

Structure–Property Relationship of Starch-Filled Chain-Extended Polyurethanes

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ABSTRACT: Chain-extended polyurethane (PU) elastomers were prepared using castor oil with 4,4'-methylene bis (phenyl isocyanate) (MDI) as a crosslinker and 4,4'-diamino diphenyl sulphone (DDS) as an aromatic diamine chain extender. A series of starch-filled (from 5 to 25% wt/wt) diamines chain-extended PUs have been prepared. The starch-filled PU composites were characterized for physico-mechanical properties viz, density, surface hardness, tensile strength, and percentage elongation at break. Thermal stability of PU/starch have been carried out by using thermogravimetric analyzer (TGA). Thermal degrada-

tion process of PU/starch were found to proceed in three steps. TGA thermograms of PU/starch shows that all systems were stable upto 235°C, and maximum weight loss occur at temperature 558°C. The microcrystalline parameters such as crystal size ($\langle N \rangle$) and lattice strain (g in %) of PU/starch have been established using wide-angle X-ray scattering (WAXS) method. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2945–2954, 2003

Key words: polyurethane; chain extender; mechanical properties; thermal properties

INTRODUCTION

The properties of elastomeric polyurethanes (PUs) depend very much on their chemical structure and morphology. They have a heterophase structure consisting of the polyol, which constitutes the soft segment, and the polyfunctional isocyanate and chain extender/crosslinker, which constitutes the hard segment. The morphology of PU depends on the state of the compatibility and microphase segregation between the two segments. The existence of the phase segregation caused by the clustering of hard and soft segments into separate domains has been a subject of continued research interest.^{1–3} Variety of polyols and diisocyanates have been used in the synthesis of PUs, and their effect on the properties have been investigated.^{4–8} Recently, the utilization of the renewable resources in polymers has become an increasing interest because of their potential for substitution of petrochemical derivatives. Many researchers have reported the use of natural polymers having more than two hydroxyl groups per molecule either as polyol or as crosslinker in the preparation of PU, by allowing them to react efficiently with the diisocyanates.^{9–11} The results of these investigations have shown that the natural products, which are mainly plant components, act as hard

segments in these PUs. These products are of great importance, as the thermal and mechanical properties can be controlled by changing the hard and soft segment contents.

Over the last few years, there has been a renewed interest in biodegradable plastics and plastics made from annually renewable, natural polymers such as starch. Numerous works have been done on study the properties of starch-based films,^{12–14} but only the last study reported the effects of different types of starch on the properties of films.

Starch has been considered as a candidate material in certain thermoplastic applications because of its known biodegradability, availability, and low cost.^{15,16} In the last decade there has been some interest in developing systems of starch and synthetic polymers. Most of the early studies have focused on the synthesis of starch-based systems.^{17–19} There have been some reports on the properties of the resulting starch/synthetic polymer systems after processing.^{20–23} Materials possessing excellent end properties can be obtained by blending starch with synthetic polymers containing reactive functional groups. Chain-extended PU elastomers have a wide range of industrial applications and they are well known for their mechanical and optical properties. A detailed literature survey reveals that the starch-filled chain-extended PU systems have not been studied for their structure–property relationship. In this research article the authors report the physico-mechanical, thermal

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TABLE I
Physico-mechanical Properties of Starch-Filled Chain-Extended PU

Samples	Density (g/cc)		Tensile strength MPa ± 1	% Improvement	Percentage elongation at break ± 2	% Improvement	Surface hardness ± 2	
	Theoretical	Experimental ± 2%					Shore A	Shore D
CO+MDI+DDS		1.094	2.35	—	47	—	89	50
CO+MDI+DDS+5% Starch	1.0953	1.0956	6.86	192	61	32	91	57
CO+MDI+DDS+10% Starch	1.0966	1.0971	6.98	197	54	17	93	58
CO+MDI+DDS+15% Starch	1.0979	1.0982	7.25	208	46	0	94	61
CO+MDI+DDS+20% Starch	1.0992	1.101	7.46	217	42	-8	96	62
CO+MDI+DDS+25% Starch	1.1005	1.1020	7.95	238	35	-24	97	68

Starch density—1.12 g/cc.

CO—castor oil.

properties, and microstructural parameters of starch-filled chain-extended PUs.

