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EFFECT OF INCREASING NCO/OH MOLAR RATIO ON THE CHEMICAL AND MECHANICAL PROPERTIES OF ISOCYANATE TERMINATED POLYURETHANE PREPOLYMER DERIVED FROM BIO-MASS

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Abstract

The study deals the effect of increasing NCO/OH molar ratio on the physico-mechanical properties of isocyanate terminated polyurethane prepolymer. The prepolymer was prepared using castor oil and toluene-2,4-diisocyanate. The NCO/OH molar ratio has been varied from 1.6 to 2.0. The formation of the prepolymer was confirmed by UV and FTIR spectroscopy. The results reveal that the curing time of the prepolymer decreased with increase in NCO/OH molar ratio. When NCO/OH molar ratio increased, the tensile strength of the polyurethane film increased, while percent elongation decreased due to increase in hard segment content.

Keywords: Polyurethane Prepolymer, Tensile strength, UV, FTIR

INTRODUCTION

Bio-based products rely upons plant-derived materials as their main ingredients. They are made from a renewable resource and generally do not contain environmentally damaging substances. By using bio-based products, the user is avoiding reliance on petroleum resources. Unsaturated triglyceride oils such as soybean, crambe, linseed and castor oil constitute one major class of renewable resources [1]. The main composition of these triglyceride oils is saturated and unsaturated fatty acids. They can be polymerized to form elastomeric network and promise alternative material resources to petrochemical derived resin [2]. Directly using these fatty acid or their derivatives from some chemical modifications are emerging applications which include painting, coating, varnishes, cosmetics and more recently polymer and composites [3]. Different types of vegetable oils have been successfully utilized to synthesize biodegradable polyurethanes. Among them castor oil is a relatively inexpensive source of secondary hydroxyl groups and a triglyceride of fatty acids with 92-95% ricinoleic acid [4]. The work on interpenetrating polymer networks (IPNs) from renewable resources to produce cost-effective and relatively was initiated by sperling and reported later on by others [5, 6].

In the literature [7] a number of methods have been reported for the preparation of IPNs, such as sequential IPNs. The first synthesized cross linked polymer I is swollen with a second monomer II containing its own crosslinker and initiator, and polymerized in situ. Besides simultaneous IPNs synthesis refers to mixing of monomers prepolymers, crosslinkers etc., and both components are then simultaneously polymerized by independent, non-interfering reactions.

The urethane linkage (- NH – COO-) in polyurethane is a result of reaction between diisocyanate's isocyanate (-NCO) group and a polyol's hydroxyl group (-OH). If a stoichiometric excess of diisocyanate is used, the resulting short urethane chain are NCO terminated and the product is called isocyanate terminated polyurethane prepolymer [8]. Monomeric diisocyanates that have high vapour pressure are strong irritants to the mucous membrane the skin and eyes. Constant inhalations of their vapor lead to asthma. Therefore, isocyanates are pre-reacted to give a safer form useful in commercial surface coatings. The easiest and safer way is to prepare prepolymer to minimize the problem of vapour pressure and toxiticity [9]. The aim of the elaboration of such types of polymer associations in general is to obtain materials with better mechanical properties, and increased resistance to degradation and a potential synergy of the properties of their components and the resulting materials exhibit a good dimensional stability [10]. Polyurethanes have proved to be potential material for biomedical applications because of their high mechanical strength, flexibility, fatigue resistance and biocompatible nature [11-15]. The aim of our work is to utilize our natural and agricultural resources to produce cost-effective and relatively eco- friendly polymers with significantly improved properties.

Therefore, the NCO/OH molar ratio is regarded as an efficient way to regulate the morphology and properties of isocyanate terminated polyurethane prepolymer. The NCO/OH ratio is defined as the equivalent ratio between the materials containing NCO groups and those containing OH group.

