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Curcumin-Based Polyurethane Coatings: A Novel Bioactive Solution

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ABSTRACT

This paper reports the preparation of polyurethane (PU) coatings using aromatic diisocyanates (methylene diisocyanate (MDI), toluene diisocyanate (TDI), and MDI/TDI mixture) with natural diols like curcumin, employing an organotin catalyst (DBTDL). The PU mixtures were applied using a brush on steel, aluminum panels, and various polymers, and their coating characteristics were evaluated, including gloss, scratch resistance, impact resistance, pencil hardness, and chemical resistance. Increasing the molar ratio of natural diols enhanced coating flexibility but reduced hardness. Additionally, the PU coatings were analysed for thermal stability using thermo gravimetric analysis, demonstrating the successful production of eco-friendly, bio based PUs through an economically viable process.

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Introduction

Significant strides have been achieved in chemistry, particularly concerning the seventh principle of Green Chemistry, emphasizing the use of renewable raw materials instead of depleting ones, whenever possible [1-3]. As sustainability gains prominence, there is a growing need to replace petroleum-derived materials with renewable alternatives, especially in polymer production [4,5]. Plants offer a crucial renewable resource, with approximately 75% of biomass being carbohydrates, 20% lignins, and around 5% oils and other components. A comprehensive understanding of the chemistry of these biomolecules is essential to ensure the sustainable utilization of biomass as a renewable feedstock [6,7].

Curcuma longa, commonly known as "turmeric," has a rich history of use in South Asian cuisine, cosmetics, and traditional Ayurvedic medicine [8-11]. Its vibrant yellow powder is extensively used as a spice and coloring agent in Indian cooking and has been revered for its therapeutic properties in Indian and Chinese traditional medicine for centuries [12-15]. This spice owes its distinct color to phenolic compounds called curcumoids, with curcumin being the principal ingredient, comprising approximately 77% of turmeric's curcumoid content, followed by demethoxy curcumin (17%) and bisdemethoxycurcumin (3%) [12,16-18]. Curcumin is a diphenolic compound and is known for its antioxidant, anticancer, anti-inflammatory, and potent anti-Alzheimer's disease activities [19-25].

In the realm of polymer chemisvtry, curcumin has found versatile applications as an environmentally friendly and cost-effective photoinitiator [26,27]. It has been utilized in the fabrication of curcumin-containing electrospun cellulose acetate mats and curcumin-incorporated collagen films [28,29]. Additionally, curcumin has been explored in the context of dendrimer curcumin conjugates and as a colorant for silicone-based elastomers [30,31]. The unique dual functionality of curcumin offers an exciting platform for the development of novel bio-polymers [32]. Furthermore, curcumin has been identified as a potential substitute for conventional diols like Bisphenol A (BPA) and ethylene glycol. The BPA does not found naturally but has become pervasive in our surroundings due to its extensive production, consumption, and subsequent introduction into the environment [33].

In summary, turmeric, with its active compound curcumin, holds significant potential in various fields, ranging from culinary traditions and traditional medicine to cutting-edge applications in polymer chemistry. Its diverse and promising properties continue

to captivate the interest of researchers, fostering exploration into sustainable and innovative solutions. In this study, turmeric was utilized as a source of curcumin to synthesize two biopolymers, CPU1 and CPU2. The curcumin was transformed into urethanes by reacting it with the -NCO (isocyanate) groups of MDI and TDI. These polyurethane compositions were then applied using a brush on steel panels, aluminum panels, and different polymers. The coating characteristics of the PU compositions were thoroughly evaluated in this investigation.

Experimental

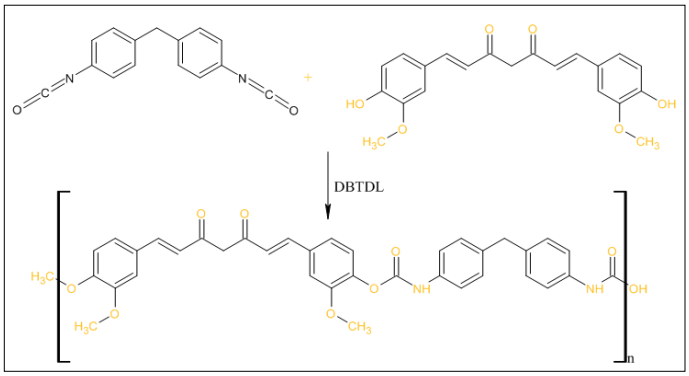
Materials

Chemicals

Curcumin extraction and purification followed a procedure outlined in existing literature [5,34]. The MDI and TDI required for the synthesis of their dimers were procured from Merk, Germany and used as received. Dibutyltin dilaurate (DBTDL), obtained from Aldrich Chemicals, UK, was of laboratory grade. All other chemicals and solvents used for synthesis or analysis were of either synthesis or analytical grade, as per their specific applications.

