GENERATIONAL ECO-FRIENDLY AND REFORMATIVE POLYURETHANE COMPOSITES

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ABSTRACT

Polymers are anexpansive class of materials which are made from units of smaller molecules called monomers. Fossil fuels used in developing plastics account for about 7% of worldwide oil and gas. The resources will be exhausted within the next few hundred years and within the next few years the peak of global oil production will occur. Polymers from biomass can not only solve the problem of petrochemical products but they also help in waste disposal. Presently, the discarding of polymers derived from petrochemical sources and this is a major concern particularly in popular countries. Therefore, there is a substantial demand for the development of eco-friendly and biodegradable polymers. In fact,many of the polymers taken from renewable resources can also be biodegradable under the suitablecircumstances. Cardanol and its derivatives have immeasurableuses in polymer based industries such as friction linings, varnishes, rubber compounding resins, paints, surfactants, laminating resins, polyurethane based polymers and wood preservatives.

Key words: Biodegradable, Polyurethane, Cardanol, Composites, Natural fibres

1. INTRODUCTION

The escalation in environmental realization and communal interest, the new environmental regulations and ingestion of petroleum led to thinking of the use of environment friendly materials[1]. These fibers contain lignocellulose in nature. They are light weight, easily accessible, sturdy, renewable, inexpensive, biodegradable and inoffensive. Natural fiber is deliberated one of the eco-friendly materials which have good properties compared to artificialfiber[2]. Natural fibers are materials which are in the form of continuous filaments. The examples of natural fibers namely kenaf, abaca, jute, hemp, cotton, flax, coir, luffaetc are widely used.

Natural fibers have proven to be used as best strengthening materials because of their decomposable and renewable characteristics in thermoset and thermoplastic matrices[3].The use of polymer composites from renewable resources has advantages over artificial sources particularly as a solution to the ecological problem created by plastic waste. Green composites are today extensively researched because of the need for inventionsin the enlargement of materials, complete biological degradability and decrease in the volume of carbon dioxide released into atmosphere. The use of these bio-composites is anticipated to mend manufacturing speed and recycling which enhances environmental compatibility[4].

Recently some microorganisms have been reported to produce humiliating enzymes[5]. Due to hydrophobicity and greater fatty acid skeleton of polymers microorganisms are incapable to transference the polymers directly through their outer cell membranes.To make it possible they break down or degrade the polymers to simpler products to simplify their transport into the cell. Biodegradation is a chemical degradation of materials incited by the action of microorganisms such as bacteria, fungi and algae[6-9].The most common definition of a biodegradable polymer is a degradable polymer where in the primary degradation mechanism is through the action of metabolism by microorganism[10].

The degradation of a polymer is affected by many factors like temperature, moisture, oxygen, sunlight, stress, living organisms and contaminants[11].Biological degradability of polymers by microorganism's decreases with increase in the molecular weight of the polymer. There is a decline in polymer solubility which makes it disapproving for microbial cell membrane and is broken down by cellular enzymes. Reiterating units of polymers like dimers and oligomers are easily degraded and mineralised[12].

2. EXPERIMENTAL

2.1 Synthesis of cardanol-furfural resin from cardanol

Cardanol-furfural resin (CFR) was synthesized by the condensation of cardanol and furfuralusing phthalic acid as catalyst. Cardanol was engaged in a three neck round bottom flask equipped with a Liebig condenser, a mechanical stirrer and a thermometer.Furfural and phthalic acid catalyst in methanol was further to the cardanol through a dropping funnel.The reaction was carried out at $120^0 \pm 5^0$C for 5 hours.The resins were cleansed by dissolving in ether and by precipitating it with distilled water. Foremostportions were collected and dehydrated using a rotary evaporator under vacuum and analyzed.