So, in the present study focus was made for better understanding of the effect of increasing NCO/OH molar ratio on the physico-mechanical and chemical properties of isocyanate terminated polyurethane prepolymer. The formation of the prepolymer was investigated by FTIR method and the physico-mechanical and chemical properties were investigated. The mechanical properties were investigated by preparing polyurethane films and the curing time of the prepolymer was determined.

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EXPERIMENTAL

Required Materials

Castor oil was obtained from the local market, toluene 2, 4-diisocyanate (TDI) from sigma aldrich. All other reagents were of analytical grade and used without further purification. [16, 17].

Preparation of Polyurethane prepolymer (PPU)

A reaction kettle, under dry nitrogen, was charged with TDI and castor oil of varying ratio of NCO/OH was added slowly with stirring. The reaction was carried out at 45°C for 1h. [18, 19].

Characterization methods

Infrared spectra

Infrared spectra of the PPU in KBr pellets were obtained from Shimadzu FTIR 4200 series spectrophotometer. Whereas in case of PPU, being a liquid, a thin film was cast over the NaCl block and its FTIR was recorded [20].

UV-spectra

UV-spectra were analyzed in Hitachi (U-2001,Tokyo, Japan) UV spectrophotometer [21].

Mechanical properties

The tensile strength and elongation at break were measured at room temperature using Instron Houns-Field universal testing machine model 4204 as per ASTM D-638 method.

RESULTS AND DISCUSSION

The Polyurethane prepolymer obtained from castor oil and TDI were characterized according to following reports.

Infrared spectroscopy

Fig. 1a shows the IR spectra's of castor oil. Fig 1 b, c, d, shows the synthesized prepolymers at different NCO/OH molar ratio. All the synthesized prepolymer shows the characteristics absorption bands of polyurethanes except in the peak associated to NCO stretching which shows higher absorption area in case of higher NCO/OH molar ratio. It was observed that all the prepolymers possess the following characteristic absorption bands, urethane NH stretching at 3343-3321 cm-1, bending at 1531-1528 cm-1, methylene or alkyl group at 2974 cm-1, carbonyl group at 1727-1730 cm-1 and C-O-C stretching at 1025-1044 cm-1. The strong characteristic absorption peak at 2272 – 2275 cm-1 is associated with NCO stretching. Presence of NCO stretching band and all the above-mentioned peaks indicates formation of isocyanate terminated polyurethane prepolymer. FT-IR spectra of the different prepolymers show NCO stretching band and the same peak does not present the castor oil. It confirms the formation of prepolymers through the FT-IR data.

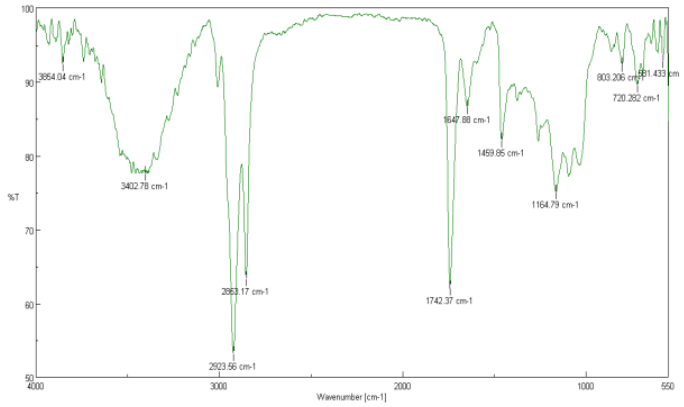

Fig.1a- Castor oil

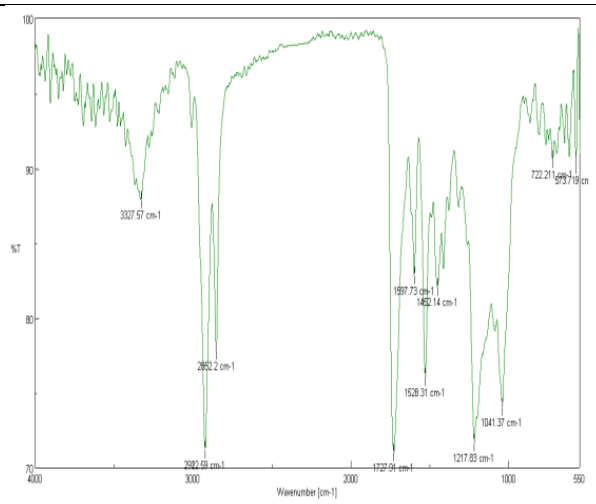

Fig.1b- Prepolymer (1.6)

