

Synthesis and Characterisation of Novel Crosslinked Biopolyurethane from Soyabean oil as ecofriendly Biodegradable Material

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Abstract: Novel cross linked Biopolyurethane were synthesized from naturally occurring soyabean oil . Polyurethane was prepared by Epoxidation followed by the formation of Polyol by thermal hydrolysis at high temperature for five hours. The formed polyol was converted into polyurethane by the addition of hexamethylene diisocyanate at different concentration. The cross linked novel biopolyurethane were evaluated by FTIR and NMR studies. The biodegradation of the formed polymer were evaluated by soil biurial test. The Chemical resistance of the crosslinked polyurethane were analysed by different solvents. As a result of these studies it shows that the newly synthesised Polyurethane was potentially biodegradable and used for the manufacture of leather and automobile parts.

Keywords: Biurial test, epoxidation, biodegradable.

1. INTRODUCTION

Soyabean oil has been found to be more useful in the preparation of rigid, semi-rigid flexible urethane resistant to moisture. Polyurethanes prepared from soyabean oil containing unsaturated linkages and contains polyfunctional groups. Polyurethane possess high hydrolic stability and good electrical insulating properties.[1]

Polyurethane was an unique material with a wide range of physical and chemical properties. Polyurethanes was an unique material with a wide range of physical and chemical properties. Polyurethanes were used as protective coatings, adhesives, fibers and thermoplastic elastomers. [2]

The Polyurethane composed of aliphatic diisocyanates demonstrated a greater rate of biodegradation than the polyurethane composed of aromatic diisocyanates. When the polyol used was polyhexamethylene adipate diol of polycaprolactone diol, the polyurethane obtained as a high rate of biodegradation in the composting condition.[3]

Vegetable oils are triglycerides of fattyacids. In order to use these compounds as starting materials for polyurethane synthesis. The preparation of polymers from vegetable oils were receiving increasing attention because of economic and environmental concerns. The polymers were mainly manufactured by the addition of diisocyanate (NCO) with polydiol of various molecular weight. The properties of Polyurethane depend on certain factors as the content of reactive groups, the degree of cross linking and the enlargement of the reacting monomers. [4]

The renewable resources have proved to be useful for the synthesis of a variety of monomers as well as linear and cross linked polymers of different types.[5]

In the present study the potential utility of edible soyabean oil used for the preparation of novel crosslinked biodegradable polyurethane as ecofriendly biodegradable material of various consumes application such as manufacture of packaging materials.

Vegetable oils were the most widely used renewable resource for the chemical and polymer industries including high degradability easy availability and possess relatively low price. [6]

Most of the worldwide market plastics derive from fossil fuels such as oil, coal and natural gas. The continuous depletion of fossil raw materials produced environmental problems.[7]

Plant oils can be used as a starting compound for the production of advanced polymers at different concentration[8]. Nowadays polymers absorb small amount of moisture content and Thermogravimetric analysis helped to determine the level of water content through degradation process.[9] For Industrial applications Soyabean oil was the most important and cheaply available in common in all over the countries.[10]. Most of these plant oils and their derivatives have been used due to their renewable nature, low cost and easy availability. A large amount of plant oils were used as alternative source for the production of polymers and they were used for making adhesives and nanocomposites.[11]

Recently Polymeric research enhances the various properties of polymers such as mechanical, optical and electrical which mainly depend upon the different advancements in science and technology. For example Hybrid fillers are developed into polymer matrices.[13]

Vegetable oils consist of mixture of isomers such as monoterpenoids, sesquiterpenes, aromatic and aliphatic compounds.[14] Plants consist of aromatic compounds have ecological functions which are used for the treatment of many infective diseases.[15] Polyurethane plays a major role in case of polymers possessing different properties and applications. The selection of polyols determine the properties of the produced Polyurethane.[16] Cross linked biodegradable polymers has been prepared from edible oils and consist of unsaturated linkages and they were used for making roof tops. [17]

Polyurethane has been developed as more versatile resin. The biodegradability depend upon the nature of vegetable oil used.[18] Oils are nonreactive raw material and certain agents were added to activate the double and ester linkages.[19] Differential thermal analysis and thermogravimetric analysis allow to determine thermal effects during physical and chemical changes.[20]

2. MATERIALS AND METHODS

Materials:

Soyabean Oil (Sigma Aldrich), 30 % Hydrogen peroxide (Rankem), Glacial acetic acid (Sigma Aldrich), Para toluene sulphonic acid (Sigma Aldrich), 1,6-hexylene glycol (Sigma Aldrich), N,N¹ Diphenylamine (Sigma Aldrich), Hexamethylene diisocyanate. (Sigma Aldrich).

