World Journal of Innovation and Modern Technology, Vol. 6, Issue 5, (Oct) **2023**
ISSN 2682-5910

DOI: 10.53469/wjimt.2023.06(05).09

Preparation and Characterization of Sweet Potato Residue based on NIPU

Zhongshu Man

Institute of International Education, Beijing University of Chemical Technology, Beijing 100029, China

Abstract: ***This research explores the synthesis of non-isocyanate polyurethane (NIPU) materials using sweet potato residue as a biomass-based raw material. The study involves a multi-step process, including oxypropylation and epoxidation reactions to activate hydroxyl groups within sweet potato residue, resulting in hydroxyl-activated sweet potato residue oil (HAPO). Subsequently, HAPO is further modified through epoxidation, leading to epoxidized HAPO (Expo-HAPO). These intermediate products are then utilized in the preparation of NIPU films by cross-linking with various polyamines. The study emphasizes the importance of maintaining specific molar ratios for optimal cross-linking. Characterization techniques, such as FT-IR and 1H-NMR, confirm the successful reactions and molecular changes during the process. Additionally, the incorporation of lignin oil enhances mechanical properties and UV resistance in the NIPU films. This research expands the application scope of NIPU materials, making them more environmentally friendly and versatile.***

Keywords: Non-isocyanate polyurethane (NIPU); Sweet potato residue; Biomass-based materials; Oxypropylation; Epoxidation.

1. INTRODUCTION

Polyurethane is a polymer material that has been important since it was first synthesized. It has excellent mechanical properties, thermodynamic properties and corrosion resistance and has been widely used in industrial production [1]. In 1937, German chemist Otto Bayer invented the industrial-scale synthesis method of polyurethane and successfully prepared polyurethane foam containing a large amount of polyurethane elastomer [2].

Due to the fact that in traditional processes, the production of polyurethane requires two primary raw materials, polyols and isocyanates, both of which are derived from the petrochemical industry, this exacerbates our consumption of finite non-renewable resources and is detrimental to environmental preservation [3]. In order to meet this challenge, using green biomass resources to prepare polyurethane has become the focus of research in the polyurethane industry and biomass industry. Since the isocyanates required for synthesis are usually obtained from petroleum and highly toxic phosgene, they can cause harm to humans and the natural environment during application. Residual isocyanates in polyurethane materials can adversely affect the human body, such as skin irritation and Long-term asthma [4]. During the disposal of waste polyurethane, toxic substances formed by burning or landfilling can also cause environmental pollution [5]. These make it more urgent for us to find more efficient and environmentally friendly synthesis strategies to prepare polyurethane.

Among the many alternative materials, the synthesis of non-isocyanate polyurethane (NIPU) is considered a more efficient, environmentally friendly and versatile strategy [6]. Among these, NIPU synthesized using cyclic carbonates and polyamines as crosslinkers is regarded as the most environmentally friendly approach.

Sweet potato residue refers to the residue left after nutritious components such as sweet potato starch, sugar and protein are extracted. It is an industrial by-product. Starch is a relatively cheap bio-based polymer with excellent thermal solubility, biocompatibility, and biodegradability, making it a promising raw material for developing biodegradable plastics [7]. Therefore, this paper selected sweet potato residue as the biomass-based basic raw material for preparing NIPU films in this experiment. Its main purpose is to enable the starch in sweet potato residue to participate in the synthesis of non-isocyanate polyurethane (starch is a high-quality composite additive), the remaining ingredients can make up for the shortcomings of pure starch in reaction stability to a certain extent.

2. MATERIALS AND METHODS

2.1 Materials

The materials involved in this study include:

anhydrous ethanol, epoxy propane, acetone, anhydrous glycerol, tetrahydrofuran, deuterated chloroform, potassium hydroxide, epoxy chloropropane, N,N-dimethylformamide, isophorone diamine, deuterated pyridine, deuterated-DMSO, tetra-n-butylammonium bromide, 1,6-hexanediamine, ethylenediamine, polyethyleneimine, diethylenetriamine, boron trifluoride etherate, CO2 gas, and oligomeric lignin oil.