Preparation of polyurethane coatings (PU) based on Curcumin

Scheme 1 presents a schematic diagram illustrating the synthesis process of polyurethanes (PUs). At room temperature, curcumin underwent a reaction with MDI/TDI. Initially, a catalyst, DBTDL (0.5%), was added to curcumin. To achieve the desired solid content (50%), dimethyl acetamide (DMAC) was mixed with curcumin. Subsequently, the complete curcumin solution was combined with MDI/TDI. The mixture was stirred for 30 minutes before being transferred onto pre-treated steel coating panels (4 × 6 inches) and evenly spread using a brush. Different PU samples were prepared by varying the ratios of -NCO/OH, such as 1:1, 2:1, and 2.5:1.



Scheme 1: Synthesis of PUs from Curcumin and MDI, TDI

Chemical Analysis of Raw Materials

The structure of Curcumin was confirmed through IR, 1HNMR, and mass spectral analysis. To determine the isocyanate content of the synthesized MDI/TDI, the n-butyl amine method was employed following the ASTM D-2572-97 standard. Additionally, the hydroxyl value of Curcumin was determined using the acetylating reagent method, following the experimental procedure recommended by ISI: 354 (1987).

Gel permeation chromatography (GPC)

The molecular weight of the PUs was determined using gel permeation chromatography (GPC) with the Agilent GPC-Addon Rev A02.02 series HPLC system, employing a PL-Gel Agilent column and THF solvent. To measure the viscosities of the polymer samples, they were dissolved in THF and then analyzed at 25ºC using the Ubbelodhe viscometer.

FTIR Spectroscopy

The FTIR spectra were acquired by scanning 50 times using a FTIR spectrometer (Shimadzu, Japan) within the range of 4000 to 500 cm−1. KBr pellets were used as the sample preparation method for the analysis.

Thermal Analysis

Thermo gravimetric analysis (TGA) of the coating samples was conducted using a thermo gravimeter instrument (TA Q500, USA). For each analysis, 3 mg of the samples were placed in a platinum pan and subjected to heating under a nitrogen atmosphere (10 mL/min) at a rate of 10 °C/min, ranging from room temperature to 550 °C. The instrument recorded the weight loss versus temperature curve during the heating process. Differential Scanning Calorimetry (DSC) analyses were performed using a Q100 model from TA Instruments, New Castle, DE, USA.

Polyurethane Coating Characterization

Gloss

The digital gloss meter (BYK Additive & Instruments, Germany) was initially calibrated using the standard sample provided by the company. Subsequently, the gloss measurement of the coated panels was conducted at an angle of 60°C.

Pencil Hardness

The pencil hardness of the coatings was assessed using a pencil hardness tester (BYK Additive & Instruments, Germany). The test was conducted following the ASTM D-3363 standard. Twenty pencils with grades ranging from 9B to 9H were employed, utilizing a standard holder. These pencils were moved over the surface of the test sample at a consistent angle and pressure, as specified by the instrument's guidelines.

Impact Resistance

The surface-coated panels were subjected to rapid deformation using a weighted indenter (4.1004 pounds) from a fixed height (5-100 cm). Following the impact, peeling and cracking of samples were observed.

Chemical Resistivity

To assess the chemical resistance of the samples, the ASTMD 543-67 (1972) method was employed. The typical procedure involved immersing the samples in various solutions, including 1N NaOH, 1N H2SO4, 1N HCl, and xylene, for a duration of 7 days. After the immersion period, the panels were dried for an hour, and the film was examined for any visible changes at regular intervals.

The anticorrosion properties of the prepared PU coatings were evaluated through immersion studies, comparing both crossed and uncrossed coated steel panels with pristine steel panels. Crossed panels were obtained by making sharp razor blade incisions (10 µm) on the panels. The immersion study was conducted in an aqueous solution of NaCl (3.5 wt %) for a total exposure time of 144 hours, with a further extension to 192 hours. The panels were continuously monitored at various time intervals through visual inspections, and the observations were recorded using a digital camera.

Biocompatibility

The clotting of blood on polymer material was investigated by Lee-White method (Cheng et al. 2003) [35]. In short, blood (5 ml) without an anticoagulant was poured in the tube coated with polymer and kept in the water bath at 37ºC; time was measured until the fluidity of blood disappeared. In a glass tube (without polymer coating) 5 ml blood was added which was used as control. All the

experiments were performed in triplicates.

Results and Discussion

In recent years, the growing interest in the development of environmentally friendly paints and coatings has underscored the necessity to seek alternatives to fossil fuels. Hence, we have opted for curcumin extracted from renewable resource materials in the formulation of polyurethanes for coatings. Numerous reports can be found in the literature detailing the production of polyurethane (PU) from renewable resources such as vegetable oils and natural diols. Nevertheless, given the rising global population, utilizing edible oils for the production of such materials is not sustainable. In accordance with the aforementioned criteria, curcumin has been selected as the renewable resource-based material for the formulation of environmentally friendly PU coatings.

