Synthesis and Characterization of Luffa Fibre Reinforced Polyurethane Composites

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Abstract: In recent years, there is increasing environmental concerns, greater attention are being paid towards the use of plant fibres taking the advantages of their abundance and availability as renewable resource and their biodegradability in the environment and economical for their cost effectiveness. The use of plant fibres as reinforcements in composite materials requires extra care regarding fibre/matrix adhesion particularly when the matrix is hydrophobic in nature. Cashewnut shell is the byproduct obtained from cashew processing industries and it is a soft honey comb structure containing a dark brown liquid known as cashewnut shell liquid (CNSL). Polyurethanes are one of the most versatile materials and are widely used in both in both industry and everyday life. The synthesis of vegetable oil based polymeric materials with excellent physical and chemical properties has drawn great interest in recent times.
Key words: Plant fibres, polyurethanes, composites, cashewnutshell liquid.

I. INTRODUCTION

In the present senerio, there has been a rapid attention in research and development in the natural fibre composite field due to its better formability, abundant, renewable, cost - effective and eco - friendly features. Natural fibre is a type of renewable sources and a new generation of reinforcements and supplements for polymer based materials [1]. Various fields where natural fibres can employed are, structural composites, automobile, geotextiles, packaging, molded products, sorbents, filters and in combination with other materials [2]. The exploitation of natural fibre composites in various applications has opened up new avenues for both academicians as well as industries to manufacture a sustainable module for future application of natural fibre composites [3]. Luffa fibre is a light weight natural material that has prospective to be as an alternative sustainable material for various engineering applications such as acoustic and vibration isolation, impact energy adsorption and packaging [4]. Alkaline treatment is the most commonly used chemical treatment of natural fibre composites in the preparation of thermoset and thermoplastic reinforced natural fibre composite material. In the alkaline treatment process the net work structure of hydrogen bonding is altered due to reaction of sodium hydroxide (NaOH). This process is increasing the surface roughness of the natural fibres. The alkalization treatment of natural fibres improves adhesion and creates better mechanical properties of natural fibre reinforced composite materials [5]. Polyurethanes are special group of polymeric materials which essentially are different from most of the plastic types. They can be incorporated into different items such as paints, liquid coatings, elastomers, insulators, elastic fibres, foams and integral skins [6]. Currently polyurethanes are one of the most common, versatile and researched materials in the world [7]. These materials combine the durability and toughness of metals with the elasticity of rubber, making them to suitably replace metal, plastics and rubber in several engineered products [8]. They have been widely applied in biomedical applications, building and construction, automotive, textiles and in several other industries due to their superior properties in terms of hardness, elongation, strength and modulus [9-11].

Fig. 1 Luffa Fibre

II. EXPERIMENTAL

A. Materials

Cardanol was procured from M/S Sathya Cashew Pvt. Ltd, Chennai. Furfural, epichlorohydrin and phthalic acid were received from Sisco Research Laboratory, Mumbai. Methanol was received from Nice Chemicals Pvt. Ltd, Cochin. Catalyst dibutyltin dilaurate and curing agent 4,4'-methylene (biscyclohexyl) isocynate was obtained from Sigma Aldrich, USA. Luffa fibres are obtained from local sources.

B. Methods

1) *Synthesis of Polyols:* Cardanol - furfural resin was synthesized using cardanol and furfural with phthalic acid as catalyst. Cardanol was taken in a three neck round bottom flask equipped with a Liebig condenser, mechanical stirrer and thermometer. Furfural and 1% phthalic acid catalyst in methanol was added to the cardanol through a dropping funnel. The reaction was carried out at 120^0 C for 5 hours. The resin was purified by dissolving in ether and by precipitating it with distilled water. Major fractions were collected and using a rotator evaporator under vacuum. The cardanol - furfural resin was epoxidized using epichlorohydrin and the resulting epoxidized resin was hydrolyzed with dilute hydrochloric acid. The synthesized polyols (SP_1 and SP_2) thus formed was purified by washing with distilled water several times and then dried over vacuum at 80^0 C.

2) *Synthesis of Polyurethanes and Polyurethane Composites:* Polyurethane sheets were prepared by synthesized polyol mixed with the curing agent 4,4'-methylene (biscylohexyl) isocyanate and the catalyst dibutyltin dilaurate . The reaction mixture was stirred manually in a small plastic cup at room temperature and poured into a flat glass mould. The polyurethane sheets (PPU_1 and PPU_2) thus formed were allowed to stand for 24 hours, and cured in a vacuum oven at 80^0C for 48 hours. Polyurethane composites ($PPULC_1$ and $PPULC_2$) were prepared by incorporating alkali treated luffa fibres into polyurethanes.