2.2 SPR's oxygenation.

Before starting the reaction, we need to thoroughly mix 10g of sweet potato residues (SPR) with ethanol and KOH solution, which initially aims to activate the hydroxyl groups in the sweet potato residue. Next, we used an electronic balance to weigh 15g of acetone, 5g of propylene oxide and 12% by weight of glycerol and added them to the mixture solution in sequence. Place it into the high-pressure reactor according to the correct operation, set the reaction temperature of the reactor to about 150°C, and set the stirring rate to 500 rpm, and the reaction duration is about two hours. After that, close the reactor and wait. After cooling to room temperature (about 25°C) and the pressure pointer pointing to 0, open the reaction kettle, take out the polytetrafluoroethylene liner, and observe and stir the prepared product solution. If small solid particles are present, we use acetone to rinse the corresponding solid part multiple times until it is completely dissolved in the product solution. Finally, we placed the mixture solution into a vacuum oven set at 30°C to dry the product. We ultimately obtained 4.02g of SPR oil with activated hydroxyl groups (Hydroxyl-activated SPR oil, HAPO).

2.3 Preparation of HAPO by Epoxidation

We used the HAPO prepared in the previous stage as raw material to prepare epoxidized HAPO (Expo-HAPO). The ultimate goal was to introduce epichlorohydrin into hydroxyl-activated sweet potato residue oil. The reaction formula of the entire stage is shown in Figure 1. Add 5 g of HAPO (0.067 mol) and the required reaction process catalyst Lewis acid $(C_2H_5)_2OBF_3$ (0.033g, 0.0023 mol). The molar ratio of the two components is 1:20 relative to the added HAPO. Mix them in a 100-mL round-bottomed flask and add the DMF (N, N-dimethylformamide) solution as the reaction solvent substrate. Stir to mix thoroughly. Then, it was placed in an oil bath for reaction; the reaction temperature was set to 90°C, and the reaction time was 4 hours. During this process, epichlorohydrin was added to the entire reaction system at a ratio of 1:1 (4.13g, 0.14 mol). After the reaction time, set the oil bath temperature to 60°C. After reaching the set temperature, weigh the same 1:1 molar ratio of sodium hydroxide (NaOH) (3.73g, 0.14 mol) and add it to the reaction system. After waiting for a while, after the sodium hydroxide is wholly dissolved and reacted, the prepared epoxidized HAPO (Expo-HAPO) is washed with an appropriate amount of acetone and DMF solution. Finally, 6.27g of Expo-HAPO is obtained. The yield of this step is approximately 76.5%.

2.4 The carbonation preparation of Expo-HAPO to produce Carb-HAPO

We conduct the preparation process of carbonated sweet potato pomace oil (Carb-HAPO). The whole process is mainly catalyzed by the TABA catalyst to fix carbon dioxide in Expo-HAPO to obtain the final product we need. First, we added Expo-HAPO (10g, 0.55 mol) and TABA (tetrabutylammonium bromide) (0.73g, 0.00272 mol) prepared in the previous stage into a 100 mL round-bottomed flask and weighed 12g of hydrogen carbonate. Sodium $NaHCO_3$ (0.14 mol) can also be added slightly more to ensure sufficient introduction of CO_2. Slowly add sodium bicarbonate in batches to the round-bottom flask. Set the oil bath temperature to 110°C and the reaction time to 10 hours to fix carbon dioxide. If there are signs of evaporation during this period, an appropriate amount of DMF solution can be added. Subsequently, the oil bath temperature was set to 90°C, and the system was stabilized for ten hours. After obtaining the prepared product, separate the solid part and rinse it with acetone and DMF solvents. After drying the product, we obtained approximately 10.73 g of Carb-HAPO, yielding approximately 83.7%.