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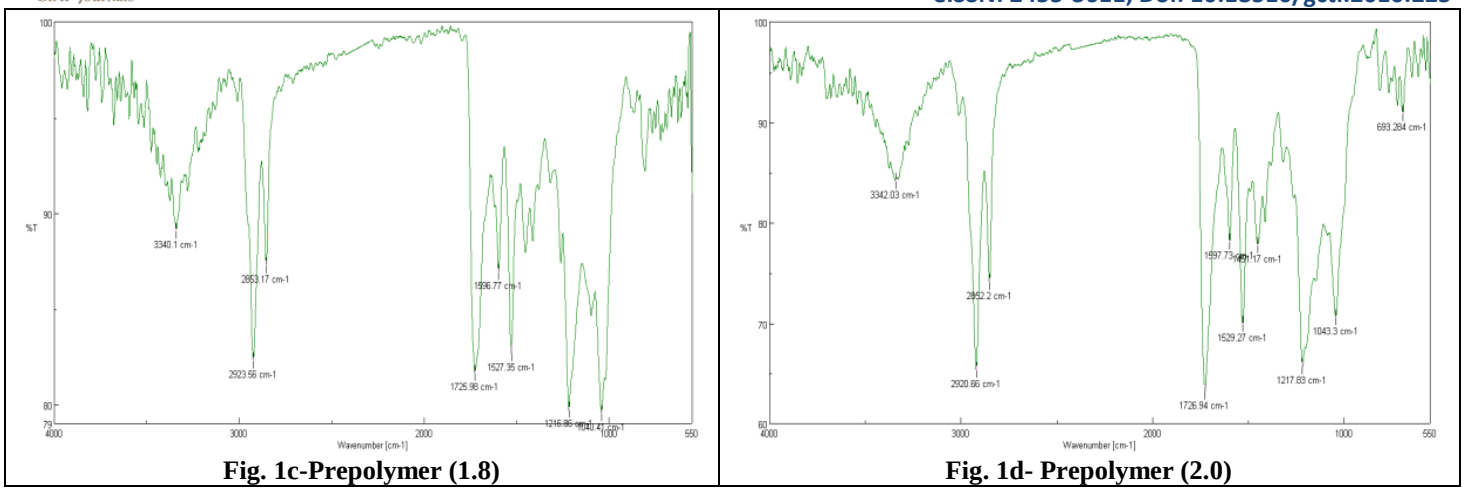

Fig. 1c-Prepolymer (1.8) **Fig. 1d- Prepolymer (2.0)**

Figure 1: FT-IR spectrum

UV study

The max values were observed at 264 nm and 263.5 nm withlow intensity due to transition for the CHBPU and MHBPU, respectively (Fig. 2). As there was no absorption peak at 286 nm,the characteristic max for TDI, so it confirmed the absence of free TDI .

