Corrosion Management **ISSN: 1355-5243**
(https://corrosion-management.com/)
Volume 34, Issue 01 – June 2024
SCOPUS

Synthesis and characterization of bio-based polyurethane for potential applications as photocatalysts and anti-microbes

[1]J.L. Jebisha, [2]S. Begila David
[1]Research scholar (Reg no:21213162032019), Department of Chemistry and research Centre,
Scott Christian college (autonomous), Nagercoil-629 003, Tamil Nadu, India.
(Affiliated to Manonmaniam Sunderanar University, Tirunelveli-627 012, Tamil Nadu, India)
[2]Research supervisor & Associate professor, Department of Chemistry & research Centre,
Scott Christian college (autonomous), Nagercoil-629 003, Tamil Nadu, India.
(Affiliated to Manonmaniam Sunderanar University, Tirunelveli-627 012, Tamil Nadu, India)
[2]Corresponding author email: begilarobin@gmail.com.

ABSTRACT:

Polyurethanes (PUs) are materials that are widely used in industry and daily life because of their versatility. The purpose of this work is to investigate the viability of producing bio-based polyurethane (PU) utilizing bio-based Salvia hispanica polyol (SHP) derived from Chia seed oil. Using, polymeric methylene diphenyl diisocyanate (PMDI), and water as a blowing agent, bio-based polyurethane powders were synthesized.Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and the thermogravimetric analysis (TGA) method are used to assess the properties of the synthesized bio-based polyurethanes.Through the use of Fourier transform infrared (FTIR) spectroscopy, the molecular structure of PU was examined. The FTIR spectrum's NCO peak disappeared around 2270–2250 cm^{-1}, indicating that the diisocyanate had fully reacted to create PU. SEM analysis was used to examine the PU film's morphological characteristics. Both the photocatalytic and antimicrobial activity of bio-based PU show good results, indicating that the synthesized PU can be used as an alternative to synthetic polyurethane.

KEYWORDS: Salvia hispanica polyol, polymeric methylene diphenyl diisocyanate, Polyurethane, FTIR, SEM.

1.INTRODUCTION:

Bioderived or biobased polymers made from various starting raw materials have been extensively manufactured and described in recent decades [A. Gandini (2008),G.-Q. Chen et al (2012)]. The primary objective of these studies is to substitute biologically based or biologically derived raw materials for the conventional ones, which are derivatives of gas and oil fossils, i.e., monomers, oligomers, and resins [A. Gandini (2008),G.-Q. Chen et al (2012),M. A. R. Meier et al (2007),J. O. Metzger,(2009)]. For instance, plastics can be made from vegetable oils [J. O. Metzger(2009)], products or byproducts derived from bacteria and microorganisms [M. Rinaudo, (2006)], and wood-based chemical technology products (cellulose, lignin, etc.) [R. T. Mathers, (2012)]. These polymeric compounds go by the names "green polymers" or "biobased polymers" [E. Zini et al (2011)].

Polyurethanes (PUs) are materials that are widely used in industry and daily life because of their versatility. They have a wide range of uses, including medical devices, flexible soft foam, industrial machinery, industrial footwear, coatings and paints, elastic fibers, and stiff insulation [Chattopadhyay D K et al (2009),Szycher M (2013),Firdaus M et al (2013)]. Year over year growth in research and development related to PUs is indicative of the PU industry's rapid expansion. The primary process for creating the polymers is the isocyanation of diisocyanate (NCO) with different molecular weights of polyol (OH) [Hepburn C (1992)]. A wide range of polyols and isocyanates are accessible, enabling the creation of polymers for a multitude of uses. PU is used by humans as adhesives, surface coatings, elastomers, stiff, semi-rigid, and flexible materials [Khemani K C (1997)].

The superior physical qualities (low flexibility, high tensile strength, resistance to tearing and abrasion, solvent resistance, etc.) and high chemical structural diversity of polyurethanes (PUs) have led to their widespread application [Lu QW et al (2004),Cao X et al (2005)]. Polyol and isocyanate react to produce PU in most cases. The petrochemical sector is the primary source of polypropylene glycol (PPG), a type of polyol [Edhi P et al (2012)]. Nowadays, research into using renewable resources to make rigid polyurethane (PU) is required because of the skyrocketing costs of petrochemical feedstock and the growing public demand for green, ecologically friendly products [Meier MA et al (2007),Gaidukov S et al (2013)].

