Polymer Bulletin 31, 679–685 (1993)

Polymer Bulletin

# Polymers from renewable resoureces: polyester resins and blends based upon anhydride-cured epoxidized soybean oil

**Joachim Rösch and Rolf Mülhaupt***

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

## Summary

A broad range of crosslinked polyesters were prepared by curing epoxidized soybean oil with various dicarboxylic acid anhydrides in the presence of cure catalysts such as tertiary amines, imidazoles, or aluminum acetylacetonate. The mechanical and thermal properties of the casting resins were dependent upon the type of anhydride. While the anhydrides of hexahydrophthalic acid, succinic acid, and norbornene dicarboxylic acid yielded highly flexible rubbery materials with glass transition temperatures below room temperature, the more rigid anhydrides of maleic and phthalic acid gave amorphous stiff polyesters with higher glass transition temperatures varying between 43 and 73°C. When the cure reaction was carried out in polypropylene melts, multiphase polymers were formed containing polyester phases dispersed in the continuous polyolefin matrix.

## Introduction

Today polymers from renewable resources are being reevaluated as potential environmentally friendly materials which biologically recycle the carbon dioxide evolved during polymer biodegradation or incineration. Moreover, the photosynthesis of biomass represents a highly efficient process for the utilization of solar energy in the production of polymeric materials (1). In addition to the abundant polysaccharides such as cellulose and starch, glycerol esters of fats and oils are attractive renewable sources of raw materials useful in polymer synthesis (2,3). Traditionally, unsaturated glycerol esters, e.g., derived from oleic, linoleic or linolenic acid, which cure upon exposure to oxygen, are beeing applied as drying oils and components of paints and printing inks.

---

*Corresponding author

Many derivatives of unsaturated oils are being produced in industrial scale. An important class of derivatives is epoxidized soybean oil (ESO) being widely applied as PVC additive which improves PVC processability, stability and flexibility. In this communication we report the preparation of thermosetting polyester resins based upon curing ESO with dicarboxylic acid anhydrides. Furthermore, the potential of in-situ anhydride cure of ESO is being evaluated in reactive processing and the synthesis of polyester blends during processing of polyolefins.

## Experimental

Materials: all raw materials are commercially available and used without further purification. Epoxidized soybean oil was supplied by Ciba-Geigy AG and contained 0.41 mmol epoxide/g as determined by titration in THF/acetic acid 1:1 in the presence of tetraethylammonium bromide with 0.1 N $HClO_4$ following endgroup titration procedures described by DIN 16945. The soybean oil contained 20 wt % saturated $C_{16}$ and $C_{18}$ fatty acids, 5 wt % linolenic acid, 50 wt % linoleic acid, and 25 wt % oleic acid. Norbornene dicarboxylic acid anhydride and hexahydrophthalic anhydride were commercial curing agents for epoxy resins and were supplied by Ciba-Geigy AG. Succinic anhydride, maleic anhydride, and phthalic anhydride, aluminum acetylacetonate, benzyldimethylamine, 2-ethylimidazole were purchased from Aldrich Co. Polypropylene (Hostalene$^{TM}$ PPN 1060, MFI(230/2.16)=2 dg/min, $T_m$=165°C, $M_n$=63000 g/mol,and $M_w$=182700 g/mol as determined by SEC analysis of 1,2,4-trichlorobenzene solutions at 135°C) was obtained from Hoechst AG. Maleic-anhydride-grafted polypropylene (Exxelor$^{TM}$ PO 2011, MFI(230/2.16) = 125 dg/min, $T_m$=164°C, Mn=30000 g/mol as determined by SEC analysis) was supplied by Exxon Chemicals.

Preparation and characterization of anhydride-cured ESO: the dicarboxylic acid anhydride, ESO, and the catalyst were mixed according to the mixing ratios indicated by the epoxy/anhydride molar ratio in Table 1, heated at 160°C, degassed for the duration of a few minutes using oil pump vacuum, and then poured into a preheated mold. The cure reaction was performed in a hot-air-circulation oven for the duration of 1 hour at 200°C to produce plates of 4 mm thickness. Rectangular bars (60 x 6 x 4 mm) were cut out of these plates to perform three-point-bending tests on an Instron 4204 according to standard procedures of DIN 53452. Glass transition temperatures were measured by dynamic mechanical analysis on the Rheometrics solids analyzer at 10 Hz and a heating rate of 3K/min.