2.2 Synthesis of polyols

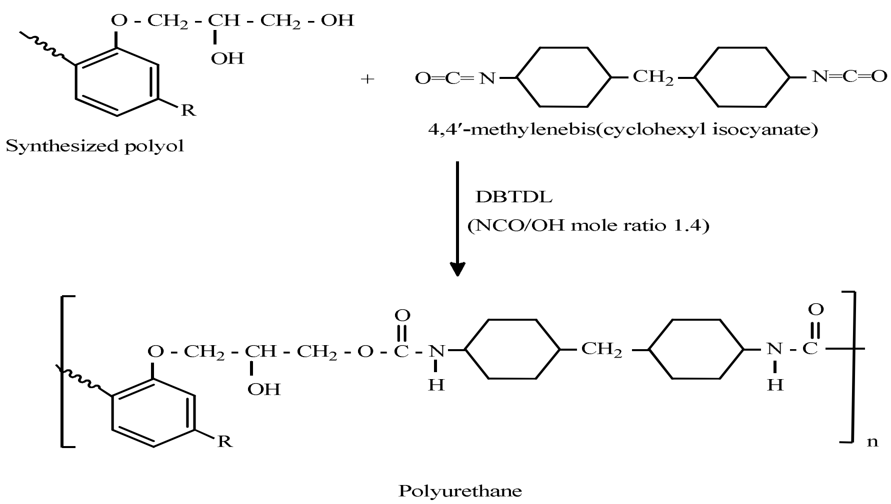
The epoxidized resins were taken in a three neck round bottom flask equipped with a Liebig condenser, a mechanical stirrer and a thermometer.Ethanol was added through a dropping funnel. The reaction was conceded out at 60 ± 5^0C for about 30 minutes.The synthesizedpolyol(CFP) thus formed were refined by eroded with distilled water several times and then dried over vacuum at 80^0C. Thus the formed synthesized polyol wasevaluated.

2.3 Synthesis of polyurethane composites

2.3.1 Pre-treatment of fibers with alkali

The fibers were washed initially and dried at room temperature. Then it was preserved in hot air oven at 50^0C to remove the excess moisture.The fibers are treated in 10% aqueous solution of NaOHfollowed by washing with distilled water and dried at 60^0C in hot air oven for 24 hours.The dried fibers are cut into 5 mm length prior to use.

Polyurethanes were prepared by using cardanol – furfural resin and synthesized polyol with the curing agent4, 4'-methylenebis(cyclohexyl) isocyanate and the catalyst dibutyltindilaurate. Polyurethane composites (CFRPUC, CFRPUS, CFRPUL, CFPPU, CFPPUSand CFPPUL) were synthesized by incorporation with 10% of fibersvia coir, sisal and luffa into the polyurethane sheets.



Scheme: 1 Formation of polyurethane

3. RESULTS AND DISCUSSION

Polyurethanes are progressively being used in anextensive range of applications where long term service in hostile environment is required.The steadiness of polymer deals with their degradation reactions and their control is a majorpre-occupation of practitioners and diverse features of modern polymer technology. Polyurethanes have enlarged tensile strength and the melting points making them more long-lasting.Their resistance to degradation by water, oils and solvents make them outstanding for the replacement of plastics.The present study reports the degradation and stability performance of the newly blended polyurethane composites.

3.1 Microbial activity studies on polyurethane composites

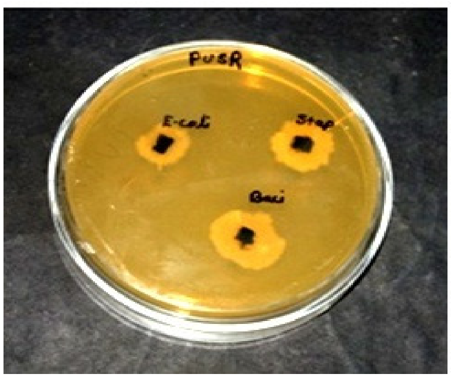
To examine the biodegradability of polymer, the polymer is exposed to microbial activity. Three microbial strains such as Escherichia coli, Staphylococcus aureus and Bacillus subtilis are selected and microbial activity is studied. The bacterial studies on samples are carried out for thirty days. The zone of degradation showed that the samples are degraded by the microorganisms. The zone of degradation of polyurethanes and polyurethane composites are presented in Table I. The data showed the gradual increase of the zone of degradation from fifteenth day to thirtieth day. This shows that the degradation of polymer samples is slowly degraded by the microorganisms. Among the three microorganisms, Bacillus subtilis exhibits higher zone of degradation when compared to others.