Environmentally friendly and renewable components are being used in the production of polyurethane (PU) due to recent changes in the market and law. In order to create an alternative to the commercial polyols that are already on the market, numerous studies have been conducted on the synthesis of polyols from various vegetable oils. Fish oil [Smith B C (1998)], castor oil [Smith B C (1998)], fatty acid [Narine S S et al (2007)], sunflower and rapeseed oil [Patton T C (1962)], palm kernel oil [Petrovic Z S (2008)], and soybean [Z. S. Petrovic, (2008)] are a few examples.

The aim of this work is to investigate the viability of producing bio-based polyurethane (PU) utilizing bio-based polyol derived from*Salvia hispanica* L. The produced bio-based *Salvia hispanica* L polyol (SHP)was used to react with polymeric methylenediphenyl diisocyanate (PMDI) to create bio-based PU. The spectral properties, biological characters and the thermal stability of the bio-based polyurethane were examined. Further investigation on photocatalytic degradation of synthetic azo dye were also carried out.

2.EXPERIMENTAL METHODS:

2.1. PREPARATION OF BIO-BASED POLYOL:

Chia seeds were purchased from the local market. In a Soxhlet device, 5g of *Salvia hispanica L.*(chia seeds) seeds were extracted with 100 ml of n-hexane as the extraction solvent. The obtained oil was treated with glacial acetic acid, tolueneand sulfuric acid in a three-necked flask that was fitted with an isobaric funnel, reflux condenser, and mechanical stirrer. In order to extract *Salvia hispanica* L polyol. (SHP), the organic phase was dried over sodium sulphate and concentrated under vacuum to remove the ethyl ether[Monteavaro, L et al (2005)].

2.2 PREPARATION OF BIO-BASED POLYURETHANE POWDERS:

The Salvia hispanica L polyol was mixed with DMCHA (gelling catalyst), coconut oil (surfactant) and distilled water (blowing agent). The mixture was continuously stirred in a magnetic stirrer until it is completely homogenized. Then PMDI (isocyanate) was added and allow to mix at the same speed. The reaction mixture was then rapidly poured into an open mold and it was left to cure for seven days at room temperature [Tatcha Sonjui et al (2017)].

3.CHARACTERIZATION TECHNIQUES:

3.1. FTIR:

The functional groups of the synthesized bio-based polymer were investigated using Shimadzu FTIR-8400S spectrophotometer. Infrared spectra were recorded in the wave number range of 4000-400 cm^{-1}. Spectra were obtained from64 scans taken at a resolution of 4 cm^{-1}.

3.2. THERMAL STABILITY:

The degradation temperature of polymer was determined by Thermogravimetric Analysis (TGA) using NETZSCH STA 449F3 Thermogravimetric Analyzer. About 3-5 mg of each sample was heated under nitrogen atmosphere from 50 to 700°C at a heating rate of 10°C/min.

3.3. XRD:

The crystal structure of the polymer was analyzed by X-ray diffraction (XRD), using an X-ray diffractometer (Rigaku Mini Flex II, Japan) employing a graphite monochromator and CuKα radiation (l nm).

3.4. SEM:

Scanning electron microscopy (SEM) was carried out on a JEOL 6300F machine at an acceleration voltage of 5KV.

3.5. ANTIMICROBIAL ACTIVITY:

Antimicrobial activity was examined using “The Kirby-Bauer Method” against the number of pathogens including both gram-positive and gram-negative bacteria and also certain fungi. The zone of inhibition of polymers against certain pathogens were also examined.

3.6. PHOTOCATALYTIC ACTIVITY:

Bio-based polyurethane’s photocatalytic activity was examined using an azo dye (Congo Red).1 mg of powder per dye was dissolved in 100 ml of deionized water to create the dye solutions, and a UV-visible spectrophotometer was used to assess the dye absorption. 50 ml of each dye solution had 1 mgof polymer powder added to it, and it was then left outside in the sun. In order to compare the dye solutions' color changes in the absence and the presence of polymer, a control set of experiments was also created. The dye solutions' absorption was measured at regular intervals of time (every 30 minutes) [Chandraker SK et al (2019)].

