Effect of Reaction Time on the Synthesis and Properties of Isocyanate Terminated Polyurethane Prepolymer

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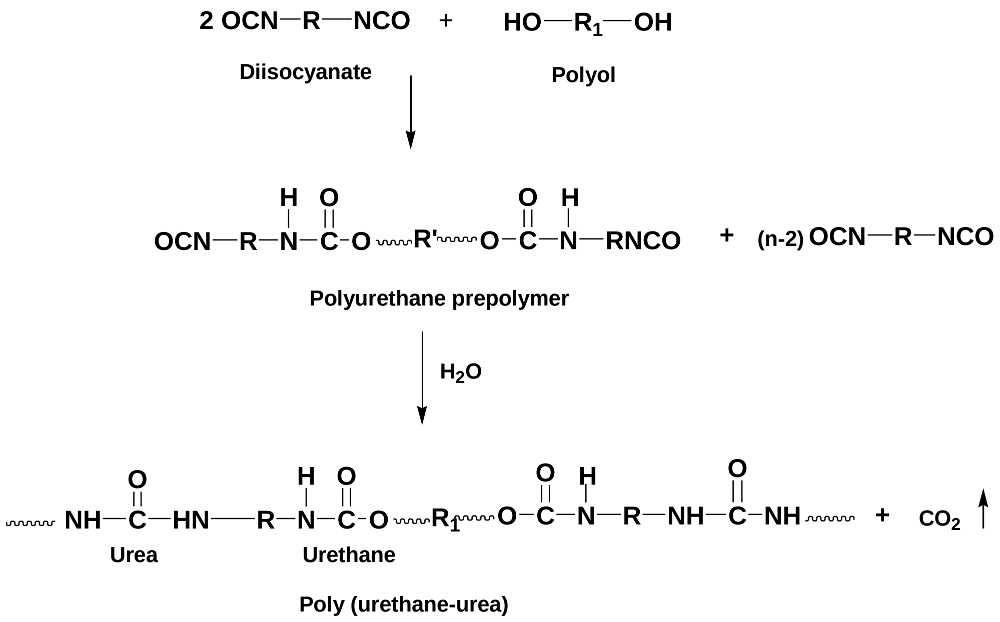
Abstract - In this study, the effect of different reaction time on the synthesis and properties of isocyanate terminated polyurethane prepolymer was studied. The isocyanate terminated polyurethane prepolymer was synthesized by reacting stoichiometric excess of methylene diphenyl diisocyanate (MDI) with poly (propylene oxide) glycol (PPG) at 60°C. The formation of the prepolymer was investigated by Fourier transform infrared spectroscopy (FTIR). The result reveals that the viscosity and weight average molecular weight of the prepolymer increases with increase in reaction time. Above 3hr reaction time, a sharp increase in viscosity and polydispersity index was observed indicating the possibility of the formation of side products. One hour reaction time was found to be insufficient for the completion of the reaction as it generates very low molecular weight. The curing time of the prepolymer was found to decrease with increasing reaction time due to lowering of isocyanate content. The glass transition temperature (T_g) of the prepolymer shift toward higher temperature range with increase in reaction time. On increasing the reaction time, the tensile strength of the polyurethane film increases upto 4hr, thereafter it starts decreasing. The percent elongation of the film also shows similar increasing pattern upto 4hr, thereafter it leveled off.

KEYWORDS: Polyurethane prepolymer, Reaction time, Structure, Viscosity, isocyanate content

INTRODUCTION

Depending on the structure, polyurethane covers a broad range of properties. Polyurethanes (PU's) are considered one of the most versatile classes of polymers for numerous commercial applications such as coating, foams, adhesives, sealants, membranes, elastomer as well as in many biomedical applications. From the application point of view, PU's can be designed to have any properties to satisfy different material requirement.