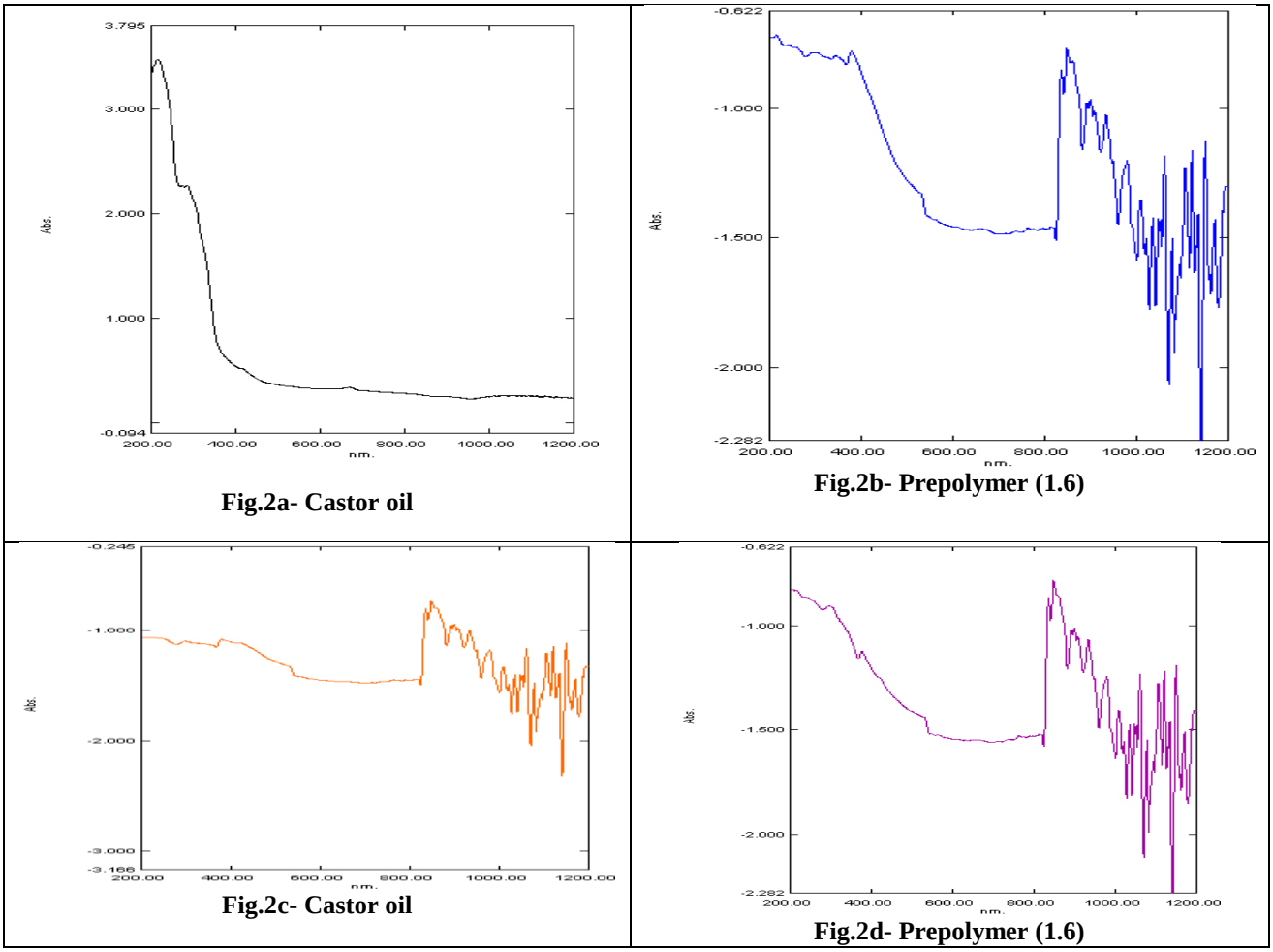

Fig.2a- Castor oil

Fig.2b- Prepolymer (1.6)

Fig.2c- Castor oil

Fig.2d- Prepolymer (1.6)

Figure 2: UV spectrum

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Mechanical properties

Mechanical properties such as elongation at break (%), and tensile strength are furnished in Figure 3 and 4. The NCO/OH has considerable effect on the molecular weight of the PPU. It also influences the compatibility between polyurethane and PPU. High NCO/OH leads to low molecular weight of PPU (Xiao et al 1983). From it is observed that tensile strength increases whereas, elongation decreases with increasing NCO/OH ratio probably due to low molecular weight of PPU at high NCO/OH ratio. As a result, PPU exhibits higher tensile strength.