4.RESULTS AND DISCUSSION:

4.1. FT-IR:

FTIR spectroscopy was used to examine the chemical structure of the bio-based polyurethane made from the bio-based Salvia hispanica polyol. Figure1 displays the FTIR spectra of PU made from the bio-based polyol. The broad absorption band at 3350 cm^{-1} was caused by the stretching vibration of a hydrogen-bonded N-H urethane. The N, C, and O group's distinctive peak, which is hardly visible at 2275 cm^{-1}, suggests that the PMDI's isocyanate groups were completely reacted [Narine S.S.et al (2007)]. The emergence of two absorption peaks indicated the development of urethane bonds. The C=O stretching of the urethane was responsible for the first peak at 1605 cm^{-1}. The other peak, located at 1539 cm^{-1}, is the result of urethane linkage's N-H bending. The discovery of the carbonyl peak (C=O) at 1747 cm^{-1} demonstrated that the hydrogen bond had formed [Badri K.B.H. et al (2010)]. The C-H stretching of the -CH$_2$ group was suggested by the bands seen between 2925 and 2850 cm^{-1}.

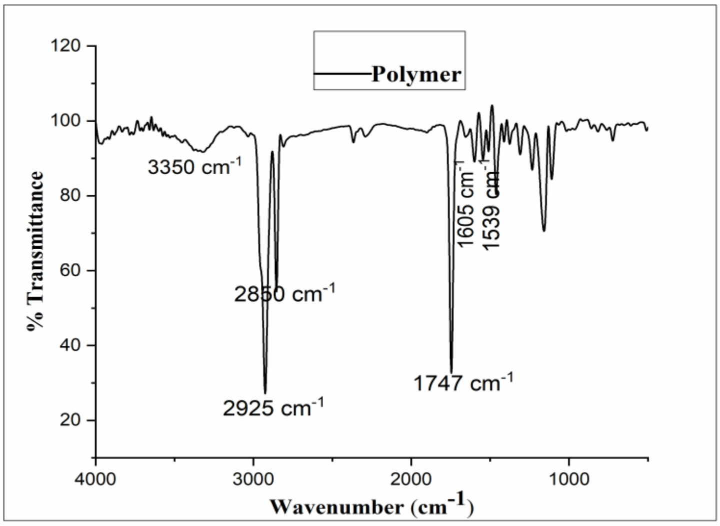

Fig 1 (FTIR spectra of PU)

4.2.XRD:

Figure 2 displays the polyurethanes' X-ray diffraction pattern. The strong broad peak around $2\Theta = 20^\circ$ indicates a crystalline phase due to the hydrogen bonding in polyurethane.

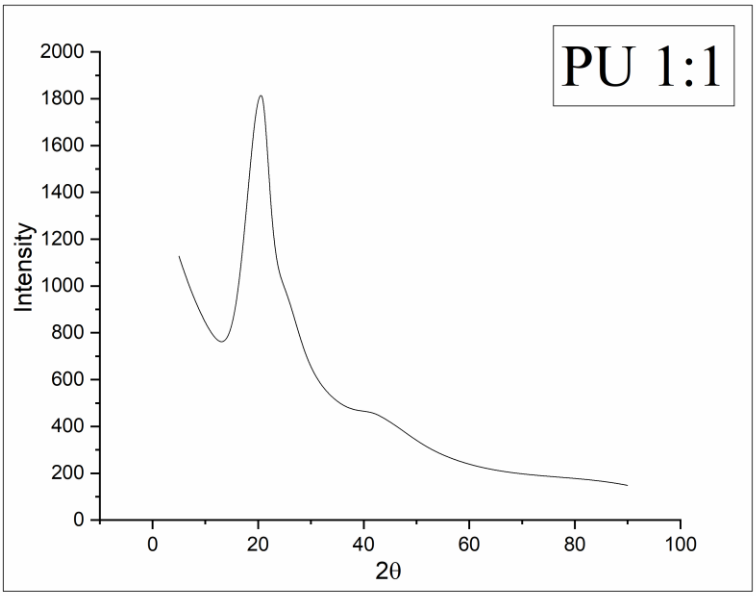

Fig 2 (XRD pattern of PU)

4.3.TGA:

Table 1 shows the % of weight loss and decomposition temperature.