III. RESULTS AND DISCUSSION

A. Physico - Chemical Properties of Synthesized Polyols

The decrease in iodine value of the polyols may be due to the steric hindrance of adjacent bulky groups to the addition of iodine monochloride. The specific gravity and viscosity of the polyols are found to be greater than that of cardanol - furfural resins. Higher specific gravity of the polyols is due to intra and inter molecular hydrogen bonding through dihydroxy propyl units. The physico - chemical properties of synthesized polyols are presented in Table 1.

Table I
Physico - Chemical Properties of Synthesized Polyols

Properties	SP_1	SP_2
Colour	Dark Brown	Dark Brown
Odour	Phenolic	Phenolic
Specific Gravity g/cc at 30^0C	0.9632	0.9681
Intrinsic Viscosity	0.0341	0.389
Iodine Value (Wij's Method)	211	202
Hydroxyl Value	228	266
Molecular Weight	1700	2300
Number of Hydroxyl Groups	7	10

B. Thermal Properties

1) *DTA Thermogram:* TG/DTA thermograms of cured polyurethanes and polyurethane composites are presented in Figure 1. The DTA curves of polyurethanes do not show any endothermic peak. But three exotherms are invariably seen in all the cured polyurethanes. The exotherm is due to the cleavage of meta substituted long alkyl side chain of phenyl ring and also due to the cleavage of allophanate linkages. The third exotherm was observed at 530^0C for polyurethanes and 540^0C for polyurethane

composites. The polyurethane composites are thermally degraded successively after the cleavage of meta substituted alkyl side chain due to higher crosslink density.

2) TGA Thermogram: The TGA curves of polyurethanes showed that the decomposition in three distinct stages. The initial weight loss is attributed to the moisture retained in the sample. The first break of the TG curves around 230^0C is due to decross linking or post curing process. The second break around at 380 - 400^0C indicates the decomposition of polyurethane moiety of the compound. The third decomposition temperature is 520 - 540^0C is due to the disintegration of the resin moiety into simpler molecules.
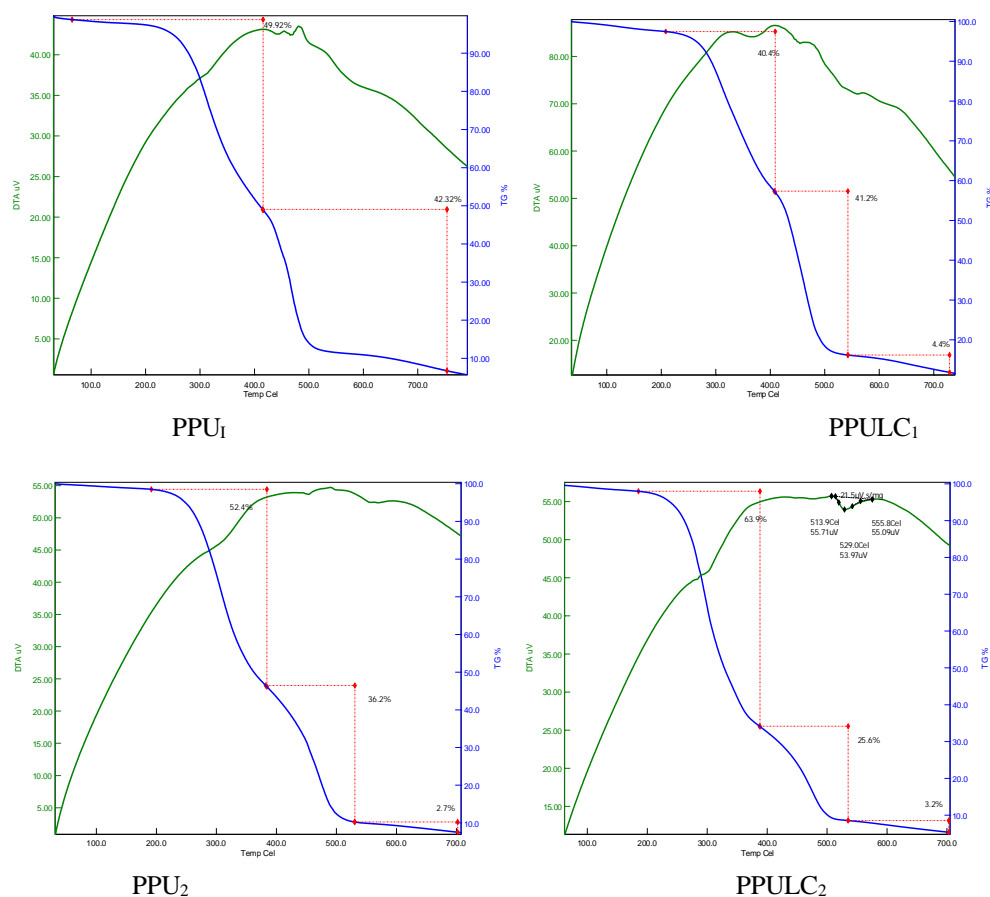