The synthesis of PUs involved the reaction between Curcumin and MDI as well as TDI, as shown in Scheme 1. Building on previous research that focused on segmented polyurethanes derived from plant-based oils and polyols, this study takes a step further by preparing PUs utilizing natural resources such as Curcumin [36].

Gel Permeation Chromatography (GPC) analysis

The Gel Permeation Chromatography (GPC) analysis of the solvent THF (tetrahydrofuran) soluble fraction of PUs revealed a molecular weight distribution typical for step growth polymerization. The GPC data and viscosity measurements of the PUs are presented in Table 1. CPU-1 exhibited a high molecular weight due to a significant degree of cross-li nking between Curcumin and MDI, facilitated by the presence of enolizable-OH groups. In contrast, the molecular weight noticeably decreased to 45164 for CPU-2, likely attributed to a reduction in the degree of cross-linking.

The intrinsic viscosities measured in THF were 0.47 for CPU-1, whereas all other samples showed values lower than 0.3 dL/g. This variation in viscosity is closely related to the molecular weights, suggesting that lower viscosity could potentially impact the mechanical properties of the PUs.

Table 1: GPC and viscosity data of CPU

Sample	Mn[a]	Mw[a]	Mw[a]/ Mn[a]	Intrinsic Viscosity[b]
CPU-1	23590	66972	2.83	0.47
CPU-2	20087	45164	2.24	0.31

[a]Data from THF soluble fraction (using polystyrene standard from GPC) [b]in THF at 25ºC

IR Spectra

The spectrum of curcumin exhibits a band at 3427 cm^{-1}, which corresponds to the -OH stretching vibrations, along with bands at 2931 and 2849 cm^{-1}, corresponding to symmetric and asymmetric -CH_2- stretching, respectively. The typical absorption peaks of polyurethanes, such as those at 3353 cm^{-1} (-NH stretching vibration), 1713 cm^{-1} (C=O stretching vibration), and 1230 cm^{-1} (C-O-C stretching vibration) for urethane, are clearly observed, indicating the presence of urethane in the synthesized Pus and which are in good agreement with the previously reported polyurethanes [37]. Furthermore, the disappearance of -OH and -NCO peaks further confirms the formation of PUs.

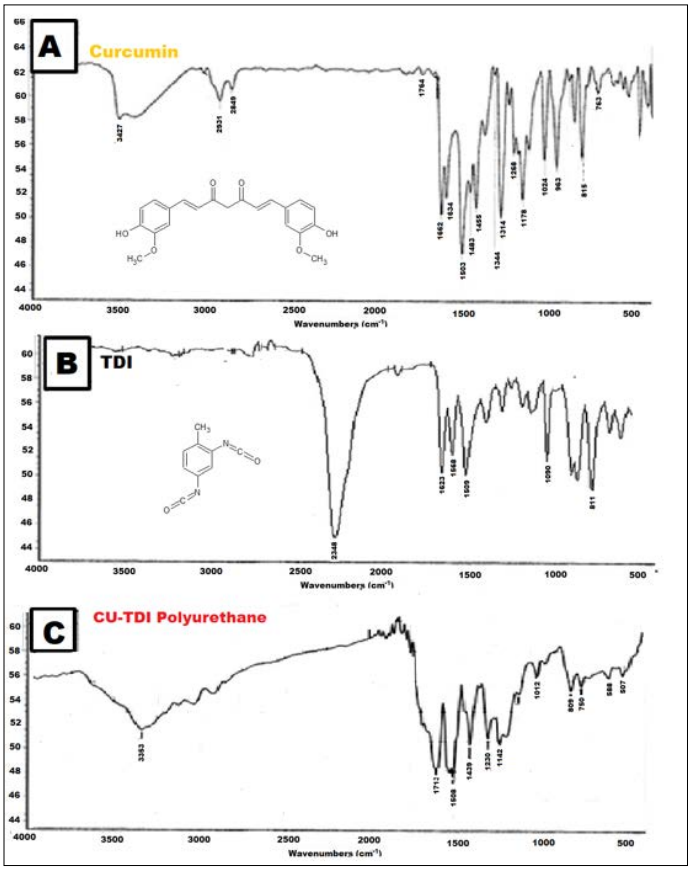


Figure 1: IR Spectra of A. Curcumin, B. TDI, C. CPU1 (CU-TDI Polyurethane)

Thermal Analysis

The TGA thermograms (Figure 2) demonstrate excellent thermal stability of the cured film, with minimal weight loss up to 250ºC, likely attributed to some unreacted components. The TGA analysis reveals a degradation process occurring in two distinct steps. In the first step, degradation through the urethane linkage may occur, leading to the formation of highly cross-linked products. Even at higher temperatures, the degradation proceeds at a slow rate, with a weight loss of 60%. However, the degradation process does not extend beyond 60% at 900 ºC. These results suggest that the development of PUs derived from natural resources, such as Curcumin, imparts enhanced thermal stability to the material compared with the already reported bio based polyurethanes by the Gaikwad et al [37]. The enhanced stability might be due to presence of the benzene rings of the curcumin.