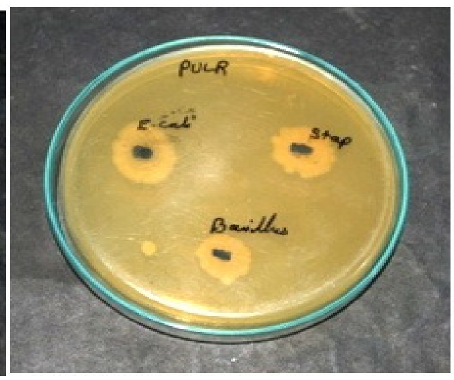
In the present study, samples CFPPUL (luffafiber reinforced polyurethane composites) higher zone of degradation. The degradation of luffafiber reinforced composites is more when compared to other samples. From this it can be concluded that, the polyurethane composites are biodegradable in nature.

Table 1 Growing Zone rate (mm) for polyurethane composites

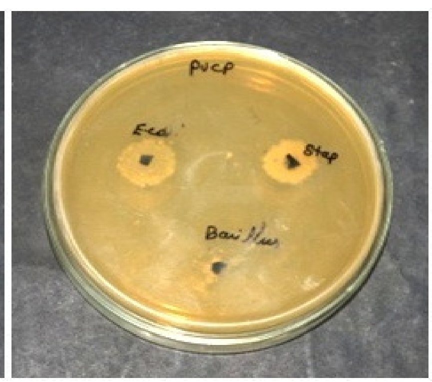
Samples	Micro organisms					
	Escherichia coli		Staphylococcus aureus		Basillussubtilis	
	15th day	30 thday	15th day	30th day	15th day	30th day
CFRPU	16	19	16	22	20	25
CFRPUC	12	15	15	19	13	16
CFRPUS	17	20	20	26	16	22
CFRPUL	21	25	19	24	18	26
CFPPU	16	20	16	19	15	21
CFPPUC	12	15	17	20	21	27
CFPPUS	16	18	16	21	14	23
CFPPUL	19	22	18	20	16	20

CFRPU **CFRPUC**

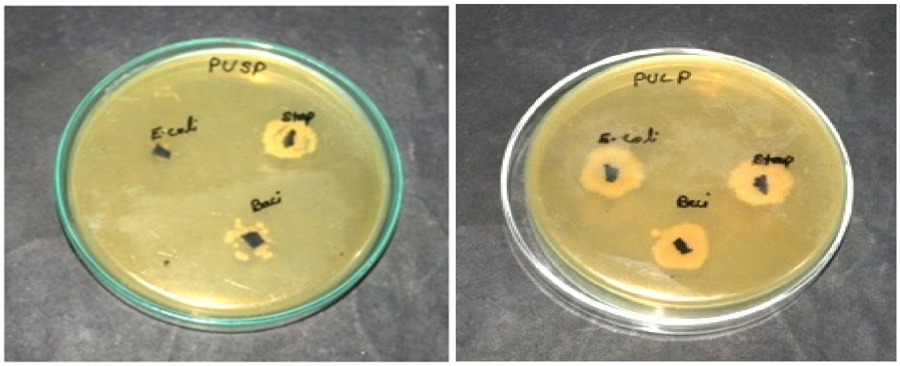




CFRPUS **CFRPUL**



CFPPU **CFPPUC**



CFPPUS CFPPUL

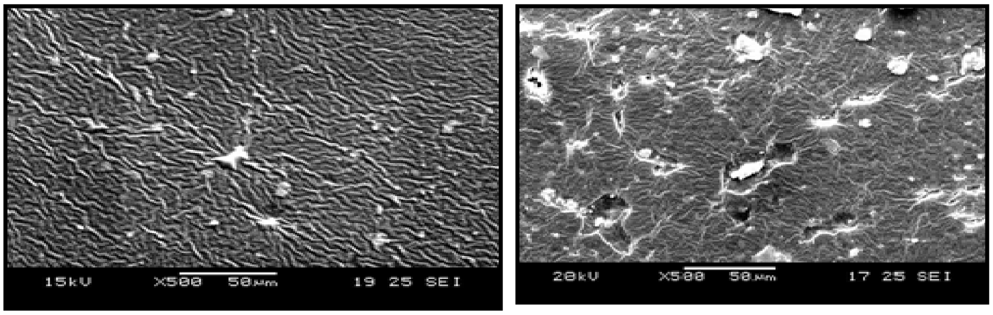
Fig. 1 Microbial activity images of polyurethane composites