Polyurethane's are segmented copolymers composed of alternating hard and soft segments or blocks. The diisocyanate which form the hard segments provide dimensional stability to the polymer whereas the polyol which form the soft segment provides elastomeric character. The urethane linkage (-NH-COO-) in the polyurethane is a result of the reaction between the diisocyanate (-NCO) groups and polyol hydroxyl groups (-OH). If a stoichiometric excess of diisocyanate is used, NCO terminated urethane chains are produced and the product is called isocyanate terminated prepolymer. The formation of isocyanate terminated polyurethane prepolymer and its subsequent curing reaction are represented schematically in scheme I:



Scheme I : Formation of isocyanate terminated polyurethane prepolymer and its curing reaction

Curing of the prepolymer takes place in presence of water to form a network of poly(urethane urea). The prepolymer formation depends upon a number of chemical as well as mechanical factors. Among the mechanical factors, the reaction time plays a major role in influencing the properties of the polyurethane prepolymer **[1]**. It has been observed that the reaction time have a marked effect on the rate of prepolymer preparation as well as on the chemical structure of the resulting prepolymer. It was reported that the viscosity build up and gelation of prepolymers was influence by reaction time **[2].** Therefore, the reaction time is regarded as an efficient way to regulate the morphology and properties of polyurethane.

In our present study, an effort was made to investigate the role played by reaction time in regulating the physico-chemical, mechanical and thermal properties of isocyanate terminated polyurethane prepolymer. The polyurethane prepolymer was synthesized using diphenyl methane diisocyanate and poly (propylene oxide) glycol by varying the reaction time from 1hr to 5hr. The structure and properties of the synthesized prepolymer was investigated by FTIR technique, different ASTM and IS methods, thermal analysis and tensile test.

EXPERIMENTAL

Materials

Diphenyl methane diisocyanate (MDI), white solid flakes (melt.pt. 40^{o}C) was obtained from Sigma-Aldrich, USA, and was used as such without further purification. Poly(propylene oxide) glycol (PPG) was obtained from Sigma-Aldrich, USA. Catalyst 2, 2´ dimorpholinodiethyl ether (DMDEE) from Degussa, Germany was procured and used as such without any purification. Hydrochloric acid (AR grade), obtained from RFCL Limited, New Delhi and di-n-butylamine (AR grade) and methyl ethyl ketone (AR grade) were procured from sdFine chem ltd, Mumbai and was used as received without further purification. Some properties of MDI and the PPG used for the synthesis of polyurethane prepolymer are given in Table 1

Table 1: Some properties of MDI and PPG 1000 used for prepolymer synthesis

Property	**MDI**	**PPG1000**
Average functionality[a]	2.0	2.0
OH number (mg KOH/g)[a]	0.0	111
NCO content (wt%)[b]	33.8	0.0
Molecular weight (M_n(g/mol))[a]	250	1000
Viscosity 25°C, (cSt)[a]	50	150

[a] Information given by supplier

[b] Obtained by titration with di-n-butylamine

Synthesis of PU - prepolymer

The synthesis was carried out in a 5-necked glass reactor equipped with teflon stirrer, thermometer pocket, condenser and nitrogen gas inlet system. The polyol was vacuum dried for 2 hours at 80°C and kept overnight in molecular sieves prior to use to ensure that the material is free from moisture (less than 0.05%). The MDI flakes was melted in a beaker and poured into the reactor under nitrogen atmosphere. Inert atmosphere was maintained throughout the reaction so as to avoid the ingress of atmospheric moisture. The required amount of catalyst, DMDEE (0.25% of the whole reaction mixture) was then added followed by addition of PPG. The PPG was added part wise to the reactor. After that, the system was maintained at 60°C for the required amount of time period at 250-270 rpm. The NCO/OH molar ratio of the reactants was maintained at 3:1. Five different reaction periods were chosen for the study e.g. 1hr, 2hr, 3hr, 4hr and 5hr. The prepolymer obtained were in the form of yellow colored viscous liquid.

Preparation of polyurethane film

For studying the mechanical properties viz. tensile strength and percent elongation, polyurethane films were prepared by casting evaporation techniques. Approximately 10% solution of polyurethane prepolymer in tetrahydrofuran was prepared and poured into a teflon mould. It was then kept at room temperature, till all the solvents gets evaporated and curing takes place to form a transparent film. The films obtained were of about 0.4 mm thickness.

Characterization

The synthesized prepolymers were characterized for the following properties:

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of the prepolymers was taken on an FTIR, Perkin Elmer Model 521 in the range of wavenumber from 400cm^{-1} to 4000cm^{-1} by coating 1mm thick layer of the prepolymer on a KBr pellet.

