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Sustainable Interpenetrating Polymer Networks using Waste Cooking Oil-Based Polyurethane and Polystyrene

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This study focuses on the synthesis of interpenetrating polymer networks (IPN) using waste cooking oil (WCO)-based polyurethane (PU) and polystyrene (PS) through a simultaneous method. The incorporation of IPN structures allows for the production of materials with desirable properties, particularly in terms of swelling behaviour due to the physical interlocking between the polymer networks. The present study aims to explore the utilisation of WCO as an environmentally friendly alternative, reducing its potential harm to the environment. WCO, being easily accessible and cost-effective, exhibits significant potential in product development. In this study, WCO was modified via transesterification to obtain WCO polyol, which was then utilised in the synthesis of the polyurethane network with methylene diphenyl diisocyanate (MDI) using stannous octoate (SnO_4) as a catalyst. Simultaneously, styrene was incorporated with benzoyl peroxide (BPO) as an initiator. The addition of trimethylolpropane triacrylate (TMPTA) in different percentages served as a crosslinking agent to form IPN, which was subsequently cast into films. The resulting films were characterised using Fourier-transform infrared spectroscopy (FTIR), and their physical properties were tested by a swelling test. FTIR confirmed the formation of IPN structures, while the swelling behaviour exhibited promising results attributed to the presence of TMPTA as a crosslinker.

Keywords: Interpenetrating polymer network; waste cooking oil; polyurethane; polyol, crosslinker

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An IPN is a combination network consisting of two or more polymers intimately joined together, forming interwoven structures. This system synthesises and cross-links one polymer in the immediate presence of another polymer. These multiple distinct polymers coexist as a continuous, interconnected network [1]. At a macroscopic level, the polymers within the system create continuous phases. IPN shares similarities with block copolymers, where domain size depends on block length. The chain length between cross-links also determines the domain size in IPN systems. However, the key distinction between copolymers and IPN lies in phase separation. In the presence of a cross-linker in the system, IPN exhibits intersecting high-entanglement network structures that promote phase continuity.

The use of eco-friendly resources in the polymer field has garnered significant attention from researchers, given their potential to replace petrochemical-based derivatives. Researchers have placed significant emphasis on exploring and developing novel materials sourced from renewable resources [2, 3]. Sustainable sources can also yield polyols, a key component of PUs [4–6]. Natural oils like rapeseed, soybean, and palm oil, after undergoing appropriate chemical modifications, serve as valuable resources for synthesising porous PU materials [7, 8]. However, it is worth noting that most vegetable oils fall into the category of first-generation bio-based raw materials. This implies that the production of polyols from edible oils competes with food production [9]. One notable resource in this context is vegetable oil, which has found widespread use in the production of bio-based polyols. These biobased polyols are instrumental in bolstering the renewable component of various products and are valued for their cost-effectiveness and outstanding performance [10]. They have been employed in several areas, including the automotive industry, the manufacturing of athletic goods, and the fabrication of flexible and rigid foams, as well as thermoplastics.

This study delves specifically into the utilisation of WCO, a byproduct resulting from cooking meals using edible vegetable oils [11]. Unfortunately, the significant quantity of WCO produced poses serious health risks for both humans and animals if ingested, and it also presents substantial environmental challenges when not handled responsibly. Regrettably, urban areas often dispose of WCO haphazardly, leading it into sewage systems, drains, open spaces, rivers, and

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wooded areas. This careless disposal results in the release of unpleasant odours, blockages in drainage systems, deterioration of concrete infrastructure, and contamination of both terrestrial and aquatic ecosystems [12]. Furthermore, inadequate management of WCO can lead to issues such as foam formation, an increase in organic content in water sources, disruption of wastewater treatment processes, decreased levels of dissolved oxygen, and disturbances in ecological balance. Therefore, finding sustainable alternative uses for WCO, such as its conversion into value-added and versatile products like PU, represents a highly practical solution [13].

In the field of materials science, where innovation and sustainability converge, IPNs represent a remarkable paradigm shift. These intricate matrices of polymers hold the potential to develop industries by combining the versatility of PU and polystyrene (PS) with the sustainable edge of WCO-based polyols. Therefore, this study aimed to observe the interaction between IPN, polyols, and polyurethanes. The revolutionary introduction of polyols based on WCO in the context of PU/PS IPN offers a promising path towards the development of sustainable materials.

