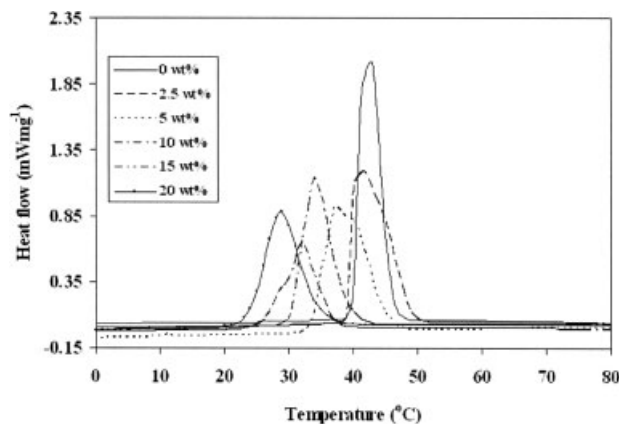$$\frac{1}{T_g} = \frac{(1-C)}{T_{g1}} + \frac{C}{T_{g2}} \quad (1)$$

Figure 6 DSC crystallization plots for various PEO/novolac blends.

where, T_g is the glass transition temperature of the blend, T_{g1} is the glass transition temperature of the phenolic resin, T_{g2} is the glass transition temperature of PEO, and C is the weight fraction of PEO. The T_g value of the blend shows a positive deviation with respect to the value calculated by the Fox equation ($-38°C$), which can be attributed to the crystallinity and interassociation H-bonding as confirmed by FTIR analysis discussed earlier.

To study the crystalline behavior all the blends were subjected to cooling scan as disclosed in the experimental section. The effect of cooling rate on crystallization of PEO is shown in Figure 5. As expected the crystallization temperature (T_c) decreases with increase in cooling rate. Figure 6 shows the DSC cooling scans for various blends using a constant cooling rate, 3°C min^{-1}. The percentage of crystallinity (% X_c) of the blends can be calculated from the following formula:

$$X_c = \Delta H_c^b = \Delta H_c^b / \Delta H_c^0 \quad (2)$$

Figure 5 Effect of cooling rate on crystallization temperature of PEO.
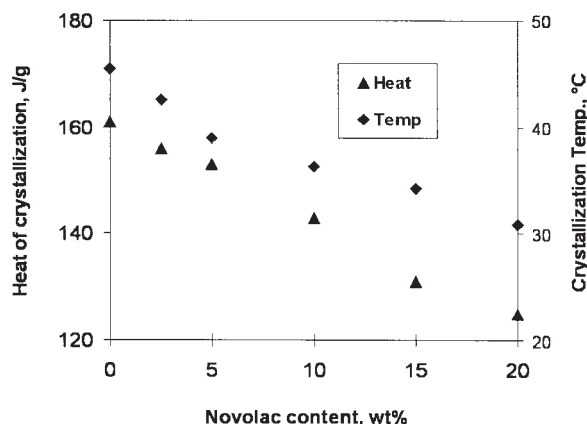

Figure 7 Effect of blending on heat of crystallization and crystallization temperature of PEO/novolac blends.
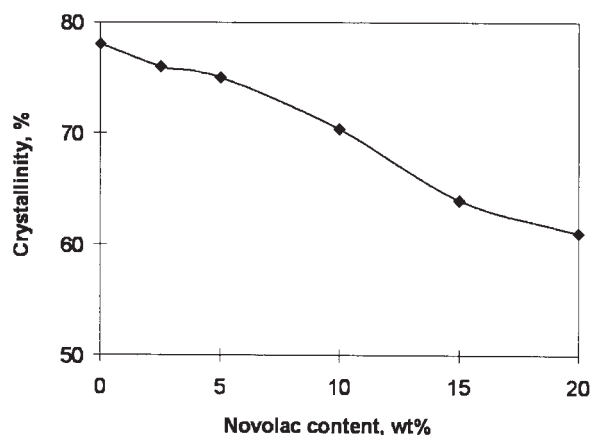
Figure 8 Effect of blending on crystallinity of PEO/novolac blends.

where ΔH_c^b is the heat of crystallization per gram of the blend and ΔH_c^0 is the heat of crystallization per gram of 100% crystalline PEO (205 J g^{-1}).[42,43] ΔH_c^b is calculated from the formula given below:

$$\Delta H_c^b = \frac{(\Delta H_c)_{\text{total}} \times 100}{w \times y} \tag{3}$$

where, $(\Delta H_c)_{\text{total}}$ is obtained from the peak area of DSC cooling curve, w is the weight of the sample taken for DSC experiment, and y is the concentration of PEO in wt%.

