CHAPTER 4

Polyurethanes from starch

4.1 Introduction

Though polyurethanes are finding increasing applications as elastomers, foams, coatings etc., unfortunately due to their thermosetting character, recycling is difficult and limited. As a result PU based waste has become an area of concern. Biodegradation of PUs can become a possible solution to this problem. Recently the utilization of the renewable resources in polymers has gained interest due to their potential for substitution of petrochemical derivatives. Hence use of renewable resources can simultaneously take care of nonbiodegradable waste and petrochemical derivatives. The synthesis of biodegradable PUs is a relatively recent development in PU chemistry, and only a few reports have been published mostly in the patent form. It is well - known that polyester-based PUs are much more succeptible to biodegradation than PUs derived from polyether diols[1]. In general, more flexible PUs, are susceptible to biodegradation[2]. Poly(ester urethanes) containing biodegradable polyester segments of lactic acid,[3,4] poly(3-hydroxybutyrate),[5] and polyethylene adipate[6] have been reported.

Natural polymers having more than two hydroxyl groups per molecule have been used either as polyol or as crosslinker in the preparation of polyurethane, by allowing them to react efficiently with the diisocyanates. Biodegradable PU composites have been synthesised using hydroxyl groups present in plant material and / or fibres and molasses using MDI as diisocynate[7]. Sakai et al[8] have developed biodegradable PUs from acasia and cryptomeria bark. Synthesis and characterisation of degradable PU elastomers containing an amino acid extender has been carried out by Skarja and Woodhause[9]. Many authors[10-18] have used a variety of lignins as polyol for the synthesis of polyurethanes.

Nakamura et al[16] synthesized polyurethanes from coffee grounds and studied their viscoelastic properties[17]. Hatakeyama et al[18] prepared polyurethanes from lignin, wood, tar residue, wood meal and molasses and showed that T_g, tensile strength and Young's modulus increase with increase in content of these plant materials. Hatakeyama et al[19] have also studied the thermal properties of PUs derived from molasses before and after biodegradation. The results of these investigations have shown that the natural products, which are mainly plant components, act as hard segments in these polyurethanes. As the thermal and mechanical properties can be controlled by changing the hard and soft segment contents, these products can be of importance. IPNs from hydroxypropyl lignin-based PU and PMMA prepared by Kelley et al[20] are reported to exhibit 2-phase morphology. The modulus behavior of the different IPNs was explained by models, which accounted for either dual phase continuity or phase inversion.

The natural products used in the investigations mentioned above have very complex structure and composition and may not be entirely pure. Hence, attempts are being made to undertake a systematic study of polyurethanes containing less complex natural products. Biodegradable polyurethane block copolymers based on depolymerised cellulose derivatives such as cellulose triacetate have been reported[21,22]. Gong and Zhang[23] have studied the properties and interfacial bonding of regenerated cellulose films with PU-chitosan IPN coatings. IPNs of polyurethanes derived from castor oil, an important commercial oil extracted from beans of plant Ricinus communis, have also been investigated[24,25]. Zetterlund et al[26] have used glucose, fructose and sucrose for the development of PUs. They have observed that the incorporation of sachharides into polyurethane structures results in a higher crosslinking and higher hard segment content. However, the use of starch in the synthesis of PUs has been reported in only a few

publications[27-35] and most of them are in PU foams. Dosmann and Steel[31] added starch to urethane systems to yield shock-absorbing foams. Bennett and co-worker[32] reported a rigid urethane foam formulation containing 10 to 40 % of starch. Alfani et al[33] have synthesised polyurethane foams based on starch and polycaprolactone triol. They studied the effect of starch content on the thermal and mechanical properties and kinetics of foams. These studies demonstrated that starch products cause foams to be more flame resistant and more readily attacked by soil microorganisms. Boggs[34] developed a method to incorporate starch as a filler and crosslinking agent in diissocyanate-modified polyesters to yield elastomers. Chen and Li[35] have studied the biodegradation and swelling behaviour of PTMO based PUs modified with starch.

We have synthesised crosslinked polyurethanes containing starch and investigated their thermal, mechanical, morphological and biodegradable properties. Comparison of the products containing starch and 1,1,1- trimethylolpropane (TMP) as crosslinkers is also made. This is the first attempt to investigate the role of starch as a crosslinker in PUs.

4.2 Experimental

4.2.1 Materials

The chemicals used in the synthesis and their sources are given in Table 1.1. The diisocyanate was used without further purification. Potato starch from Qualigens, India and TMP were dried before use, as described in section 1.3.1.

4.2.2 Synthesis of polyurethanes

The prepolymer was synthesized in a five neck reaction kettle fitted with a mechanical stirrer, nitrogen inlet and a dropping funnel. The polyol was dried under vacuum at 80 °C for about an hour. A calculated quantity of the dried starch was mixed with the polyol and stirred in the reactor until a fine dispersion was achieved. Owing to the insolubility of starch in PPG 2000 it forms only a fine suspension. TDI was added dropwise over a period of 15 minutes. The mixture was stirred continuously for about 45 minutes followed by the addition of the catalyst dibutyl tin dilaurate. Stirring was continued further for about five minutes until the viscosity of the mixture increased. The air bubbles entrapped were removed by degassing and the mixture was poured into preheated and cooled glass moulds. The curing was carried out at room temperature for 15 hours and at 80 °C for 3 hours. After curing the polyurethanes were used for testing.

4.2.3 Characterisation

Specimen preparation for tensile testing and methods of determination of tensile properties, shore hardness, morphology, thermo-mechanical properties and transport properties are discussed in section 1.1.2.

Soil degradation studies

Biodegradation of all the polymers was studied by the soil burial method[36]. For this purpose a number of plastic containers of about 200 cm^3 capacity were filled with 1:1 mixture of compost and soil. Circular polymer samples of about 0.2g weight were placed in the containers at a depth of about 5 cms. The soil was kept moist by sprinkling water at regular time intervals. The

excess water was drained through the hole at the bottom of the container. The containers were stored at about 30 to 35 °C. The degradation of the samples was studied at regular time intervals of 15 days by removing the samples carefully from the soil and washing them gently with distilled water to remove the soil adhering on the surface. The samples were dried at 60 °C under vacuum until constant weight. Weight loss of the polymer with respect to time was recorded as a measure of degradation. In some cases the weight loss was checked only after 90 days.