Experimental Procedure:

The technique adopted for the synthesis of Polyurethane was Stepwise polycondensation. In this method the reaction started with the preparation of epoxy resin followed by the ring opening of epoxide linkage to polyol in presence of an acidic medium such as para toluene sulphonic acid. Finally the polyol was converted to polyurethane by the addition of a monomer such as hexamethylene diisocyanate.

About 100g of the Soyabean oil was taken in a three necked flask. 18 g of glacial acetic acid was added to the soyabean oil. About 120ml of 30% hydrogen peroxide was added dropwise for about two hours. The setup was heated for about 60 to 70 °C for about ten hours. At last the epoxidised soyabean oil was formed and washed again with light warm water and keep it for about 110 °C for half an hour.

The next step was the conversion of epoxidised soyabean oil to polyol. To a small amount of epoxy resin add 1,6-hexamethylene glycol in the ratio of 1:2. Then to the mixture add para toluene sulphonic acid and it was kept at 250 °C for 6 hours. At last a dark brown viscous liquid was formed and it indicated the polyol synthesis.

The final step was the addition of a monomer to the polyol in the ratio of 1:2. After the addition of hexamethylene diisocyanate to the polyol add two drops of diphenyl amine as a catalyst. Finally the product was transferred to a preheated mould at 110 °C for about one week. At last a thin film of Polyurethane was formed and its thermal stability was analysed by TG-DTA analysis.

3. RESULT AND DISCUSSION

The Polyurethane crosslinked polymer was analysed by FTIR, NMR and TG-DTA analysis. The thermal properties and the extent of degradation was also analysed by thermogravimetric analysis. The biodegradability was studied by Sem Analysis. The Surface phenomena explained briefly about the particle degradation before and after soil burial test. The chemical resistance of the polymer against different solvents were analysed.

FTIR Spectral studies:

FTIR spectrum showed the presence of polymeric products. The presence or absence of absorptions at certain wavelengths in the infrared spectrum can be interpreted in terms of certain features in the compound. In the FTIR Spectrum of soyabean oil the absorption band at 1738 cm^{-1} showed the presence of carbonyl group. The absorption band in the region of $3000\text{-}3370\text{ cm}^{-1}$ indicate the presence of OH stretching frequencies. The spectral region at 1230 cm^{-1} and 1159 cm^{-1} showed the presence of the stretching vibrations of C-O bond in esters.

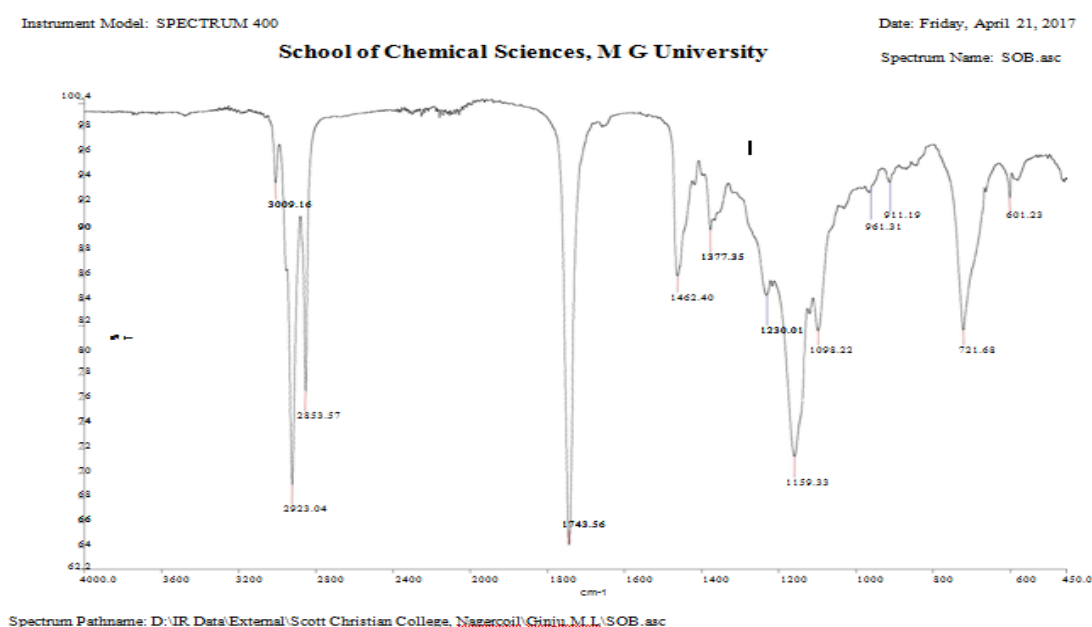


Fig. 1. FTIR Spectrum of Soyabean oil.