EXPERIMENT

Chemicals and Materials

WCO was collected from a residence and purified using coconut husk-activated carbon (AC). This work used the following materials: sodium hydroxide (NaOH), ethanol, phenolphthalein indicator, phthalic anhydride-pyridine reagent, pyridine, potassium hydroxide, diethanolamine (DEA), monomer ethylene glycol (MEG) and phthalic anhydride (PA), MDI, stannous octoate as catalyst, styrene, benzoyl peroxide (BPO) as co-initiator, and trimethylolpropane triacrylate (TMPTA) as a crosslinker. Meanwhile, toluene, chloroform, and tetrahydrofuran (THF) were used as solvents in the solubility test.

Methodology

A sample of WCO was obtained from waste palm oil used after cooking meals in a household. The initial step involved the treatment process of WCO by filtering the WCO using filter paper to eliminate any suspended particles. Subsequently, 100 mL of the filtered WCO was heated within the temperature range of 95–125 °C. Approximately 0.5 grams of activated carbon derived from coconut husks were introduced into the WCO and left in contact for 24 hours. Following this, the adsorbed WCO was agitated at 500 rpm and maintained at a temperature of 110 °C for 1 hour. The adsorbed WCO was then subjected to filtration using filter paper and analysis through FTIR spectroscopy to determine the percentage of free fatty acids (% FFA) [5].

To create a polyhydric compound used for transesterification, DEA, MEG, and phthalic PA were mixed homogeneously in a ratio of 90:7:3. This solution was thoroughly stirred and left to stand overnight. The transesterification reaction was executed by mixing the adsorbed WCO-based polyol with the polyhydric compound solution in a ratio of 80:20, respectively. The resulting mixture was heated and continuously stirred at a temperature range of 185–195 °C with a continuous stirring rate of 200 rpm for 20 minutes. This process resulted in the formation of polyol, which was subsequently analysed using FTIR spectroscopy, % FFA, acid value, and hydroxyl (OH) value.

To synthesise the PU/PS IPN, a mixture involving the PU (NCO/OH ratio: 0.6, 0.8, and 1.0) and styrene in an 80:20 weight ratio was used. Methylene diphenyl diisocyanate (MDI) was incrementally introduced to epoxidized transesterified palm WCO polyol while the mixture was being mechanically stirred; this process was conducted at temperatures ranging from 45°C to 50°C. Stannous octoate was included as a catalyst throughout the 2-hour reaction. Additionally, styrene monomer was introduced into the mixture during the reaction.

The IPN formation process involves the incorporation of an initiator, benzoyl peroxide (BPO), at a concentration of 1.4% by weight of styrene. The co-initiator and crosslinker, TMPTA, were added at different concentrations of 0.5%, 1.0%, 1.5%, and 2% by weight of styrene. Following the addition of these components, the reaction proceeded and was subsequently allowed to stand for 24 hours at room temperature.

Characterization Methods

Chemical Properties

The characterization of WCO encompasses the assessment of the acid values and percentage of free fatty acids (% FFA), while the hydroxyl (OH) value determination of WCO polyol conforms to the rigorous specifications outlined in ASTM D4274-05 [16].

Fourier Transform Infrared (FTIR)

The FTIR spectra of the samples were recorded with a PerkinElmer 400 spectrometer. The acquisition parameters were done with a total of 8 accumulations at 4 cm^{-1} resolution with a spectral range of 4000–500 cm^{-1}.

Solubility Test

The solubility test was performed by keeping the 0.01–0.03 g of polymer film in 20 ml of solvent (chloroform, THF, toluene, and DMSO). The solubility test was conducted in three ways: first, by immersing the semi-rigid PU samples at room temperature for 4 hours, and then by agitation for 4 hours. If there were no changes in the weight loss, the test was continued by heating for 4 hours with agitation. The mixture was filtered through filter paper (porosity 2µm) and dried under vacuum to a constant weight. Then, from the weight of the dissolved polymer, the soluble fraction was measured using equation (1):

Solubility fraction (%): $[((Wo - Wt)/Wo)x\ 100]$ (1)

where Wo is the weight of the original films and Wt is the weight of residual films after the solubility test.