3.2 Soil burial test

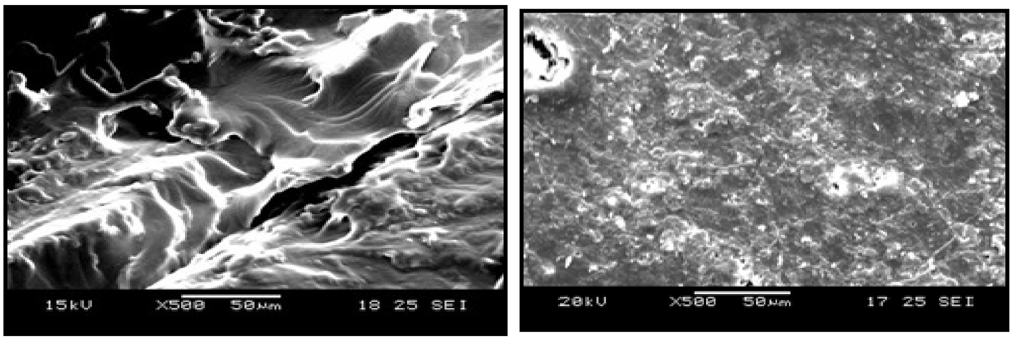
To find out the ecological resistance, polyurethane composites are characterized by soil burial test.There is a small weight loss observed in polyurethane composites after the completion of soil burial test. Polyurethane composites displayextreme weight loss when compared to neat polyurethane sheet.This may be due to the presence of natural fibers.Hence these polyurethane composites are biodegradable.The samples were measured by SEM images.

Table 2 Weight loss percentage of polyurethane compositesunder soil burial test

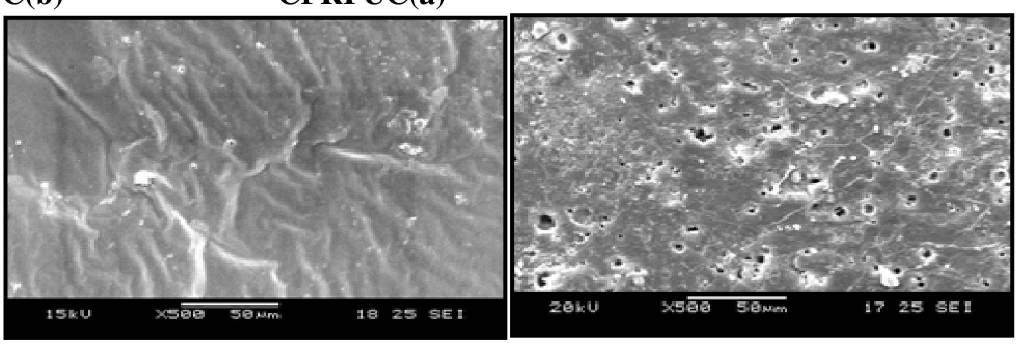
Samples	Weight loss (%)
$CFRPU_4$	0.007
$CFRPUC_4$	0.015
$CFRPUS_4$	0.016
$CFRPUL_4$	0.019
$CFPPU_4$	0.009
$CFPPUC_4$	0.016
$CFPPUS_4$	0.014
$CFPPUL_4$	0.019



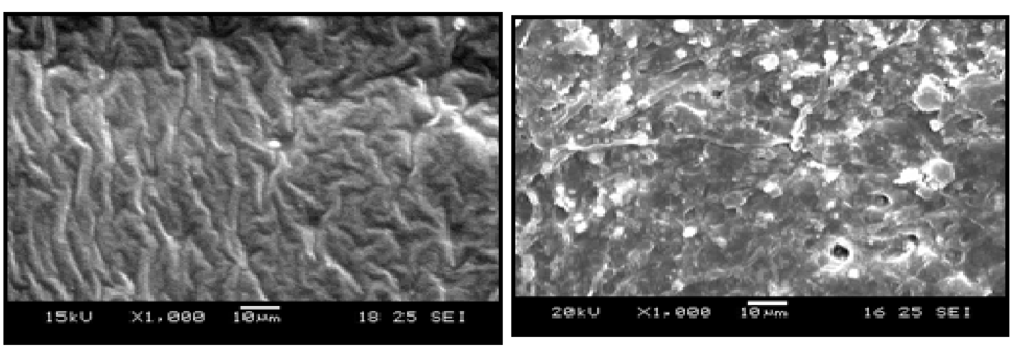
CFRPU(b) CFRPU(a)