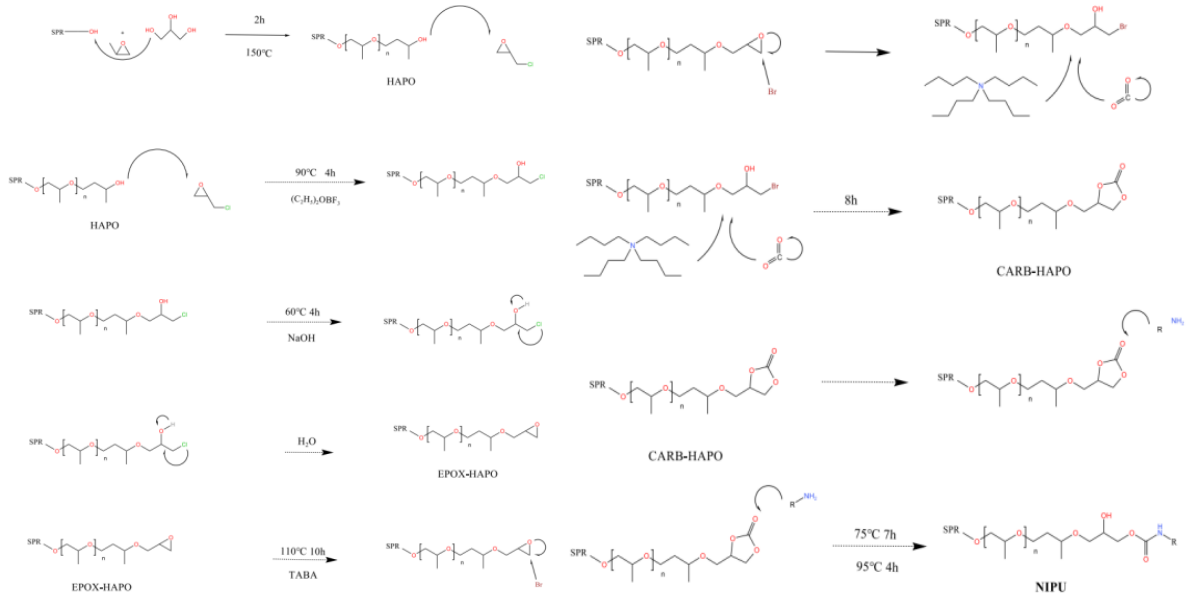

Figure 1: Reaction process for preparing NIPU by SPR

2.5 Characterization

Calculate the yield of reaction product samples at each stage.

$$\text{Yield (\%)} = m1/m2 \times 100\%$$

m1: The mass of the lignin sample obtained after processing.

m2: The mass of initial biomass added before treatment.

Gel Permeation Chromatography (GPC);Fourier Transform Infrared Spectroscopy (FT-IR) characterization;

Proton Nuclear Magnetic Resonance (1H-NMR) characterization; Apparent Structure Characterization of NIPU Thin Films; Ultraviolet Resistance Characterization of NIPU Thin Films.

3. RESULT

3.1 Synthesis and characterization of functionalized SPR as NIPU precursor

By employing the oxypropylation reaction, we successfully activated the hydroxyl groups within the sweet potato residue (SPR). To ensure optimal conditions for the entire reaction, it was imperative to maintain an alkaline environment. This was achieved by carefully proportioning the quantities of glycerin and potassium hydroxide introduced into the reaction substrate, thereby enhancing the adaptability of the sweet potato residue and promoting its reactivity throughout the process.

Throughout the reaction, the temperature initially exceeded our predetermined setpoint. However, it subsequently exhibited a gradual decline before stabilizing. This temperature profile indicates the smooth progression of the oxypropylation process, which is inherently exothermic. It's worth noting that variations in temperature also influence the pressure within the reactor to some extent.

Over the course of the two-hour oxypropylation reaction, we achieved a remarkable liquefaction efficiency of sweet potato residue, exceeding 90%. This conclusion is supported by the gel permeation chromatogram (GPC spectrum) depicted in Figure 2. In this figure, the resulting product (HAPO) exhibits a narrow distribution within the GPC spectrum. This observation signifies that the molecules derived from sweet potato residue (SPR) are relatively uniform in size after two hours of liquefaction. Consequently, the liquefaction efficacy of the entire process is distinctly evident.