4.3 Results And Discussion

The compositions of the polyurethanes synthesized are given in Table 4.1.

The polyurethanes were obtained in the form of films of about 2 mm thickness which were transparent where TMP was used as crosslinker (TMP - PU) but translucent possibly due to partial phase separation where starch was used as crosslinker (St - PU). The molar concentration of either TMP or starch was 1.3, 1.4 and 1.5 at NCO:OH equivalent ratio of 1.2. Starch based polyurethanes were also prepared by varying the NCO:OH equivalent ratios from 0.86 to 1.3. Another set of polyurethanes was synthesized using 75 / 25, 50 / 50 and 25 / 75 mole percentages of starch and TMP (St-TMP PUs). The concentration dependence of the additive effect of starch and TMP on thermo-mechanical properties of polyurethanes was studied using equimolar mixture of starch and TMP at 1.5, 2 and 2.5 molar concentration.

Table 4.1 : Molar composition of polyurethanes

Crosslinker	PPG / TDI / Crosslinker	NCO:OH ratio	% Hard segment
Starch			
	1.2 / 3.0 / 1.3	1.2	21.60
	1.1 / 3.0 / 1.4	1.2	23.46
	1.0 / 3.0 / 1.5	1.2	25.50
	1.0 / 3.25 / 1.5	1.3	26.61
	1.0 / 3.0 / 2.0	1.0	26.95
	1.0 / 3.0 / 2.5	0.86	28.36
TMP			
	1.2 / 3.0 / 1.3	1.2	21.00
	1.1 / 3.0 / 1.4	1.2	22.68
	1.0 / 3.0 / 1.5	1.2	24.70
Starch+TMP (mole %)			
75:25	1.0 / 3.0 / (1.125+0.375)	1.2	25.03
50:50	1.0 / 3.0 / (0.75+0.75)	1.2	25.09
25:75	1.0 / 3.0 / (0.375+1.125)	1.2	24.90
Starch+TMP (equimolar)			
	1.0/ 3.0 / (0.75+0.75)	1.2	25.09
	1.0 / 3.0 / (1.0+1.0)	1.0	26.45
	1.0 / 3.0 / (1.25+1.25)	0.86	27.7

4.3.1 Tensile Properties

The tensile strength and elongation at break were determined for all the polyurethanes. The results are given in Figs. 4.1- 4.4.

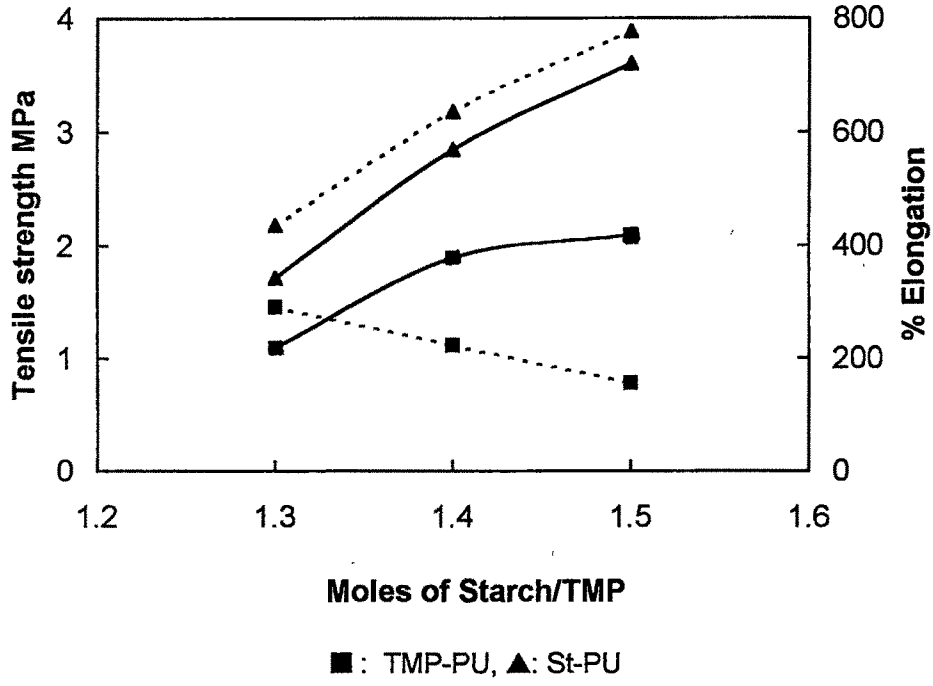


Fig. 4.1 : Dependence of tensile strength (___)and % elongation (----) on starch/TMP concentration.