ΔH_c^b [obtained from eq. (2)] and T_c for various blends are presented in Figure 7. The effect of blending on crystallinity [calculated from eq. (1)] of the blends is shown in Figure 8. It is clear that the rate of crystallization decreases as evident from the decrease in T_c with the incorporation of novolac in PEO. This can be attributed to the presence of amorphous novolac, which exert disturbing effect during crystallization. The crystallinity decreases up to 20 wt % of novolac concentration. The blend with 30 wt % novolac does not show a clear crystallization peak because of break down of crystalline structure as confirmed by POM analysis. It is interesting to note that by addition of 20 wt % of novolac it is possible to change T_c of about 20°C and still 60% crystallinity is retained. Hence the blends having 0–20 wt % of novolac can be used in shape memory polymer structured system as a crystallizable component. The requirement of switching temperature for medical application (~35°C) for a shape memory polymer can be achieved by using the developed blends as crystallizable component.

POM analysis

The microscopic analysis was carried out for both crystallized from solution as well as from the melt. The microphotographs for the samples crystallized from solution are shown in Figure 9. PEO spherulites having regular shape with well defined bound-
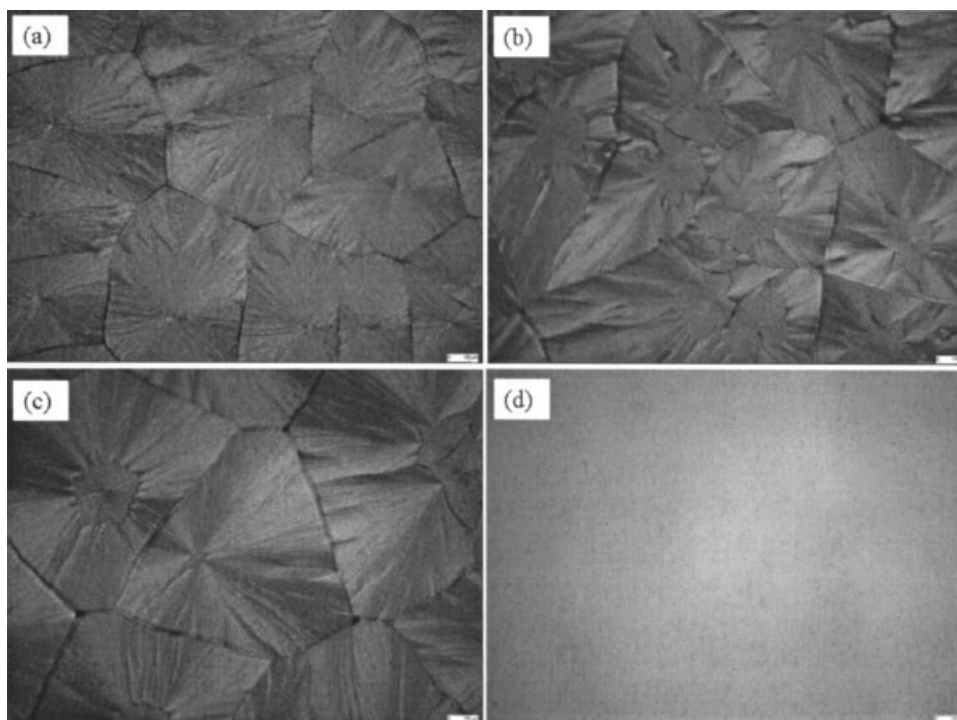

