

Synthesis and characterization of biobased polyurethanes from modified castor oil and palm oil based isocyanate: Effect of NCO/OH molar ratio

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Abstract— In this paper the effect of varying NCO/OH molar ratio on the properties of synthesized PUs has been investigated. The PUs have been synthesized from monoglycerides of CO with palm oil based isocyanate and 1,3 propanediol in the presence of catalyst dibutyltin dilaurate. The effect of NCO/OH on the physical properties such as the acid value, hydroxyl value, viscosity and isocyanate value have been investigated. Fourier transform infrared spectroscopy (FTIR-ATR) study has been carried out to evaluate the extent of hydrogen bonding (H-bonding). Atomic force microscopy studies have been studied to evaluate the morphological properties. Thermogravimetric analysis (TGA) demonstrates that with increase in NCO/OH molar ratio the thermal stability of the synthesized resins also increases.

Keywords—castor oil, Tolonate X FLO 100, FTIR-ATR, acid value.

I. Introduction

Polyurethanes (PUs) have gained enormous importance due to their diverse application in the field of coatings, adhesives, foams¹. Owing to their wide application to the investigation of structure-property relationship in PUs has been a hot topic of research. In the past years, various reports^{2, 3} are available regarding the effect of NCO/OH molar ratio, the structure of the hard and soft segments, molecular weight on the physicochemical properties of PUs. Further, the hard segments usually constitute the diisocyanate and the chain extender while the soft segments constitute the polyol². Nowadays, vegetable oils (VOs) have been used as polyol for the synthesis of PUs since they are cost effective, environment friendly and renewable. Amongst this VOs castor oil (CO) has been highly taken into consideration due to the presence of the inherent hydroxyl group⁴. However CO has its own limitations which can be improved through transesterification reaction with various alcohols⁵. The other component being used for the synthesis of PUs is the petrobased isocyanate, which are derived from toxic phosgene releasing free diamines and hydrogen chloride on decomposition⁶. Hence, in this paper, we aimed to synthesized PUs from transesterified CO with a palm oil based isocyanate. Further, the effect of varying NCO/OH molar ratio on the synthesized PUs was investigated through various characterization techniques.

II. Materials and method

A. Materials

Castor oil (CO) was procured from M/s. SD Fine chemicals (Kolkata, India). The palm oil based isocyanate was kindly provided by M/s. Vencorex Chemical, France. 1, 3 propanediol, pentaerythritol and lead oxide (PbO) were procured from M/s Himedia, India. The tin catalyst dibutyltin dilaurate (DBTDL) was supplied by M/s. Sigma Aldrich, Germany and was used as received. Analytical grade acetone was procured from M/s Fischer Scientific, USA.

B. Synthesis and Characterization

Synthesis of transesterified CO (TCO): The TCO was synthesized by the transesterification of CO with pentaerythritol. The reaction was carried out in a round bottomed flask equipped with stirrer, thermometer and reflux condenser. The temperature of the oil bath was maintained around 230 °C for a specified period of time. After attaining the desired hydroxyl value the reaction was stopped and the TCO synthesized was kept under vacuum for drying.

Synthesis of PUs with varying NCO/OH molar ratio: The synthesis of PUs with varying NCO/OH ratio (1, 1.1, 1.2) was synthesized by one step polymerization technique. A calculated amount of moisture free TCO was taken in three necked round bottom flask equipped with stirrer, nitrogen inlet and thermometer. Thereafter, the palm oil based isocyanate and 1,3 propanediol were added to the TCO mixture and stirred for a specified period of time in the presence of a DBTDL. After the desired viscosity was attained the solution was casted onto the teflon sheet and was cured at 90 °C for 12 hrs. The PU s obtained were named as TBPU 1, TBPU1.1 and TBPU 1.2 respectively.

Characterization: FTIR-ATR method was carried out to determine the structural characteristics of the synthesized TPUs, TCO and CO in the range of 4000-400 cm⁻¹. AFM study was done to evaluate the effect of NCO/OH on the morphological behavior of TPUs. TGA analysis was carried out to investigate the effect of NCO/OH on the thermal stability of PUs at a rate of 10 °C/min from ambient temperature to 550 °C. The mechanical properties of TPU films were accessed with a test speed of 10mm/min. The water absorption measurement was carried out at room temperature with distilled water to determine the gel content with varying NCO/OH molar ratio.

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III. Results and Discussion

A. Fourier transform infrared spectroscopy (FTIR-ATR)

Structural characterization of CO and TCO: The FTIR spectra of CO and TCO has been illustrated in Fig. 1. From the spectra, it is revealed that there is an increment in the band at 3400 cm^{-1} for TCO as compared with CO. This increase in the intensity can be attributed to the increase in the hydroxyl value (OH) of TCO. Further, the other characteristic absorption bands at $2923\text{--}2854\text{ cm}^{-1}$, 1745 cm^{-1} (-COOH), 1159 cm^{-1} (-C-O-C) remains unaltered.