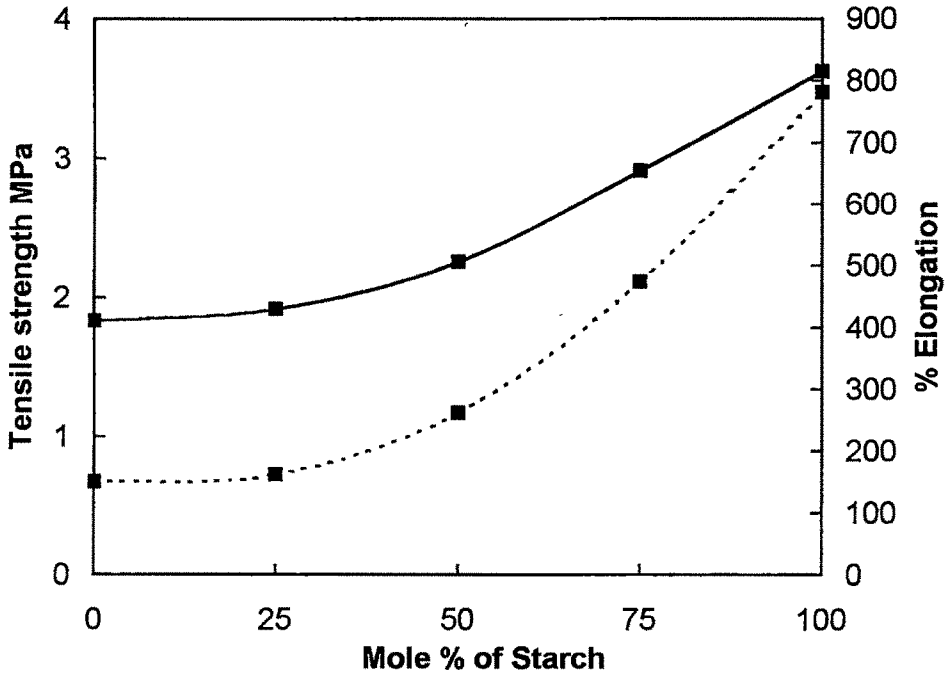


Fig. 4.2 : Effect of starch concentration on tensile strength (____)and % elongation (----) of starch-TMP based PUs. Total St-TMP molar concentration =1.5

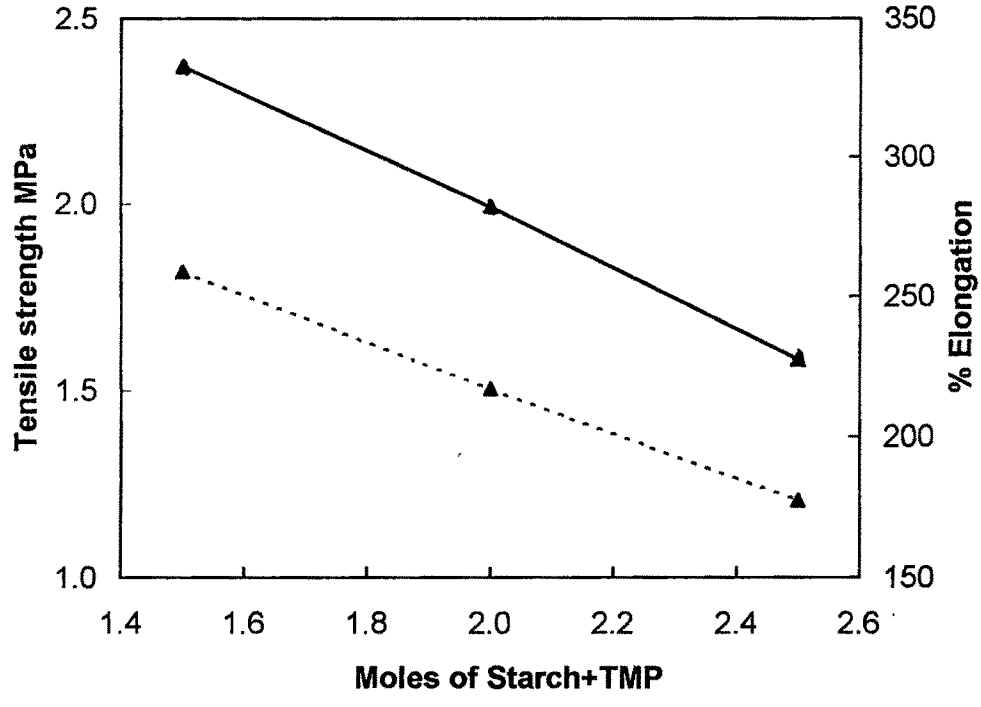


Fig. 4.3: Effect of molar concentration of equimolar starch-TMP mixture on tensile strength (___) and % elongation (----)

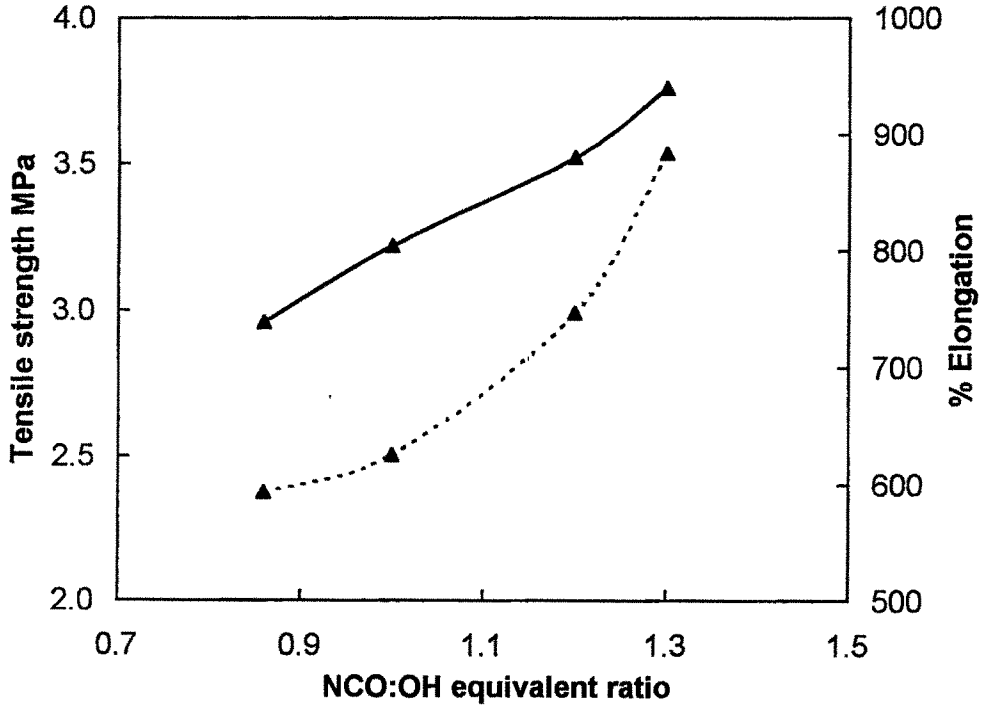


Fig. 4.4: Dependence of tensile strength (___) and % elongation (----) on NCO:OH equivalent ratio in St-PUs.