Weight loss %			**Total weight loss (%)**	**Residue after 600˚C (%)**
Td1 (264-354˚C)	Td2 (350-494˚C)	Td3 (490-590˚C)	97.91	2.09
11.12	82.23	4.56		

The thermogravimetric curve for PU is shown in figure 3. There are three distinct stages of decomposition. The % weight loss after decompositionsand the decomposition temperatures Td,are listed in Table 1. At 264°C, the first deterioration stage, or Td1, is detected. Tmax, the maximum temperature, is reached at 271°C. The urethane linkage degradation is correlated with the Td1. Polyurethane's thermogravimetric curve shows that the material is thermally stable at room temperature until it begins to break down. Td2, the second stage of thermal deterioration, is shown between 350°C and 494°C. From 490 to 590°C is when the third stage of thermal deterioration, or Td3, starts. Td2 is associated with the release of free isocyanate, while Td3 is linked to the breakdown of the PU's soft section [Corcuera M A et al(2011),Su'ait M S et al (2014)]. According to the TGA result, the PU appears to be stable up to 264°C.

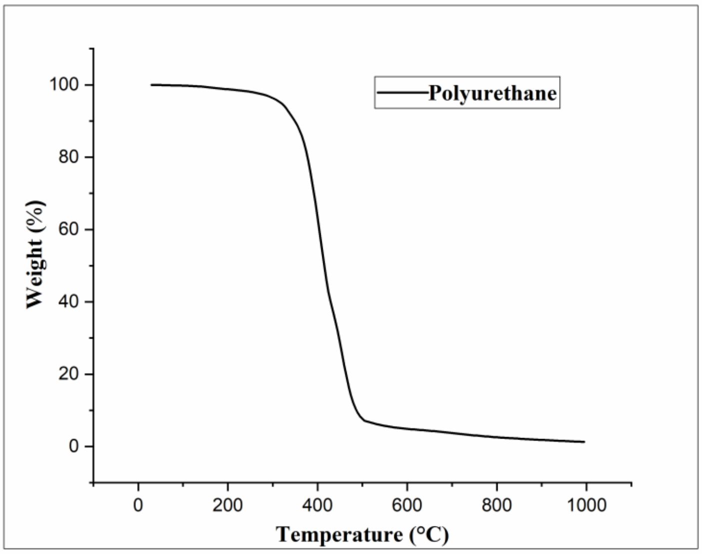

Fig 3 (TGA curve of PU)

4.4 SEM:

The morphology and dimensions of polyurethane was examined by SEM. The synthesized polyurethane reveals the formation of irregularly shaped particles with an average particle size of 132.2 nm. The histogram (fig 4) reveals the particle size distribution of the polyurethane. The SEM image (fig 5) also depicts the presence of spherical shaped particles with smooth surface which are fused together to form a chunk like morphology.

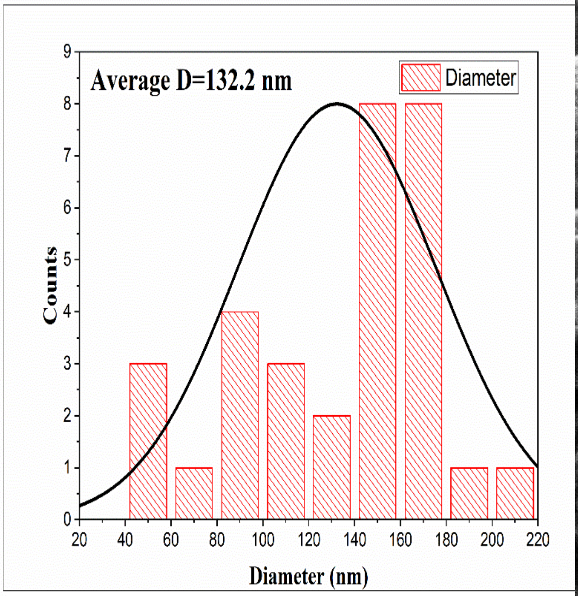

Fig 4 (histogram)