RESULTS AND DISCUSSION

Chemical Properties

Table 1 provides a summary of the characteristics of waste cooking oil (WCO) and polyol derived from WCO. The utilisation of activated carbon from coconut husk in the purified process led to a decrease in the percentage of free fatty acids (% FFA) and the acid value in the WCO sample. Next, a transesterification reaction produced polyol from the purified WCO. Transesterification is a chemical reaction that typically involves the replacement of alcohol in an ester with another substance [14]. The obtained polyol has an OH value of approximately 449 mg KOH/g. The polyols derived in this step exhibit a highly desirable hydroxyl index, ranging between 400 and 600 mg KOH/g. The obtained value categorises the products within the group of polyols commonly employed in the synthesis of commercial PU rigid foams and films [10].

FTIR Analysis

With the aid of the FTIR spectrometer depicted in Figures 1 and 2, the structure of the polyol derived from WCO was determined. The polyol consisted of chains of fatty acids with carboxylic acid groups. The confirmation of the synthesis of WCO-based polyols was achieved through the presence of peaks at 3290 cm^{-1}corresponding to the hydroxyl (-OH) group, respectively. The C-H stretching peaks were observed at 2923 cm^{-1} and 2852 cm^{-1}[14], while the peaks for O-H bending were located at 1121 cm^{-1} [15, 16].

Table 1. Characteristic of WCO, adsorbed WCO, and WCO-based polyol.

Properties	**Raw WCO**	**Purified WCO**	**WCO-based polyol**
Free Fatty Acids (% FFA)	2.82	1.12	-
Acid Value (mgKOH/g)	5.61	2.24	-
OH value (mg/KOH/g)	-	-	449.02

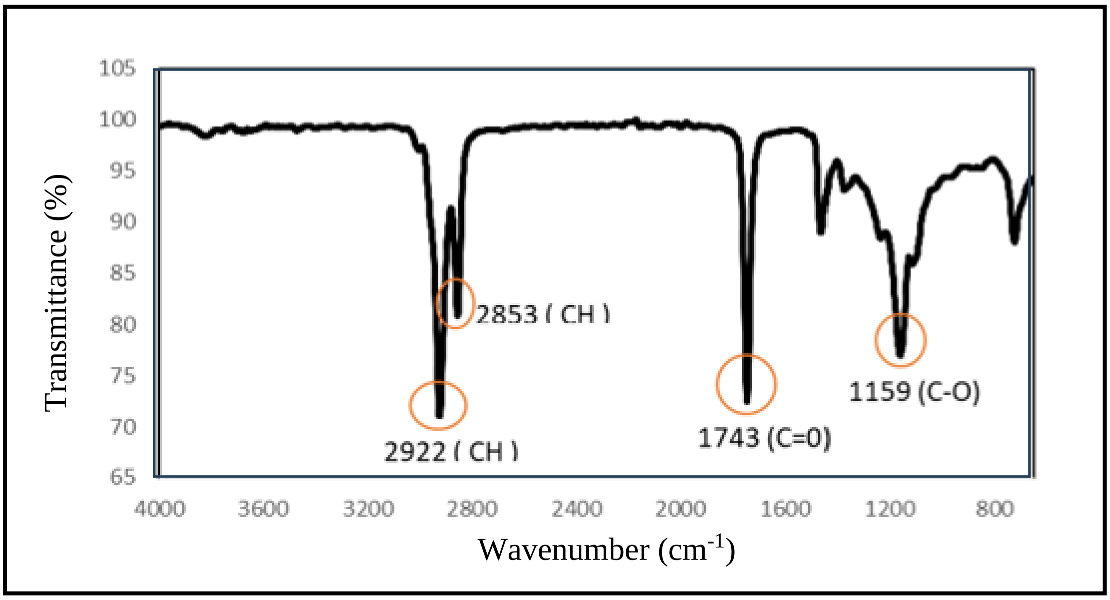

Figure 1. The FTIR spectrum of purified WCO.

