Studies on epoxidised oil and its blend with polystyrene and poly(methyl methacrylate)

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Received 21 September 2000; accepted 7 February 2001

Attempts have earlier been made to replace aromatic epoxies by renewable resource based vegetable oil epoxies. However the latter lack in toughness and strength. To improve these properties linseed oil epoxy was blended with polystyrene and poly(methyl methacrylate). The polyblends were prepared in varying proportion of oil epoxy and polystyrene/poly(methyl methacrylate), for investigation of their physical and mechanical characteristics with reference to their use in coatings. The blend formation was confirmed by DSC, FT-IR and solution tests. The epoxy equivalent, hydroxyl value, iodine value, viscosity, refractive index, and specific gravity of oil epoxy, oil epoxy-polyastyrene blends and oil epoxy-poly(methyl methacrylate) blend were determined. Glass transition temperatures of linseed oil epoxy-polystyrene blends were found to occur in the range of 60-77.6°C and for the linseed oil epoxy-poly(methyl methacrylate) blends in the range of 75-82.4°C in the composition range investigated. Distinct shift in IR peaks of epoxy ring, ester group and hydroxyl group was observed in both the polyblends systems indicating electrostatic interaction between the constituents of the blends. Linseed oil epoxy was found to turn into rigid mass by the addition of these polymers to the extent of only 16.6% (w/w). Preliminary investigations also revealed higher toughness and rigidity in linseed oil epoxy-poly(methyl methacrylate) blends than in linseed oil epoxy polystyrene blends. Both the polyblends systems show solubility in various organic solvents.

Aromatic epoxy resins are a class of versatile thermosetting polymers which have wide application in surface coatings and paints in addition to their application in adhesives, composites and laminates. Epoxies have high strength, low creep, very low cure shrinkage, resistance to corrosion and show good adhesion to the surface of many substances. However, the major drawback of these epoxies is that, in the cured state they are brittle having fracture energy far less than engineering thermoplastics and metals. Furthermore the use of petroleum based polymers is expected to go down in coming years because of their spiraling prices and the high rate of depletion of stocks. In recent years, the use of renewable resources has attracted the attention of many workers as a potential substitute for petrochemicals. Keeping these facts in mind, a long chain aliphatic epoxy from linseed oil (a renewable resource) has been synthesized through the epoxidation of unsaturation present in fatty acid chain. It is expected to show high flexibility and good corrosion resistance properties, particularly against water and acids because of its long hydrophobic chains. However, these aliphatic epoxies fail to give satisfactory mechanical properties like toughness, hardness and possess low load bearing capacity. With a view to improve these properties the linseed oil epoxy (LOE) has been blended with hard and brittle polymers like polystyrene and poly(methyl methacrylate). Polystyrene (PS) is a hard, brittle and transparent polymer which show low weathreability. It is also susceptible to environmental stress cracking. Poly methyl methacrylate is a hard, brittle and transparent polymer which has been found to show good weathreability. Literature survey reveals that no work has been reported on the blending of oil epoxy with these polymers. In present work the vegetable oil epoxy has been chosen with the objective of using a precursor obtained from a renewable resource and enhancing the physico mechanical properties of the epoxy through blending with polystyrene and (poly)methyl methacrylate so that it can be used as an anticorrosive coating material.

Experimental Procedure

Materials

Oil was extracted from linseed (obtained from local market) through Soxhlet apparatus. Petroleum ether

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Fig. 1—$^1$H-NMR spectra of LOE

(b.p. 60-80°C) was used as solvent. Fatty acid composition of the oil is given in Table 1. Hydrogen peroxide (30%), sulphuric acid, glacial acetic acid, and benzene used were of analytical grade (Merk, India). The poly(methyl methacrylate) (PMMA) of Mw 350,000 ($T_g$ 120°C) and polystyrene (PS) of Mw 140,000 ($T_g$ 94°C) were procured from Aldrich Chemical Company, SA.