The isocyanate content in the prepolymer was determined as per ASTM D 2572-91. The isocyanate present in the prepolymer was reacted with an excess of di-n-butyl amine and then titrated with standard 0.1N HCl solution. Since a known amount of amine was added, the amine consumed by the prepolymer is due to the presence of free isocyanate which was determined. The data given are the average of three measurements.

Dynamic viscosity of the prepolymer was determined by Brookfield viscometer DV Pro II (Brookfield Engineering Laboratories Inc, USA). The measurements were performed at 35 ± 1°C at 12rpm using spindle No.4.

Molecular weight of the prepolymer was determined by gel permeation chromatography using 2414 RI Detector (Make –Waters) and polystyrene as a standard. The samples were prepared in duplicate by dissolving 0.5% and 0.1% by wt of prepolymer in tetrahydrofuran (THF). THF was also used as a carrier solvent at the rate of 0.5ml/min.

Storage time was determined as per the method mentioned in US Patent 5,66,5056. For determining the storage stability about 50 ml of the PU prepolymer is poured in a polypropylene bottle and hermetically sealed under nitrogen atmosphere. The bottle was kept in an oven controlled at 130°C and the time till the resin was flow able was recorded. An average of three measurements was taken as the result.

The set to touch time was determined according to ASTM D1640 – 03 (2009). A thin film (approx thickness 12.5µm) of PU prepolymer was coated on a glass plate. From time to time, the tip of a clean finger was lightly touched on the test film and immediately placed the fingertip on a piece of clean, clear glass plate. Observed, if any of the prepolymer was transferred to the glass plate. If no prepolymer was transferred, the time was noted as the set to touch time of the polyurethane prepolymer. The test was carried out at 30-32°C and relative humidity of 40-45%. An average of three measurements was taken as the result.

Tack-free time was determined according to IS 101 (Part 3/Sec1) -1986. A thin film of PU prepolymer was coated on a glass plate. The plate was then placed in one pan of suitable balance and counterpoised with weights. Placed a further weight of 2.25kg and press on the dried film surface of the plate with thumb till the two pans are balanced. Hold for one minute and then slowly release. If no sign of stickiness appears on the thumb, the time was noted and reported as tack-free time of the prepolymer. Temperature was maintained at 30-32°C and relative humidity of 40-45%. The data given was the average of three measurements.

The tensile strength and percent elongation of the polyurethane films were measured in a universal testing machine (Tinius Olsen, H5KL). The dimension of the test specimen was 10cm x 2cm x 0.04cm and the measurement was performed under load cell of 250N with a crosshead speed of 5mm/min at room temperature. The data taken are the average of three measurements.

Differential Scanning Calorimetry (DSC) measurement of the prepolymers were carried out under nitrogen atmosphere on a DSC – 2910 (TA instrument). The heating rate was of 10°C / min in the temperature range of -100°C to 100°C.

RESULTS AND DISCUSSION

Effect of reaction time on structure

Fig.1 shows the IR spectra of the prepolymers synthesized at different reaction time. All the prepolymers shows the characteristics absorption bands of polyurethanes except in the peak associated to NCO stretching which shows higher absorption area at lower reaction time due to presence of higher isocyanate content. It was observed that all the prepolymers possess the following characteristic absorption bands, urethane NH stretching at 3300cm^{-1}, bending at 1516cm^{-1}, methylene or alkyl group at 2974cm^{-1}, carbonyl group at 1700cm^{-1} and C-O-C stretching at 1100cm^{-1}. The strong characteristic peak at 2272 - 2275cm^{-1} is associated with NCO stretching. Presence of NCO stretching band and all the above-mentioned bands indicates formation of isocyanate terminated polyurethane prepolymer.