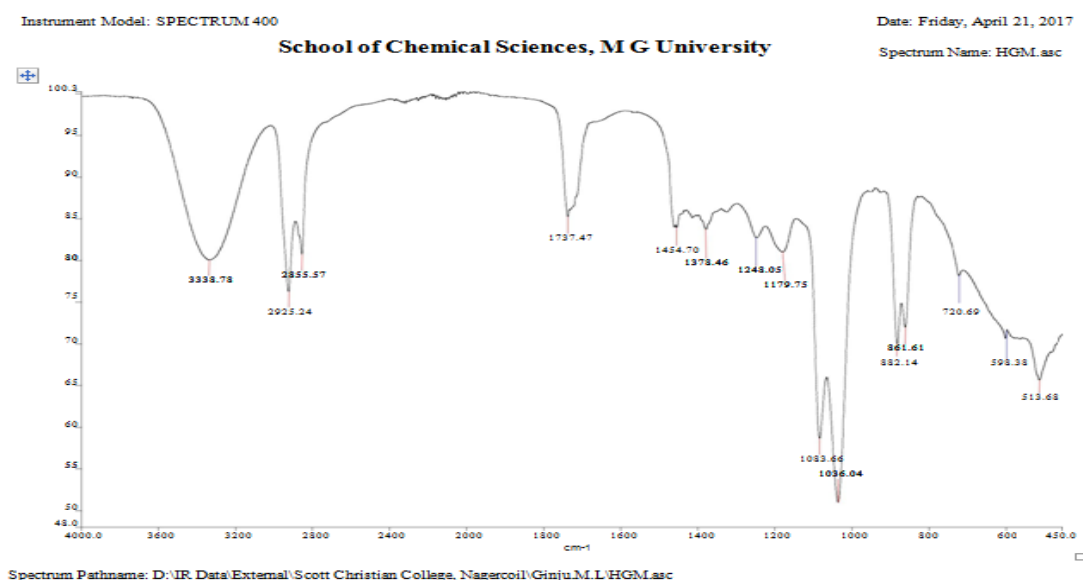


Fig. 2. FTIR Spectrum of Soyabean polyol.

The epoxidised soyabean oil showed an absorption band at 869 cm^{-1} due to the presence of epoxy group. Then the epoxy group disappear in the polyol spectrum due to the oxirane ring opening. The spectra of polyol showed the broad stretching peak around 3333 cm^{-1} .

H¹ NMR Analysis:

The H¹ NMR spectra recorded for soyabean oil, epoxidised soyabean oil and soyabean polyol. The region δ between 5 to 5.4 ppm indicate the presence of olefinic proton. This peak disappeared for the epoxidised soyabean oil. The peak ranges from 5-5.4 ppm was disappeared in the spectrum of soyabean polyol and the peaks appear at 3.4-4.3 ppm correspond to methylinic proton associated with -OH groups.