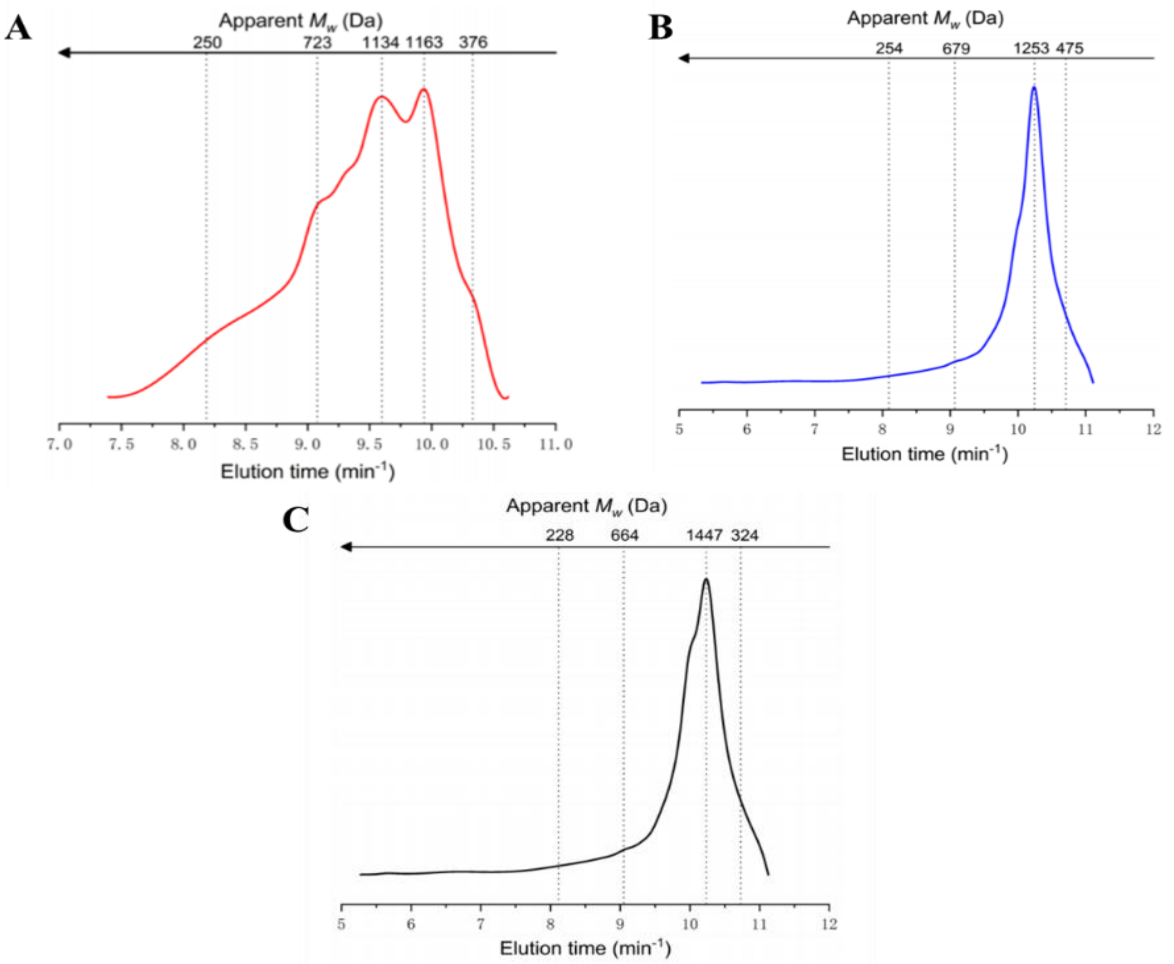

Figure 2: A GPC spectrum of SPR derivative HAPO; B GPC spectrum of SPR derivatives Expo-HAPO; GPC spectrum of C SPR derivative Carb-HAPO

In this study, we employed FT-IR (Fourier transform infrared spectroscopy) and 1H-NMR (hydrogen nuclear magnetic resonance spectroscopy) to characterize the products resulting from the oxypropylation reaction of sweet potato residue (SPR). The spectra obtained from these techniques were presented in Figure 3.

While it is important to note that this study does not allow for a direct comparison between the complex raw materials of sweet potato residue and the corresponding products following the oxypropylation reaction, the experiments reveal distinct features in the FT-IR spectrum of the reaction products. Specifically, Figure 3 highlights prominent absorption peaks at 2927 cm^{-1} and 2861 cm^{-1}, which correspond to the stretching vibrations of two specific aliphatic groups, $-CH_2$ and $-CH_3$. The robust signal associated with the characteristic peak at 2861 cm-1 is of particular significance, attributed to the -CH3 aliphatic group. This signal is compelling evidence of the effective extension of the oxypropyl chain during the activation of hydroxyl groups within SPR.

Additionally, there is a noteworthy vibration peak at 3442 cm^{-1} in the FT-IR Fourier transform spectrum. This intense peak corresponds to the hydroxyl-OH groups and is a distinctive indicator of the hydroxyl groups' presence. The existence of this characteristic peak signifies that during the oxypropylation reaction of sweet potato residue (SPR), the breakdown of macromolecules within SPR frequently occurs in tandem with the extension of the entire oxypropyl chain and the successful activation of the corresponding hydroxyl groups.

Similarly, in the 1H-NMR spectrum at this stage, we observe the detection of aliphatic methylene protons in the 3.80 to 3.85 ppm range. This finding strongly corroborates the conclusions drawn from the FT-IR spectrum analysis. Therefore, it can be confidently stated that following the oxypropylation reaction, SPR undergoes effective dissolution and liquefaction, transforming it from its original solid state. Moreover, the results from the analysis of the liquefied sweet potato residue (SPR) reveal a more pronounced liquefaction effect, a relatively uniform molecular weight distribution, and the successful exposure of highly activated hydroxyl groups. These findings collectively lay a solid foundation for the subsequent hydroxyl activation of sweet potato residue and the further epoxidation of HAPO to prepare EXPO-HAPO, marking significant progress in this research endeavor.