Figure 9 POM microphotographs for the solution cast blend samples with various novolac contents (a) 5 wt %, (b) 10 wt %, (c) 20 wt %, and (d) 100 wt % (all photographs are taken with a magnification of 40).
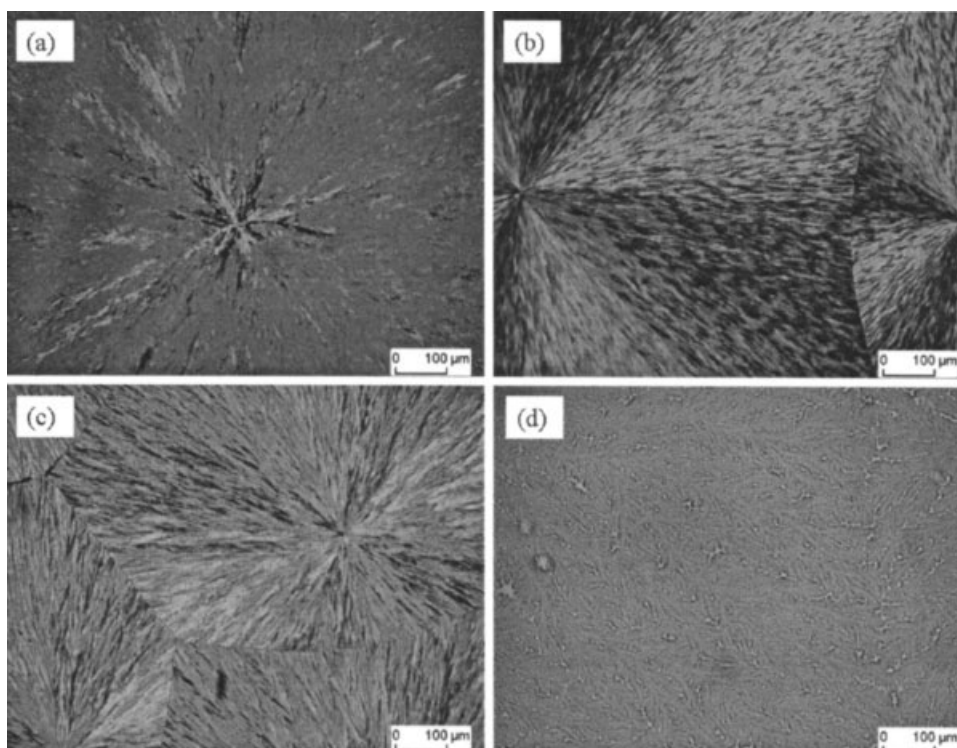
Figure 10 POM microphotographs for the blend samples with different novolac contents crystallized from melt using a hot-stage facility: (a) 0 wt %, (b) 10 wt %, (c) 20 wt %, and (d) 30 wt % (all photographs are taken with a magnification of 100).

ary are clearly discernible whereas the novolac is featureless. One can see in the microphotographs of blend samples that the boundary area for characteristic crystalline pattern increases and regularity of the pattern decreases with increase in novolac content. The characteristics Maltese cross spherulitic structure was not very clearly observed for the solution cast samples. However, the clear Maltese cross microstructures were observed when crystallization from melt was studied using a hot-stage facility. The microphotographs for pure PEO and blends are shown in Figure 10. PEO displays a Maltese cross birefringence pattern having regular shape. With increase in novolac concentration the Maltese cross section increases and order arrangement is lost as observed for solution cast samples. This can be attributed to disturbance of radial orientation caused by amorphous novolac during crystallization process. This is presumably because the amorphous PEO/novolac mixture engulfed in interlaminar region during the crystallization of PEO. The blends with higher concentration of novolac show leaf-like structure due to anisotropy of the total crystallization process. This supports the DSC results that no crystallization peak was observed for the blend with 30 wt % novolac. It may be noted that there is no evidence of segregation of noncrystallizable novolac in the inter-spherulitic contact zones form the micro photographs.

CONCLUSION

PEO/novolac blends were prepared by solution cast technique and their crystallization behavior was investigated. DSC and optical microscopic studies of the blends indicate that novolac is completely miscible with the amorphous phase of PEO and the crystalline phase remains as separate one. A significant decrease in crystallization temperature and crytallinity were observed as a result of incorporation of novolac in PEO. The blend systems will find application in the development of crystallizable component for a shape memory polymer system where the switching temperature can be manipulated by changing the blend compositions.

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