

Synthesis and Characterization of Polyurethanes Based on Hydroxylated Tung Oil (HTO) and PAPI

W Q Yang^{1,2}, J X Zhang², Z Y Ren^{2*}, L Jiang², Y Fu² and S Q He¹

¹ School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, China

²High & New Technology Research Center of Henan Academy of Sciences, Zhengzhou, China

*zyren23@163.com

Abstract. Two novel polyurethane films were successfully synthesized. One was from hydroxylated tung oil (HTO) and polymethylene polyphenyl isocyanate (PAPI), which was designated as HTO-PAPI; and the other was from HTO end-capped a traditional polyurethane prepolymer and PAPI, which was designated as PP-HTO-PAPI. FTIR and NMR results show that the prepared HTO-PAPI and PP-HTO-PAPI are the expected structures. Mechanical testing result shows that the Young's modulus and elongation at break for HTO-PAPI and PP-HTO-PAPI are 282.13 MPa, 1.8 MPa and 14.15%, 218.23%, respectively, indicating that the two polyurethane films have very distinctive properties. And the properties can be controlled by incorporating different ratio of HTO and prepolymer. The present work provides a good foundation for the synthesis of novel polyurethane adhesives that will be hopefully used in different applications.

Keywords: polyurethane; hydroxylated tung oil (HTO); mechanical properties; characterization; PAPI.

1. Introduction

Polyurethane is a typical segmented copolymer generally composed of soft and hard segments. The soft segment has a long chain polyol (usually polyether or polyester polyol) with molecular weight of 1000-3000g/mol while the hard segment consists of an isocyanate and a small molecular chain extender, usually a diol or diamine. The soft segment offers elasticity while the hard segment acts as the physical crosslinking point and plays the key role in determining mechanical properties[1].

Hydroxyl-modified tung oil or hydroxylated tung oil (HTO), which is prepared from a natural plant oil, namely tung oil, is a type of new polyol[2-3]. According to its structure and molecular weight (Figure 1), it is neither a typical polyol as soft segment, nor the typical chain extender as one part of hard segment. The same conjugated triene structure as tung oil makes HTO have post-polymerization function [4] while the long pendent chain possibly has some plasticization. Therefore HTO is a type of special new polyol that have shown its special function in polyurethane dispersion in our previous work [5]. Among the different isocyanates, polymethylene polyphenyl isocyanate (PAPI) has functionality of over 2, which can be used for preparing crosslinked materials [6-7]. However, there are few reports on PAPI related polyurethane, possibly because the reaction involved is hard to control.



In the present work, we briefly report the synthesis and structure/mechanical characterization of two novel polyurethanes HTO-PAPI and PP-HTO-PAPI. It is of important significance to incorporate both HTO and PAPI into polyurethane chain not only because HTO is from a renewable source, but also the function of HTO is special and worth to be deeply studied.

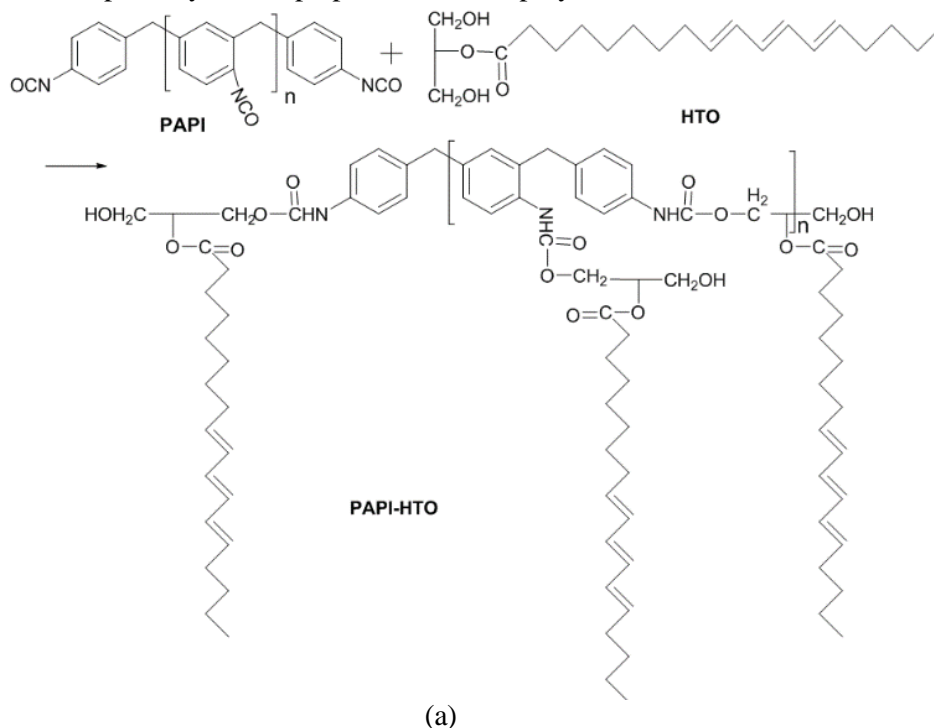
2. Experimental

Synthesis of HTO-PAPI. The HTO dried in a vacuum oven was added to a four-necked flask with nitrogen protection, and PAPI was added at a certain ratio. An appropriate amount of solvent dimethyl carbonate (DMC) was added. A drop of phosphoric acid was added when the temperature is about 40°C. Then temperature was raised to 60~70 °C and was maintained for one and half hours.