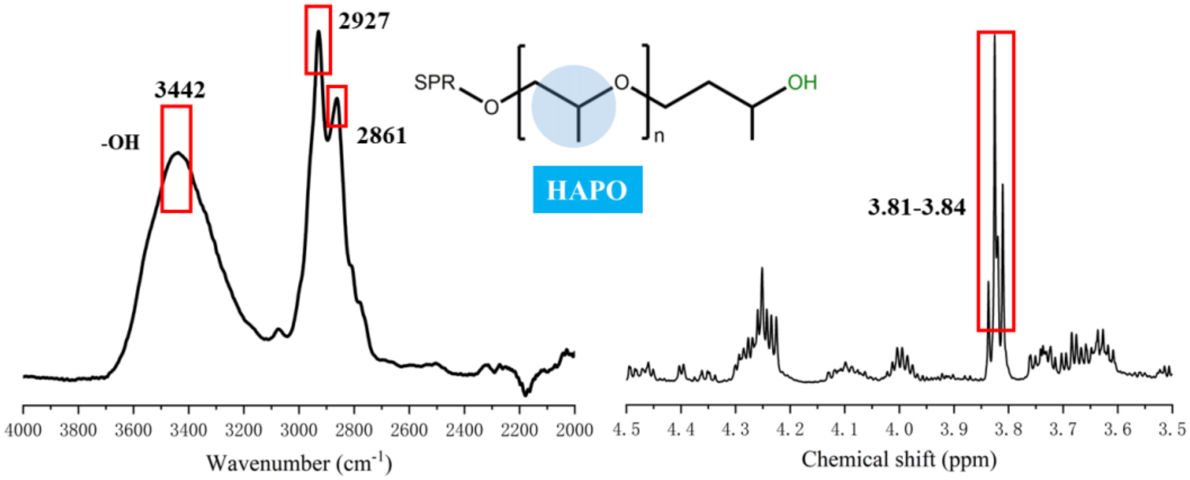

Figure 3: The characterization of SPR during the functionalization process. FT-IR (left) and 1H-NMR (right) spectra of HAPO

The epoxidation reaction of HAPO is a crucial chemical process with extensive applications across various fields. The experimental procedure for this reaction is outlined in Figure 4, and the entire process can be divided into two distinct stages.

In the first stage, HAPO derived from sweet potato residue (SPR), as prepared in the preceding step, undergoes a reaction with epichlorohydrin, yielding two important substances: epoxy resin and o-chlorohydrin resin. To facilitate this reaction, we employ a Lewis acid $(C_2H_5)_2O \cdot BF_3$ as a catalyst. The role of this Lewis acid is pivotal in catalyzing the reaction effectively. During this reaction stage, the -BF3 group introduced by the Lewis acid serves as an initiator, enabling the successful occurrence of the reaction. This initiation step promotes the cationic ring-opening polymerization of epichlorohydrin within the solution and facilitates its interaction with the hydroxyl groups present in the solution.

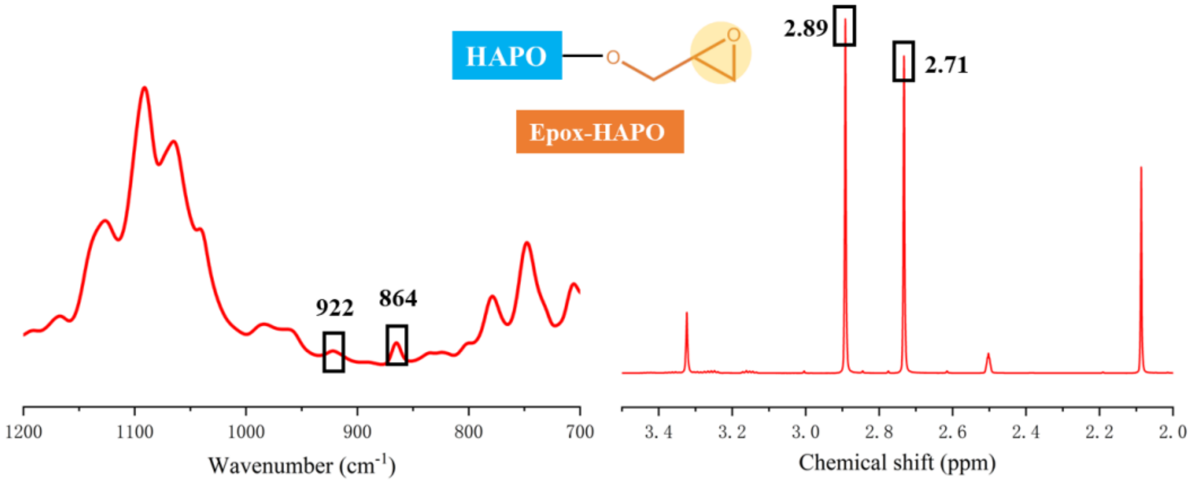

Figure 4: The characterization of SPR during the functionalization process. FT-IR (left) and 1H-NMR (right) spectra of Expo-HABO