CFRPUC(b) CFRPUC(a)



CFRPUS(b) CFRPUS(a)



CFRPUL(b) CFRPUL(a)

Fig. 2SEM images of polyurethane composites (before (b) and after (a) soil burial test)

3.3 Hydrolytic stability test

The weight loss of polyurethanes and polyurethane composites in the media such as water, ethanol and sodium chloride (salt solution) was estimated by immersing the samples for the total period of 60 days under ambient conditions.The medium was changed at the interval of one week.The weight loss was determined.

Table 3 Weight loss of percentage of hydrolytic conditions in polyurethane composites

Samples	Weight loss (%)		
	Water	Ethanol	Salt water (1N NaCl)
CFRPU	0	0	0
CFRPUC	0.04	0	0.01
CFRPUS	0.05	0	0.03
CFRPUL	0.02	0	0
CFPPU	0	0	0
CFPPUC	0.05	0	0.02
CFPPUS	0.03	0	0.04
CFPPUL	0.02	0	0.01

3.4 Chemical resistance test

The degradation of polyurethanes and polyurethane composites were studied by an acid, base and oxidant medium. Dilute hydrochloric acid (1N), sodium hydroxide (1N) and hydrogen peroxide (30%) were used.The medium was reformed once in a week and the samples were kept in new solvents.At the end of the assessmentweight loss was calculated.

Table 4Weight loss percentage chemical resistant test in polyurethane composites

Samples	Weight loss (%)		
	Acid (1N HCl	Base (1N NaOH)	Oxidant (30% H_2O_2)
CFRPU	0	0	0
CFRPUC	0	0	0.05
CFRPUS	0	0	0.03
CFRPUL	0	0	0.07
CFPPU	0	0	0
CFPPUC	0	0	0.04
CFPPUS	0	0	0.04
CFPPUL	0	0	0.08

3.5Solubility in organic solvents

Solubility of polyurethane composites in organic solvents such as ethyl methyl ketone, chloroform, toluene, dimethyl acetamide and acetone was carried out. The samples were immersed into the solvents in an airtight container for sixty days.The medium was changed once in a week.After the completion of sixty days the samples were taken out from a solvent, dried under vacuum.The weight loss was calculated using electronic balance.

Table 5 Weight loss percentage of organic solvents in polyurethane composites

Samples	Weight loss (%)				
	Ethyl methyl ketone	Chloroform	Toluene	Acetone	Dimethyl acetamide
CFRPU	0	0.04	0.04	0	0.08
CFRPUC	0	0.06	0.09	0	0.11

CFRPUS	0	0.08	0.07	0	0.16
CFRPUL	0	0.14	0.03	0	0.09
CFPPU	0	0.03	0.13	0	0.02
CFPPUC	0	0.14	0.10	0	0.17
CFPPUS	0	0.16	0.07	0	0.15
CFPPUL	0	0.10	0.03	0	0.11

4. Conclusion

The ageing performance shows the stability of polyurethanes and polyurethane composites against hydrolytic, chemical, organic solvents and temperature.In hydrolytic stability test there is a small deviation in water and salt solution but the samples are stable in ethanol.In chemical resistance test, the samples are given slight variation in oxidizing agent, but they are stable towards acid and base.The constancy of organic solvents shows some weight loss in chloroform, toluene and dimethyl acetamide, but there is no weight loss in ethyl methyl ketone and acetone. Polyurethanes and polyurethane composites are thermally stable.There is a small weight change during thermal stability test. Perforation studies showed that the polyurethanes and polyurethane composites are biodegradable in nature.

5. References

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