Synthesis
Linseed oil epoxy was prepared using a reported method for the synthesis of vegetable oil epoxy. Linseed oil 40 g (I.V. 180) equivalent to 0.2899 mol of unsaturation, 40 mL of benzene, 7.995 mL (0.1326 mol) of glacial acetic acid, and one mL of concentrated sulphuric acid were taken in a three neck round bottom flask equipped with a mechanical stirrer, dropping funnel and thermometer. The flask was then immersed in cold water bath, 48.5 mL (0.427 mol) of 30% hydrogen peroxide was added drop wise with continuous stirring. The temperature of the reaction mixture was kept at 20°C during the addition of entire hydrogen peroxide. The temperature was then raised to 60°C which was maintained till the reaction continued. The progress of the reaction was monitored by determining the epoxy equivalent at regular intervals.

Preparation of blends
Linseed oil epoxy-polystyrene (LOE-PS) and linseed oil epoxy-poly(methyl methacrylate) (LOE-PMMA) blends were prepared by solution method.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Linseed oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid value (mg of KOH)</td>
<td>8.3</td>
</tr>
<tr>
<td>Saponification value</td>
<td>160</td>
</tr>
<tr>
<td>Iodine value</td>
<td>181</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.896</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.478</td>
</tr>
<tr>
<td>Fatty acid composition</td>
<td></td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>44%</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>14%</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>20%</td>
</tr>
</tbody>
</table>

60% solution (w/v) of PS and PMMA were mixed in varying ratios with 60% solution (w/v) of LOE separately in different reaction vessels under vigorous stirring at room temperature. The solvent was evaporated slowly in a fuming cupboard under exhaust till it appears to be dry. The remaining solvent is removed in a vacuum oven at 40°C for 24 h. The compositions of LOE-PS and LOE-PMMA polyblends are summarized in Table 2. The formation of blends were checked by observing that no separation of phases occurred under boiling and cold conditions of the blend solutions. The formation of blends were also confirmed by glass transition temperature ($T_g$) of blend samples recorded with the help of DSC.

Characterization
The iodine value, hydroxyl value, colour value, epoxy equivalent, specific gravity, refractive index of oil epoxy and its blends were determined by standard methods. Solubility of these blended polymers were checked in various organic solvents at room temperature. The blend formation was also studied by FT-IR spectroscopy. The spectra of these polymers were recorded on Perkin Elmer 1750 FT-IR spectrometer on NaCl cell. The formation of oil epoxy was also confirmed by the $^1$H-NMR spectra. $^1$H-NMR spectra was recorded on JEOL 200 MHz FX100 spectrometer using DMSO as solvent and TMS as an internal standard. The thermal analyses of these polymers were carried out by DSC (910 Dupont) in N$_2$ atmosphere at a heating rate of 10°C/min. The polymeric film of LOE, LOE-PS and LOE-PMMA were applied on aluminium coupons (70x25x1) mm for specular gloss (at 60°), scratch hardness (BS 3900) and impact resistance test (IS: 101, Part 5/Sec 3).
Table 2—Physico-chemical properties of LOE and its blend with PS and PMMA

<table>
<thead>
<tr>
<th>Properties</th>
<th>LOE</th>
<th>LOE-PS Polyblends (LOE:PS) w/w</th>
<th>LOE-PMMA Polyblends (LOE:PMMA) w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour value</td>
<td>1</td>
<td>1, 1, 1, 1, 1, 1</td>
<td>1, 1, 1, 1, 1, 1</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.486</td>
<td>1.482, 1.481, 1.480, 1.479, 1.478</td>
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<tr>
<td>Specific gravity</td>
<td>1.142</td>
<td>1.132, 1.118, 1.108, 1.102, 1.091</td>
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<tr>
<td>Inherent viscosity</td>
<td>0.78</td>
<td>1.13, 1.21, 1.22, 1.31, 1.32</td>
<td></td>
</tr>
<tr>
<td>Epoxy equivalent</td>
<td>320</td>
<td>385.7, 448.4, 511.8, 574.2, 634.8</td>
<td></td>
</tr>
<tr>
<td>Iodine value</td>
<td>18.5</td>
<td>15.41, 13.28, 11.25, 10.2, 9.12</td>
<td></td>
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<tr>
<td>Hydroxyl value</td>
<td>21.0</td>
<td>17.5, 14.64, 12.81, 11.38, 10.25</td>
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</tbody>
</table>