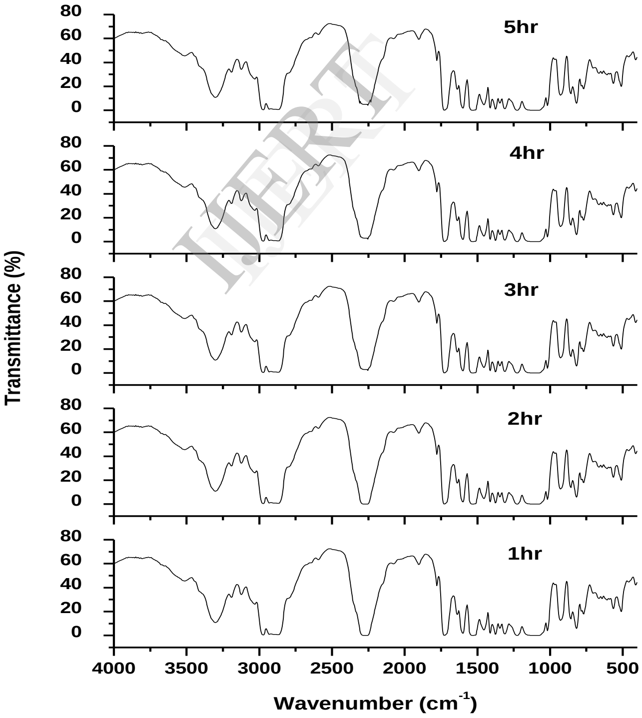


Fig. 1. IR spectra's of the polyurethane prepolymers synthesized at different reaction time

Effect of reaction temperature on physico-chemical properties

The effect of different reaction time on the physico-chemical properties of isocyanate terminated polyurethane prepolymer was shown from Fig. 2 to 7.

It was observed from Fig. 2 that as the reaction time increases, the isocyanate content of the prepolymer decreases, thus giving clear evidence that chain extension and other NCO-consuming side reactions are taking place on increasing the reaction time **[3].**

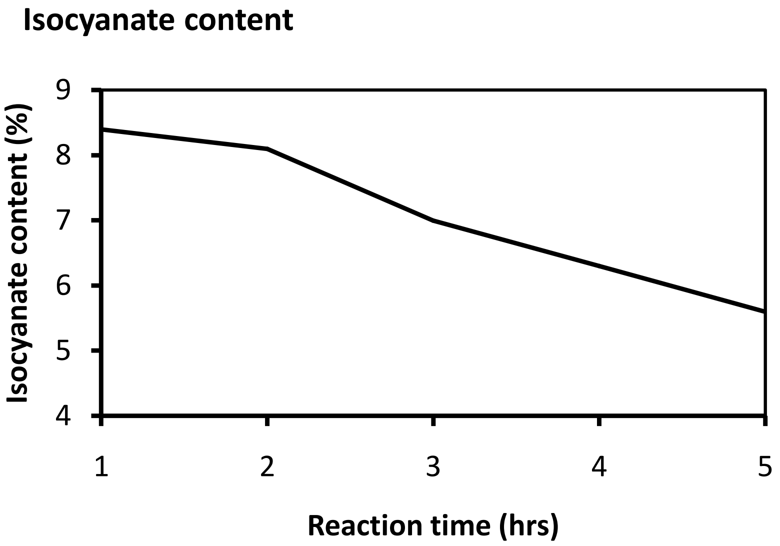


Fig.2. Isocyanate content of the prepolymer at different reaction time

It can be seen from Fig. 3 that with increase in reaction time period, the viscosity of the prepolymer increase gradually upto 3hr, but above 3hr a sharp increase in viscosity was observed. The weight average molecular weight the prepolymer was found to increase gradually with increasing reaction time (Fig. 4). The polydispersity index of the prepolymer shows a sharp increase above 3hr, indicating the possibility of the formation of side products such as allophanate and dimers (Fig. 5). This may be the reason behind the sharp increase in viscosity above 3hr as the prepolymer becomes very viscous due to formation of side products. The increase in molecular weight in the initial 3hr reaction period can be attributed to the chain extension reaction between PPG and MDI **[4]**, but the high molecular weight above 3hr might be due to the formation of large allophanate content and other side products. One hour reaction time is found to be insufficient to allow complete reaction, since it generates very low molecular weight