EXPERIMENTAL

Materials

Castor oil (CO) was procured from the local market. Its molecular weight (M_n) is 930 and its hydroxyl group/molecule is 2.24. 4,4'-methylene bis (phenyl isocyanate) (MDI), dibutyl tin dilaurate (DBTL) and 4,4'-diamino diphenyl sulphone (DDS) were obtained from Sigma (St. Louis, MO). They were used as received. Starch was procured from M/s. Riddhi Siddhi Chemicals (I) Ltd., India.

Synthesis of starch-filled chain-extended PUs

A series of PU/starch systems were prepared with different weight ratios of starch viz., 5, 10, 15, 20, and 25%. The prepolymer was synthesized in a four-necked reaction kettle fitted with a mechanical stirrer, nitrogen inlet, condenser, and a dropping funnel. The castor oil was dried under vacuum at 80°C for about an hour, and then it was dissolved in MEK. The required amount of (MDI : castor oil is 1 : 0.6) methylene diisocyanate (MDI) was added dropwise over a period of 15 min. The mixture was stirred continuously for about 45 min followed by the addition of the catalyst dibutyl tin dilaurate. Stirring was continued further for about 5 min until the viscosity of the mixture increased. DDS dissolved in MEK was added to the reaction flask with further stirring. A calculated quantity of the dried starch was mixed until a fine dispersion was achieved. The air bubbles entrapped were removed by degassing and the mixture was poured into a glass mold. The mold was allowed for 24 h at room temperature. After curing, PU/starch sheets were released slowly from the mold.

Techniques

The PU/starch composites were characterized for physical properties like density and surface (shore A and shore D) hardness according to ASTM D 792-86 and ASTM D 785, respectively. The mechanical properties such as tensile strength and percentage elongation at break have been measured as per ASTM D 638 using 4302 model Hounsfield universal testing machine (UTM), UK. A minimum of five samples were tested at room temperature for each formulation, and the average values are reported.

The thermal stability of all PU/starch samples were measured with a TG METLER Polymerchemie Marburg FB 14, thermogravimetric analyzer (TGA). The TGA studies have been carried out in the temperature range from ambient to 600°C at a heating rate of 20°C/min in air media, and the weight loss with respect to temperature was recorded. The instrument was calibrated using pure calcium oxalate sample before analysis.

The relative thermal stability of the PU/starch were evaluated by comparing decomposition temperatures at various percent weight losses and integral procedural decomposition temperature (IPDT). The IPDT is defined as a means of summing up the whole shape of the normalized TGA data curve. IPDT is an index of thermal stability, was determined from the thermogram area using the method reported in the literature.²⁴ The oxidation index (OI) was calculated based upon the weight of carbonaceous char (CR) as related by the empirical equation:

$$OI \times 100 = 17.4 \times 0.4 CR \quad (1)$$

X-ray recording and profile analysis

X-ray diffraction data on PU/starch samples were collected on a STOE/STADIP X-ray powder diffrac-

