

STUDIES ON ADDITION CURABLE CASTOR OIL BASED BIOPOLYESTERS FOR THE DEVELOPMENT OF NANOFILLERS

T. Jothy Stella¹

Abstract-Biodegradable crosslinkable bio polyester thermosets were prepared using addition curable fumarate esters of castor oil,(poly castor oil fumarate) and copolymerized using the crosslinking agents vinyl acetate (VA), methylacrylate (MA) and methyl methacrylate (MMA) respectively. These biopolyesters were characterized by cross link density, thermal stability, mechanical property and resistance towards various chemicals. These polymers can be used as the precursors for the development of polymer networks, mechanical property and biodegradability for the application as nano fillers in the polymer composites.

Keywords: Polymer composites, Biopolyesters, Vinyl acetate (VA), Methylacrylate (MA), Methyl methacrylate (MMA), Nano fillers

1. INTRODUCTION

The use of renewable resources as starting materials for the synthesis of polymers has been the area of research activity for more than 20 years [1-6]. In recent past years a remarkable research has been carried out to the synthesis of biodegradable polymers from renewable resources [7-8]. Natural oils are now considered as the most important class of raw materials for the preparation of polymeric materials and these biopolymers are often biodegradable as well as non-toxic [8].

In the last decade, synthesis and usage of biodegradable polymers have been very popular. Especially, biodegradable polyesters are useful materials for medical purposes. In this respect, ricinoleic acid-based copolymers were prepared and characterized [8-9]. In the present study biodegradable poly (castoroil fumarate) polyester has been synthesized from the naturally available, ricinoleic acid containing castor oil and is obtained from the seed of a plant *Ricinus communis* of the family *Eurphorbiaceae*. The plant is grown in all tropical and subtropical regions and India is the world's largest exporter of castor oil [10].

Castor oil is chemically a triglyceride of fatty acids that contains 87-90% of ricinoleic acid (cis-12-hydroxy octadec-9-enoic acid) with a hydroxyl number of 163mg KOH/g, and average functionality of about 2.7. Ricinoleic acid is an unsaturated omega-9-fatty acid having 18-carbon on its backbone with one hydroxyl group on the 12th carbon atom and a cis double bond between 9th and 10th carbon atoms. Castor oil is mostly used in the form of its modified derivatives such as dehydrated, hydrogenated, alkoxy-lated, sulphated and the halogenated derivatives [11-13].

The polar hydroxyl groups in castor oil account for its relatively high viscosity and specific gravity. It 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 [10]. The hydroxyl functionality of castor oil has been widely utilized to esterify it and synthesize CFR, castor oil fumarated resin [14]. In the present study, poly (castoroil fumarate) polyester Resin, CFR is made to react with the cross linking agent, vinyl monomers like vinyl acetate, methyl acryllate and methyl methacryllate in different molar proportions, and are cured to form rigid biodegradable crosslinked poly esters, and these polyesters are biodegradable and used for medical purposes, as surgical sutures. They are used as a precursor for the development of polymer networks. In bio-applications their biocompatibility and biodegradability play an important role as nano fillers in polymer composites [8].

2. MATERIALS

Castor oil (acid value-2.0mg KOH/g, hydroxyl value-162 KOH/g, iodine value-82 (wij method) Specific gravity (0.957-0.961) was obtained from Sri Ram industries, Madurai. Sodium acetate, benzoyl peroxide and dimethylaniline (Ranbaxy, NewDelhi), Maleicanhydride (CDH, Bombay), Morpholine (Paxmy chemicals, Chennai) vinyl acetate (Loba chemic Pvt. Ltd., Mumbai), methylacrylate (MA) and methyl methacrylate (MMA) (Sisco Research Lab Pvt. Ltd) were received and used as such.