Reactive blending and blend characterization: ESO was cured with anhydrides in polypropylene melts using a Haake Rheomix 90 equipped with a 60 ml double-screw blender which was preheated at 200°C. In a typical run, 40 g of the polypropylene was fed to the mixing chamber and melt kneaded for 2 minutes. Then 8 g of the liquid mixture of ESO, dicarboxylic acid anhydride and catalyst was added. Approximately 2 minutes after the initial torque decay following the addition of the low-viscosity mixture, the torque increased substantially. After mixing for an additional 4 minutes, the blend was removed quickly and quenched. Then sheets of 1.5 mm thickness were compression molded under vacuum at 260°C using a Schwabenthan Polystat 100 press. After annealing them at 260°C for 10 minutes, the samples were quenched bewteen water-cooled metal plates. For tensile testing dumpbell-shaped tensile bars (according to DIN 53455) were cut and machined. Stress/strain measurements were performed at a crosshead speed of 10 mm/min on an Instron 4204 at 23°C to determine Young's modulus. Morphological studies were carried out using the Zeiss CEM 902 transmission electron microscope (TEM). Thin sections suitable for TEM analysis were obtained after staining and hardening the samples in ruthenium tetroxide vapors for 6 hours. With the Reichert Jung Ultracut E microtoming equipment and a diamond knife the thin sections of 80 to 100 nm thickness were cut.

## Results and discussion

The cure reaction of multifunctional epoxy resins with dicarboxylic acid anhydrides is well known to yield highly crosslinked amorphous polyester materials. Mechanical and thermal properties depend upon the chemical nature of the anhydride curing agents, type and concentration of cure accelerators, cure reaction conditions, and epoxy conversion which is closely related to the epoxy/anhydride molar ratio, the catalyst efficiency, and the reactivity of the anhydrides (4-6). As summarized in Table 1, ESO was cured with various anhydrides, e.g., anhydrides of norbornene dicarboxylic acid, hexahydrophthalic acid, succinic acid, maleic acid, and phthalic acid in the presence of aluminum acetylacetonate, benzlydimethylamine (BDA), or 2-ethylimidazole (EI) as cure accelerators. Similar to the conventional epoxy/anhydride-based thermoset resins, the anhydride/epoxy molar ratio was varied between 0.75 and 1.0 with accelerator contents varying between 0.5 and 2 wt % with respect to the anhydride/epoxy mixture. Preferably, the anhydride cure of ESO was performed at 200°C for the duration of 1 hour. At this temperature gelation occurred within few minutes without causing extensive thermal and oxidative degradation.

Table 1. Cure conditions and properties of polyesters prepared by curing ESO with various dicarboxylic acid anhydrides at 200°C.

| Run No | Anhydride Type | Curing Agent Anhydride/Epoxy (mol/mol) | Catalyst Type | Catalyst (wt %) | Flex.Modulus (MPa) | Tg[a] (°C) |
|---|---|---|---|---|---|---|
| 1 | Norbornenedicarboxylic anh. | 0.75 | Al(acac)$_3$[c] | 2.0 | b) | -5 |
| 2 | Hexahydrophthalic anh. | 0.75 | " | 2.0 | b) | 3 |
| 3 | Succinic anh. | 0.75 | " | 2.0 | b) | 10 |
| 4 | Maleic anh. | 0.75 | " | 2.0 | 520 | 43 |
| 5 | Maleic anh. | 1.00 | " | 2.0 | 650 | 49 |
| 6 | Phthalic anh. | 0.75 | " | 2.0 | 830 | 71 |
| 7 | Phthalic anh. | 0.75 | " | 1.0 | 520 | 58 |
| 8 | Phthalic anh. | 0.75 | " | 0.5 | 380 | 53 |
| 9 | Phthalic anh. | 1.00 | " | 2.0 | 930 | 73 |
| 10 | Phthalic anh. | 1.00 | BDA[d] | 1.0 | 840 | 67 |
| 11 | Phthalic anh. | 1.00 | EMI[e] | 1.0 | 980 | 75 |

a) determined by dynamic mechanical analysis, b) highly flexible, c) aluminum acetylacetonate, d) benzyldimethylamine, e) 2-ethylimidazole

From the data listed in Table 1 it is possible to conclude that, in addition to the nature of the anhydride curing agent, the epoxy conversion is the critical parameter governing polymer properties. At low epoxy conversions, i.e., using low accelerator content or less reactive anhydrides such as the cycloaliphatic anhydrides, the resulting crosslinked polyesters were highly flexible and rubber-like. In the case of norbornene dicarboxylic acid anhydride (run 1), hexahydrophthalic anhydride (run 2) and succinic anhydride (run 3), the glass transition temperatures remained well below room temperatures. With maleic anhydride and especially with more rigid and more reactive aromatic dicarboxylic acid anhydrides, stiffer polyesters with flexural moduli in the range of 500 to 1000 MPa and glass transition temperatures varying between 43 and 75°C were obtained. Highest stiffness and thermal resistance were observed for stoichiometric ratios of epoxy and anhydride groups and 2 wt % content of aluminum acetylacetonate or benzyldimethylamine accelerators respectively. Similar to the aliphatic anhydrides, the reduction of the accelerator concentration adversely affected stiffness and glass transition temperature. For example, when the aluminum acetylacetonate content is lowered from 2 to 0.5 wt % (run 6 versus run 8), the flexural modulus is reduced by approximately 50 %, while the glass transition temperature was reduced by 18°C. This experimental evidence demonstrates that the change in crosslink densities is associated with the conversion of the cure reaction. As a consequence, variations of accelerator concentration and anhydride type permit control of the mechanical properties over a very wide range.