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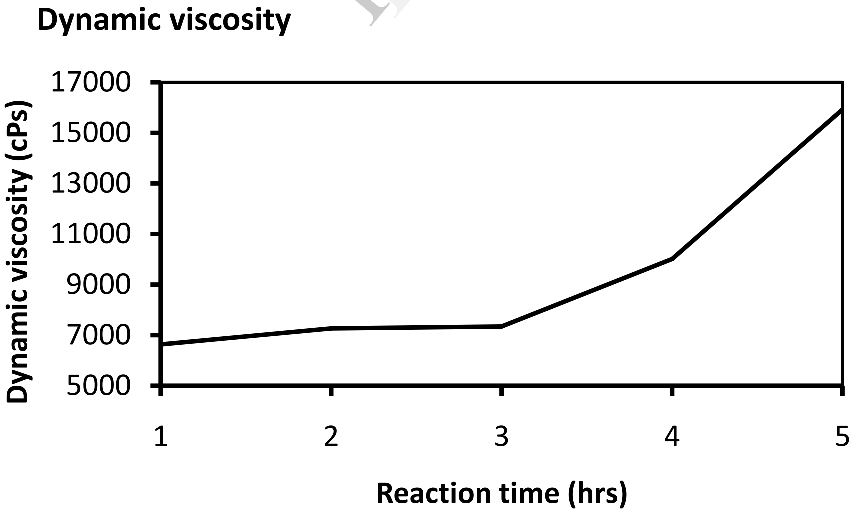

Fig.3. Viscosity of the prepolymer at different reaction time

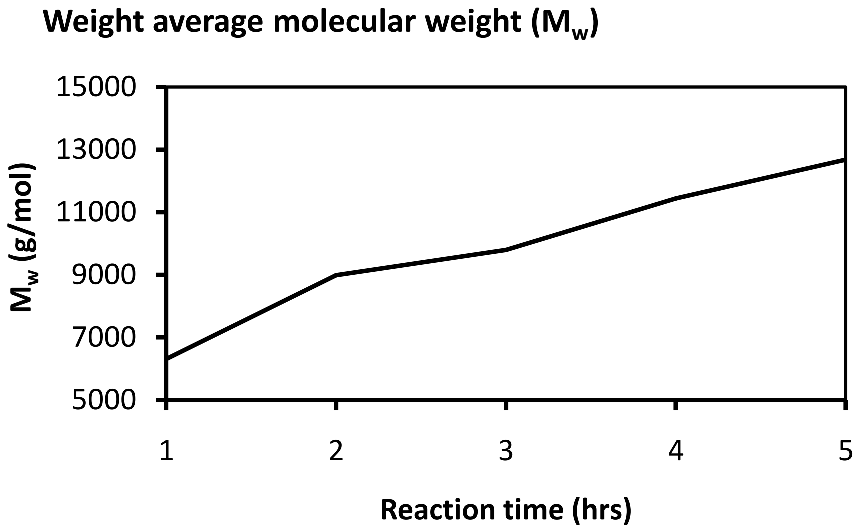

Fig. 4. Weight average molecular weight of the prepolymer at different reaction time

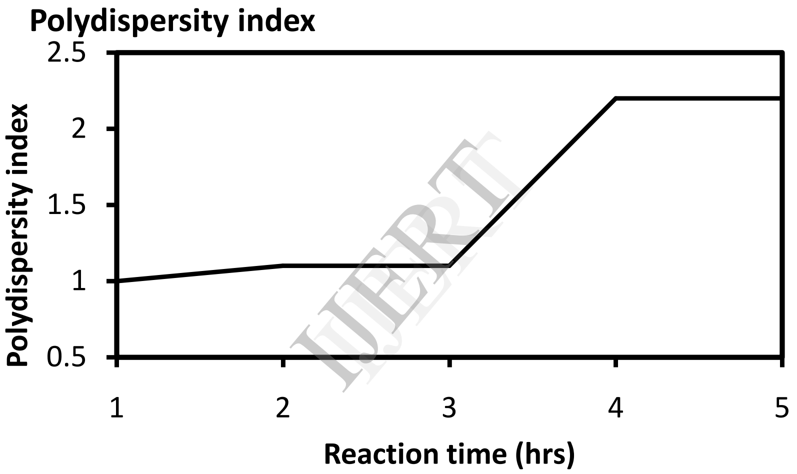

Fig. 5. Polydispersity index of the prepolymer at different reaction time

The storage time of the prepolymer (as shown in Fig. 6) was found to decrease with increasing reaction time, since with increasing chain extension reaction and formation of side products, the onset of gelation occurs faster.