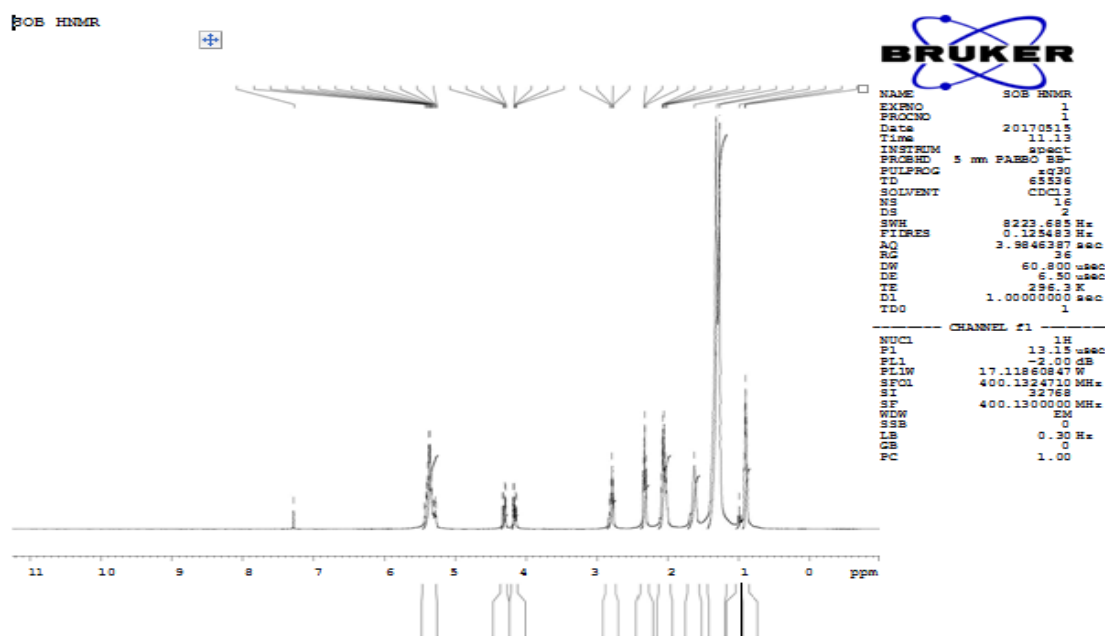


Fig. 3. H¹ NMR spectrum of Soyabean oil.

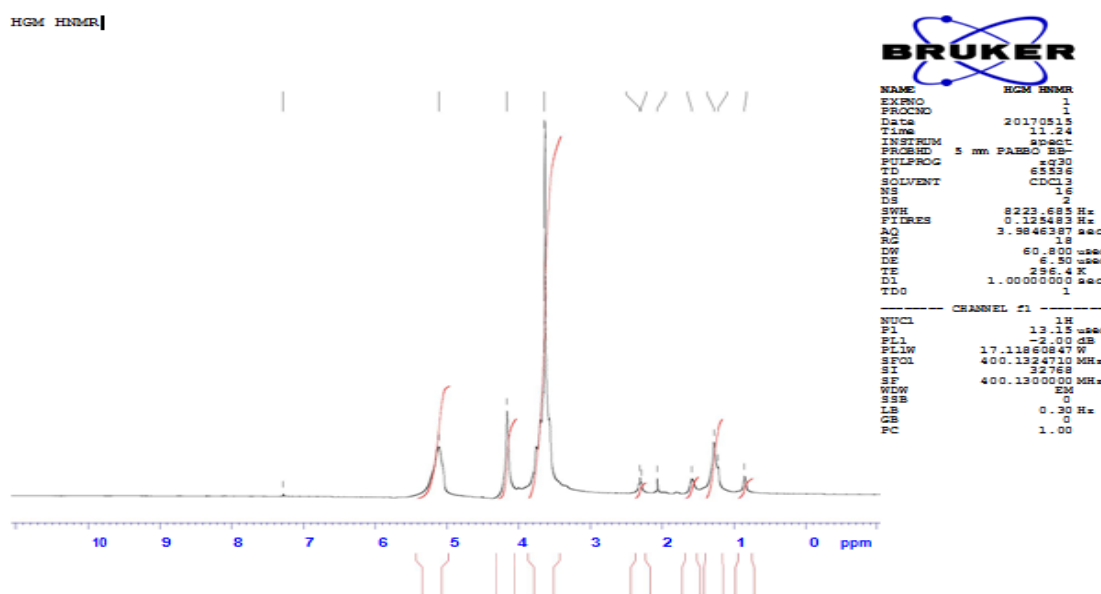


Fig. 4. H¹ NMR spectrum of Soyabean Polyol.

Thermal Analysis:

The thermal studies showed that the prepared soyabean oil was thermally stable. In the TG-DTA analysis of soya polymer the degradation started from 206.66⁰ C and gradually the polymer weight decreases and finally reached 445.64 ° C. The polymer formed was thermally stable upto 450°C. The degradation of water molecule also studied at different time intervals with increase in temperature. From this study the thermal stability of the thin film of Polyurethane were analysed systematically.