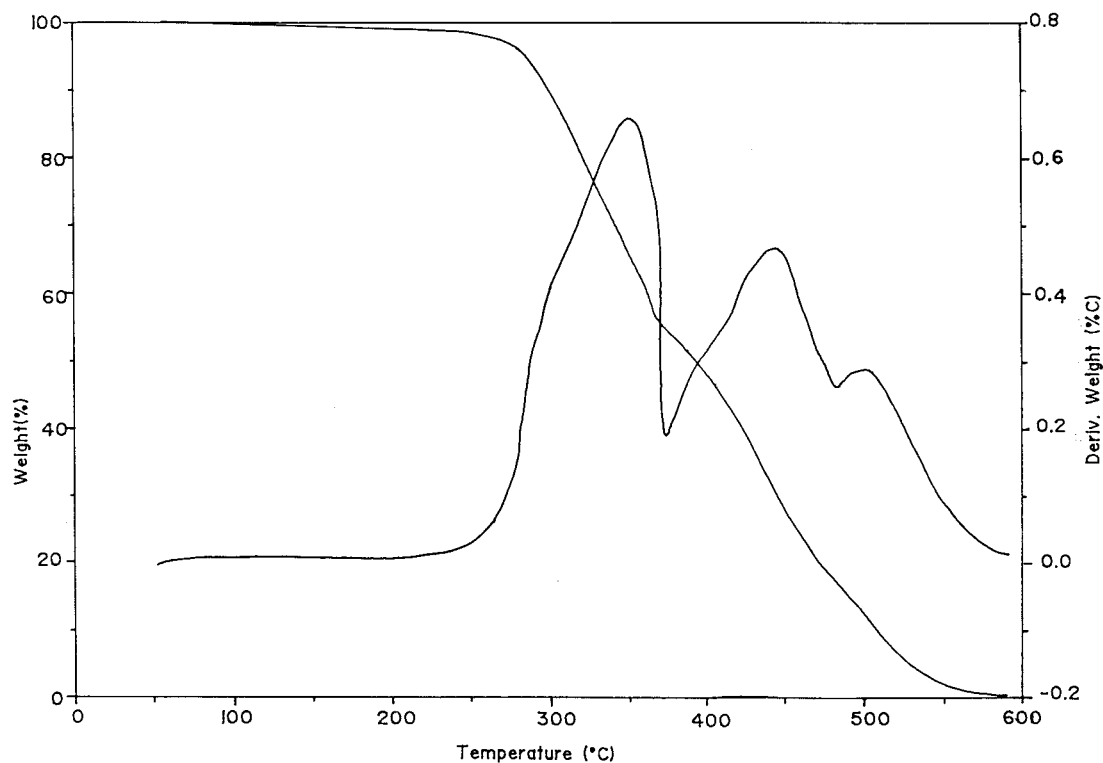


Figure 1 TGA and its derivative thermograms of 10% starch-filled PU.

tometer with germanium monochromated $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation in a transmission mode, using a curved position sensitive detector (CPSD) in the 2θ

range from 5 to 50° at a step size of 0.03° . The trial and error indexing program (TREOR)²⁵ was used in determining the unit cell parameters.

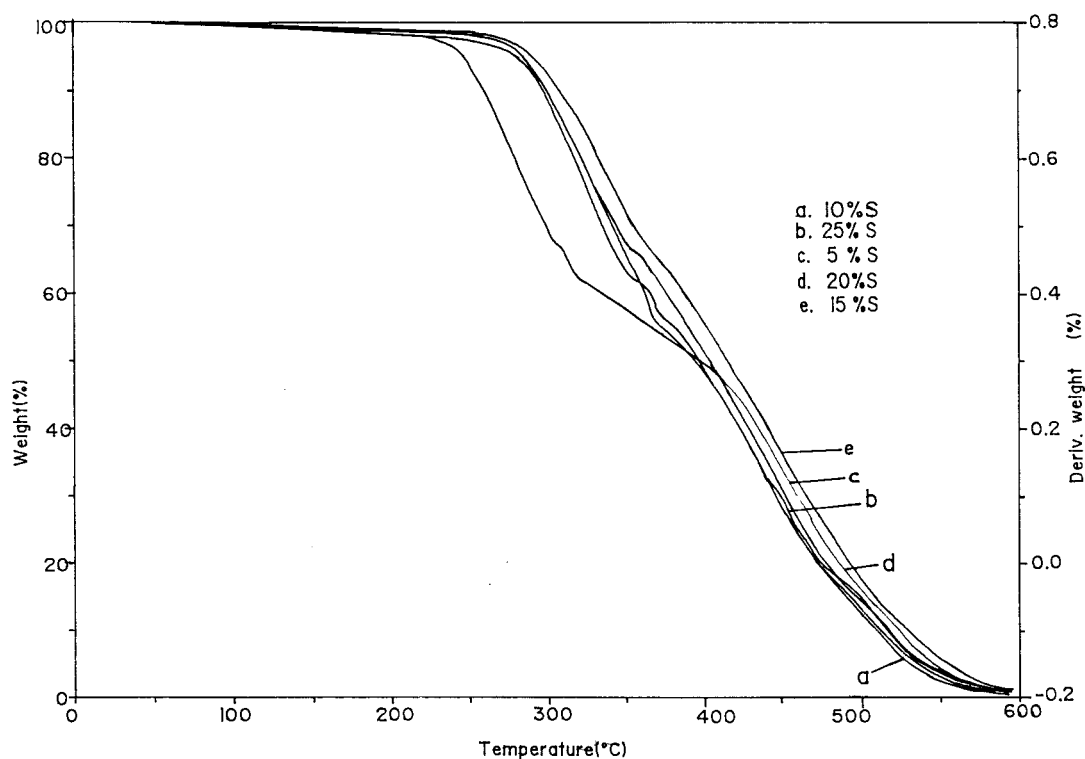


Figure 2 TGA thermograms of all PU/starch systems.