Effect of starch or TMP concentration

Fig. 4.1 gives the comparison of the tensile strength and elongation properties of polyurethanes containing starch or TMP. It can be seen that St-PUs show higher tensile strength and better elongation as compared to TMP-PUs. Moreover, in the case of TMP-PUs the tensile and elongation properties show opposite trend. With increasing concentration of TMP the tensile strength increases and elongation decreases, as expected. However, on replacement of TMP by starch, both tensile strength and elongation were observed to increase with increasing starch content. This may be because of the presence of multiple hydroxyl functionality in the starch molecules, which increases the crosslink density, and hence the stress-strain properties. The observed increase in elongation with increasing starch content may be due to factors other than crosslink density and can be explained on the basis of internal bond strength, which according to Saraf and Glasser[11], is a property influenced more by chain breakage than by chain slippage. Presence of multiple hydroxyl groups in starch results into increasing number of urethane bonds with increased starch content. Increasing starch content serves as a bridge with the multiple hydroxyl groups forming more number of urethane bonds. Hence, if fracture depends on the bonds produced in the polyurethane synthesis[11] it may occur only at higher elongation. In addition, the observed higher tensile properties further support the existence of phase segregation in St-PUs.

The effect of starch and TMP on the mechanical properties of PUs in the presence of each other was also studied by using different mole percentages of starch and TMP. The total concentration of starch-TMP mixture in polyurethane was kept constant at 1.5 moles at NCO:OH equivalent ratio 1.2. From the

results given in Fig. 4.2 the tensile strength and elongation were observed to increase as the mole percentage of starch increases as discussed earlier.

Significant rise in stress-strain properties was observed above equimolar ratio of starch-TMP. Hence, the dependence of mechanical properties on starch-TMP concentration was further studied at equimolar ratio (Fig. 4.3). With increasing starch-TMP concentration, decrease in the mechanical properties was observed. When 2.5 moles of equimolar mixture of starch-TMP was taken, due to stoichiometric imbalance between OH and NCO groups, starch and TMP compete for reaction with the isocyanate. As primary –OH reacts faster than the secondary OH[37], it can be assumed that TMP may be used up faster than starch. As a result the unreacted starch brings a discontinuity in the matrix leading to poorer mechanical properties.

Effect of NCO: OH equivalent ratio

Though mechanical properties were observed to be dependent on starch content in polyurethanes, the other important factor governing these properties is NCO: OH ratio (R value). Hence, its effect on tensile strength and elongation was studied. The results obtained are given in Fig. 4.4. It was observed that as the R value increases from 0.86 to 1.3, there is a steady rise in the stress-strain properties. When R value is 1.2 the polyurethanes formed are -NCO terminated. The free NCO groups react further with the urethane linkage increasing the chemical crosslinking[38] leading to a change in morphology thus affecting the mechanical properties.

At R value 1 due to lack of rigidity offered by the three dimensional structure mentioned earlier, there is a decrease in tensile strength as well as elongation at break. When the starch

content is 2.5 moles (R=0.86) the excess of starch forms separate phase and gets dispersed as observed from the morphology (Fig. 4.5). This indicates that the unreacted starch particles may act as the origin of cracking rather than as reinforcing filler in this PU system. This further creates a discontinuity in matrix and decreases the tensile strength and elongation. The unreacted components and free chain ends act as plasticisers resulting in lower crosslink density and give rise to a mechanically weaker polymer.

When the TDI content was increased from 3 to 3.25 moles (R=1.3) keeping starch content constant the resulting polymer showed not only greater tensile strength but also higher elongation indicating dependence of these properties on NCO concentration. This can be explained as follows. When the TDI content was less (3 moles) there existed certain domains in the samples due to incomplete crosslinking or possible structural inhomogenities developed due to the reaction of some of the NCO groups with moisture during curing[38]. Whereas excess of diisocynate develops a firm network by linking together the dangling chains or reacting with urethane groups through crosslinking, resulting into higher stress-strain properties.

The results of the shore hardness measurements and stress and strain at yield are given in Table 4.2. All the properties showed similar trend as observed in tensile properties.

4.3.2 Scanning Electron Microscopy

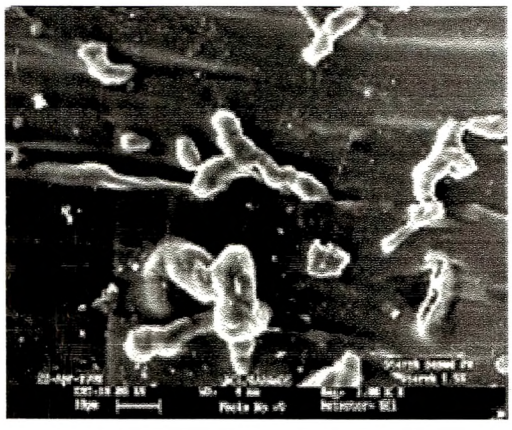
Figure 4.5 shows the morphology of tensile fractured specimens of polyurethanes containing TMP, starch and TMP-starch (50:50) mixture at 1.5 molar concentration. It can be seen that in St-PU the fractured surface shows the presence of fibrillar

