



Studies on Swelling Properties of IPNs of Cross Linked Biopolyesters of Castor Oil and Cardanol

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Abstract

Biodegradable polyester thermosets and interpenetrating networks were prepared using addition curable fumarate esters of castor oil and methylolated cardanol and crosslinking agents vinyl acetate (VA), vinyl pyrrolidone (VP), acrylonitrile (AN), methylacrylate (MA) and methyl methacrylate (MMA) respectively. The swelling properties of these cross linked biopolyesters and IPNs were studied under standard conditions.

Keywords: Swelling Properties, Castor Oil, Cardanol.

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Introduction

Plant oils containing hydroxyl fatty acids are important raw materials for the polymer production. They can be polymerized to form elastomeric networks and are used as alternative material resources to petrochemical derived resins. The polymers obtained from plant oils are biopolymers; they are often biodegradable as well as non-toxic. [1]. One of the most naturally and abundantly occurring plant oil is castor oil (Ricinus oil). It is a triglyceride of fatty acids which occurs in the seed of the castor plant, Ricinus Communis. It is produced by cold pressing the seeds and subsequent clarification of the oil by heat. In comparison with other oils, it presents high viscosity, high polarity, very low vapour pressure and optical activity. The ester linkages, double bonds and hydroxyl groups in castor oil provide reaction sites for the preparation of many useful derivatives. Castor oil plasticizes a wide variety of natural and synthetic resins. Castor oil has become an important raw material for the production of polyurethanes, IPNs, biodegradable polyesters etc. Castor oil can generate high polymer with limited crosslink density and offers toughening characteristics to brittle and highly cross linked composite materials [1].

Cashew nut shell liquid (CNSL), an agricultural renewable resource contained in the spongy mesocarp of the cashew nut shell (*Anacardium occidentale* L). It holds considerable importance, because it is a source of unsaturated hydrocarbon phenol and behaves as an excellent monomer for thermosetting polymer production. Cardanol, a major constituent of CNSL is a meta substituted phenolic compound. Cardanol is obtained by distilling the cashew nut shell liquid (CNSL). The unique feature that makes cardanol as an

interesting monomer is the presence of a Meta substituent of a C₁₅ unsaturated hydrocarbon chain with 1-3 double bonds and the phenolic character of the cardanol. Compared with conventional polymeric materials, cardanol based polymers can have improved functional characteristics (such as toughness, process ability and hydrophobicity) due to the long meta substituent alkyl chain and rigid phenyl group [2-3].

Experimental methods

Preparation of IPNs of fumarate resins of cardanol and castor oil

The fumarate resin of castor oil (CFR) and cardanol (MCFR) were blended in weight ratio of 1:1 with constant stirring for 30 minutes. The resin blend was then mixed with the monomers, acrylonitrile (AN), methyl acrylate (MA) and methyl methacrylate (MMA) in the weight ratio of 1:0.5 in presence of benzoyl peroxide and dimethyl aniline and then casted on a clean silicone oil-coated glass plate, cured in hot air oven at 80°C for 6h. The general scheme of crosslinking in IPN formation is given in Figure 1. The IPNs prepared with vinyl acetate (VA), vinyl pyrrolidone (VP), acrylonitrile (AN), methyl acrylate (MA) and methyl methacrylate (MMA) were coded as CFMCF-VA, CFMCF-VP, CFMCF-AN, CFMCF-MA and CFMCF-MMA respectively.

Swelling studies on IPNs of fumarate resins of cardanol and castor oil

All the IPNs were subjected to swelling experiments. The density of the present IPNs was determined as per ASTM D 792. Samples (1x1 cm) with uniform thickness were punched out from the sheets and their thickness, length and breadth were accurately measured by means of a screw gauge and Vernier calipers respectively. Therefore, the accurately weighed IPNs were allowed to swell in the solvents having different solubility parameters viz. hexane, benzene, N,

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N-dimethyl acetamide, N,N-dimethyl formamide, ethyl alcohol, n-butyl alcohol, and ethylene glycol in diffusion test bottles for 2 days at room temperature.

