Studies on the effect of hard segment cross-linking on the polyurethane properties

Anupama Mogha* and Anupama Kaushik
Dr. S.S. Bhatnagar University Institute of Chemical Engineering and Technology, Panjab University, Chandigarh, 160014, India
Email id: anupumapawar85@gmail.com

Abstract: The studies focus on the preparation of the polyurethane sheets. Polyurethanes belong to the polymers that have the wide spectrum of applications. The polyurethane based materials are getting worldwide attention and demand, due to their superior properties over the other materials available. The pure polyurethane as well as cross linked polyurethane sheets was prepared using the polymerization process. The prepared polyurethanes were characterized by scanning electron microscopy (SEM), Fourier transformation infrared (FTIR) spectroscopy and thermo gravimetric analysis TGA-DTG analysis. The compositional and structural studies indicate the formation of polyurethane linkages. Also the thermal stability is indicated by the TGA analysis. The SEM image provides the morphological studies for the polyurethane samples.

1. INTRODUCTION

Polyurethanes belong to the larger class of polymeric compounds. Polyurethanes, are generally synthesized from an isocyanate reaction with a polyol [8]. Diisocyanate and polyhydroxy compounds are the main components that undergo polyaddition polymerization reaction for the production of polyurethanes. Polyurethanes were commercially used as malleable elastomers, coatings [2], adhesives, flexible foams [1], and rigid polyurethane. Polyurethanes are intensively studied due to their potential application in the field of flame retardancy [9], biomedical and tissue engineering [5], etc. Polyurethanes are produced in extensive densities and stiffness for a large number of applications.

Depending upon the application, their density ranges from 6 to 1,220 kg/m³ and polyurethane vary from elastomers to flexible, rigid, and hard foams. For the last 15 years, their worldwide utilization is growing at an average rate of 7% annually. Thus, polyurethanes play an important role in insulation panels to automobiles [18, 13]. Crosslinking agents/ chains extenders and catalysts are also used in the polyurethane preparation. The largest user share of polyurethane goes to Asia-Pacific and second largest used is European countries. The properties of polyurethane can be tailor made and depend upon the chemical composition of the isocyanate and polyol, NCO: OH ratio as well as the chain extender used[14]. NCO:OH ratio can be controlled by using isocyanates, polyols, and chain extender components [7]. The structure of the molecular backbone and the chain extender imparts enhanced mechanical and thermal properties of polyurethanes. Difunctional BDO (1,4-butandiolene) is used as urethane chain extender. The crosslinker reacts with the isocyanate to create the hard segment while the polyol is used to create a soft segment for the polyurethane [3]. Hence from the above information polyurethanes can be prepared by using polyol, and diisocyanate resources using a suitable crosslinker for the desired properties.
The studies were focused upon the synthesis of pure polyurethane and the crosslinked polyurethanes, using BDO as crosslinker. The comparison studies between the pure polyurethane and the crosslinked polyurethane were done using FTIR, TGA-DTG, and tensile curves. Also the prepared can find numerous biomedical and commercial applications.

2. MATERIALS AND METHODS

1,4 Butanediol (BDO) is used as a chain extender as well as a crosslinker in the polyurethane nanocomposite preparation. 1,4-butanediol (BDO) with molecular weight 90.12 g/mol, and molecular formula $\text{C}_4\text{H}_{10}\text{O}_2$.

Castor oil with molecular formula $\text{C}_{57}\text{H}_{104}\text{O}_9$ is supplied by CDH fine chemicals. Castor oil as the main polyol content and source of the soft segment is used for the preparation of polyurethane nanocomposites. Dehydration of castor oil is done at 105 °C, to eliminate moisture content from the sample. The oil after dehydration is stored in a moisture free environment with molecular sieves [17].

The hard segment comprises of diisocyanate in the polyurethane matrix. In current studies, MDI (1,4 Diphenylmethane diisocyanate) is used as a hard segment to complete the reaction with the polyol component. The molecular formulae for MDI are $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$, and are kindly supplied by Shivaadhin, Baddi, India.

2.1. Fabrication of pure polyurethane sheets

The dehydrated castor oil was taken in the three necks round bottom flask and adjusted on mechanical stirrer under the nitrogen environment. To this dropwise, MDI (1,4 Diphenyl methane diisocyanate) was added. The reaction mixture is heated from 50-70 °C, so that the urethane formation takes place. When the mixture becomes viscous it was poured in petridish to complete the reaction. Then the dried sample is recovered from the dish in the form of thin films.

2.2 Fabrication of pure polyurethane sheets with crosslinker/ chain extender

The above process is repeated with the addition of 1,4 Butanediol (BDO) is used as a crosslinker/chain extender [4]. Then the dried sample is recovered from the dish in the form of thin films.