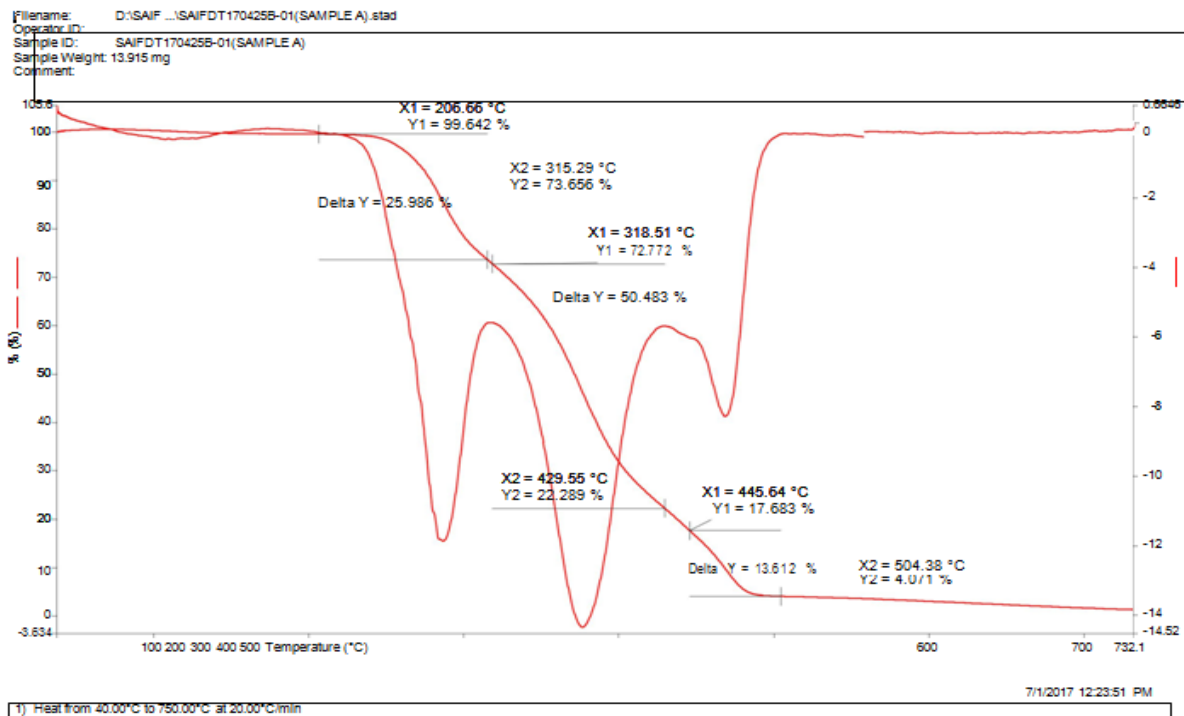
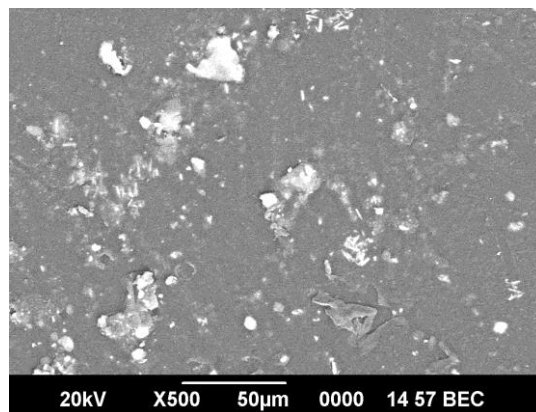
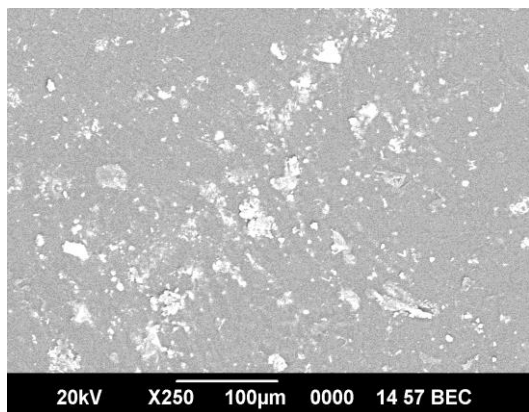


Fig: 5. TG-DTA curve of Soyapolyurethane

SEM Analysis:

Sem Analysis were clearly studied by soil biurial test. In Soil biurial test around 1.5 cm² thin film was cut into square shape and buried into the soil. Before the soil biurial test the sem image was taken. Daily spread water over the surface of the soil. After 72 days the polymer was taken from the soil and washed with distilled water and dried over oven at 110⁰ C. Then after soil biurial again the sem image was taken and compare the two images. From these it was concluded that the prepared polymer was biodegradable in nature. Sem analysis helped to find out the distribution of particles in the polymer synthesised from natural oils. The Scanning micrograph of SPU at 100 µm to 2 µm magnification represented in the following figure.