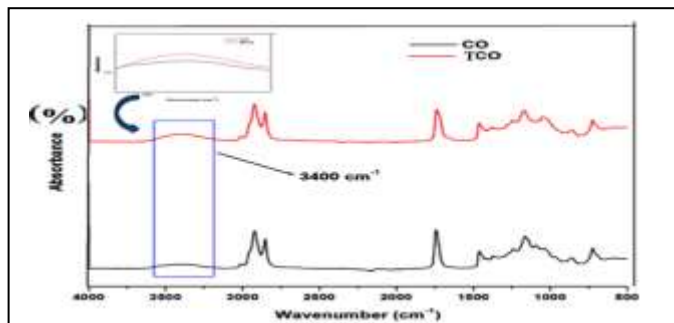


Figure 1. FTIR Curve of CO and TCO.

Structural characterization of TPUs with varying NCO/OH molar ratio: The FTIR spectra of TPUs with different NCO/OH molar ratio is represented in Fig. 2. The absence of peak at 2260 cm^{-1} for NCO indicates the complete polymerization reaction. Moreover, the absence of peak at 3400 cm^{-1} for OH group also signifies the formation of PUs. To investigate the effect of NCO/OH on the extent of H-bonding of TPUs the band corresponding to ν (N-H) from 3500 cm^{-1} to 3350 cm^{-1} and ν (C=O) from 1735 cm^{-1} to 1685 cm^{-1} was accessed². Generally in PUs the H-bond is formed between the -NH and C=O of hard segment or with the ether oxygen and carbonyl of soft segment⁷. It has been reported that in H-bonded PUs the ν (N-H) and ν (C=O) appear at lower wavenumber as compared to the ones devoid of H-bonding². Based on the above reports it is observed that TPU 1.2 exhibits higher H-bonding since the ν (N-H) and ν (C=O) are shifted to lower wavenumber. This might be due to the formation of more H-bonds between the NH and C=O of the hard segment with higher content of the NCO.

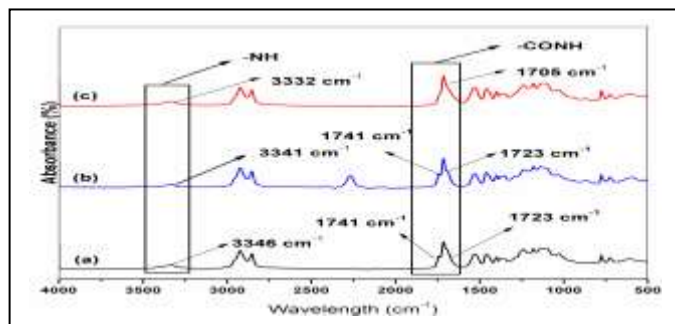


Figure 2. FTIR curve of (a) TPU 1 (b) TPU 1.1 (c) TPU 1.2

B. Thermogravimetric analysis (TGA)

The thermal stability curves of TPUs with varying NCO/OH molar ratio is shown in Fig. 3. and the results are summarized in table I. From the results it can be concluded that the NCO/OH had profound effect on the thermal stability of TPUs. All the TPUs showed three stage degradation profile. It has been reported that the first stage corresponds to the degradation of urethane bonds while the second stage signifies the degradation of soft segments and finally the third stage corresponds to the degradation of the remaining segments⁷. Fig. 4 indicates that with an increase in the NCO/OH molar ratio the degradation temperature increases. This might be attributed to the fact that with increase in NCO/OH molar ratio greater than 1 more urethane linkages are formed due to the presence of free NCO groups that react during the crosslinking process to form allophante, biuret and urethane linkages. Thus, the urethane linkages decompose at higher temperature resulting higher thermal stability in TPU 1.2. Moreover, the higher crosslinking also leads to closer packing and compact structure resulting higher thermal stability.

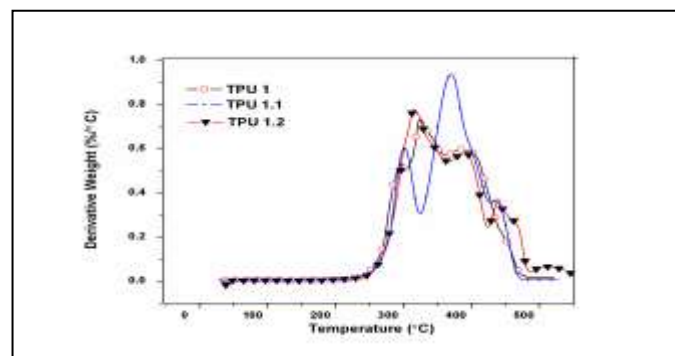


Figure 3. TGA curve of TPUs.

