Synthesis and Dynamic Mechanical Behavior of Crosslinked Copolymers and IPNs from Vegetable Oils

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ABSTRACT: Crosslinked copolymers and IPNs were synthesized from vegetable oils (e.g., cottonseed oil, castor oil, and tung oil). The dynamic mechanical behavior of the polymer blends was studied by Dynamic Mechanical Spectroscopy (DMS). The tan δ–temperature curves of these kinds of copolymers and IPNs show a single peak, which indicate good compatibility. They represent a kind of damping materials with high tan δ values over wide temperature ranges. Thus a new way has been found to use natural products of agriculture to produce damping materials. Effects of various factors on the dynamic mechanical behavior were studied. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1840–1842, 2003

Key words: crosslinked copolymer; IPNs; dynamic mechanical behavior

INTRODUCTION

Damping materials that can be used over wide temperature ranges are usually made from semicompatible polymer blends. Because most polymeric materials are incompatible with each other, it is an important method to obtain semicompatible polymer blends through formation of IPNs or crosslinked copolymers.[1–5] Vegetable oils are rich and renewable resources. It is of significant practical and theoretical value to study and determine if vegetable oils can be transformed into crosslinked copolymers and/or IPNs that can be used as damping materials.

Sperling and his coworkers[6–8] reported on the IPNs from castor oil-based polyurethanes and styrene monomer. They found that the mechanical properties of these IPNs were increased by increasing TDI content of the castor oil based polyurethanes. Patel et al.[8–11] prepared IPNs from polyurethanes based on castor oil with other vinyl monomers and found that the IPNs formed were tougher than the corresponding homopolymers.

A series of crosslinked copolymers and IPNs from epoxidized vegetable oils and maleinized tung oil were synthesized. These crosslinked copolymers and/or IPNs were tested by means of Dynamic Mechanical Spectroscoy (DMS) to investigate their compatibility and damping property.

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EXPERIMENTAL

Synthesis of epoxidized castor oil

Castor oil 400 g was mixed with 48% H_2O_2 200 mL and formic acid 20 mL. The reaction was carried out at 50°C with continuous stirring for 9 h. The product obtained was washed with distilled water until free of acid and hydrogen peroxide.

Synthesis of adducts of tung oil with maleic anhydride

Tung oil (1 mol) was mixed respectively with 1, 2, and 3 mol maleic anhydride at 80–90°C under N_2 with continuous stirring for 3 h. Three different adducts of tung oil with maleic anhydride were obtained.

Synthesis of polyurethane prepolymer

TDI 2mol was mixed with 1 mol PPO(polypropylene oxide glycol $\bar{M}_n$ 2000) oligomer in a flask and heated in an oil bath at 75°C with stirring under dry N_2, until the reaction was complete (about 3.5 h).

Synthesis of crosslinked copolymers

Crosslinked copolymers were synthesized by mixing epoxidized vegetable oils and adducts of tung oil with maleic anhydride in different proportions; 2% by weight DMP-30 was added. The mixture was stirred for 3 min to form a homogeneous solution. The bubbles were removed under vacuum. Then the mixture was poured into a mold and cured subsequently at 100°C for 24 h and at 135°C for 24 h.

TABLE I
Dynamic Properties of Crosslinked Polymers

Sample	Composition	T_g (°C)	Tan δ max	Temperature range of tan $\delta > 0.3$
ABCP-1	ECA:DMT-1:4	46.2	0.835	20.2–73.4°C
ABCP-2	ECA:DMT-1:1	39.2	0.782	20.3–60.9°C
ABCP-3	ECA:DMT-4:1	6.1	1.305	−27.8–33.2°C
ABCP-4	ECA:TMT-1:4	55.3	0.963	25.4–79.2°C
ABCP-5	ECA:TMT-1:1	51.2	0.797	30.4–71.6°C
ABCP-6	ECA:TMT-4:1	9.3	1.120	−16.5–36.5°C
ABCP-7	ECO:TMT-1:4	37.0	0.975	4.3–66.1°C
ABCP-8	ECO:DMT-1:4	45.1	1.119	13.9–69.1°C

Synthesis of IPNs

Polyurethane prepolymer was mixed with epoxidized vegetable oils (or exoxy resin) and adducts of tung oil maleic anhydride in a predetermined proportion. To this, a suitable chain extender (dihydric alcohol) and DMP-30 were added and the mixture was cured.

Characterization

The Dynamic Mechanical Spectroscopy was conducted using a Rheovibron Dynamic Viscoelastometer (model DDV-III-EA, Baldwin Co., Japan). The temperature range employed was from −60 to +200°C, with a heating rate of 3°C per minute. A frequency of 35 Hz was applied.