TABLE II
Data Obtained from TGA Thermograms for Starch-Filled DDS Chain-Extended PUs

Samples	Process	T_0 (°C)	T_{\max} (°C)	T_c (°C)	Weight loss (±%)
CO+MDI+DDS	1	254	336	391	50.1
	2	391	462	528	42.9
	Ash	—	—	—	7.0
CO+MDI+DDS+5% Starch	1	249	329	367	32.0
	2	367	411	482	35.0
	3	482	508	558	32.3
	Ash	—	—	—	0.6
CO+MDI+DDS+10% Starch	1	241	320	358	34.0
	2	379	452	491	20.0
	3	491	508	582	35.8
	Ash	—	—	—	1.2
CO+MDI+DDS+15% Starch	1	244	323	382	36.5
	2	382	446	480	29.0
	3	480	511	576	33.1
	Ash	—	—	—	1.4
CO+MDI+DDS+20% Starch	1	246	322	381	38.4
	2	381	454	490	28.9
	3	492	516	580	30.7
	Ash	—	—	—	2.0
CO+MDI+DDS+25% Starch	1	235	323	380	39.2
	2	380	455	491	24.0
	3	491	520	576	34.2
	Ash	—	—	—	2.6

CO—castor oil.

We have estimated these parameters by simulating the profile by employing the procedure described earlier²⁶ for Bragg reflection at $19.56 (2\theta)$. The following equations have been used to simulate X-ray reflection:

$$I(s) = I_{N-1}(s) + I_N^1(s) \quad (2)$$

where, $I_{N-1}(s)$ is computed using,

$$I_N(s) = 2 \cdot \text{Re} \left[\frac{(1 - I^{N+1})}{(1 - I)} + \frac{I\nu}{d(1 - I)^2} \{I^N(N(1 - I) + 1) - 1\} \right]^{-1} \quad (3)$$

where,

$$\nu = 2ia^2s + d \text{ and } I = I_1(s) = \exp(-a^2s^2 + ids) \quad (4)$$

Also,

$$I_N^1(s) = \frac{2a_N}{\mathcal{D}(\pi)^{1/2}} \exp(i\mathcal{D}s) [1 - a_N s \{2\mathcal{D}(a_N s) + i(\pi)^{1/2} \exp(-a_N^2 s^2)\}] \quad (5)$$

where, $a_N^2 = N\omega^2/2$, ω is the standard deviation of nearest neighbor probability function²⁷ and $\mathcal{D}(a_N s)$ is the Dawson's integral or the error function with purely complex argument and can be easily computed. $\langle N \rangle$ is the number of unit cell counted in a direction perpendicular to the (hkl) Bragg plane, d is the spacing of the (hkl) planes. Re refers to the real part of the expression, s is $\sin \theta/\lambda$, λ is the wavelength of X-ray used, a is related to the standard deviation, ω is lattice distribution function, and D is the crystal size

TABLE III
Data Obtained from TGA Scans for Starch-Filled DDS Chain Extended PU

Samples	Temperature at different weight loss (°C) ±2%						IPDT ±2	OI
	T_0	T_{10}	T_{20}	T_{30}	T_{50}	T_{\max}		
CO+MDI+DDS	254	308	327	350	396	504	487	0.063
CO+MDI+DDS+5% Starch	265	310	332	355	410	515	406	0.062
CO+MDI+DDS+10% Starch	268	305	325	365	385	520	448	0.084
CO+MDI+DDS+15% Starch	275	308	325	340	365	518	408	0.084
CO+MDI+DDS+20% Starch	266	310	330	345	460	560	426	
CO+MDI+DDS+25% Starch	250	300	318	335	380	525	506	0.186

CO—castor oil.