In the second stage of the reaction, the o-chlorohydrin resin or epoxy resin, which was produced in the first stage, undergoes a dehalogenation process under the influence of NaOH, ultimately yielding Expo-HAPO. Throughout this entire reaction process, we employed two characterization techniques, namely FT-IR and 1H-NMR, to monitor the reaction's progress in real time. As depicted in Figure 5, we can discern two distinctive characteristic peaks in the FT-IR spectrum. The first of these is the prominent peak at 922 cm^{-1}, which conveys crucial information. This peak represents the asymmetric absorption of the epoxy group, while the second characteristic peak, observed at 864 cm^{-1}, corresponds to the symmetric absorption of the epoxy group. Furthermore, our analysis of the 1H-NMR spectrum confirms the successful completion of the entire epoxidation reaction. Notably, the presence of two distinct single peaks at 2.71 ppm and 2.89 ppm in the spectrum confirms the transformation of HAPO into Expo-HAPO.

Also, the molecular weight of Expo-HAPO, as prepared in the experiment, tends to be slightly higher than that of HAPO. It is worth noting that after the epoxidation reaction is concluded, the signal intensity of the PO homopolymer segment, present in the solution from the previous stage, experiences a certain degree of attenuation. This phenomenon suggests that the PO homopolymer, featuring two hydroxyl groups at the end of its molecular chain, may interact with other similar molecules, thereby undergoing cross-linking and ultimately forming a complex macromolecular structure.

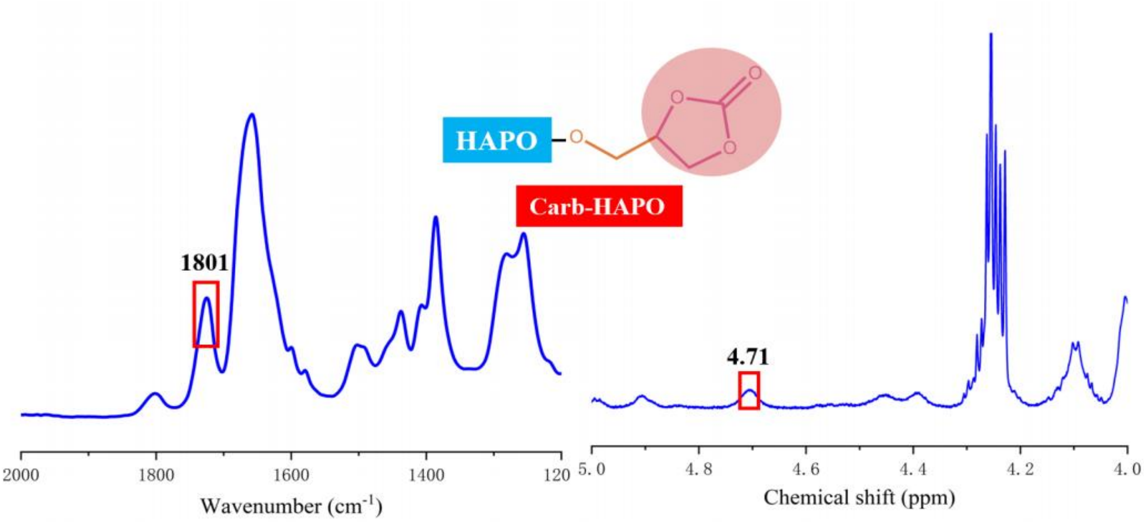

Figure 5: The characterization of SPR during the functionalization process. FT-IR (left) and 1H-NMR (right) spectra of Carb-HABO

3.2 Relevant characterization of NIPU films prepared by SPR-derived Carb-HAPO from sweet potato residues

In our experimental setup, we utilized five distinct polyamines to facilitate the cross-linking and solidification process in conjunction with the previously prepared Carb-HAPO, ultimately yielding Non-Isocyanate Polyurethane (NIPU). A critical consideration in this process is the precise molar ratio that should exist between the polyamines and the corresponding Carb-HAPO they react with.This ratio is of paramount importance when producing NIPU because it significantly influences the cross-linking properties of the final product. An excess of amino groups, for instance, can compete with hydroxyl groups in the solution, leading to suboptimal cross-linking performance in the resulting NIPU product. Conversely, an excessive amount of Carb-HAPO can result in incomplete cross-linking of the film. To ensure the NIPU film we ultimately create possesses desirable mechanical properties, we maintain a molar ratio of approximately 1:1 between the amino groups and Carb-HAPO during the cross-linking process in this study.