PPU$_I$

PPULC$_1$

PPU$_2$

PPULC$_2$

Fig. 1 TG/DTA curves of polyurethanes and polyurethane composites

C. Coats - Redfern Method

Coats - Redfern equation have been used to calculate the kinetic parameters such as order of decomposition reaction (n), activation energy (E$_a$), pre - exponential factor (Z) and rate decomposition constant (k). The activation energy values of decomposition of cardanol based polyurethanes and polyurethane composites have been determined by Coats - Redfern equation. For first order reaction process, Coats and Redfern provided an approximation. This is an integral form of the rate equation. The simplified form of the equation is,

$$\frac{\log g(\alpha)}{T^2} = \log \frac{AR}{\phi E_a}(1 - 2RT/E_a) - \frac{E_a}{2.303RT}$$

Where,

    T = Temperature

    A = Pre - exponential term

    R = Gas constant

E = Energy of activation

ϕ = Heating rate

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f}$$
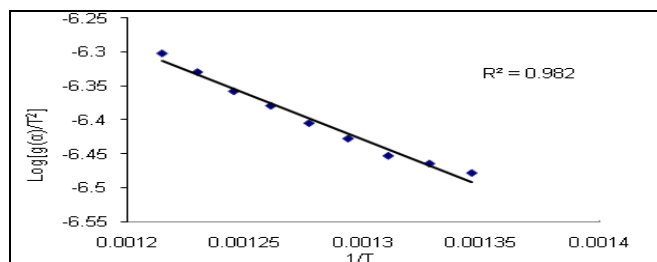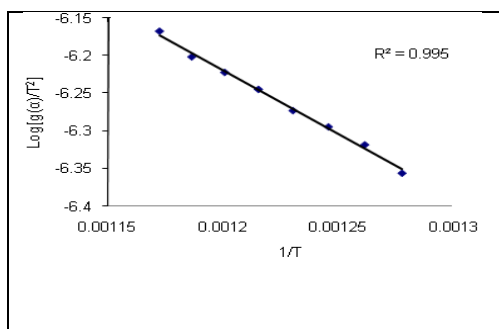
Where,

W_0 = Initial weight of the sample

W_t = Residual weight of the sample at the temperature

W_f = Final weight of the sample

Microsoft Excel spread sheets are used for data entry such as temperature range, initial weight of the sample and the residual weight of the sample. Energy of activation of polyurethanes and polyurethane composites with maximum R^2 values are tabulated in Table 2. The computerized plots of log $[g(\alpha)/T^2]$ versus $1/T$ based on Coats - Redfern equation are presented in Fig 2.

Table II
Energy of Activation of Polyurethanes and Polyurethane Composites with Maximum R^2 Values

Samples	Stage I		Function	Stage II		Function
	R^2	E_a Kcal/mol		R^2	E_a Kcal/mol	
PPU_1	0.984	3.172	R_2	0.992	1.098	R_3
PPU_2	0.967	8.781	D_3	0.984	1.305	MPL^0
$PPULC_1$	0.979	7.450	A_4	0.985	3.622	$MPL^{2/3}$
$PPULC_2$	0.988	6.236	A_4	0.985	3.098	R^2

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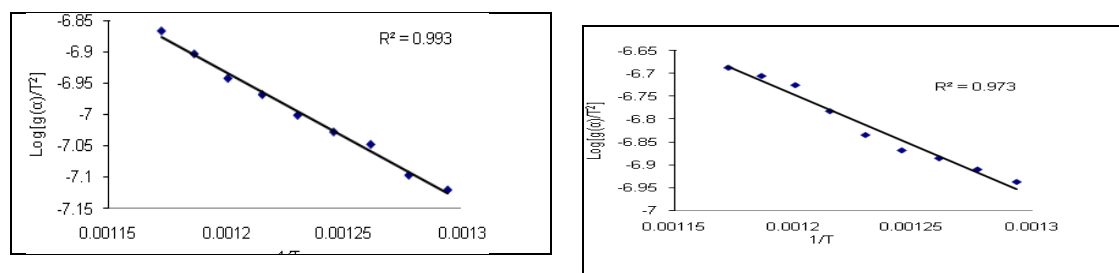*Volume 6 Issue IV, April 2018- Available at www.ijraset.com*