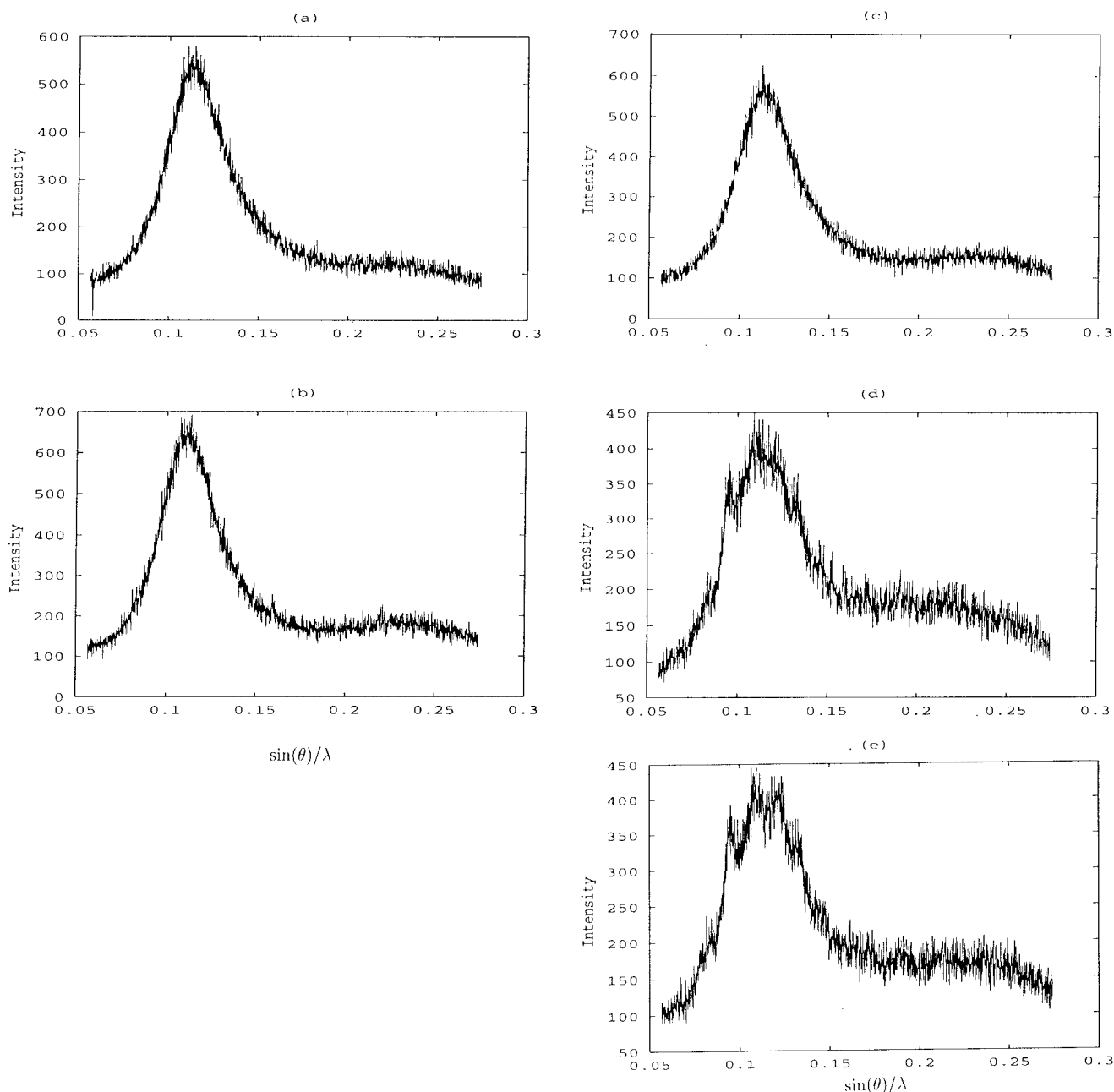


Figure 3 X-ray diffractograms of starch-filled chain-extended PUs. (a) CO+MDI+DDS+5% Starch; (b) CO+MDI+DDS+10% Starch; (c) CO+MDI+DDS+15% Starch; (d) CO+MDI+DDS+20% Starch; (e) CO+MDI+DDS+25% Starch.

$(= \langle N \rangle d_{hkl})$. $I_N(s)$ is the modified intensity for the probability peak centered at D .

RESULTS AND DISCUSSION

A series of PU/starch composites (95/5, 90/10, 85/15, 80/20, and 75/25% wt/wt PU/starch) have been prepared using DBTL as catalyst. The obtained PU/starch sheets were tough, rigid, and opaque. The flexibility of PUs decreases with increase in starch content.

Physicomechanical properties

Physicomechanical properties such as density, tensile strength, percentage elongation at break, and surface hardness (shore A and shore D) of all PU/starch systems were given in Table I.

