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Swelling Studies of Cross Linked Biopolyesters of Polycastor Oil Fumarate

T. Jothy Stella

Assistant Professor, Department of Chemistry, Dr.Sivanthi Aditanar College of Engineering, Tiruchendur, Tamilnadu, India.

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Abstract

Biodegradable cross linked biopolyesters of castor oil were prepared using addition curable fumarate esters of castor oil with 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 were studied under standard conditions.

Keywords: Biodegradable, biopolyesters of castor oil, crosslinking agents, swelling properties.

Introduction

The polymers synthesized using plant oils exhibit appreciable properties at reduced costs [1]. Plant oils containing hydroxyl fatty acids are important raw materials for the polymer production [2]. The polar hydroxyl groups in castor oil account for its relatively high viscosity and specific gravity. Castor oil is not only compatible with, but also plasticizes a wide variety of natural and synthetic resins. The ester linkages, double bonds and hydroxyl groups in castor oil provide reaction sites for the preparation of many useful derivatives [3].

Castor oil (Ricinus oil) presents singular chemical and physical properties. It is a triglyceride of fatty acids which occurs in the seed of the castor plant, Ricinus Communis. The ester linkages, double bonds and hydroxyl groups in castor oil provide reaction sites for the preparation of many useful derivatives. Castor oil can generate high polymer with limited crosslink density and offers toughening characteristics to brittle and highly crosslinked composite materials.

Experimental methods

Preparation of crosslinked biopolyesters

The fumarate resins of castor oil (CFR) was prepared as reported elsewhere [4]. Simillarly the fumarate resin of castor oil was prepared by heating 3 moles of castor oil with 1 mole of maleic anhydride using morpholine and sodium acetate as catalysts. The polyesters based on castor oil fumarate (CFR) were prepared by reacting the respective fumarat resin with the monomers, vinyl acetate (VA), vinyl pyrrolidone(VP), acrylonitrile (AN), methyl acrylate (MA) and methyl methacrylate (MMA).CFR was mixed with monomers in the weight ratio of 1:0.5 in presence of benzoyl peroxide and dimethyl aniline, then casted on a clean silicone oil-coated glass plate and cured in hot air oven at 80^0C for 6h. The polymer sheets obtained with vinyl acetate,vinyl pyrrolidone, acrylonitrile, methyl acrylate and methyl methacrylate were coded as CFR-VA,CFR-VP,CFR-AN,CFR-MA and CFR-MMA respectively.

Correspondence
T. Jothy Stella,
E-mail: jothybeno@gmail.com, Ph. +9175986 53030

Swelling studies on crosslinked biopolyesters of poly castor oil fumarate

The entire cross linked biopolyesters of castor oil were subjected to swelling experiments. The density of the present polyesters 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 polymer materials were allowed to swell in the solvents having different solubility parameters viz. hexane, benzene, N, 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. Solubility parameters of the various solvents are given in Table 1.

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:

Swelling coefficient (Q) = (Weight of the solvent in swollen polymer / Weight of the swolled polymer) X (Density of polymer / Density of solvent).

The swelling coefficient of the polymer films 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).

Table I. Solubility Parameters of the Solvents

Solvent	**Solubility Parameter (Cal/cc) ½**
Hexane	7.3
Benzene	9.2
Dimethyl acetamide	10.8
Dimethyl formamide	12.1
Ethanol	12.7
n-Butyl alcohol	13.6
Ethylene glycol	14.6

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 (Mc), (reciprocal of crosslink density) of the cured material were determined using the modified Flory-Rehner equation as reported elsewhere [5].

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

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_o = Molar volume of the solvent

χ = Polymer – solvent interaction parameter

M_C = Molecular weight between two cross links

Results and Discussion

Crosslink density and voids play an important role in determining the properties of crosslinked polymers. Castor oils were used to prepare biostable polyester resins respectively using condensation polymerization. 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. In the present studies addition polymerization and crosslinking was adopted to generate void-free polyesters. The present crosslinked biopolyesters (CBP) 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 used, N, N-dimethyl formamide with solubility parameter, 12.1 imparts maximum swelling for all crosslinked biopolyesters (CBP). Therefore the solubility parameter of the present crosslinked biopolyesters is taken as 12.1. The variation of swelling co-efficient with solubility parameter is given in Figure 1.

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 poly castor oil fumarate is comparatively higher than the corresponding vinyl monomer based materials. (Table 2).

Figure I. The Variation of Swelling Coefficient With Solubility Parameter for the Crosslinked Biopolyesters Of Poly (Castor Oil Fumarate)

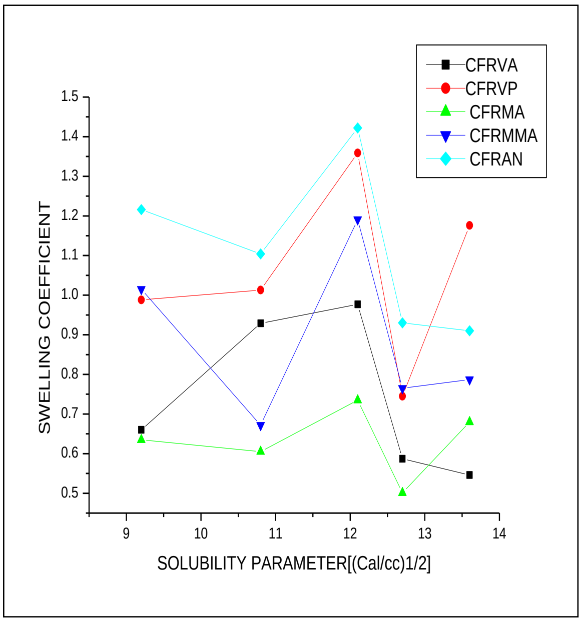

Table II. Crosslink Properties of Crosslinked Biopolyesters of Poly (Castor Oil Fumarate)

Crosslinked Material	Density (g/cc)	Crosslink Density (mol cm^{-3}) ($\times 10^3$)	Molecular Weight Between Crosslinks (mol^{-1})
CFR-VA	1.04582	2.478	403
CFR-VP	1.08098	2.886	346
CFR-MA	1.2769	1.145	873
CFR-MMA	1.2392	3.183	314
CFR-AN	1.2581	1.534	651

Conclusion

The present crosslinked biopolyesters of poly castor oil fumarate do not exhibit any tackiness, internal cracks, and voids. The crosslinked biopolyesters also have mar resistance. The swelling studies reveal that the crosslink density of the crosslinked biopolyesters based on methyl methacryllate of poly castor oil fumarate is comparatively higher than the corresponding vinyl monomer based materials.

References

1. H.Figen Balo, Lutfi Yucel, Aynur Ucar (2010), J.Porous Mater, 17, 553.
2. Vinay Sharma, P.P. Kundu, (2006), Prog.Polm.Sci, 31, 983-1008.
3. Patel, B.P., Patel,H.S. (2004) H.S. E-Journal of Chemistry, 1, 11-16.
4. T Jothy Stella; K Sathiyalekshmi; & G Allen Gnana Raj International Journal of Polymeric Material**,** 2012, 61, 466-482.
5. Vinoy Thomas, Jayabalan,M, J.Biomed. Mater. Res. 2001, 56, 144-157.