In this study, Fourier Transform Infrared Spectroscopy (FT-IR) was employed as a crucial tool to characterize the NIPU film that we meticulously prepared. The results unequivocally confirmed the successful formation of the essential urethane bonds between Carb-HAPO and polyamine, a pivotal achievement.

This result also proves that an extensive NIPU cross-linked network is formed in the product. For the urethane bond, the corresponding characteristic peaks of the carbonyl group contained therein appear at the two positions of 1703 cm^{-1} and 1250 cm^{-1} respectively in Figure 6. These findings collectively underscore the favorable cross-linking properties and mechanical attributes of the NIPU film we have produced. This augurs well for its prospective utility in numerous practical applications in the future.

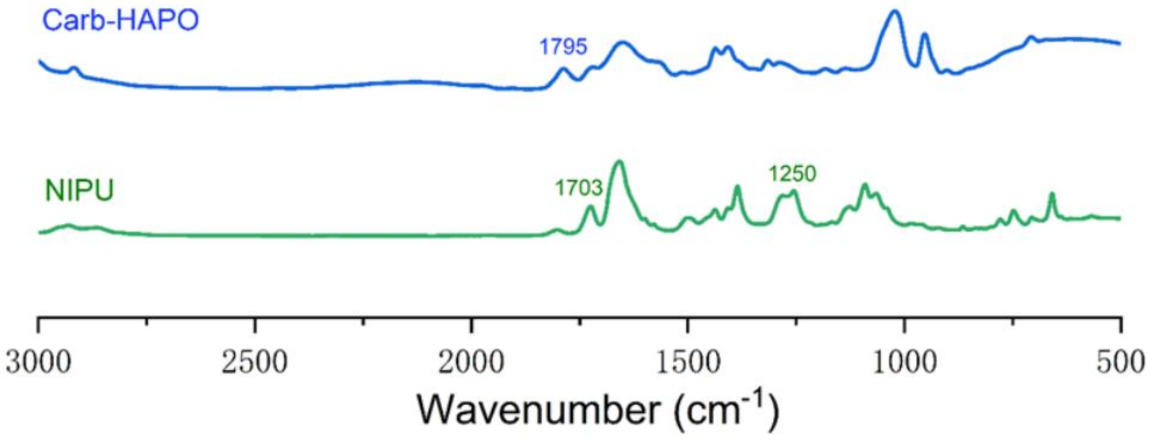

Figure 6: Infrared characterization of the NIPU synthesizing process

In final step, we opted for polyethyleneimine (PEI) to engage in a cross-linking reaction with Carb-HAPO, resulting in the production of the NIPU film(shown in Figure 7). Subsequent mechanical property tests revealed striking results: PEI-based NIPU exhibited significantly superior tensile strength and Young's modulus than the other three polyamine-based NIPU film groups. Impressively, the tensile strength reached an astonishing 6.6MPa, while the elongation at break also achieved a commendable 19.6MPa. The only area where PEI fell short was in Young's modulus, which, at 66MPa, was less than optimal.

This remarkable enhancement in mechanical properties can be attributed to the unique interaction of polyethyleneimine. Specifically, PEI seems to cross-link further with any remaining unreacted hydroxyl groups from the epoxidation process during SPR preparation. This additional cross-linking process results in a denser and stronger overall NIPU product structure, leading to the outstanding mechanical performance observed in our tests.