3. METHODS

3.1 PREPARATION OF POLY (CASTOR OIL FUMARATE) POLYESTER RESIN

The Poly (Castoroil Fumarate) Polyester Resin was prepared by heating 3 moles of castor oil with 1 mole of maleic anhydride using morpholine as the catalyst. In a typical reaction 45.8 g of castor oil, 14.7g of maleic anhydride, 1g of sodium acetate along with few drops of morpholine were placed in a three necked flask with a stirrer. The reaction was carried out

¹ Assistant Professor, Chemistry Department, Dr. Sivanthi Aditanar College of Engineering, Tiruchendur,

at $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 60 minutes and then at $180^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 10 minutes under vacuum condition using rota mantle to yield yellowish transparent liquid resin, CFR poly (castor oil fumarate) Polyester Resin.

3.2 SYNTHESIS OF POLY (CASTOR OIL FUMARATE) POLYESTER RESIN BLEND WITH VINYL MONOMERS

Three biodegradable and crosslinked biopolyesters were prepared by mixing, Poly (Castor oil Fumarate) Polyester resin CFR with the cross linking agent, vinyl acetate (VA), methyl acrylate (MA) and Methyl methacrylate (MMA) in presence of benzoyl peroxide (initiator) and dimethyl aniline (accelerator) and then casted on a clean silicone oil spreaded glass plate, cured in hot air oven at 80°C for 6 hours .

3.3 CHARACTERIZATION OF POLY (CASTOR OIL FUMARATE) POLYESTER RESIN BLENDS

Crosslink density plays an important role in determining the properties of crosslinked polymers. The crosslinked polymers 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), n-butyl alcohol (13.6), and ethylene glycol (14.6) were used in the present studies to determine the swelling coefficient. Among the solvents N, N-dimethyl formamide imparts maximum swelling.

Tensile strength of the resin blends were determined using dumbbell shaped specimens as per ASTM Standard D412, using an Inston universal testing machine. The gauge length was fixed as 50 mm and the area of cross section was 10mm. The Polyester resin blends were subjected to differential thermal analysis (DTA)/ Thermogravimetric analysis (TGA) studies at a rate of 10K/min in Nitrogen atmosphere using SDT Q 600 V8.3. Acid, alkali and solvent resistance were estimated according to the ASTM Standard D3137 C267. Polyester resin blends (3x1x0.1cm) were immersed in the medium (100 ml) for a total duration of 60 days under ambient conditions. The medium was changed and fresh medium was added at an interval of one week. The loss of weight was determined using an electronic weighing balance.

4. RESULTS AND DISCUSSION

The crosslinked polyester resins are synthesized from unsaturated polyester resin and crosslinker by free radical mechanism. The hydroxyl functional group on the twelfth carbon causes castor oil to be polar. Biodegradable unsaturated poly (castor oil fumarate) polyester was prepared using castor oil as per reaction scheme shown in Figure 1. The reaction between a hydroxide compound and anhydride proceeds in two steps, in the first step, esterification of the anhydride occurs to form a free acid group, which is esterified in the second step. Since the castor oil contains three hydroxyl groups, the final oligomeric resin contains fumarate ester linkages in all the three ricinoleic branches.

The molecular weights between crosslinks and crosslink density of the present materials confirm the crosslinked character. The crosslinking of unsaturated polyester involves the reaction of the unsaturated sites in the polymer chain with a monomer which may be of vinyl type such as acrylonitrile etc. Unsaturated polyester resin prepared from maleic anhydride and a hydroxyl compound, propylene glycol may be co polymerized with a vinyl monomer [15].

Thermal properties of poly (castor oil fumarate) polyester Resin blends studied are influenced mainly by molecular weight between crosslinks and the degree to which segments form stiff sequence and elastically active branch points. The segments constituting stiff sequences are vinyl monomers substituted fumarate groups. DTA curves show multi stage endothermic peaks characterizing thermal decomposition. The DTA curves of the polyesters indicate more than three endotherms above 200°C chain scission and degradation. This is well exhibited by the weight loss starting from this temperature in the TGA curves. The TGA curves for decomposition of Poly (Castor oil Fumarate) Polyester Resin blends with vinyl monomers shows that they are invariably stable under high temperature conditions. The decomposition is a complex process to follow. All these polyesters have higher starting temperature (T_{start}) for the degradation and weight loss and get decomposed in more than two stages. 10% weight loss occurs only at reasonably high temperatures. The first stage of degradation and weight loss is due to the initial degradation of vinyl monomer present in fumarate ester linkage chain at low temperature which is due to flexibility of the vinyl groups even in the cross linked state of polyesters . The thermo gravimetric data of the samples are given in Table 3, shows that they possess higher thermal stability. The reaction scheme for the synthesis of poly (castor oil fumarate) is shown in Figure 1.