Table 4.2 : Mechanical properties of PUs

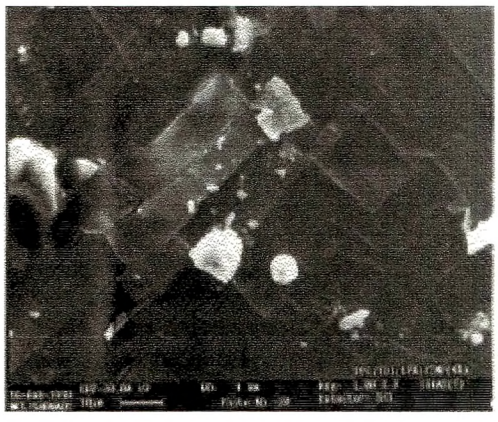
Crosslinker	Hard segment %	Hardness Shore A	Modulus at 50 % strain Mpa X 10^2	Yield stress Mpa	Yield Strain %
Starch					
	21.60	72	48.3	19.0	15.6
	23.46	75	82.7	36.1	17.5
	25.50	78	83.5	38.5	19.0
	26.95	75	81.4	33.2	17.3
	28.36	72	80.7	32.1	16.9
	26.61	80	85.5	39.0	19.8
Starch + TMP (mole %)					
75:25	25.03	69	46.9	23.7	16.3
50:50 (1.5)	25.09	67	55.2	16.3	12.5
50:50 (2.0)	26.45	65	50.3	14.5	10.2
50:50 (2.5)	27.77	70	49.6	14.3	9.6
25:75	24.90	65	55.2	13.2	8.8

structure developed due to gradual fracture (Fig. 4.5A) and some extent of phase separation as discussed earlier. Whereas in TMP-PUs no such structures are observed. Moreover, it shows cracks developed due to sudden fracture (Fig. 4.5B). The St-TMP PU showed mixed features such as fibrillar structure as well as a few cracks (Fig. 4.5C).

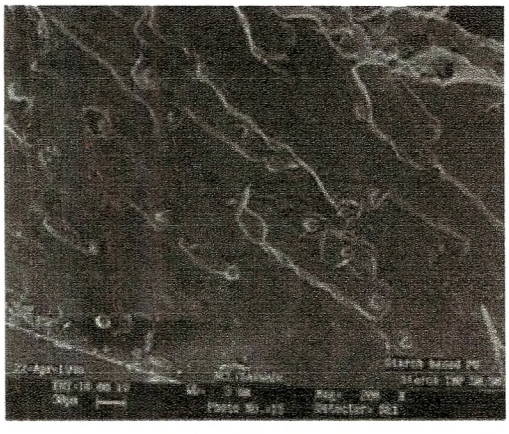
Fig. 4.5D shows morphology of PU containing 2.5 moles of starch. Due to excess of starch, unreacted starch granules as well as holes created due to easy pulling out of these granules during fracture are clearly seen in the micrograph. This morphology supports the poor mechanical strength observed for this particular polyurethane.



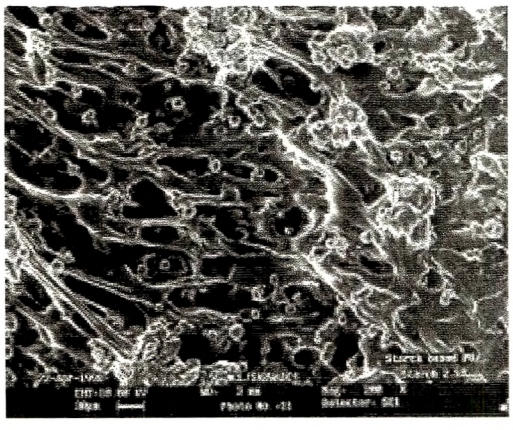
(A) (1KX)



(B) (1KX)



(C) (200 X)



(D) (200 X)

Fig. 4.5 : SE Micrographs of tensile fractured surface of polyurethanes containing 1.5 moles of (A) starch, (B) TMP, (C) equimolar starch + TMP and (D) 2.5 moles of starch

4.3.3 Thermal Analysis

4.3.3.a Differential Scanning Calorimetry

Fig. 4.6 exhibits representative thermograms of starch, TMP and starch-TMP based polyurethanes. The Tg value for the PU containing 1.5 moles starch is somewhat higher than that of the PU containing equal amount of TMP (Fig. 4.6A and C respectively). The Tg of the polyurethane containing equimolar mixture of starch and TMP at 1.5 molar concentration (Fig. 4.6B) falls in between that of the PU containing only starch or TMP. It was further observed that starch based polyurethanes show two Tgs whereas in the case of TMP and TMP-starch containing polyurethanes only one Tg was observed. This may be due to the smaller change in calorific value for the transition of the hard segment, which is below the detection level[39] as in the present case. Further if the hard segment content is low the observation of glass transition becomes still difficult.

In case of St-PUs there is increase in crosslink density because of the presence of a number of hydroxyl groups per molecule of starch. This results into higher concentration of hard segment. The second Tg may be due to the incompatibility of starch-TDI, and PPG-TDI segments. This further supports the observed phase separation in St-PUs. The higher Tg value obtained on replacement of TMP with starch may be attributed to the higher crosslink density resulting into restricted main chain motion of the polymer. When the starch content is increased from 1.5 to 2.5 moles, Tg decreases (Fig. 4.6D) due to the plasticizing effect of the excess starch, which also affects the mechanical properties as discussed earlier. The observed shift in soft segment Tg due to the change in starch content was significant and also influenced phase separation.