TABLE I. THERMAL DATA OF TPU FILMS

Sample	Thermal properties		
	T_d onset (°C)	T_d end (°C)	Char residue at 500 °C
TPU 1	240	496	2.1
TPU 1.1	260	500	3
TPU 1.2	268	540	10.1

C. Water absorption measurement

For the water absorption measurement the different TPU films with dimension $12 \times 15 \times 1\text{ mm}$ ($l \times b \times h$) were immersed in distilled water for 72 hours. The weight of the samples (W_a) before immersion and the weight (W_b) after 72 h of immersion was recorded. Thereafter the water absorption (W%) was calculated using equation 1.

$$W(\%) = \frac{W_b - W_a}{W_a} \times 100 \quad (1)$$

For determining the gel content (%) a known weight of sample (W) was placed in toluene at 100°C and then swelled to equilibrium. After attaining a constant value the sample was dried and weighed (W^1) to determine the level of crosslinking. The gel content (%) was determined by using equation 2 on the basis of the level of crosslinking.

$$\text{Gel content (\%)} = \frac{W^1}{W} \times 100 \quad (2)$$

It can be inferred from table II that TPU 1.2 shows maximum gel content and lower water absorption characteristics. This might be due to the highly crosslinked network owing to higher H-bonding as indicated in the FTIR studies. The results obtained are in agreement with that reported by Gurunathan et.al.²

TABLE II. SWELLING DATA OF TPU FILMS

Sample	Swelling properties	
	Water absorption (%)	Gel content (%)
TPU 1	11.4	76
TPU 1.1	8.9	84
TPU 1.2	6.2	86.3

D. Atomic force microscopy (AFM)

The AFM topography images of TPU films with NCO/OH molar ratio 1.1 and 1.2 are indicated in Fig. 3. Generally the H-bonding is responsible for the phase separation behaviour⁸. Higher the interurethane H-bonding higher is the phase segregation. To investigate the phase segregation behavior of TPU films the AFM study was carried out in tapping mode. Usually the brighter region indicates the hard segments while the lighter region signifies the softer segments⁷. It is observed from figure 6 that TPU 1.2 indicates aggregation of hard domains in compact areas well dispersed in the matrix formed by the soft segments. This signifies the phase separated morphology of TPU 1.2 due to higher interurethane H-bonding. This result obtained are in agreement with that observed in FTIR study.

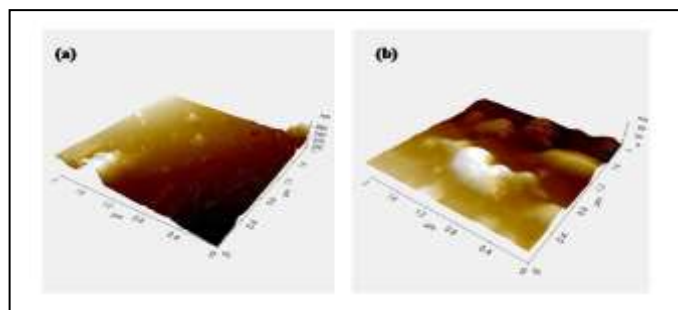


Figure 4. AFM Topography images of (a) TPU 1.1 and (b) TPU 1.2.

E. Mechanical test

It has been reported that the mechanical behavior of PUs depends upon the chemical interactions, hard segment content, and the crosslinking density². Table III shows the tensile data of TPU films with varying NCO/OH molar ratio. The OH groups in MCO are located in the primary position which shows higher reactivity towards the NCO groups, thus indicating good mechanical properties for all TPUs. However, TPU 1.2 indicates higher tensile stress as compared with TPU 1.1 and TPU 1 respectively. The higher strength in TPU 1.2 can be attributed to the higher crosslinking density and the higher H-bonding. Moreover, with an increase in the hard segment content (NCO + 1,3 propanediol) leads to higher intermolecular interaction thereby restricting the motion of the soft segments.

TABLE III. MECHANICAL DATA OF TPU FILMS

Sample	Tensile properties		
	Tensile strength (MPa)	Elongation at break (%)	Young's Modulus (MPa)
TPU 1	17 ± 0.45	260 ± 0.5	21.8 ± 0.5
TPU 1.1	19 ± 0.6	240 ± 0.7	27.9 ± 0.6
TPU 1.2	26 ± 0.5	180 ± 0.6	30.1 ± 0.4

The phase segregation behavior⁹ can be another reason for the higher tensile strength in case of TPU 1.2. Similar results were reported by various authors.

IV. Conclusion

In this study TPUs with varying NCO/OH molar ratio were synthesized with transesterified castor oil (TCO) and palm oil based isocyanate, 1,3 propanediol in the presence of a catalyst. The FTIR studies reveal the successful synthesis of TPUs which indicates that the palm oil based isocyanate can be a candid alternative to petrobased isocyanate for the synthesis of PUs. It was also concluded that higher the NCO content higher is the interurethane H-bonding and network formation. TGA results indicated three step degradation mechanism wherein the thermal stability of each step increases with increase in the NCO / OH ratio owing to higher urethane content and cross linking. Further, the water absorption results also reveal the increase in gel content to increase in the NCO / OH ratio due to higher crosslinking. The AFM studies reveal phase segregation in TPU 1.2 due to higher H-bonding as indicated through FTIR studies. The results obtained are in further agreement with the mechanical test findings, which reveal the higher crosslinking due to higher hard segment content in TPU 1.2.

Thus, in summary the detailed study exposed that the hard segment content has profound influence on the properties of TPU. Thus, this work can open a new pathway for the synthesis of bio-based polyurethane from renewable resources with efficient properties with the concept of sustainable development.

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