Synthesis PP-HTO-PAPI. The dry HTO was added to a four-necked flask, and the PP (prepared from polytetrahydrofuran (PTMG) and diphenylmethane diisocyanate (MDI)) was added at a ratio of -NCO:-OH = 1:2. After this step of reaction was over, PAPI was added at a ratio of -NCO:-OH = 1:1.

NCO content was determined to trace the extent of polymerization during above syntheses. When the reactions were over at certain condition, the product was poured into polytetrafluoroethylene (PTFE) disc to dry at room temperature.

Figure 1 shows the pathway for the preparation of two polyurethanes.



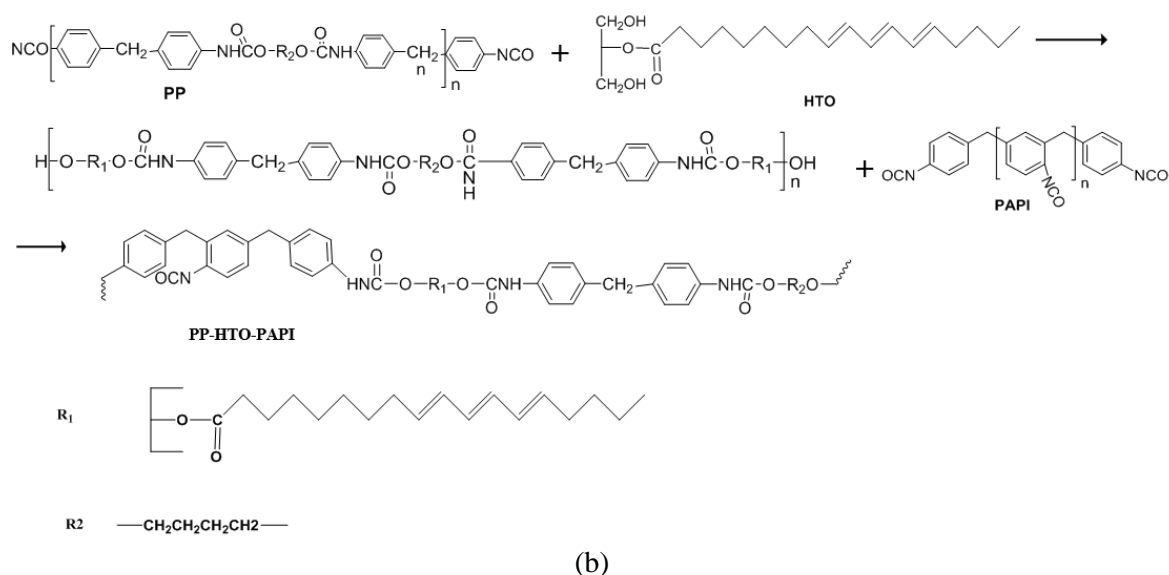


Figure. 1. Synthesis routes of two polyurethanes **a:** PAPI-HTO; **b:** PP-HTO-PAPI

3. Results and discussion

3.1. Structural characterization

Figure 2 is the comparative FTIR spectra of two polyurethanes based on different compositions. It can be observed that the characteristic bands of urethane in both PP-HTO-PAPI and PAPI-HTO are very obvious, including the ν_{NH} band at 3326cm^{-1} , the urethane $\nu_{\text{C=O}}$ band at 1727cm^{-1} as well as the amide II and amide III bands [8-9] at 1534cm^{-1} and 1219cm^{-1} , respectively. It is also seen that there is small band at around 993cm^{-1} [4], showing the triene structure remains in two polyurethanes.