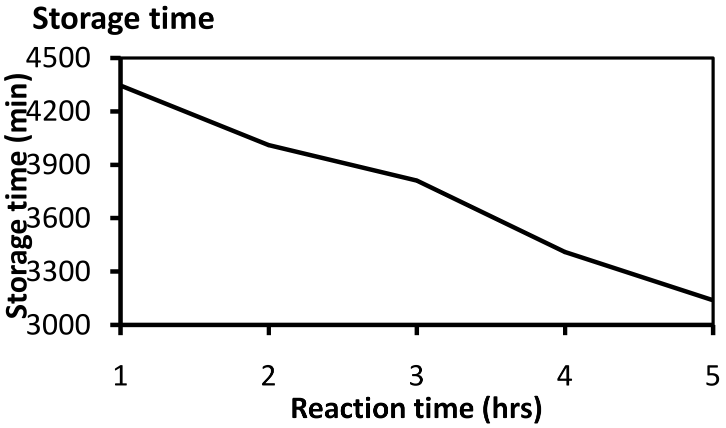

Fig. 6. Storage time of the prepolymer at different reaction time

The curing time of the prepolymer was determined by observing the set to touch time and tack free time of the prepolymer (Figure 7). It was observed that both the set to touch time and tack free time of the prepolymer decreases with increase in reaction time due to lowering of isocyanate content.

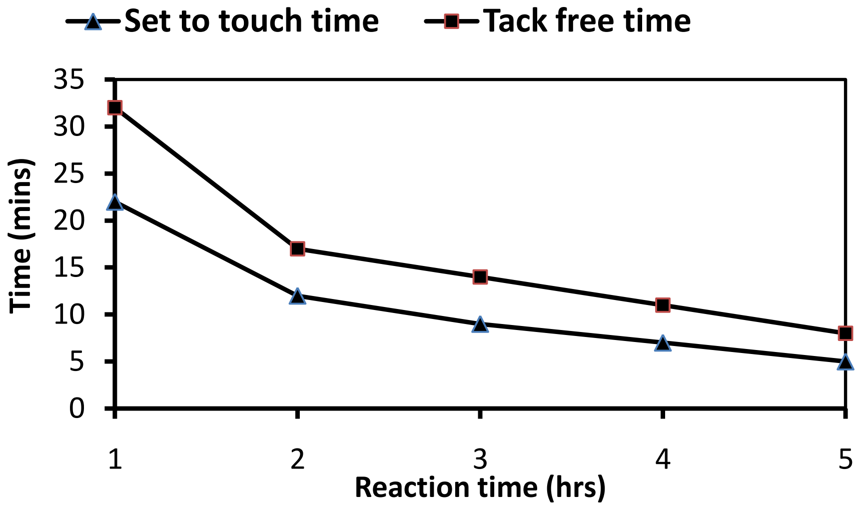

Fig. 7. Curing time of the prepolymer at different reaction time

Effect of reaction time on mechanical properties

The mechanical properties of the prepolymer were observed by preparing polyurethane film (Fig. 8). It can be seen that the tensile strength of the polyurethane film increases upto 4hr reaction time, thereafter decreases. The percent elongation of the film increases upto 4hr reaction time, and on further increasing the reaction time upto 5hr the elongation of the film decreased. This may be due to the formation of side products which increases the stiffness and decreases the flexibility of the polyurethane film.