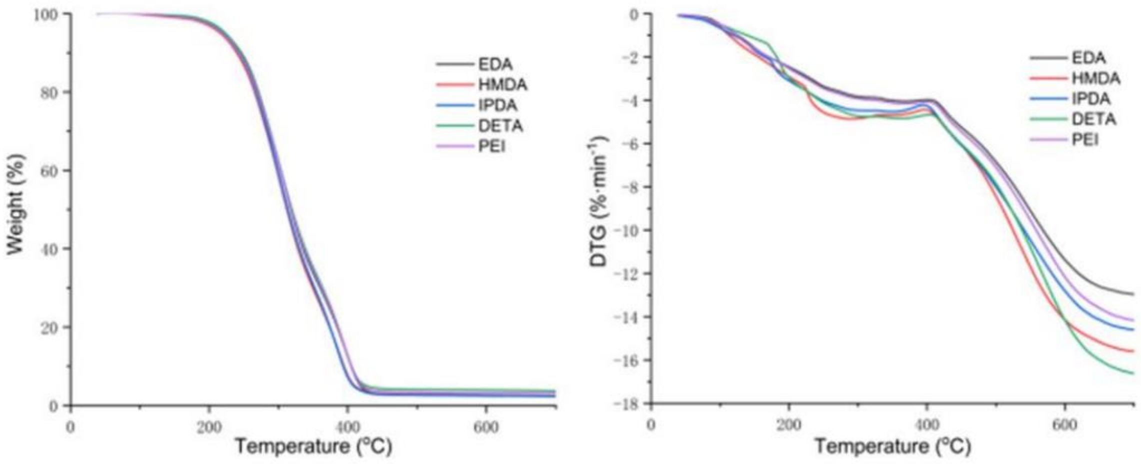

Figure 7: TGA and DTG curves of NIPUs

In the depicted figure, the characterization data clearly indicate a notable trend: as the proportion of added lignin oil increases, the UV resistance of the NIPU film product experiences a marked improvement. This enhancement can be attributed to the higher presence of functional groups, particularly phenolic hydroxyl groups, within the product. These functional groups effectively hinder the passage of UV rays through the material. Consequently, from a UV resistance standpoint, the prepared products exhibit promising potential for a wide range of practical applications.

4. DISCUSSION

In the selection of raw materials, we used waste residue from the starch industry, sweet potato residue containing a large amount of starch and cellulose as biomass-based raw materials and expanded it from the original use of only the preparation of fertilizers or feeds to the research on the synthesis of biomass-based materials. It was subjected to an oxygen propylation reaction to enhance its reactivity and fluidity. For high-quality products, lignin oil is added to give the product better mechanical properties and UV resistance. This significantly expands the application range of NIPU materials, making it a more environmentally friendly polymer material with broader prospects for future use.

5. CONCLUSION

This paper utilizes starch industrial waste sweet potato residues as the biomass-based reactant material. It focuses on modifying and chemically synthesizing epoxy resins from the functional groups within sweet potato residues and fixing CO_2 to prepare cyclic carbonates. Preparation of sweet potato pomace-based NIPU materials by cross-linking biomass-based cyclic carbonates with different kinds of polyamines and oligomeric lignin oil was added to the products with good performance in proportion to test the UV resistance and mechanical properties. The tensile strength of NIPU film can reach up to 6.6MPa. After adding different proportions of oligomeric lignin oil, it can reach a maximum of 8.4MPa and shows a certain degree of UV resistance. Pretreatment and modification of biomass can improve its reactivity. Cross-linking cyclocarbonate with amine to form NIPU and adding lignin oil can improve its mechanical properties and UV resistance. This further broadens the application scope and applicability of NIPU materials.

However, the availability of sweet potato residue as a biomass source may be limited in certain regions, which could restrict the widespread adoption of this approach. Future research can Investigate other biomass sources beyond sweet potato residue to expand the range of sustainable raw materials for NIPU production, potentially addressing limitations related to resource availability.

REFERENCES

[1] R.S. Malani, V.C. Malshe, B.N. Thorat, Polyols and polyurethanes from renewable sources: past, present, and future—part 2: plant-derived materials, Journal of Coatings Technology and Research 19(2) (2022) 361-375.
[2] R.L. Howard, E. Abotsi, v.R.E.L. Jansen, S. Howard, Lignocellulose biotechnology: issues of bioconversion and enzyme production, African Journal of Biotechnology 2(12) (2003) 18-.
[3] Paulina, Parcheta, Janusz, Datta, Environmental impact and industrial development of biorenewable resources for polyurethanes, Critical Reviews in Environmental Science & Technology (2017).
[4] S. Samanta, S. Selvakumar, J. Bahr, D.S. Wickramaratne, M.P. Sibi, B.J. Chisholm, Synthesis and Characterization of Polyurethane Networks Derived from Soybean Oil-Based Cyclic Carbonates and Bio-Derivable Diamines, Acs Sustainable Chemistry & Engineering (2016) acssuschemeng.6b01409.
[5] J.O. Akindoyo, M.D.H. Beg, S. Ghazali, M.R. Islam, N. Jeyaratnam, A.R. Yuvaraj, Polyurethane Types, Synthesis and Applications - A Review, RSC ADVANCES (2016).
[6] S.J. Groszos, E.K. Drechsel, Method of preparing a polyurethane, 1957.
[7] J.S. Amaral, M. Sepúlveda, C.A. Cateto, I.P. Fernandes, M.F. Barreiro, Fungal degradation of lignin-based rigid polyurethane foams, Polymer Degradation and Stability 97(10) (2012) 2069–2076.