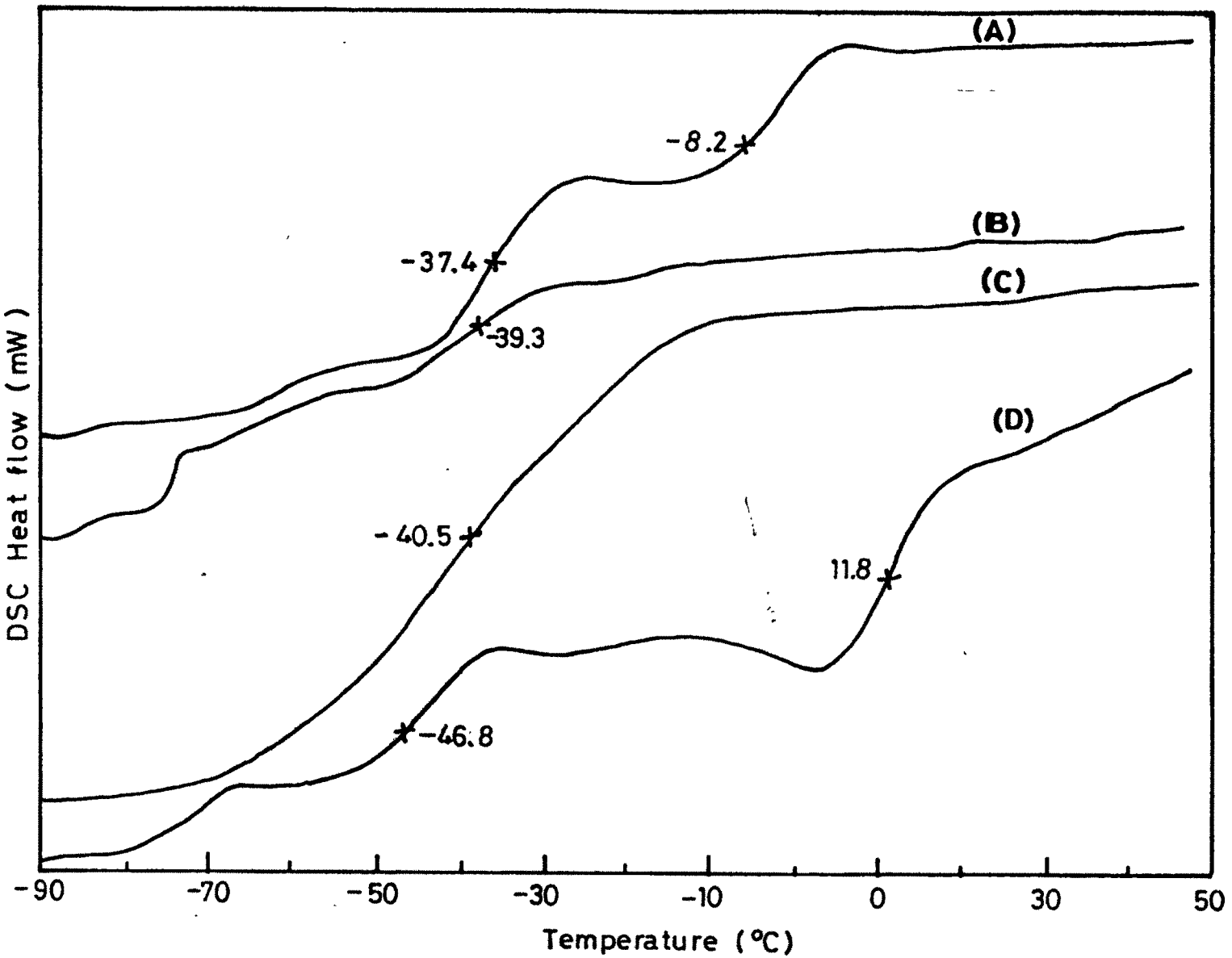


Fig. 4.6 **DSC** Thermograms of PUs containing 1.5 moles of **(A)** starch **(B)** equimolar starch TMP mixture **(C)** TMP and **(D)** 2.5 moles of starch.

4.3.3b Thermo-gravimetric Analysis

The Thermo-gravimetric curves of the blends (Fig. 4.7) show that although starch has low thermal stability the polyurethane containing 1.5 moles starch exhibited good thermal stability upto 300 °C. In comparison with TMP - PU, the St - PU showed higher thermal stability due to more rigid network.

4.3.4 Dynamic Mechanical Analysis

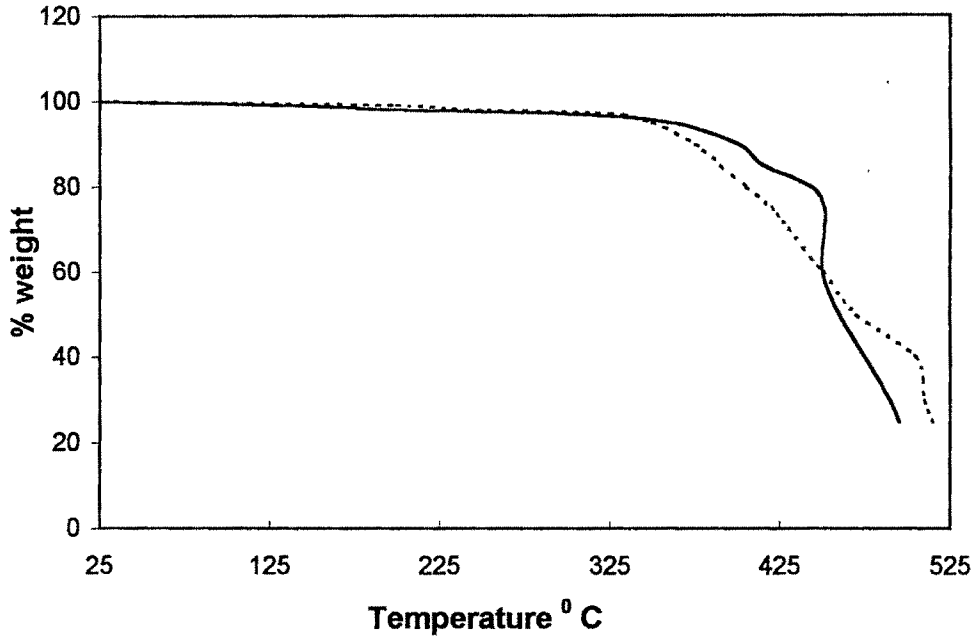
The DM plots at 1, 2, 5 and 10 Hz for PU containing 1.5 moles of starch, are given in Fig. 4.8 (A and B). Due to α relaxation a sudden decrease in E' and large peaks for E" and tan δ were observed at -55.5 and -37.6 °C respectively. The activation energy calculated as discussed in section 2.3 was found to be about 69 kcal/mol. The Tg values obtained from DSC and DMA do not vary to a large extent (Table 4.3).