Result and Discussion

The conversion of linseed oil into linseed epoxy has been confirmed by FT-IR and 1H-NMR spectropic analyses. The IR spectra of oil epoxy shows the presence of the characteristic absorption bands of oxirane ring at 910-950 cm⁻¹. The other peaks observed were methyl and methylene groups at 2900-3000 cm⁻¹, olefinic double bond at 1635 cm⁻¹, ester group of oil at 1760 cm⁻¹. The strong band at 3554 cm⁻¹ indicates the formation of OH group. 1H-NMR spectra of LOE (Fig. 1) shows proton of terminal methyl group at δ = 0.85-0.9 ppm, chain CH₂ at δ = 1.25-1.30 ppm, methylene group attached to carbonyl at δ = 2.1-2.3 ppm, proton of the oxirane ring of LOE at δ = 2.7 ppm, proton of glyceryl methylene group at δ = 3.60 ppm, proton attached to olefinic double bond at δ = 5.3 ppm. The presence of characteristic peak of epoxy ring at 910-950 cm⁻¹ and the 1H-NMR value for protons of epoxy ring at δ = 2.7 ppm confirm the formation of LOE.

**LOE-PS Polyblend**

Characteristic absorption bands of LOE-PS at 900-930 cm⁻¹ for epoxy, 1630 cm⁻¹ for double bond, 1740 cm⁻¹ for ester of oil, 1650 cm⁻¹ for phenyl group of styrene, 2900 cm⁻¹ for aromatic proton, 3460 cm⁻¹ for OH were observed.

**LOE-PMMA Polyblend**

Characteristic absorption bands of LOE-PMMA polyblend are observed at 900-915 cm⁻¹ for epoxy, 1630 cm⁻¹ for double bond, 1460 cm⁻¹ for deformation mode of methylene group, 1730 cm⁻¹ for ester and 3400 cm⁻¹ for OH group. The presence of bands at 910-930 cm⁻¹ for epoxy, 3460 cm⁻¹ for OH in LOE-PS.
and corresponding peaks at 900-915 cm\(^{-1}\), and 3400 cm\(^{-1}\) in LOE-PMMA confirm the presence of both the oxirane ring as well as hydroxyl group in the blends. The above observations lead to the conclusion that there is no chemical interaction between the constituent polymers in the formation of the blends. However the shifting of bands to low frequency indicates electrostatic interaction between partially charged positive and negative sites on both the constituent polymers in the blends\(^{20-21}\). The shifting of bands are higher in the case of LOE-PMMA polyblend due to higher polarity of PMMA.

Table 2 shows the effect of blending on the value of epoxy equivalent (EEW), hydroxyl value, specific gravity, iodine value. The EEW is found to increase as the ratio of PS and PMMA in the blend; hydroxyl value and iodine value also decreases in the same manner, but remains constant for the same amount of LOE used in blending. These observations also confirm that no chemical changes occur in blending, only physical interactions occur between LOE and PS/PMMA phases. The solubility of the polymers were visually tested in solvents like DMSO, ethanol, methanol, carbon tetra chloride, chloroform, acetone, toluene, xylene and benzene. LOE-PS shows good solubility only in DMSO, benzene, toluene, chloroform and xylene. In the rest of the above solvents the solubility is poor. The LOE-PMMA is also soluble in ethanol, methanol, acetone besides the other solvents used for solubility test of LOE-PS.

Surprisingly LOE-PMMA shows solubility both in polar and nonpolar solvents. It is presumed that the PS and PMMA phases in the LOE-PS and LOE-PMMA polyblends envelop LOE phase at molecular level, which results in the restricted solubility of LOE-PS polyblends and fairly good solubility of LOE-PMMA blends. The observed solubility trend of these blends match with the solubility behaviour of polystyrene and poly methyl methacrylate.