Poly (castor oil fumarate) polyester resin

Figure 1 Scheme for the synthesis of poly(castor oil fumarate)polyester resin

The reaction scheme for the synthesis of poly (castor oil fumarate) biopolyester is shown in Figure 2.

Poly (castor oil fumarate) biopolyester resin

+

Vinyl monomer	X	R
Vinyl acetate	OCOCH ₃	H
Methyl acrylate	COOCH ₃	H
Methylmethacrylate	COOCH ₃	CH ₃

Crosslinking of poly (castor oil fumarate) polyester resin with vinyl monomers

Figure2: Scheme for the synthesis of poly (castor oil fumarate)

Table 1: The DTA Data Of Crosslinked Biopolyesters Poly (Castor Oil Fumarate)

Material	Endothermic response ($^{\circ}\text{C}$)					Exothermic response ($^{\circ}\text{C}$)	
	Softening	1st endo	2nd endo	3rd endo	4th endo	1 st exo	2nd exo
CFR-VA	75.50	234.40	426.26	507.96	641.73	473.90	582.11
CFR-MA	88.17	350.70	-	495.25	543.31	199.0,439.11	-
CFR-MMA	87.44	345.83	410	512.84 540.64	644.68	163.46 453.66	569.55

Table 2: TGA Data of Crosslinked Biopolyesters of Poly (Castor Oil Fumarate)

Polyesters	Temperature ($^{\circ}\text{C}$) at the each stage of degradation (Weight remaining %)		
	T _{Start}	I _{Stage}	II _{Stage & Final}
CFR-VP	222.27 (95.44%)	488.34 (12.92%)	637.08 (6.27%)
CFR-MA	204.72 (96.23%)	598.28 (10.89%)	710.99 (6.246%)
CFR-MMA	222.27 (95.38%)	462.47 (12.74%)	507.74 (7.56%)

Table 3: Tensile Properties of Crosslinked Biopolyesters of Poly (Castor Oil Fumarate)

Polyesters	Tensile strength (MPa)	Elongation (%)	Modulus (MPa)
CFR-VA	0.375±0.04	30.6±3	1.23±0.05
CFR-MA	0.1066±0.01	53.06±3	2.00±0.01
CFR-MMA	0.652±0.01	61.73±3	1.46±0.02

The present crosslinked biopolyesters do not exhibit any tackiness, internal cracks, and voids. The crosslinked biopolyesters also have mar resistance. The thermal studies of the crosslinked biopolyesters reveal softening, decomposition and crosslinking. The data of mechanical properties of all the cured samples are presented in Table 3. The higher tensile strength and modulus observed in CFRMMA. The lower tensile strength is observed in CFRMA. The high strength and high modulus reflect the strong and hard character of these poly esters. Among the crosslinked biopolyesters, methyl acrylate based biopolyesters have lower tensile strength due to lower crosslink density. The percentage weight loss of poly(castor oil fumarate) polyester Resin blends were determined in 1N HCl, 1N NaOH, Acetone, Saline solution, etc and the results are furnished in the Table 4-6. All the poly (castor oil fumarate) polyester Resin blends are stable in 1N HCl, H₂O₂, H₂O, Saline solution and unstable in Acetone, Toluene, CCl₄, DMA, DMF.

Polymer degradation in chemically active media is mediated by various processes such as adsorption of medium on the polymer surface, diffusion and absorption of the medium into the polymer bulk, chemical reaction with the chemically unstable bonds in the polymer, desorption and transport of the degradation products out of the polymer matrix and polymer surface. Sathiyalekshmi *et al.* have studied the performance of rigid polyurethanes based on hydroxyl alkylated cardanol – formaldehyde resin under aging conditions [16-18]. The stability of the present biopolyesters is influenced by crosslink density, hydrolytically labile ester groups.