The samples after the immersion in solvent were removed from the bottles and the wet surfaces were quickly dried using tissue paper. The weight of the swollen specimens was measured. Thickness and width of the swollen specimen were also measured. The swelling coefficient is the ratio of volume of solvent in the swollen polymer to that of swelled polymer and is defined by the relation:

$$\text{Swelling coefficient (Q)} = \frac{\text{Weight of the solvent in swollen polymer}}{\text{Weight of the swolled polymer}} \times \frac{\text{Density of polymer}}{\text{Density of solvent}}$$

The swelling coefficients of the IPNs were plotted against solubility parameters of solvents. The solubility parameter of the solvent which induces maximum swelling and higher swelling coefficient (Q) was considered as the solubility parameter of polymer. In the present biopolyesters, maximum swelling was observed in dimethyl formamide (DMF).

Cross link density, γ or degree of cross linking is a measure of the total links between chains in a given mass of materials. The effective cross link density (mol/cm^3) and number average molecular weight between cross-links (M_c), (reciprocal of crosslink density) of the cured material were determined using the modified Flory-Rehner equation as reported elsewhere [4].

$$\gamma = - \frac{[V_\gamma \gamma + \chi V_\gamma^2 + \ln(1 - V_\gamma)]}{d_\gamma \cdot V_0 \left(V_\gamma^{1/3} - \frac{V_\gamma}{2} \right)} = \frac{1}{M_c}$$

Where V_γ = Volume fraction of the polymer in the swollen state

$$V_\gamma = 1/1+Q$$

Q = Swelling coefficient

d_γ = Density of the polymer

V_0 = Molar volume of the solvent

χ = Polymer – solvent interaction parameter

M_c = Molecular weight between two cross

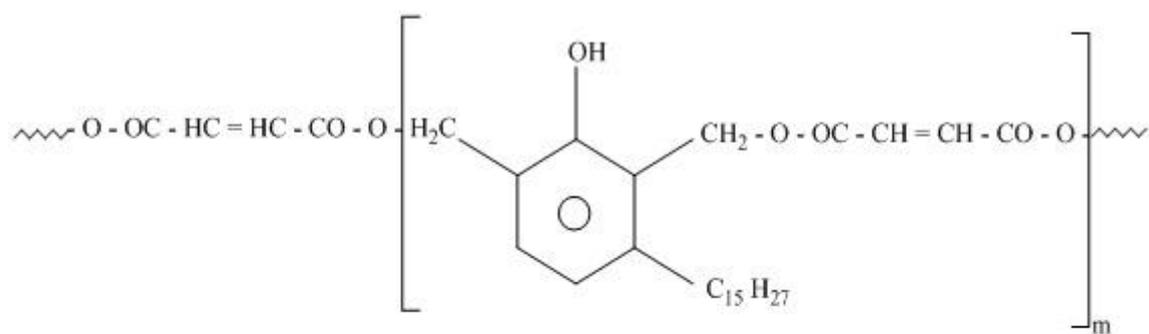
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Results and Discussions

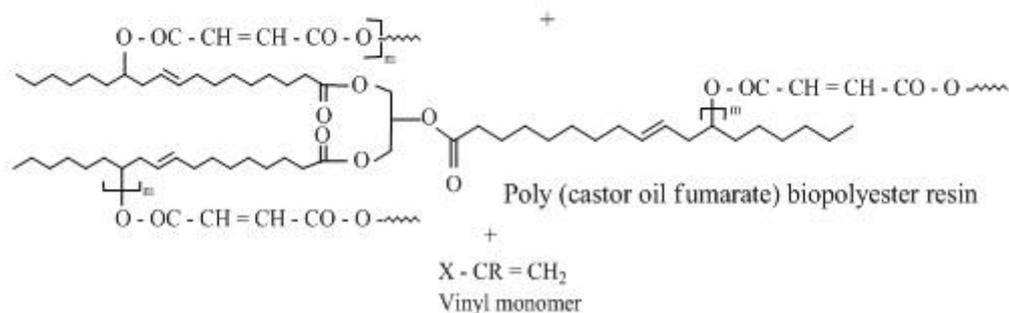
Crosslink density and voids play an important role in determining the properties of crosslinked polymers. Generally such condensation polymerization leads to generation of water and formaldehyde in the former and water alone in the latter and consequent formation of voids. The present IPNs only swell and do not dissolve in a non-reactive solvent. The degree of swelling in a non-reactive solvent determines the degree of crosslinking and the molecular weight between crosslinks. Among the solvents N, N-dimethyl formamide with solubility parameter, 12.1 imparts maximum swelling for all IPNs Therefore the solubility parameter of the present IPNs is taken as 12.1. The