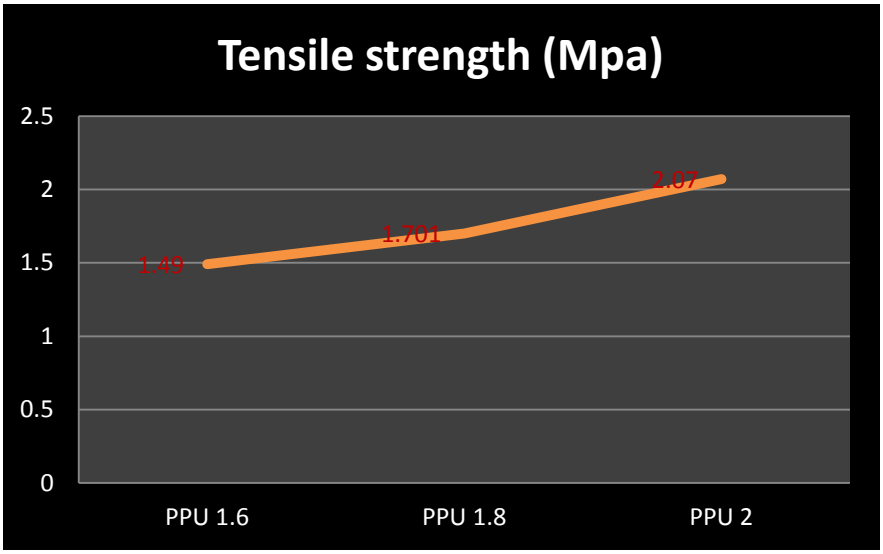

Figure 3: Tensile strength

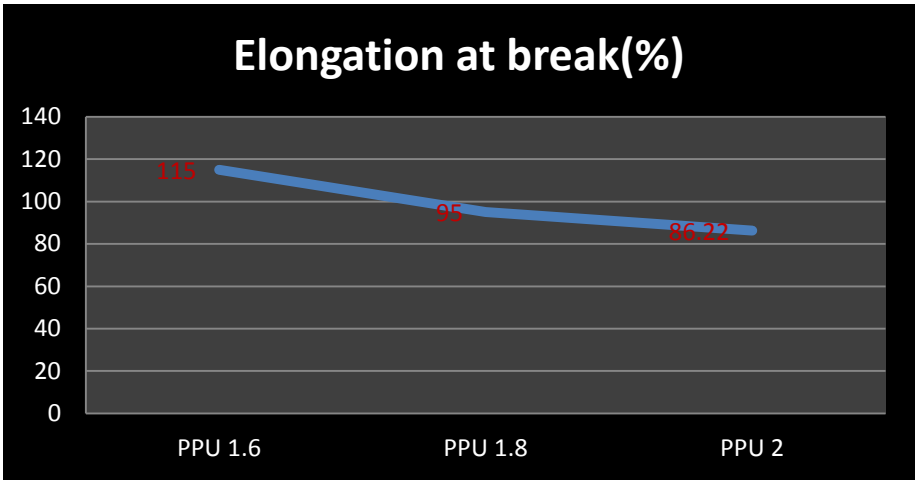

Figure 4: Elongation at break

CONCLUSION

Nowadays, there is a growing interest to produce agricultural waste and natural oil based biopolymers, particularly after the shortage of petroleum based monomers. These polymers have many advantages compared with polymers prepared from petroleum based monomers and in many cases are cheaper than petroleum polymers. The present study is aimed at synthesizing cost effective, eco-friendly and highly crosslinked polymers with enhanced thermal property from agro-based renewable resources for various sustainable industrial applications. Prepolymers showed excellent chemical resistance, hardness, elongation and tensile strength. The mechanical properties studied on polyurethane films shows that tensile strength increase, while percent elongation decreases with increase in NCO/OH molar ratio.

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