Table 4: Stability of Crosslinked Biopolyesters in Hydrolytic Conditions

Crosslinked biopolyesters	Weight loss (%)			
	Water	Alcohol	1 N NaCl	Boiling water
CFR-VA	12.50	9.62	9.52	16.67
CFR-MA	12.9	10.04	14.28	19.67
CFR-MMA	4.28	3.46	8.88	5.26

Table 5: Stability of the Crosslinked Biopolyesters in Hostile Chemicals

Crosslinked biopolyesters	Weight loss (%)			
	1N HCl	1N NaOH	Alc.KOH	H ₂ O ₂
CFR-VA	7.14	6.67	5.63	3.70
CFR-MA	22.7	8.45	34.01	23.07
CFR-MMA	15.38	6.16	14.7	4.76

Table 6: Stability of the Crosslinked Biopolyesters in Organic Solvents

Crosslinked biopolyesters	Weight loss (%)		
	Acetone	Toluene	CCl ₄

CFR-VA	61.54	55.93	18.75
CFR-MA	45.45	30.76	32.39
CFR-MMA	15.38	12.16	15.84

5. CONCLUSION

The poly (castor oil fumarate) polyester resin blend with vinyl monomers is definitely a biodegradable polyester used in biomedical applications and setting and crosslinking of the polymer depends on the monomer. The presence of fatty acid chain in the polymer structure improves some physical properties of polymer in terms of flexibility, and resistance of water and chemicals. These polyesters can be used for the development of Interpenetrating polymer networks with mechanical property and biodegradability for the application as nanofillers in the polymer composites.

6. REFERENCES

- [1] Gandini. A and M. N. Belgacem, Prog.Polym.Sci25,1203-1379, (1997).
- [2] Fengkui Li, Richard C. Larock, J. Polymers and the Environment, Vol 10, (2002)
- [3] Seniha Guner. F, Yusuf Yagci, A. Tuncer Erciyas, Prog.Polym.Sci.31, 633 (2006)
- [4] Kendaganna Swamy. K, Siddaramaiah, J. Materials Science38, 451 (2003)
- [5] Vinay Sharma, P. P. Kundu, Prog.Polym.Sci.31, 983 (2006)
- [6] Ruixiang Zhao, Peter Torley, Peter, J. Mater Sci 43, 3058 (2008)
- [7] Pim-pahn Kiatsimkul, William R. Sutterlin, J. Molecular Catalysis B:Enzymatic 41, 55 (2006).
- [8] Slivniak R, Domb A J, Macromolecules, 38:5545-5553, (2005).
- [9] Miha M. K, M. Jayabalan, J. Mater Sci, Mater Med10 (2008).
- [10] Ogunniyi D. S, Bioresource Technology, 97, 1086-1091, (2006).
- [11] Patel. P, H. S. Patel, E-Journal of Chemistry Vol. 1, 11-16, (2004).
- [12] Lower E.S, Hydrogenated Castor oil, 1993, 70, 87. ChemAbstr, 119, (1993).
- [13] Schwitzer M. K, Perspectives, prospects of world castor oil Industry, Oleagineux, 38, 253, (1983).
- [14] M.Jayabalan, K. T. Shalumon, J. Mater Sci, Mater Med10,20.1379-1387, (2009).
- [15] Muhammad Ihsan Ul Haq, Russian J.Applied Chemistry, 80, 1256, (2007).
- [16] T Jothy Stella; K Sathiyalekshmi; & G Allen Gnana Raj, International Journal of Polymeric Material, 61, 466-482, (2012).
- [17] Sathiyalekshmi,K.;Gopalakrishnan,S.;*Plastics,Rubber&Composites*, 29(2), 63, (2000)
- [18] Sathiyalekshmi,K.; Gopalakrishnan, S. *J. Adv. polymer Tech.*, 23 (2), 91, (2004).