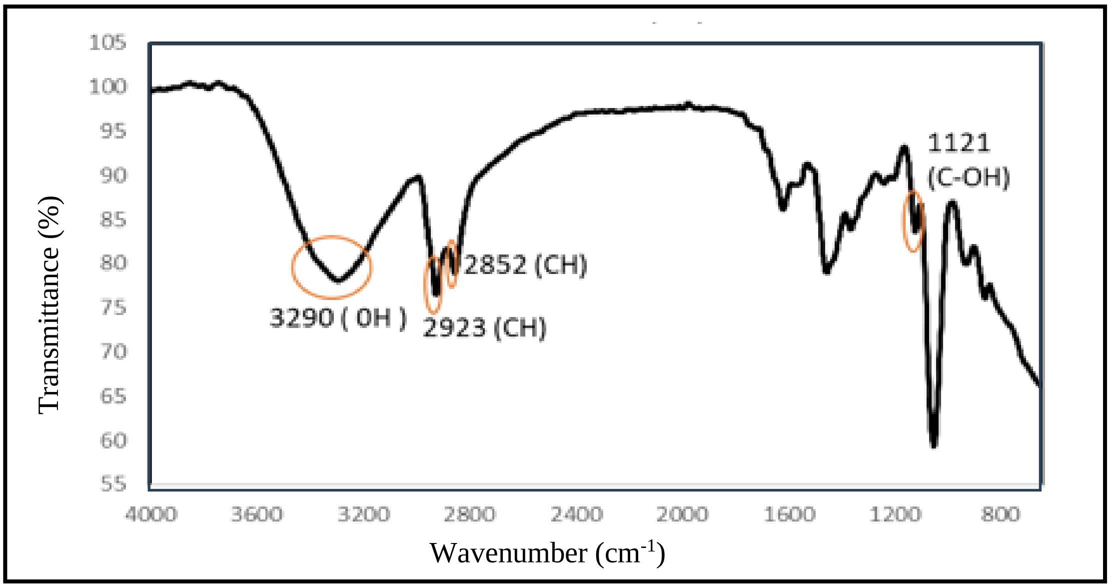

Figure 2. The FTIR spectrum of WCO polyol.