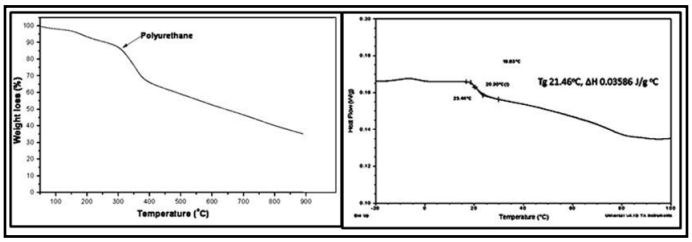


Figure 2: DSC and TGA Thermaograms of PUs

Application properties on PUs coatings

The application properties of PUs coatings with different MDI/TDI content are shown in Table 2.

Table 2: Effect of molar ratio of diols on coating properties

Molar Ratio of -NCO/OH	Dry Time[a] Hrs	Gloss 60°	Pencil Hardness	Impact Resistance [b, c]
1:1	9	81.2	2H	1.2 kg m
2:1	6	78.6	1H	>0.5 kg m
2.5:1	5	74.5	1H	>0.5 kg m

[a]Touch Dry time in hours; bDirect Impact Resistance; cReverse Impact resistance.

Table 2 demonstrates that the film performances of the samples meet the requirements for coating applications. The observed coating properties of the obtained CPU1 was due to the presence of the two benzene rings of the curcumin building block and in the chain. Further, the obtained CPU coatings shown the similar coating properties compared with the urethanes obtained by using the Karanja oil as polyol [37]. The molar ratio of MDI/TDI had minimal impact on the application properties of the PUs coatings, except for dry time, gloss, and impact resistance. The findings from the impact resistance tests indicate that an increase in the molar ratio of natural diols enhances the coating's flexibility while decreasing its hardness. Moreover, the gloss of the PUs coatings diminishes with an increase in the molar ratio of natural diols, including Curcumin.

Chemical Resistivity

The chemical resistivity of the PUs was assessed by subjecting them to various solvents. The PUs were placed in closed jars containing different solvents for 7 days, and their resistivity was monitored at 24-hour intervals by observing changes in their weights. The chemical resistivity data is presented in Table 3.

From the data, it became evident that all the prepared PUs displayed resistance to methanol, 1N sulfuric acid, 1N hydrochloric acid, and 1N NaOH. However, they showed susceptibility to a range of organic solvents, including acetone, DMSO, DMAC, NMP, and THF. This susceptibility provides a choice of solvents for processing in coating applications [32,37]. Furthermore, the PUs demonstrated resistance to both acid and alkali, indicating their potential for developing a variety of acid and alkali-resistant coating applications.

Table 3: Chemical Resistivity

Solvents	CPU1	CPU2
Methanol	-	-
Acetone	#	#
DMSO	#	#
DMAC	#	#
Chloroform	-	-
NMP	#	#
THF	#	#
1N H_2SO_4	-	-
1N HCl	-	-
1N NaOH	-	-

Note: '+' is soluble, '-' is insoluble and '#' is swelling. CPU1- Curcumin and MDI, CPU2- Curcumin and TDI

Biocompatibility

The blood clotting time on the CPU1 and CPU2 surface was used to assess the blood compatibility. Blood clotting time significantly increased as compared to reference glass, indicating the polymer's biocompatibility (Table 4). Similar blood compatibility was demonstrated by polymers that combine polyethylene glycol (PEG) and poly (3-hydroxybutarate) (PHB) [38,39].

Table 4: Biocompatibility of CPU polymers

Material	Blood Coating Time in Minutes
Glass	6.3±02
CPU1	8.1±0.3
CPU2	8.3±0.2

Conclusion

Successfully synthesized, a pair of PUs containing naturally derived diols like Curcumin exhibited remarkable thermal stability and resistance to both acids and alkalis, providing a wide range of solvent options for coating development. A preliminary assessment of application properties indicated that the PUs coatings showcased excellent flexibility, hardness, and chemical resistance. Interestingly, an increase in the molar ratio of natural diols, namely Curcumin, resulted in decreased gloss and hardness of the PUs coatings. It can be concluded that the curcumin based polyurethanes have excellent potential property for the coatings applications.

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Conflict of Interest

No Conflict of Interest.

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