RESULTS AND DISCUSSION

Crosslinked copolymers

The results of DMS measurements show that the crosslinked copolymer from epoxidized oils and adducts of tung oil with maleic anhydride have good compatibility. They all show single damping peaks in tan δ–temperature curves. The widths of the peaks are about 50−60°C at tan $\delta > 0.3$. The width, the peak value of tan δ, and T_g are affected by the content of epoxidized vegetable oils and different kinds of tung oil–maleic anhydride adducts (see Table I). This fact may come from the difference in the degree of crosslinking. The higher the network density of the copolymer, the better the compatibility. The content of epoxy resin in these crosslinked copolymers has some effect on the width of the tan δ peak. As the addtion of exoxy resion would decrease the opportunity of epoxidized vegetable oils to react with the adducts of tung oil, the compatibility of epoxidized vegetable oils and tung oil decreases. Epoxidized castor oil has hydroxyl groups that can form hydrogen bonding with carbonyl groups in tung oil, and it is more reactive with tung oil adducts than epoxidized cottonseed oil. Thus, the migration of polymer chains that causes phase separation can be prevented. That is the reason why the crosslinked copolymers from castor oil have a narrower tan δ peak and higher T_g than that from cottonseed oil.

Dynamic mechanical spectroscopic results show that IPNs prepared from vegetable oils and polyurethane have good compatibility, with a single tan δ peak in most cases (see Figs. 1–4). This fact can be explained by the existence of chemical bonding betweed the two polymer networks. Other factors, such as the difference in the degree of crosslinking and chain extender, etc., have little effect on the dynamic mechanical behavior. The IPN prepared from epoxy resin E51, compared with that from E44, has a wider tan δ peak. The IPN in which DMP-30 was used as a catalyst during synthesis has a narrower tan δ peak than those without DMP-30. These can be explained

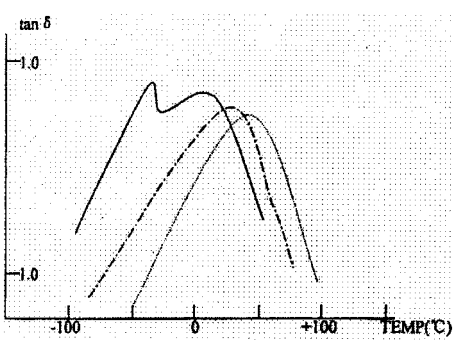

Figure 1 Damping of factor (tan δ) vs. temperature. __ IPN containing 70% PU; - · - · - 50% PU; ---- 30% PU.

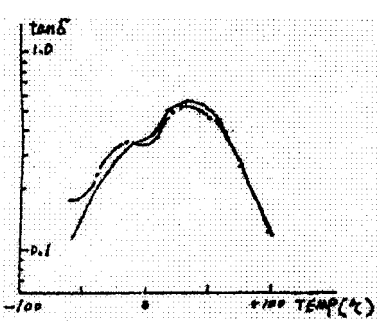

Figure 2 Damping factor (tan δ) vs. temperature. __ IPN from E44, $\bar{M}_n$454; ·-·-·- *IPN.* From E51, $\bar{M}_n$392.

by the competition between two processes in IPN formation, namely, the migration of polymer chains, which caused phase separation and the interpenetration (chain entanglement) between the two networks, which prevent phase separation. Hence, epoxy resin with a higher viscosity and addition of catalyst DMP-30 both favor higher compatibility. The IPN prepared from castor oil has better compatibility than that from cottonseed oil. The reason may be that the castor oil contains some hydroxyl groups that can form hydrogen bonds with urethane groups and epoxidized castor oil is more reactive than expoxidized cottonseed oil. The rapid reaction of epoxidized castor oil with anhydride make it possible to retard the extent of chain migration and enhance chain entanglement effect between the two networks.

CONCLUSION

Crosslinked copolymers and IPNs were prepared from vegetable oils. In most cases, there is a single peak in the tan δ–temperature curve. There exists intercrosslinking between the two networks in IPNs that greatly influence the compatibility and dynamic mechanical behavior of the IPNs. During the formation of IPNs, the migration of polymer chains and interpenetration between the two networks take place simultaneously. Increase in the viscosity of reactants or addition of catalysts will retard the extent of chain migration. These make the IPNs have high tan δ values over wide temperature ranges. The polymer blends prepared can be used as damping materials.

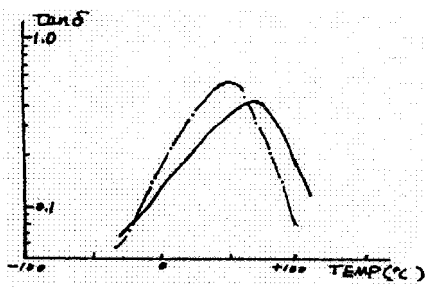

Figure 3 Effect of catalyst on DMS OF IPN. -·-·- uncatalyzed; __ catalyzed.

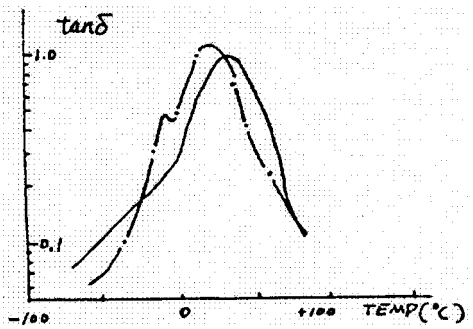

Figure 4 tan δ vs. temperature. -·-·- IPN from epoxidized oil; __ IPN from epoxidized castor oil.

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