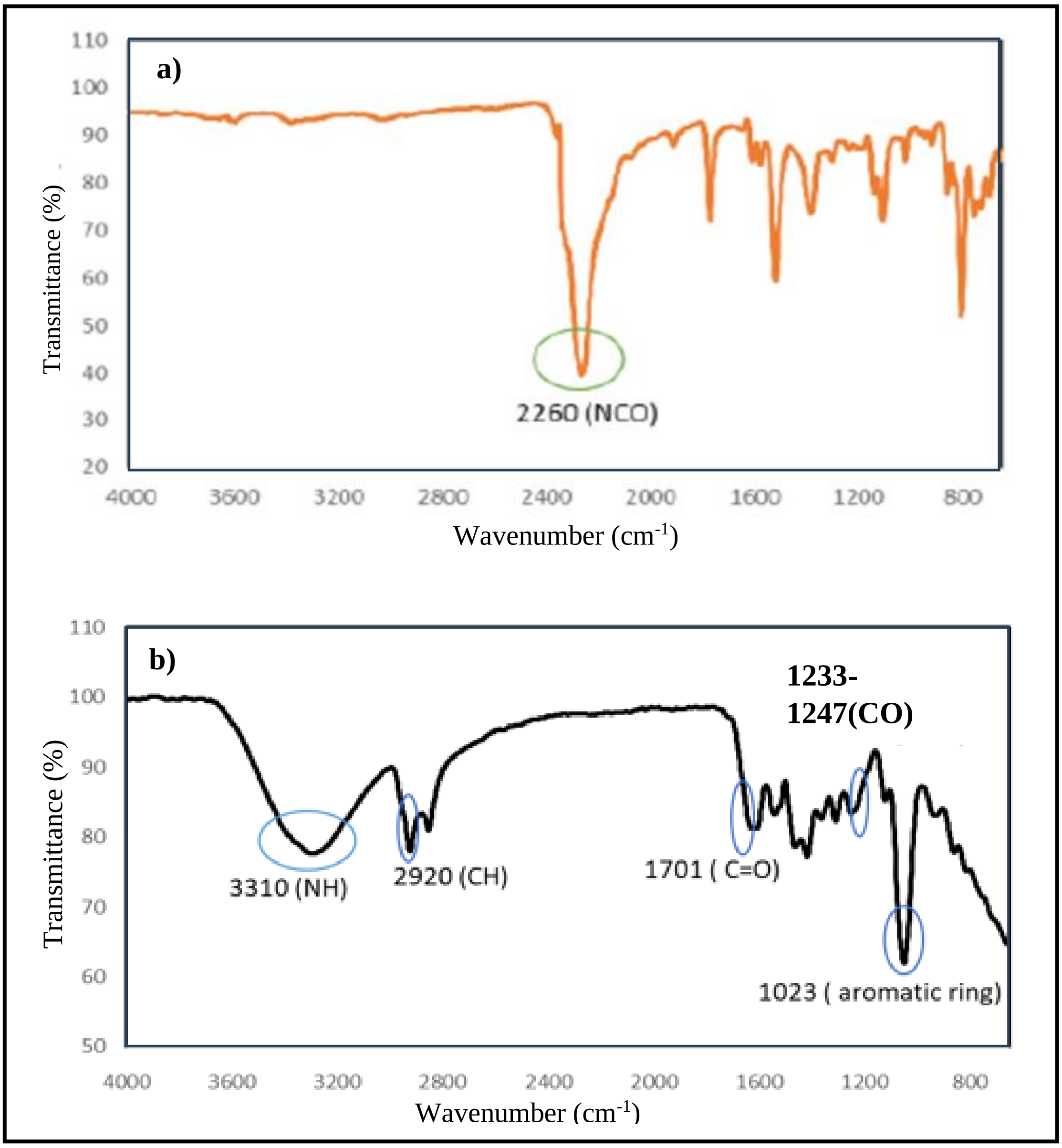

Figure 3. The FTIR spectra of a) MDI and b) PU/PS IPN.

The FTIR spectra of MDI and PU/PS IPN are shown in Figure 3. The prominent peak at 1701 cm^{-1}1) signifies the presence of the -C=O (carbonyl) group in the urethane linkage. The N-H stretching vibrations of the urethane linkage manifest as a broad band extending to 3310 cm^{-1} [14, 15]. Meanwhile, the bands around 1023 cm^{-1} indicate the presence of the PS aromatic ring. The absence of the peak at 2260 cm^{-1} suggests that each -NCO group has interacted with the -OH group of the polyol, forming a urethane bond [3]. Additionally, a distinctive peak at 2920 cm^{-1} is an overlapped peak that corresponds to CH_2 stretching in PU and the methylene group in PS. Meanwhile, the peak around 1223–1247 cm^{-1} is attributed to CO and -CH_2 of the aliphatic chain of PU [3, 15].

Solubility Behaviour

THF and toluene exerted a significant influence, particularly in the non-polar domain. As indicated in Table 2, the NCO/OH ratio plays a pivotal role in dictating solubility behavior, as observed in PU samples with NCO/OH ratios of 0.6, 0.8, and 1.0. A higher NCO/OH ratio within a sample enhances solvent resistance and augments crosslinking in the polymer. This increased crosslinking renders the sample less soluble in the solvent used for solubility testing. The highly crosslinked network poses a barrier for solvent molecules, making it challenging for them to infiltrate and disrupt intermolecular interactions, consequently leading to reduced solubility of the sample [16].

In the solubility test, adding a higher amount of TMPTA to the sample leads to reduced solubility in the chosen solvent. The nature of TMPTA as a crosslinking agent, at elevated concentrations, promotes the formation of a more crosslinked polymer network [17, 18]. The increase in crosslinking hinders the movement of polymer chains and diminishes the available sites for solvent interaction. Consequently, the highly crosslinked polymer exhibits decreased solubility, presenting a challenge for the solvent molecules to dissolve the sample during the solubility test.

Toluene is characterised by a predominantly nonpolar molecular structure consisting of carbon (C) and hydrogen (H) atoms. It lacks significant polar functional groups or bonds, limiting its ability to establish robust hydrogen interactions with polar molecules. The solubility behaviour of the IPN blend in toluene is influenced by the relative polarity of its polymer components. PS, as a nonpolar polymer featuring repeated phenyl groups, exhibits exceptional compatibility with toluene, a nonpolar solvent. This compatibility arises from the matched nonpolar characteristics of both the solvent and the polymer, facilitating rapid dissolution of the PS component in toluene during the solubility test [19]. Conversely, the PU component of the IPN blend incorporates polar functional groups like carbonyl groups (C = O) and urethane linkages (-NHCOO-). The presence of these polar groups may limit solubility in nonpolar toluene, as the solvent's nonpolar nature hinders strong interactions with the polar polymer. Consequently,

Table 2. Solubility behaviour of PU/PS IPN based on different NCO/OH ratio of PU

Samples	**Solvents**		
	Toluene	**Chloroform**	**THF**
0.6 NCO/OH ratio & 0.5% (TMPTA)	++*	±*	++*
0.8 NCO/OH ratio & 0.5% TMPTA)	++	±	++
1.0 NCO/OH ratio & 0.5% TMPTA)	-	-	-