Table 4.3 : Dynamic Mechanical data of ST-PU containing 1.5 moles of starch

Frequency Hz	T_g °C	tan $\delta_{max.}$	$E"_{max}$ N/m^2
1	-42.4	0.750	4.80×10^8
2	-41.4	0.760	4.74×10^8
5	-38.7	0.770	4.73×10^8
10	-37.6	0.775	4.70×10^8

4.3.5 Swelling behavior

A number of solvents of varying solubility parameters were used for the swelling behaviour of the PUs under study. From the plots of solubility parameter vs. swelling coefficient (α) of polyurethanes (Fig. 4.9), the solubility parameter for the St-PUs



------ P/T ——— ST-PU

Fig. 4.7 : Thermogravimetric plots for PUs

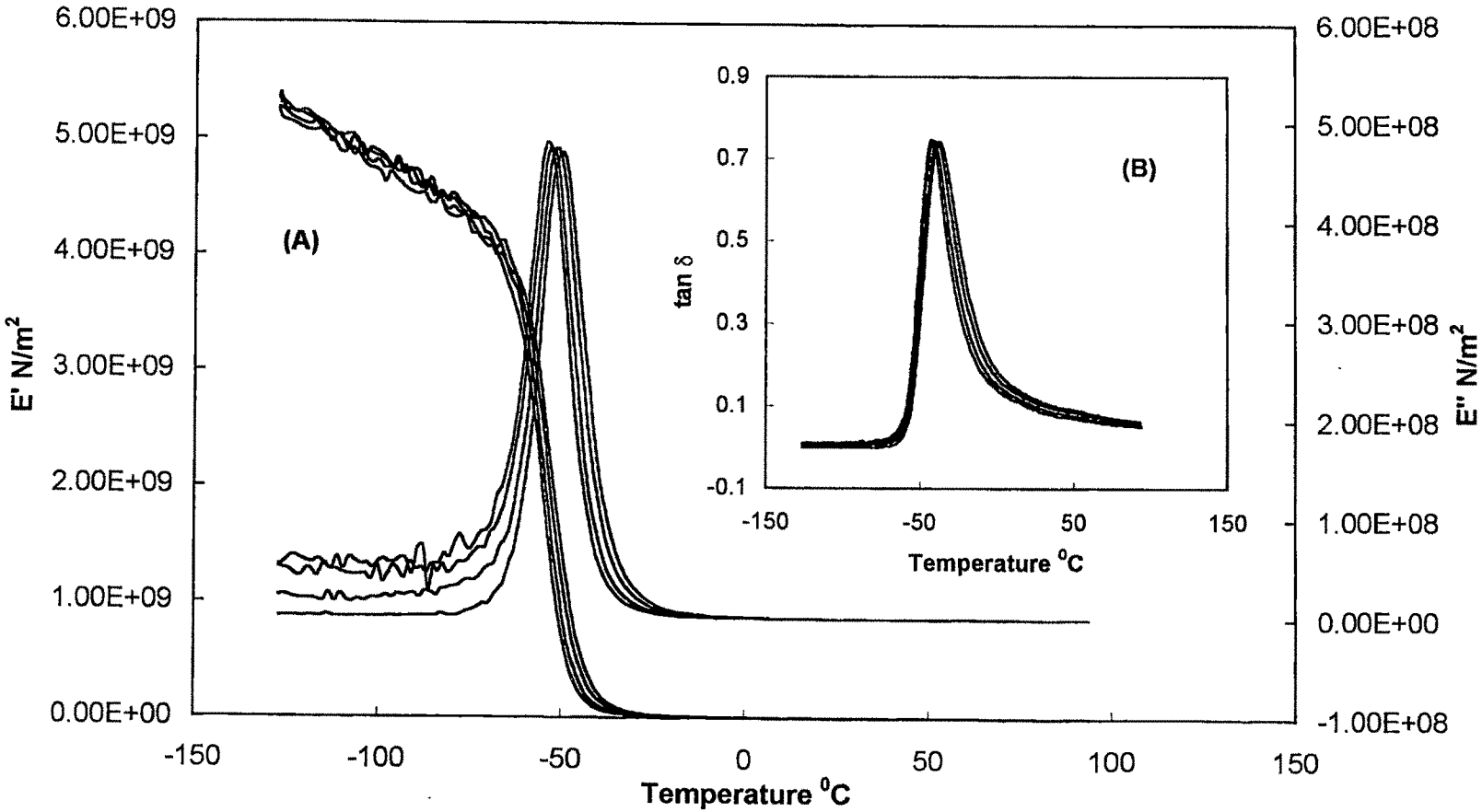


Fig. 4.8: Dynamic Mechanical plots for PU containing 1.5 mole starch.

was found to be 10.1 (cal / cm^3)$^{1/2}$ corresponding to that of acetic acid. The solubility parameter of polyurethane with 1.5 moles of TMP was observed to be 9.7 (cal / cm^3)$^{1/2}$. Using the swelling data the molecular weight between crosslinks Mc was calculated from Flory - Rehner equation[40] (Section 1.3f), The values of χ, Mc, ν and ν_e are given in Table 4.4. The higher Mc values obtained in the case of TMP-PU indicate lower crosslink density, which supports the other results. The large variation in Mc with changing solvents is due to the limitations of the Flory - Rehner theory for a heterogeneous system. Similar results have been reported earlier[41]. As discussed earlier the degree of crosslinking and crosslink density were observed to be higher in the case of St-PU.

4.3.6 Biodegradation studies

The plot of percentage weight loss due to soil burial vs. time is given in Fig. 4.10 for the samples containing 1.5 moles of TMP and starch as well as 2.5 moles of starch. The observed weight loss was much higher in the case of starch based polyurethanes and was directly proportional to the starch content. The observed weight loss in TMP based polyurethanes may be due to the presence of nitrogen in the polyurethanes, which is utilized by microbes. At higher concentration of starch (2.5 moles) unreacted starch is readily available to micro-organisms resulting into higher weight loss and poor mechanical properties as discussed earlier.