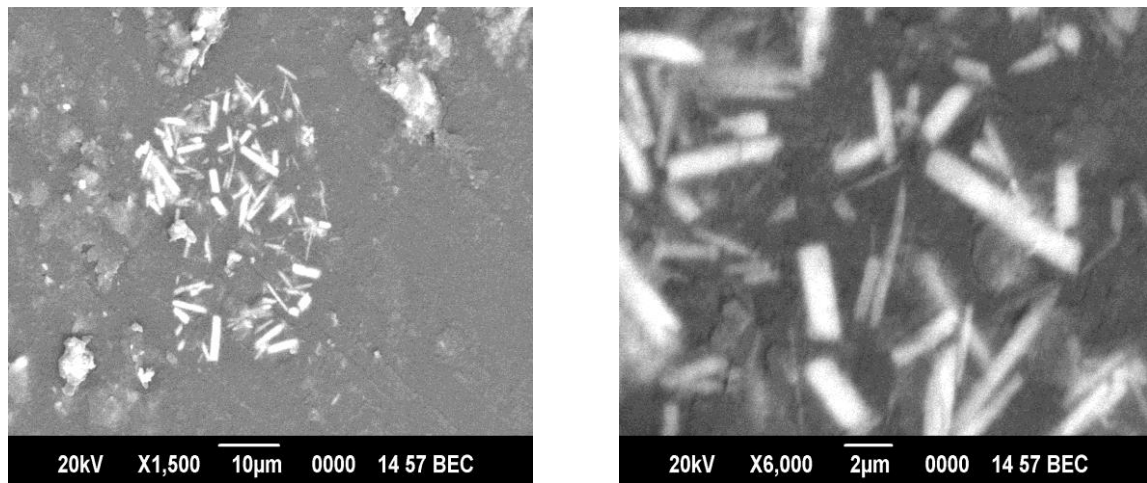


Fig:6. Sem images of Soyabean polyurethane before soil biurial test.

The surface sem images of SPU were uniformly distributed before biurial test. The sem images of SPU after biurial under the magnification from 100 µm to 2 µm showed that they were not uniformly distributed and the polymer synthesised were biologically degradable.