### Thermal studies

Table 3 shows the variation of \(T_g\) with the amount of PS and PMMA added to LOE as determined by DSC. The \(T_g\) values were determined from the inflexion point on the heat curves. From the figure and data on \(T_g\) following inferences can be drawn:

(i) Apparently the polyblends exhibit a single \(T_g\), a characteristic of single phase systems\(^{22-23}\).

(ii) \(T_g\)’s of polyblends of LOE-PMMA are higher than those of LOE-PS. In case of LOE-PMMA the increase in \(T_g\) values with the increasing amount of PMMA is sluggish while in case of LOE-PS blends the rate of increase in \(T_g\) values with increasing amount of PS in the blends is more pronounced. In case of LOE-PS blends the total variance of \(T_g\) has been found to be 17.6°C, while in case of LOE-PMMA blends this variance was found to be only 7.4°C. This may be due to the relatively smaller size of the PS chain as evident by lower viscosity of LOE-PS system (Table 2). Smaller size of PS molecule causes the incorporation of progressively larger number of chains per unit mass of LOE-PS blends as compared to LOE-PMMA blends which results into more pronounced increase in \(T_g\) values in LOE-PS blends. In the DSC thermograms (Fig. 2) of polyblends only singe glass transition temperature, \(T_g\) is observed. This clearly indicates the homogeneous miscibility of constituents in LOE-PS and LOE-PMMA blends. Several authors\(^{22-27}\) have used \(T_g\) value in blends to deduce complete miscibility of constituent phases in the blends.

### Film properties

The films of LOE, LOE-PS and LOE-PMMA were cast on aluminium coupons for studying such coating characteristics as impact resistant, flexibility and scratch hardness. Film of LOE takes 48 h in turning from dry to hard while LOE-PMMA and LOE-PS films take 16 and 18 h respectively for this change. All blend samples pass the impact test (100 lbs/in) which indicates good adhesion of the film to the metal surface. The scratch hardness results show that it increases on increasing the ratio of PS and PMMA in polyblends, which indicates the increasing rigidity of the film with the increasing amount of PS and PMMA in the blends. PMMA films were found to show higher scratch resistance, which may be attributed to higher molecular interaction in LOE-PMMA blends because of the presence of polar group in PMMA and epoxy. Flexibility of the films of these blends was
found to decrease regularly with an increasing amount of PS and PMMA in the blends but passed the bend test (1/8” conical mandrel). Small cracks were observed in case of LOE-PS (10:10) blend; presumably because of the presence of closely spaced benzene rings of styrene in the polyblend. Interestingly no cracks appear in LOE-PMMA polyblend films in their entire composition range due to longer chain length PMMA molecule and the absence of any stiffening moiety like benzene ring in the polyblend.

Conclusions

(i) LOE-PMMA and LOE-PS make miscible homogeneous blends as shown by the presence of single glass transition temperature in these blends and shifting of IR peaks of OH group, oxirane ring and ester groups in these blends.

(ii) Only a small amount of PMMA and PS (16.6% w/v) in LOE turns it into a rigid mass.

(iii) LOE-PMMA blends are found to be more rigid and tough as compared to LOE-PS blends.

(iv) Polyblends are not transparent like pure PS and PMMA but are faintly white with a color value of 1.

(v) These information can be used in making high performance coatings and paints.

Acknowledgment

This work was funded by ARDB (Ministry of Defence, India) through grant No. Aero/RD-134/110/106/034.

References

2 May C A & Tanaka G Y, *Epoxy Resin Chemistry and Technology* (Marcel Dakker, New York), 1973
27 Ming-Shu Li, Chen-Chi M Ma, Ming-Siu Lu, Miaw-Ling Lin, Jyh-Leun Chen & Feng-Chih Chang, *Polymer*, 38 (1997) 845