variation of swelling co-efficient with solubility parameter is given in Figure 1. The effective crosslink density is the total sum of chemical and physical crosslinks. Physical crosslinking is the result of micro heterogeneous two phase morphology. This is a consequence of morphological differences between two different chain blocks as observed with the present IPN materials. The hard blocks comprise aromatic phenyl units. The soft blocks comprise aliphatic side chains. The minor hard blocks aggregate to form domain under ambient conditions and get dispersed in major soft blocks. The hard blocks act as chemical crosslinks to hold together the soft blocks in the crosslinked network.

The physical crosslinks of hydrogen bonding interaction exert its influence under solid state, but not in solvated and swelled state. Therefore the higher crosslink density of the present IPN is attributed to the disruption of physical crosslinks observed in N, N dimethyl formamide solvent. Among the IPNs methyl methacryllate based one is having higher crosslink density (Table 1). The synthesis of interpenetrating polymer networks (IPNs) is a useful technique for an interpenetrating polymer network; IPN is an intimate combination of two or more polymers in the form of networks, where at least one of them has been formed in the presence of others. However there is no chemical linkage between the distinct networks. One or more polymer is synthesized and crosslinked in the presence of the other. IPNs typically consist of a flexible elastomer and one or more rigid, high modulus component. IPNs generally possess enhanced physico-mechanical properties against the normal polyblends of their components. IPNs derived from castor oil and other polymers have gained wide spread acceptance in industrial applications. Various IPNs are synthesized using known polymers by processing either with cardanol or castor oil based polymer. However there is no report on the IPNs derived by interpenetrating cardanol and castor oil based polymers. The effective crosslink density is the total sum of chemical and physical crosslinks. Physical crosslinking is the result of micro heterogeneous two phase morphology. This is a consequence of morphological differences between two different chain blocks as observed with the present IPN materials. The hard blocks comprise aromatic phenyl units. The soft blocks comprise aliphatic side chains. The minor hard blocks aggregate to form domain under ambient conditions and get dispersed in major soft blocks. The hard blocks act as chemical crosslinks to hold together the soft blocks in the crosslinked network. The molecular weights between crosslinks and crosslink density of the present materials confirm the crosslinked character. The crosslink density of the crosslinked biopolyesters based on methyl methacryllate of polycardanol fumarate is comparatively higher in the corresponding vinyl monomer based materials. (Table 1).