Another objective of this research was to cure ESO in polyolefin melts to produce polyester blends via reactive processing. In the presence of cure accelerators, the cure reaction of ESO with dicarboxylic acid anhydrides at 200°C is fast enough to form the crosslinked polyester within few minutes during polypropylene processing. The in-situ polymerization of ESO with phthalic anhydride in polypropylene melts was performed using an anhydride/epoxy molar ratio of 0.75 in order to prevent undesirable sublimation of unreacted phthalic anhydride. In order to enhance interfacial adhesion to the polypropylene matrix, maleic-anhydride-grafted polypropylene (PP-g-MA) was added. In spite of the low polarity of both polypropylene and ESO, the resulting blends were phase separated containing polyester phases dispersed in the continuous matrix of the excess polypropylene blend component. It was possible to incorporate 60 vol-% of the ESO-based polyester into polypropylene. The morphological and mechanical properties are summarized in Table 2.

According to the transmission electron microscopic analysis, the irregularly shaped polyester phases were fairly large with average domain sizes varying between 100 to 800 μm over the entire blend composition range. Interestingly, the addition of the succinic-anhydride functional compatibilizer PP-g-MA, known es polymeric dispersing agent, did not improve the dispersion process. Most likely, due to the rapid gelation of the low viscosity ESO/phthalic anhydride mixture, the time between highly viscous and gelled state was too short to effect fine dispersion in the viscous polypropylene melt.

The drastic decay of the Young's modulus and yield stress with increasing polyester volume fraction clearly indicates the presence of low-modulus polyesters which are highly flexible with respect to the more rigid polypropylene matrix. Such rubbery or soft phase separated components adversly affect the load-bearing properties of the blend. It appears likely that under the reaction conditions typical for reactive blending the short reaction time of few minutes is not sufficient to afford complete epoxy conversion. Therefore the resulting crosslinked polyesters, which are plasticized by only partially reacted ESO, are rubber-like low $T_g$ materials.

Table 2. Reactive blending of polypropylene with ESO/phthalic anhydride at 200°C in the presence of aluminum acetylacetonate cure accelerator.

| Composition[a] | ESO-based polyester (vol.-%) | Domain size (μm) | Young's modulus (MPa) | Elongation at break (%) | Yield Stress (MPa) |
|---|---|---|---|---|---|
| PP | 0 | - | 1150 | 800 | 32 |
| ESO/PA | 20 | 100-500 | 390 | 400 | 22 |
| ESO/PA+PP-g-MA | 20 | 100-500 | 430 | 24 | 25 |
| ESO/PA | 40 | 100-500 | 260 | 17 | 10 |
| ESO/PA+PP-g-MA | 40 | 100-500 | 290 | 10 | 14 |
| ESO/PA | 60 | 100-800 | 150 | 8 | 7 |

a) PP: polypropylene, ESO: epoxidized soybean oil, PP-g-MA:maleic anhydride grafted polypropylene (5 wt %).

In addition to stiffness also elongation at break was reduced dramatically with increasing polyester volume fraction, especially when the PP-g-MA compatibilizer was present. This behavior is similar to that of multiphase polypropylenes containing adhering or non-adhering inclusions respectively. When the adhesion of the dispersed phase is improved, debonding and void formation during plastic deformation are prohibited and brittle failure occurs with cracks being initiated at the interfacial boundaries of the dispersed phases. At higher polyester content the negative impact of the compatibilizer was less pronounced because of the markedly reduced ductile deformation of the blend which contained large amounts of the crosslinked polyester.

In conclusion, the investigation of anhydride cure of ESO indicates that ESO offers interesting potential for the synthesis of new polymers derived from renewable resources. On one hand, anhydride-cured ESO is of interest in typical epoxy application, e.g., coatings and casting resins. On the other hand, the injection of

ESO/anhydride mixtures into polyolefin melts affords flexibilized thermoplastic multiphase polyolefins which could be tailored to match the performance of flexible PVC-type materials.

## References

1 Gandini A, "Comprehensive Polymer Science", First Suppl., Pergamon Press, Oxford 1992, p.527.

2 Gunstone FD, "Chemistry and Biochemistry of Fatty Acids and Their Glycerides", Chapman and Hall, London 1967

3 Solomon DH, "The Chemistry of Organic Film Formers", Krieger, Huntington, New York 1977

4 Takahashi K, Hitoshi F, Adv.Polym. Sci. 80, 173 (1986)

5 Trappe V, Burchard W, Macromolecules 24, 4738 (1991)

6 Steinmann B, J. Appl. Polym. Sci. 1990, 38.

Accepted November 8, 1993 C