Conclusion

The St-PUs were found to show better mechanical properties than TMP-PUs. Not only the tensile strength but also the elongation was observed to increase. However, these properties were also found to depend on the NCO:OH equivalent ratio. With

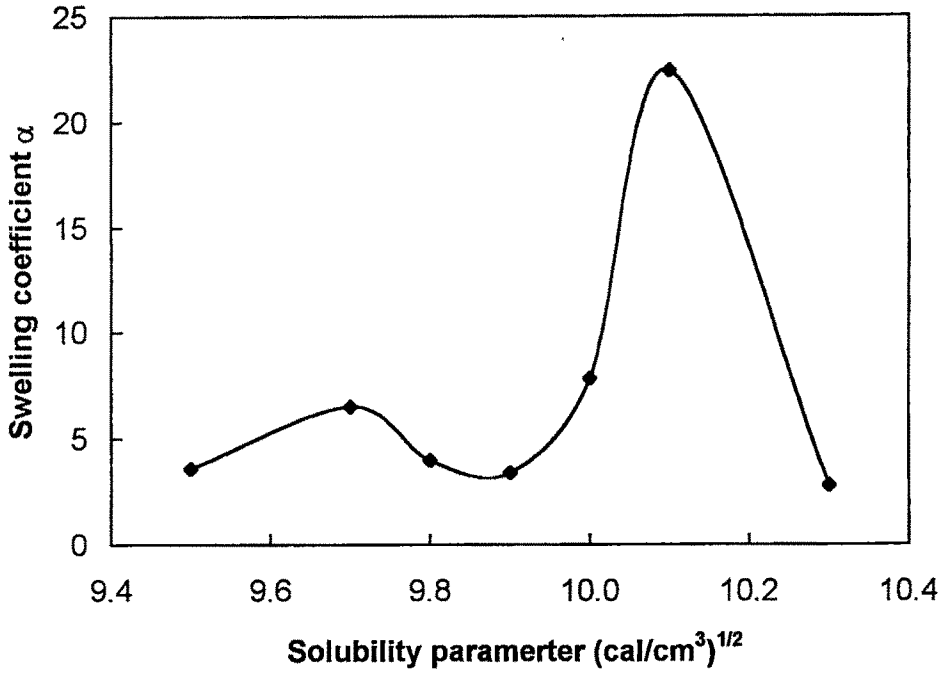


Fig. 4.9:Variation of swelling coefficients of PU containing 1.5 mole starch with solubility parameters of solvents.

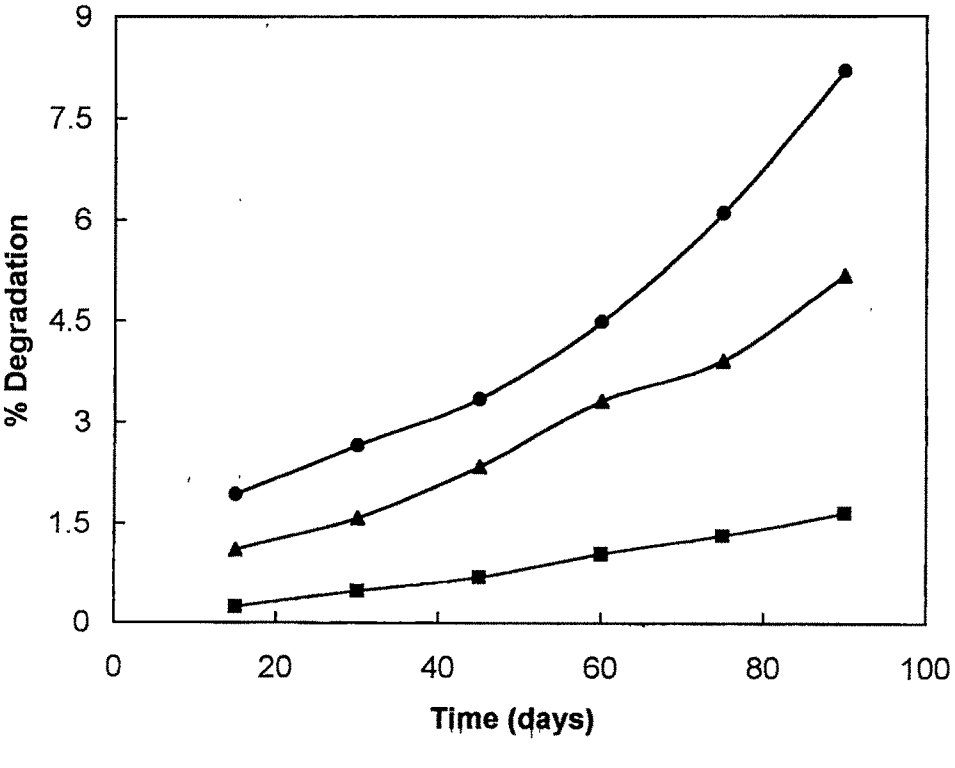


Fig. 4.10 : Biodegradation studies of PUs containing ■ :1.5 mole TMP, ▲ :1.5 mole starch, ●: 2.5 mole starch

Tabel 4.4 : Swelling data for St-PU and TMP-PU

Solvents	χ		Mc		ν x 10^4		νex10^4	
	ST-PU	TMP-PU	ST-PU	TMP-PU	ST-PU	TMP-PU	ST-PU	TMP-PU
Chlorobenzene	0.402	0.345	8699	9122	0.575	0.548	1.31	1.22
Dichloroethane	0.351	0.343	3028	4501	1.650	1.110	3.76	2.47
Acetone	0.345	0.345	4320	5031	1.160	0.994	2.64	2.21
n-octanol	0.343	0.420	4346	5102	1.150	0.980	2.62	2.18

increasing R value, the stress-strain properties were observed to be increase. The DSC thermograms of TMP-PUs showed the appearance of only one glass transition whereas thermograms of St-PU showed two indicating phase seperation. The Tg of St-PU obtained from DSC was in good agreement with that obtained from DMA. The activation energy calculated from DMA analysis was found to be 69k cal/mol. The solubility parameter from the swelling data of St-PU and TMP-PU was found to be 10.1 and 9.7 $(cal/cm^3)^{1/2}$ respectively. Hence starch based polyurethanes were observed to be better in the thermo-mechanical properties as well as showed potential for biodegradability.

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