Fig. 2   Coats - Redfern plots of PPU_1, $PPULC_1$, PPU_2, $PPULC_2$
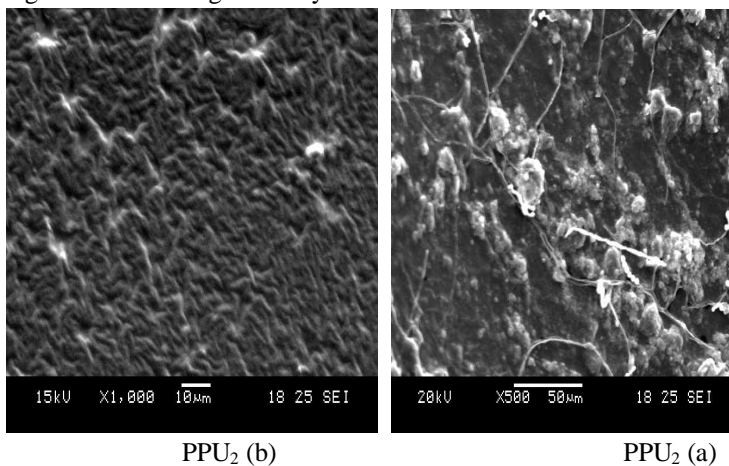
D. Mechanical Properties

 The tensile properties in terms of Tensile strength, hardness, Young's modulus and percentage of elongation are tabulated in Table 3. The data shows a gradual increase in all mechanical properties from PPU_1 to $PPULC_2$. This is due to the higher crosslink density of polyurethanes and polyurethane composites. Polyurethane composites possess higher hardness than polyurethanes. This is due to the fact that as the chain length is decreased the crosslink density also increases which results in more rigid network with better mechanical properties.

Table III
Mechanical Properties of Polyurethanes and Polyurethane Composites

Samples	Shore A Hardness	Tensile Strength	Elongation at Break (%)	Young's Modulus
PPU_1	22	4.2	195	2.1
$PPULC_1$	36	8.6	182	4.7
PPU_2	57	8.3	186	4.4
$PPULC_2$	61	13.3	161	8.2

E. Test for Biodegradability

1) Soil Burial Test: The environmental resistance of the synthesized polyurethanes and polyurethane composites was carried out using soil burial test. The samples were buried in the soil at a depth of 30 cm from the ground for 60 days. The test samples were periodically removed from the soil to access the changes in weight loss, and surface damage if any. The removed samples were washed clearly and dried in vacuum oven. The extent of degradation was examined by weight loss and surface observation. Scanning electron microscope (SEM) was used to access the degradation. Very small variations in the chemical structures of polymer could lead to large changes in their biodegradability.

PPU$_2$ (b)   PPU$_2$ (a)
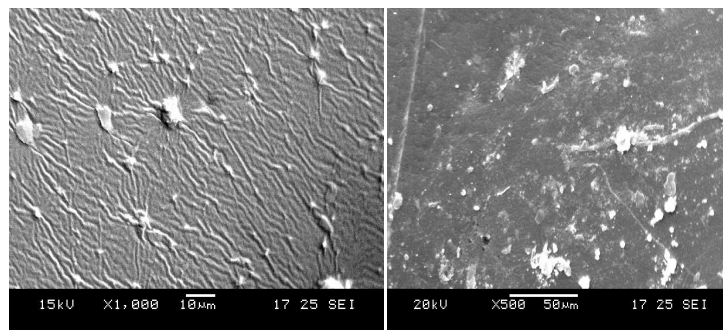
PPULC$_2$ (b)   PPULC$_2$ (a)

IV. CONCLUSION

The polyurethane composites showed better thermal and mechanical properties than polyurethanes. From the Coats - Redfern method it is concluded that the Mampel equation gives reasonable energy of activation and maximum R^2 values for both polyurethane and polyurethane composites. From the soil burial test it can be concluded that the polyurethanes and polyurethane composites are biodegradable in nature.

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