Poly (cardanol fumarate) biopolyester resin



Dibenzoyl peroxide | Dimethyl aniline
↓

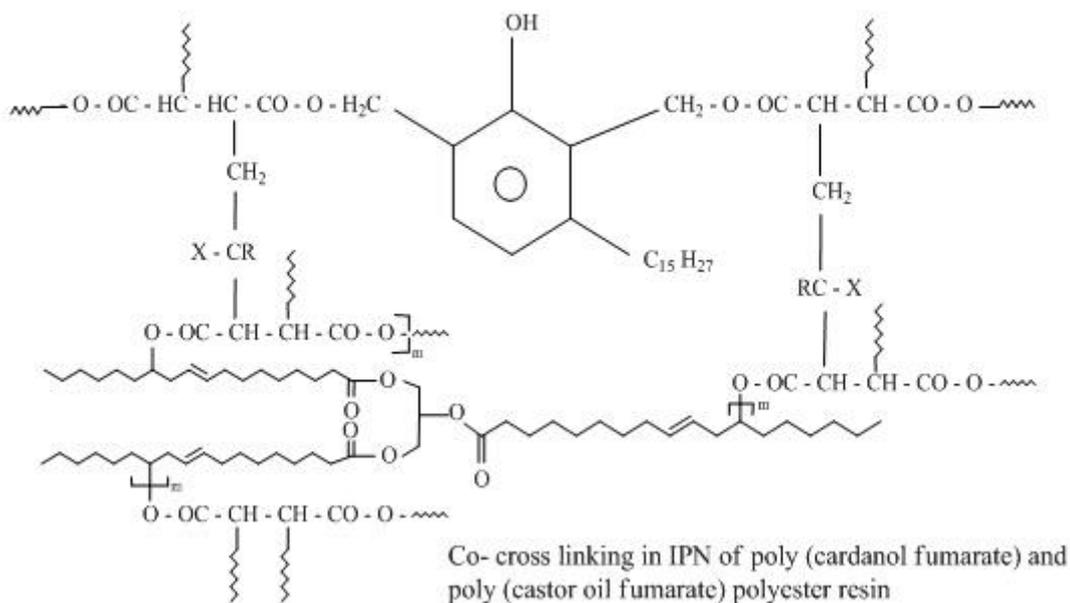
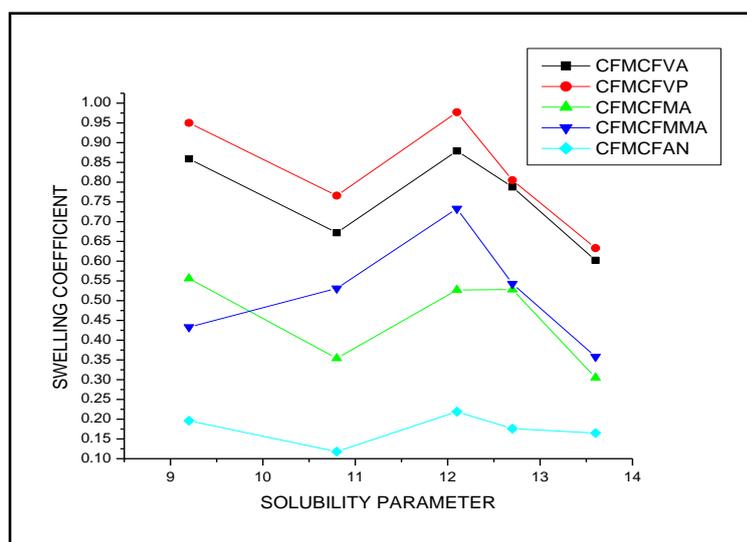


Figure I. Co-Crosslinking of Poly (Cardanol Fumarate) and Poly (Castor Oil Fumarate) Through the Vinyl Monomer

Table I. Crosslink Properties of IPNs of Poly (Cardanol Fumarate) and Poly (Castor Oil Fumarate) Biopolyester Resin

Crosslinked material	Density	Crosslink Density ($\times 10^3$)	Molecular Weight Between Crosslinks (mol^{-1})
CFRMCFR-VA	1.10827	1.879	532
CFRMCFR-VP	1.13624	2.409	415
CFRMCFR-MA	1.3430	1.380	724
CFRMCFR-MMA	1.3525	9.646	104
CFRMCFR-AN	1.3336	3.474	288

Figure II. Variation of Swelling Co-Efficient Of IPNs with Solubility Parameter of Solvents

Conclusion

Interpenetration of polymer networks were prepared using addition-curable, multifunctional and mutually soluble poly (cardanol fumarate) and poly(castor oil fumarate) biopolyester resins by addition-curing with vinyl monomers [vinyl acetate (VA), acrylonitrile (VC), methyl acrylate (MA), n-vinyl pyrrolidone (VP) and methyl methacrylate (MMA)]. Molecular interpenetration and co-crosslinking of poly (cardanol fumarate) and poly (castor oil fumarate) through the vinyl monomer favours better interpenetration of polymer networks. The present

interpenetration of polymer networks are free from tackiness, internal cracks, and voids. The interpenetration of polymer networks also has mar resistance.

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