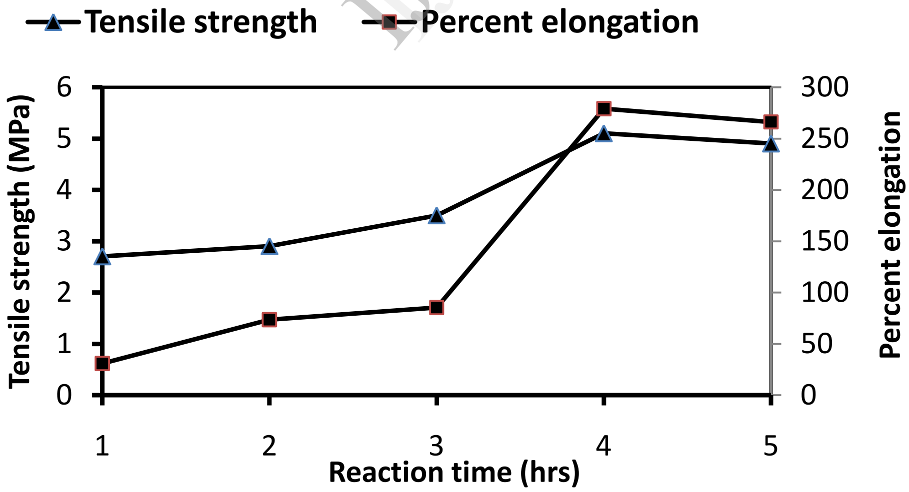

Fig. 8. Tensile strength and percent elongation of the polyurethane film at different reaction time

Effect of reaction time on thermal properties

The thermal properties of the synthesized polyurethane prepolymer were investigated by DSC technique (Fig.9).

It can be seen from the thermograms, that all the prepolymers shows only one T_g indicating proper mixing and no phase separation between hard and soft blocks at all reaction time. With increase in reaction time period, the T_g was found to shift towards higher temperature region from -40.8°C to -25.4°C. This may be due to the increase in molecular weight of the prepolymer which increases the T_g of the prepolymer.

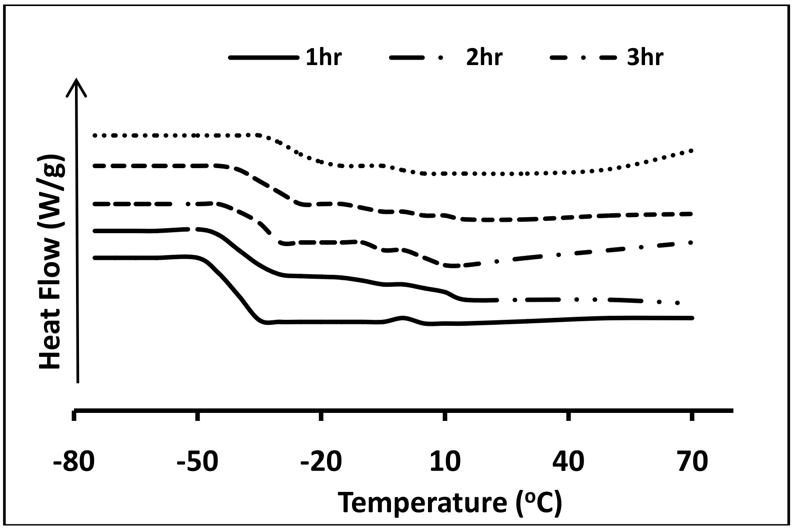

Fig. 9. DSC thermograms of the polyurethane prepolymer at different reaction time

CONCLUSION

It was observed that the synthesis of polyurethane prepolymer at different reaction time has a marked effect on its, physico-chemical, mechanical and thermal properties. The reaction time of one hour was found insufficient for the polymerization reaction as the molecular weight obtained was too low. Above 3hr reaction time, a sharp increase in viscosity of the prepolymer was observed. Polydispersity index also increases sharply above 3hr reaction time, indicating formation of side products. The curing time of the prepolymer decreases as the reaction time was increased. The mechanical properties of the polyurethane film increases upto 4 hr reaction time, above this it declines. The T_g of the prepolymer shift towards higher temperature region with increase in reaction time period.

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REFERENCES

1. J.H Saunders and K. C Frisch, *Polyurethane: Chemistry and Technology II, Technology*, Vol XVI, Part II, Interscience publisher, US, 1964, pp. 8-10. .
2. Saunders J.H and Frisch K C, *Polyurethane: Chemistry and Technology II, Technology*, Vol XVI, Part II, Interscience publisher, US, 1964, pp. 12-14.
3. Amy M. Heintz, Daniel J. Duffy and Shaw L. Hsu, Effect of reaction temperature on the formation of polyurethane prepolymer structure, 36, pp. 2695-2704, 2003.
4. Neil B. Graham, Jianwen Mao, Microgels Part 2. Solution polymerization using a urethane stepgrowth mechanism, *Colloid and Surface A: Physicochemical and Engineering Aspects*, 118, pp. 211-220,1996.