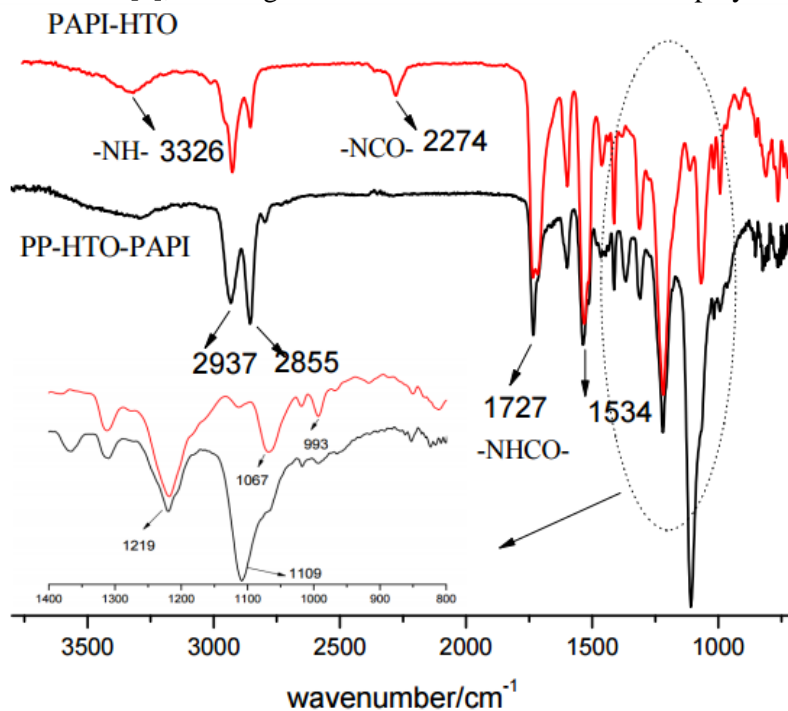


Figure. 2. FTIR spectra of PP-HTO-PAPI and PAPI-HTO

Moreover, it can be noted that the band intensity at 2855cm^{-1} and at 1109cm^{-1} are significantly stronger in PP-HTO-PAPI than that in PAPI-HTO. This result shows that PP prepared by MDI and PTMG has been introduced into PP-HTO-PAPI, as PTMG contains more CH_2 group and ether oxygen bond.

In addition to FTIR, ^1H NMR was also used to characterize the two structures. Among the chemical shifts, the peak standing for carbamate hydrogen at δ 6.8 ppm as well as the group peaks representing conjugated double bonds at δ 5.38-6.35 ppm from HTO [4, 10] all show that the HTO structure bearing triene bonds have been introduced to two polyurethane chains.

Above results show that the expected polyurethane structures have been successfully synthesized in PP-HTO-PAPI and PAPI-HTO films.

3.2. Mechanical properties

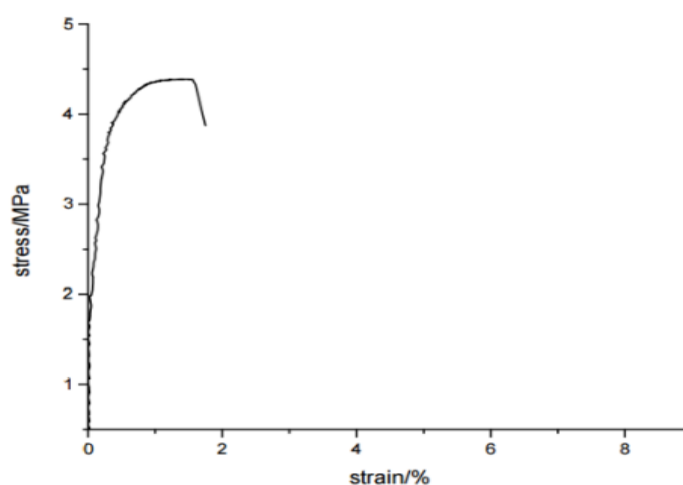


Figure. 3. Stress-strain curve of PAPI-HTO film

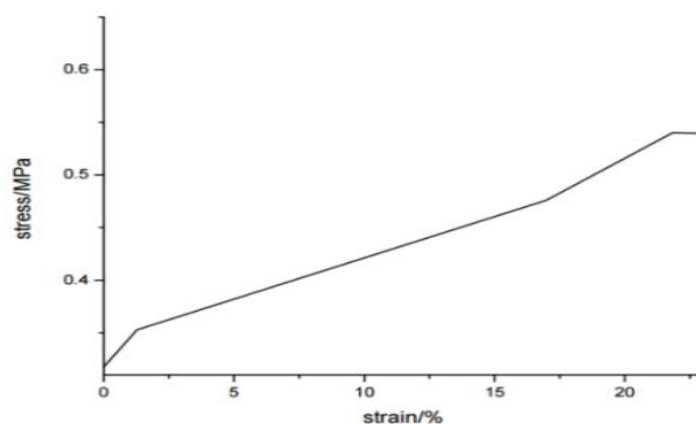


Figure. 4. Stress-strain curve of PP-HTO-PAPI film

Table 1 .Mechanical Properties of two types of polyurethane films

Sample	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PAPI-HTO	41.37	282.13	14.15
PP-HTO-PAPI	4.56	1.80	218.23