Note of solubility: ++ = soluble; - = insoluble; ± = partly soluble; * = room temperature

Table 3. Solubility behaviour of PU/PS IPN based on different percentage of TMPTA

Samples	**Solvents**		
	Toluene	**Chloroform**	**THF**
1.0 NCO/OH, 0.5% (TMPTA)	±*	±*	++*
1.0 NCO/OH ratio & 1.0% TMPTA)	±	±	±
1.0 NCO/OH ratio & 1.5% TMPTA)	-	-	±
1.0 NCO/OH ratio & 2.0% TMPTA)	-	-	-

Note of solubility: ++ = soluble; - = insoluble; ± = partly soluble; * = room temperature the toluene solubility test may result in partial dissolution or swelling of the IPN blend, with the PS component demonstrating greater solubility than the PU component. For applications requiring complete dissolution of the IPN blend, exploration of alternative solvents with higher polarity or enhanced compatibility with both PU and PS is recommended.

In the solubility test of the PU/PS IPN, chloroform serves as a moderately polar solvent with a low dielectric constant. Due to its moderate polarity, chloroform exhibits the capability to dissolve both polar and nonpolar compounds to some extent. Because of its interactions with polar functional groups, chloroform is more likely to dissolve polar substances (PU) effectively, but it can also interact to some extent with nonpolar compounds (PS) [20, 21]. The solubility behaviour of the IPN blend in chloroform can be intricate, leading to partial solubility or swelling.

THF is employed as the solvent in the solubility test involving PU/PS IPN. Due to the fact that THF is a liquid with the capacity to partially dissolve both polar and nonpolar compounds, it successfully dissolves both the polar PU and the nonpolar PS components of the IPN. In this context, polar signifies the presence of electric charges that attract other molecules, while nonpolar indicates the absence of significant electric charges. The ability of THF to dissolve both components of the IPN blend makes it effective in creating a solution containing both polymers. This contributes to a better understanding of how these polymers interact with each other [20].

TMPTA acts as a crosslinking agent for most IPN components [17, 22–24], creating covalent bonds between the polymer chains of PU and PS in this IPN product. The interweaving of these two polymer networks results in a more robust and cohesive material with enhanced resistance to solvents. The crosslinked structure imparted by TMPTA enhances the chemical resistance of the IPN [24]. When subjected to a variety of solvents and chemicals, the closely interlocked networks make the material less susceptible to chemical attack or degradation. This attribute proves particularly valuable in applications where the IPN is exposed to harsh chemicals or challenging conditions.

Table 3 shows that the crosslinking rate in the IPN can be changed by fine tuning the concentration of TMPTA and changing the reaction conditions. This precision enables meticulous management of the material’s curing duration, a critical aspect in tailoring the IPN’s characteristics and processing parameters during manufacturing. TMPTA, acting as a crosslinking agent, not only enhances adhesion between the PU and PS phases in the IPN, but also forms covalent bonds at the interface, leading to increased interfacial contacts and overall improved adhesion between the two polymer networks [18]. This heightened adhesion significantly contributes to the mechanical integrity and durability of the IPN.

Additionally, TMPTA exhibits UV curability [17, 18], indicating its ability to cure rapidly upon exposure to UV light. This attribute proves beneficial in specialised applications requiring swift processing and curing. TMPTA-based UV-curable IPNs can be effectively utilised in a variety of industrial processes, including 3D printing and coatings, offering efficient and time-saving solutions.

CONCLUSION

In conclusion, WCO emerges as a prospective substitute for petroleum and virgin vegetable oils in the production of PU/PS IPN films. The pretreatment of WCO using activated carbon effectively eliminated impurities, leading to enhanced colour and odour. To generate polyol from the adsorbed WCO, a transesterification reaction was employed, introducing OH groups into the structure. The presence of an OH absorption peak in the FTIR spectrum confirmed the successful synthesis of WCO-based polyol. Furthermore, the researchers successfully synthesised a rigid PU/PS IPN-based polyol, as evidenced by the presence of urethane linkage in the FTIR spectra and the disappearance of the NCO peak at 2260 cm^{-1}. The study also investigated the impact of TMPTA as a crosslinking agent on the formation of PU/PS IPN, demonstrating favourable solubility behaviour in the resulting films.

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