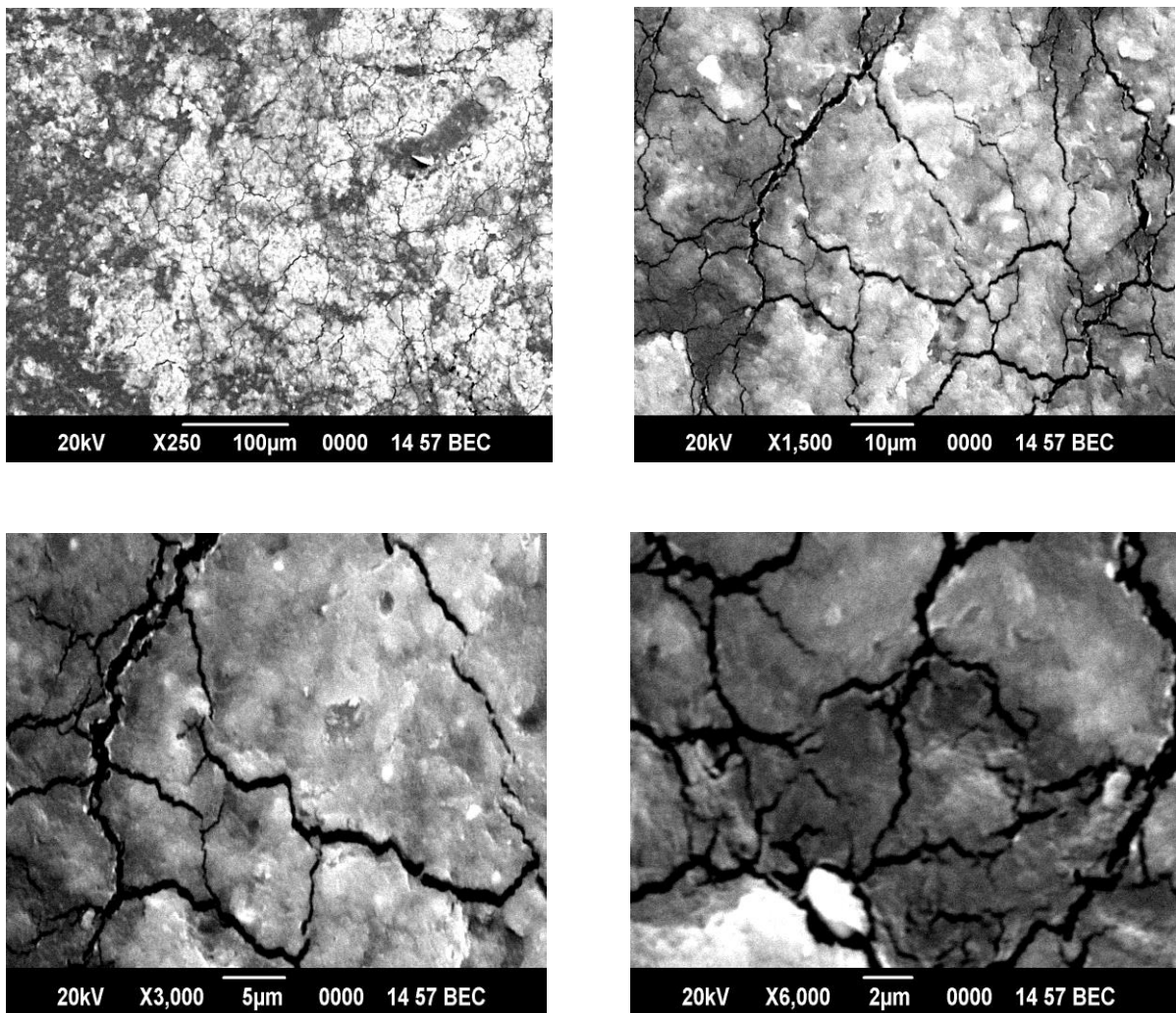


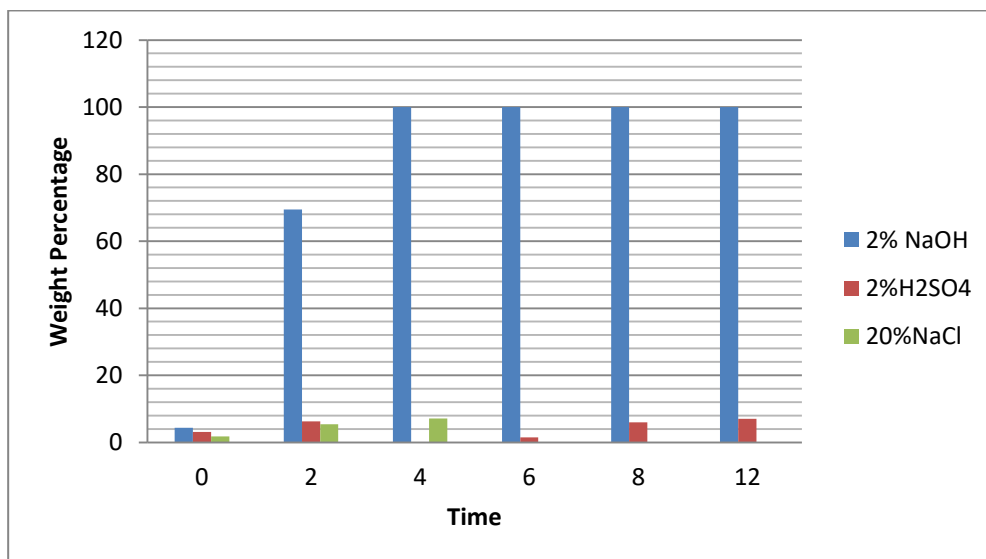
Fig: 7: Sem images of SPU after Soil biurial test.

Swelling Analysis:

The percentage of swelling in Polyurethane were studied systematically. The samples for swelling analysis suspended in alkaline and acidic medium. All the polymeric samples shows minimum swelling in basic medium. But the polymeric sample shows swelling in case of acidic solvents such as sulphuric and sodium chloride.

The polymeric samples were allowed to immersed in different solvents for 72 hours at room temperature. Then the samples were weighed after 2,4,6,8,12,24,48 and 72 hours.

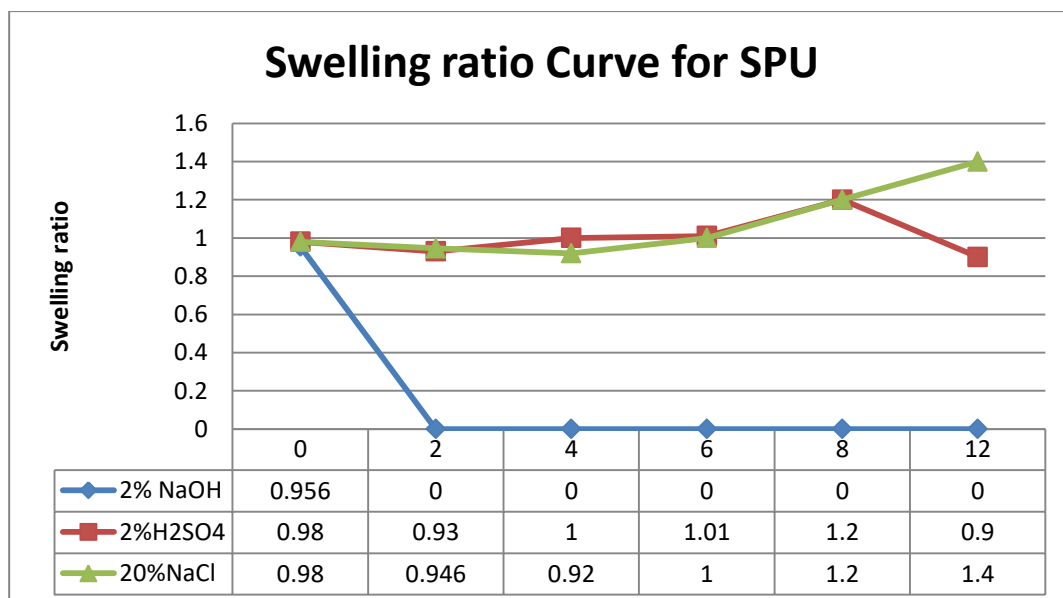
Weight Percentage of SPU



Degree of Swelling and Swelling Ratio:

Squares of 1.5 cm² of thin film of Soyapolyurethane were finely cut into pieces and dried at 60 °C and initially the weight of the polymer (w₁) was taken. Then the sample was immersed in distilled water at 30 °C for a minute. The samples were taken out from the water and moisture was removed by using filter paper. They were weighed again and it was noted as (w₂). The samples were weighed again drying at 60 °C and noted as (w₃). The degree of swelling is calculated by using the equation

$$\text{Degree of Swelling} = (w_2 - w_3) / w_3$$



4. CONCLUSION

The biodegradable soya polyurethane was prepared by stepwise polymerization technique. The method used for the preparation was simple and easily carried out. The presence of epoxy, alcoholic group was analysed by FTIR spectrum. The nature of protons in the product was clearly explained by NMR analysis. The thermal stability of the polymer was studied by TG-DTA analysis. The removal of moisture content at different stages were analysed by thermogravimetric analysis. The SEM images obtained after soil burial test explained the biodegradability of the polymer. The difference in swelling phenomena indicated that the difference in weight of the polymer was due to the nature of the solvent taken for swelling analysis. Swelling analysis influenced the physical properties of the soyapolyurethane polymer.

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REFERENCES

- [1] Sailsu.A.A ,Chem Search Journal 2012, The use of castor oil as a flame Retardant in Polyurethane foam.
- [2] Krushna Chandra Pradhan and P.L. Nayak etal, Advances in Applied Science Research. Synthesis and Characterisation of Polyurethane nanocomposite from Castor oil- Hexamethylene diisocyanate.
- [3] Kim.Y.D & Kim.S.C. Polymer degradation and stability ,62,p.343 (1997)
- [4] S.Ibrahim et al , Bullet of Material Science Vol.38.September 2015. Synthesis and Characterisation of Castor-oil based polyurethane for potential application as host in polymer electrolytes.
- [5] S.J.Park etal , Journal of Macromolecule Rapid Community 2004, 724-727.
- [6] Patel M.K etal, Journal of Resources conservation. Surfactant production and uses in Germany.
- [7] Zhang. C.etal . Journal of Polymer Sciences 2017, Recent advances in Vegetable based polymers and their composites.
- [8] Nikesh B.Samrath etal, Open journal of Organic polymeric materials, Januaryn 2015.
- [9] W.J.Sichina etal , Characterisation of Polymers using TGA,Journal of Thermal Analysis .
- [10] Z.S. Petrovic etal, Polymers from Biological oils.2010.
- [11] Wool.R.P and Sun.X.S Polymers and Composite Resins from plant oils in Bio-based Polymers and Composites.Elsevier Academic Press- 2005.
- [12] Nikesh.B.Samrath, Prakash .A.Mahanwar, Modified Vegetable oil based additives as a future Polymeric material- Open journal of Organic Polymeric materials.2015.
- [13] Ritu Tomar and Dr. Chirag .R.Sharma,Experimental studies on PVP/KI ion conductive polymer composite, International Journal of Scientific Research Engineering & Technology,Volume 2 August 2013.
- [14] Zhao.C.X,Liang.Y.Z,Fang .H.Z.Temperature Programmed Retention indices for a Gas Chromatography-mass spectroscopy analysis of plant essential oils. Journal of Chromatography.2005.
- [15] Tepe.B.Antimicrobial and antioxidant activity of essential oil and various extract of Cyclotrichium.Manden and Scheng, Journal of Food Engineering,2005.
- [16] Chaoqun Zhang , Soy-castor based polyols prepared using a solvent free Method.Journal of Green Chemistry-2013.
- [17] Meier MAR, Metzger J O and Schubert US, Chem Society, Revised 2007.
- [18] Schiffgraben ,Hannover Polyol from Castor oil and Epoxy resin for Polyurethane Coatings,European Coatings Journal, November 2003.
- [19] Z.S.Petrovic , Polymers from Biological oils- Contemporary Materials.2010.
- [20] M.Jesitor, D.Myszka,Thermal Analysis of selected polymer materials for Precision castings Models-Archives of Foundry Engineering-2013.