Figure 3 and Figure 4 are the stress-strain curves of both PAPI-HTO and PP-HTO-PAPI films; Table 1 presents the Young's modulus and elongation at break. It is seen that the two polyurethane films have very distinctive properties. The Young's modulus and elongation at break of HTO-PAPI are 282.13 MPa and 14.15%, while those of PP-HTO-PAPI are 1.80 MPa and 218.23%, respectively. These results indicate that the HTO-PAPI film is a hard and strong material that breaks before the material cracks whereas the PP-HTO-PAPI film is soft and tough material. The results also show that the structure of soft and hard segments in polyurethane has obvious effect on their properties. For PAPI-HTO, the post-polymerization [11-12] of the three conjugated double bonds in HTO is expected to make additional contribution on the hard and strong properties in addition to PAPI's polyfunctional cross-linking[13-14], while for PP-HTO-PAPI, the introduction of soft segment reduces the crosslinking density and increases the elasticity. Therefore, polyurethane adhesives with different properties based on above compositions can be hopefully used for different applications. More research work is under way.

4. Conclusions

In summary, two types of polyurethane PAPI-HTO and PP-HTO-PAPI were successfully synthesized, and FTIR and ¹H-NMR were used to characterize their structures. The mechanical properties can be adjusted from hard and strong to soft and tough via selection of compositions, whereas the multi-functional NCO groups in PAPI and the post-polymerization properties of the conjugated triene bonds in HTO would give the film good properties. The results can provide a good theoretical basis for the preparation of novel polyurethane adhesive.

Acknowledgements

This study has been supported by the Henan Science and Technology Project Foundation (the basic and frontier research project) (162300410023).

References

- [1] Petrović Z S, Ferguson J. Polyurethane elastomers, *Prog. Polym. Sci., Rubber Technology*, 1991, **16**(5), 695–836.
- [2] Xiao H X, U.S. Pat., 7,462,679, 2008.
- [3] Mosiewicki M A, Casado U, Marcovich N E, et al. Polyurethanes from tung oil: Polymer characterization and composites, *Polym. Eng. Sci.*, 2009, **49**(4), 685–692.
- [4] Ren Z Y, Liu L, Wang H F, Fu Y, Jiang L, Ren B X, Novel Amphoteric Polyurethane Dispersion with Postpolymerization Crosslinking Function Derived from Hydroxylated Tung Oil: Synthesis and Properties, *RSC Advances, (Communication)* 2015, **5**(35), 27717-27721.
- [5] Ren Z Y, Zhang C L, Jiang L, Wang H F, Zhao W, Fu Y and Zhang Y B. Facile Synthesis and Newly Found Biological Activity of Aminolized Tung Oil Components with Conjugated Double Bonds, *RSC Advances (Communication)*, 2013, **3** (39), 17712-17716.
- [6] Jr C U P, Xu X and Wang L, et al. Characterizing semi-interpenetrating polymer networks composed of poly(vinyl chloride) and 5-15% of oligomeric MDI isocyanate cross-linked networks, *Polymer*, 2000, **41**(14), 5405-5413.
- [7] Lubguban A A, Tu Y C and Lozada Z R, et al. Functionalization via glycerol transesterification of polymerized soybean oil. *J. Appl. Polym. Sci.*, 2009, **112**(1), 19-27.
- [8] Q Ge, H Wang, Y She, et al. Synthesis, characterization, and properties of acrylates-modified tung-oil waterborne insulation varnish. *J. Appl. Polym. Sci.*, 2015, **132**(10), pp 27-47.
- [9] Zhang C X, Ren Z Y, Qian H Y, Ma D Z, Amide II and Amide III Bands in Polyurethane Model Soft and Hard Segments, *Polym. Bull.*, 2008, **60**, 97-101.
- [10] Zhao W, Wang H F, Ren Z Y, Jiang L, Fu Y and Wang X L, Structural Confirmation of A New Hydroxylated Tung Oil Compound by NMR, *Magn. Reson. Chem.* 2015, **53**(2), 160-162.

- [11] Huang Y, Pang L and Wang H, et al. Synthesis and properties of UV-curable tung oil based resins via modification of Diels-Alder reaction, nonisocyanate polyurethane and acrylates, *Prog. Org. Coat.*, 2013, **76**(4), 654-661.
- [12] Thanamongkollit N, Miller K R and Soucek M D. Synthesis of UV-curable tung oil and UV-curable tung oil based alkyd, *Prog. Org. Coat.*, 2012, **73**(4), 425-434.
- [13] Kessler M R. Bio-based Polyurethanes Prepared from Different Vegetable Oils, *ACS Appl. Mater. Inter.*, 2014, **7**, 1226-1233.
- [14] Lu Y S, Larock R C. Soybean oil-based, aqueous cationic polyurethane dispersions: Synthesis and properties, *Prog. Org. Coat.*, 2010, **69**(1), 31-37.