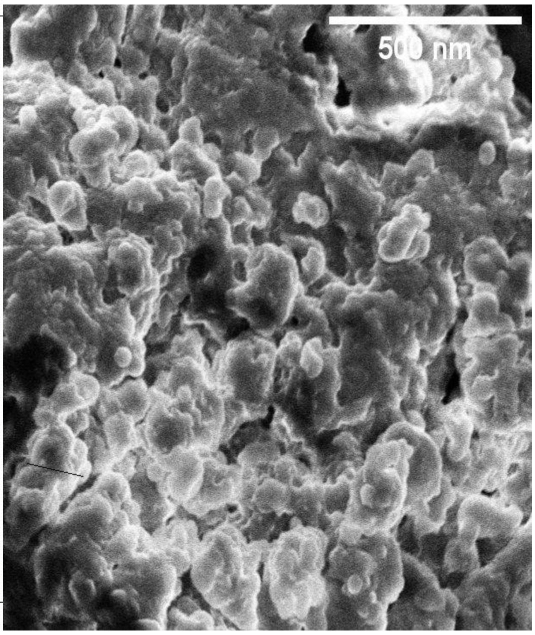

Fig 5 (SEM image of PU)

5.APPLICATIONS:

5. 1. ANTIMICROBIAL ACTIVITY:

Two bacterial cultures including Proteus mirabilis (gram positive), Salmonella typi(gram negative) and a fungal culture C.albicans were used to check the antimicrobial potential of the polymer. Amikacin was used as a control against bacterial cultures while Nystatin was used as a control against fungal cultures. The zone of inhibition against both bacteria and fungi were listed in the table:2.

Table 2 shows the zone of inhibition against certain microbes

Bacteria	Zone of inhibition	
	Polyurethane	Control (Amikacin)
Proteus mirabilis	17 mm	16 mm
Salmonella typi	16 mm	16 mm
Fungi	Zone of inhibition	
	Polyurethane	Control (nystatin)
Candida albicans	15.2 mm	13 mm

5.2. PHOTOCATALYTIC ACTIVITY:

In this photocatalytic experiment CONGO RED was effectively degraded by bio-based polyurethane. Room temperature was used for the dye degradation reaction, which was monitored at regular intervals with a UV-visible spectrophotometer. Aqueous dye solutions were left in the sun without polymer catalyst, and after more than two hours, the dye's color remained the same. However, the color of Congo red dye changed from red to colorless after two hours with the addition of the catalytic amount of polyurethane to the aqueous solution of dye in the presence of sunlight. Fig:6 shows that the UV absorption peak was decreased from 0.98 to 0.1 at 498nm.

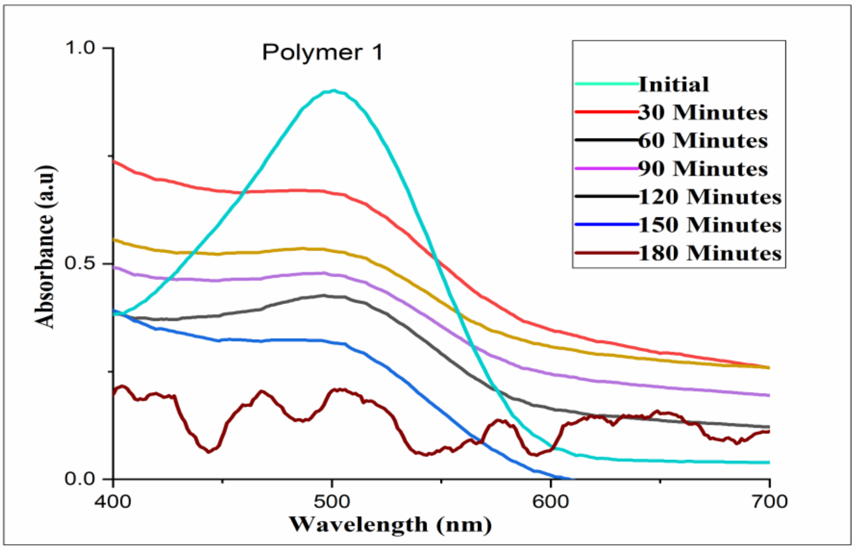

Fig 6 (UV spectra of CR dye)

6.CONCLUSION:

A bio-based polyurethane was successfully synthesized using Salvia hispanica polyol (SHP). It was confirmed using FT-IR and XRD analysis.The TGA result shows that the PU appears to be thermally stable up to 264°C.The morphology and dimensions of polyurethane was examined by SEM and the average particle size was found to be 132.2 nm.The antimicrobial potential of the prepared polymer was tested against certain bacteria and fungi.The bio-based polymer haseffective photocatalytic activity against carcinogenic azo dye CR.

CONFLICTS OFINTEREST;

The authors declare that they have no potential conflicts of interest.

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