Original Article

ISSN: 2349 - 4891

International
Journal of Recent Research and Applied Studies
(Multidisciplinary Open Access Refereed e-Journal)

Swelling Studies of Cross Linked Biopolyesters of Poly Cardanol Fumarate Biopolyesters

T. Jothy Stella

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

Received 17th June 2015, Accepted 26th August 2015

Abstract

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

Keywords: Biodegradable, Biopolyesters of Cardanol, Swelling Properties.

Introduction

Cashew nut shell liquid (CSNL), 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 (CSNL). The unique feature that makes cardanol as an interesting monomer is the presence of a meta substituent of a C_{15} 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. [1-3].

The polymers obtained from plant oils are biopolymers; they are often biodegradable as well as non-toxic [4]**.** In the past decade, considerable attention has been paid to the synthesis of polymers based on cardanol, a naturally available meta-substituted phenol from cashew nut shell liquid (CNSL). The phenolic nature and unsaturated side chain in cardanol makes it suitable for polymerisation into resins.

Experimental methods

Preparation of crosslinked biopolyesters

The fumarate resin of cardanol (MCFR) was prepared using methylolated cardanol as reported elsewhere [5]. Methylolated cardanol was prepared using mol ratio 1:0.8 of cardanol to formaldehyde and oxalic acid as catalyst.

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

The fumarate resin of cardanol was prepared by heating 1 mole of methylolated cardanol with 2 moles of maleic anhydride using morpholine and sodium acetate catalyst. The polyesters based on methylolated cardanol fumarate resin, (MCFR) were prepared by reacting the respective fumarate resin with the monomers, vinyl acetate (VA), vinyl pyrrolidone(VP), acrylonitrile (AN), methyl acrylate (MA) and methyl methacrylate (MMA). MCFR 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 prepared with vinyl acetate,vinyl pyrrolidone,acrylonitrile, methyl acrylate and methyl methacrylate were coded as MCFR-VA, MCFR-VP, MCFR-AN, CFR-MA and MCFR-MMA respectively.

Swelling studies on cross linked biopolyesters of polycardanol fumarate

All the biopolyesters 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.

Table 1. 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

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).

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 [6].

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

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

V_γ = 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

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

Crosslinked Material	Density (g/cc)	Crosslink Density (mol cm^{-3}) (×10^3)	Molecular Weight Between Crosslinks (mol^{-1})
MCFR-VA	1.01232	2.502	400
MCFR-VP	1.19626	3.101	322
MCFR-MA	1.3147	1.162	860
MCFR-MMA	1.3241	5.096	196
MCFR-AN	1.2958	1.646	607

Results and Discussion

Crosslink density and voids play an important role in determining the properties of crosslinked polymers. Cardanol was used to prepare biostable phenolic and 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. Solvents with different solubility parameters, hexane (7.3), N, N-dimethyl acetamide (10.8), N,N-dimethyl formamide (12.1), ethyl alcohol (12.7) and n-butyl alcohol (13.6) were used in the present studies to determine the swelling coefficient. Among the solvents 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.

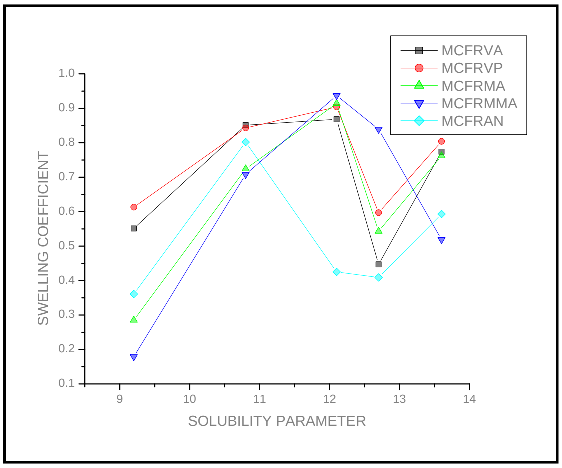

Figure I. The Variation of Swelling Coefficient with Solubility Parameter for The Crosslinked Biopolyesters of Poly (Cardanol Fumarate).

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 2).

Conclusion

The present crosslinked biopolyesters of poly cardanol 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 cardanol fumarate is comparatively higher than the corresponding vinyl monomer based materials.

References

1. P Das; A Ganesh Biomass and Bioenergy.2003, 25, 113.
2. JHP Tyman; D Wilczynski; MA Kashani J. Am. Oil. Chem. Soc. 1978, 55, 663.
3. JHP Tyman; V Tychopoulos; P Chain J. Chromatogr.1984, 303, 137.
4. Vinay Sharma, P.P.Kundu, (2006),Prog. Polm. Sci,31, 983-1008.
5. T Jothy Stella; K Sathiyalekshmi; & G Allen Gnana Raj International Journal of PolymericMaterial, 2012, 61, 466-482.
6. Vinoy Thomas, Jayabalan,M , J.Biomed. Mater. Res. 2001, 56, 144-157.

Please cite this article as: T. Jothy Stella. Swelling Studies of Cross Linked Biopolyesters of Poly Cardanol Fumarate Biopolyesters. *International Journal of Recent Research and Applied Studies*, 2015, 2, 8(14), 56 - 58.