2.3. Characterizations

For identification of organic as well as inorganic materials, Fourier Transform-Infrared Spectroscopy (FTIR) is used. FTIR analysis of samples was done using an infrared spectrophotometer. FTIR spectra in the range of 4000–500cm$^{-1}$ with a resolution of 2 cm$^{-1}$ for each sample was recorded. TGA-DTG analysis of samples for studies of thermal stability was done on SII 6300 EXSTAR model. Scanning Electron Microscope (SEM) is done on LEO 435 VP model. Studies like Surface morphology, Particle size analysis, and distribution, Grain boundary and Micro-crack location etc, are done using scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

Pure polyurethane samples with and without cross-linker BDO (1,4-butanediol) was shown in Figure 1. Characteristic peak of the alkane stretching vibration for symmetrical and asymmetrical peak are visible at 2920 and 2852 cm$^{-1}$ and C=O stretching peaks at 1724 cm$^{-1}$is visible. The N-H stretching peak at 3340 cm$^{-1}$ of urethane is visible, which is very approachable to hydrogen bonding[6]. The table below shows the main peaks and their representations. The characteristic bands of polyurethane 3300, 1720, 1600, 1230, 1110, and 950 cm$^{-1}$ are present. The functional groups for PU are observed, the C-N stretching at 1535 cm$^{-1}$, -C-H bending at 1380 cm$^{-1}$, C=C stretching at 1460 cm$^{-1}$, and C=O
stretch 1724 cm\(^{-1}\) [1, 10, 12]. The major peaks observed were shown in the Table 1.

![Figure 1. FTIR analysis for pure polyurethane compared with the cross-linked polyurethane.](image)

**Table 1. Major peaks for the FTIR analysis of polyurethanes.**

| Band cm\(^{-1}\) (a) | Assignment                        |
|----------------------|-----------------------------------|
| 1380                 | -C-H bending                       |
| 1460                 | C=C stretching                     |
| 1724                 | C=O stretch                        |
| 2852                 | -CH\(_2\) stretching Non-symmetric |
| 2920                 | -CH\(_2\) stretching Symmetric    |
| 3340                 | Hydrogen bonded N-H               |

3.2. **TGA-DTG Analysis**

The TGA curve shown in Figure 2, indicates the comparison between the pure polyurethane and the cross-linked polyurethane. While for the detailed studies DTG curves were studied. The polyurethane degradation process will occur in three stages as displayed in the Figure 3 and Figure 4, primarily due to deprivation of hard segment and in the second stage, it’s due to the soft segment and third one is for decomposition of oxidized char. The first weight loss occurs at 306-375 °C, can be ascribed to the thermal decomposition of the ester bonds between the ricinoleic fatty acid and castor oil glycerol backbone. Urethane bond decomposition is also the dominant factor for the first stage of decomposition. The loss in weight at higher alteration was probably due to polymer constituent, while the association of the quantity of residue with the amount of unreacted isocyanate in polymers shows that the first stage of disintegration is due to the urethane bond decomposition[11]. The second peak 404-466 °C corresponds to the decomposition of stable isocyanurate structure, formed as a result of side reaction. As there is a formation of metastable oxidation products in this range. The third peak arises near 500 °C is due to the formation of small amount of high temperature residue [16].
Figure 2. Thermograms for the polyurethane and the crosslinked polyurethanes.

Figure 3. Comparative TGA-DTG curves for the pure polyurethane.
Figure 4. Comparative TGA-DTG curves for the crosslinked polyurethane.

3.3. SEM Analysis

Morphological studies by SEM analysis for pure polyurethane sample as well as cross-linked samples were done to check the composition of the polyurethanes. The SEM image for the polyurethane samples was shown in Figure 5.

Figure 5. SEM images for the (a) surface and (b) cross-section of polyurethane.

SEM analysis can be used to study morphology as well as the composition of the polyurethane samples. The SEM images for the surface and cross-section of the polyurethane were shown. The surface image shows the smooth and clear vision of the polyurethane sample without any irregularities, indicates the homogeneous morphology. While the cross-section image show the heterogeneous morphology. There are holes and irregularities observed, that might be due to the effect of the cross-linker. The cross-linker helps in the miscibility of both the hard and soft segment of the polyurethane [19, 15]. Hence the images indicate better rigidity of the cross-linked sheets over the pure polyurethane sheets. Their stability can further be studied using tensile analysis.
4. CONCLUSION

Pure polyurethane and the cross-linked polyurethane samples were successfully synthesized. The BDO cross-linked polyurethane has higher thermal stability in comparison to the pure polyurethane sample as indicated by the TGA-DTG studies. The SEM analysis also influences of the BDO as cross-linker. The images show a better cross-link density. The FTIR analysis provides the studies for the composition of the polyurethane sheets. The urethane and other N-H, methyl stretching peaks are well observed in the FTIR curves. Therefore, the cross-linked polyurethane sheets result with the enhanced properties.

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SCOPE FOR FUTURE

The prepared polyurethane sheets find a large number of applications in the field of science and technology. They can be used as a base matrix for the preparation of smart composites. And further be studied for tensile, DMTA analysis.

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