The density values of PU/starch systems lie in the range of 1.0956–1.102 g/cc. As the proportion of the starch content increases in the PU matrix, the density values increase correspondingly, since more and more

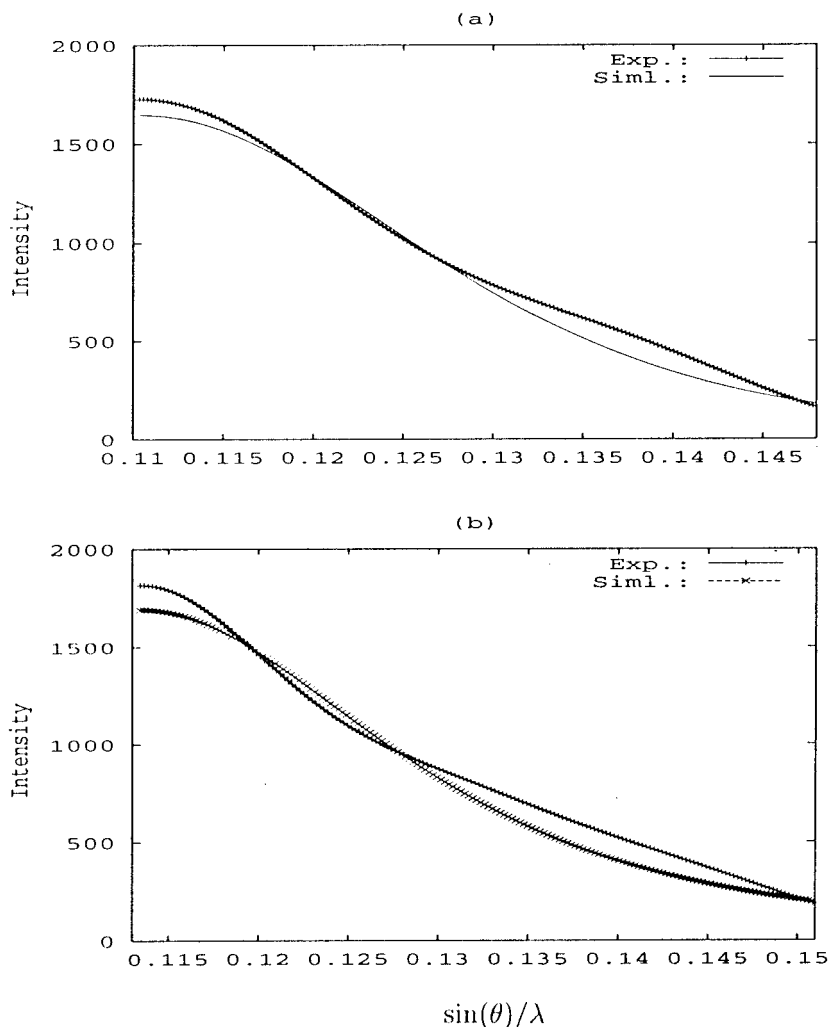


Figure 4 Simulated X-ray patterns for starch-filled chain-extended PUs. (a) CO+MDI+DDS+5% Starch; (b) CO+MDI+DDS+10% Starch; (c) CO+MDI+DDS+15% Starch; (d) CO+MDI+DDS+20% Starch; (e) CO+MDI+DDS+25% Starch.

dense starch has been incorporated in the PU. We have also calculated theoretical densities by the volume additive principle, which states that $[d = w_1d_1 + w_2d_2]$, where, d is the density of starch-filled PUs; w_1 and w_2 are the weight fractions of the constituents; d_1 and d_2 are corresponding densities. Tensile strength increases from 6.86 to 7.95 MPa with an increase in starch content from 5 to 25% in the PU system. A sudden jump of about 192% in tensile strength in 5% starch-filled PU compared to unfilled PU may be due to: (1) a higher degree of interaction between PU and starch (both dipole–dipole interaction and hydrogen bond formation), (2) an increase in crosslink density, (3) starch acts as a reinforcing filler in the matrix of PU,²⁸ and also (4) it may act as chain extender.

The percentage elongation at break of PU is 47 and after incorporation of 5% starch, the percentage elongation at break increases to 61 (about 32% improvement). The percentage elongation at break decreases

from 61 to 35 with increase in starch content. From Table I, an increase in percentage elongation up to 10% starch content in the PU system is noticed. The observed increase in percentage elongation with increasing starch content up to 10% may be due to factors other than crosslink density. It may be explained on the basis of internal bond strength, which, according to Saraf and Glasser,¹⁰ is a property more influenced by chain breakage than chain slippage. The presence of multiple hydroxyl groups in starch results in an increase in the number of urethane bonds with increased starch content. An increase in starch content serves as a bridge with the multiple hydroxyl groups forming more urethane bonds. Hence, fracture depends on the bonds produced in the PU synthesis.¹⁰ This may occur only at higher elongation. In addition, the higher tensile properties further support the existence of phase segregation.

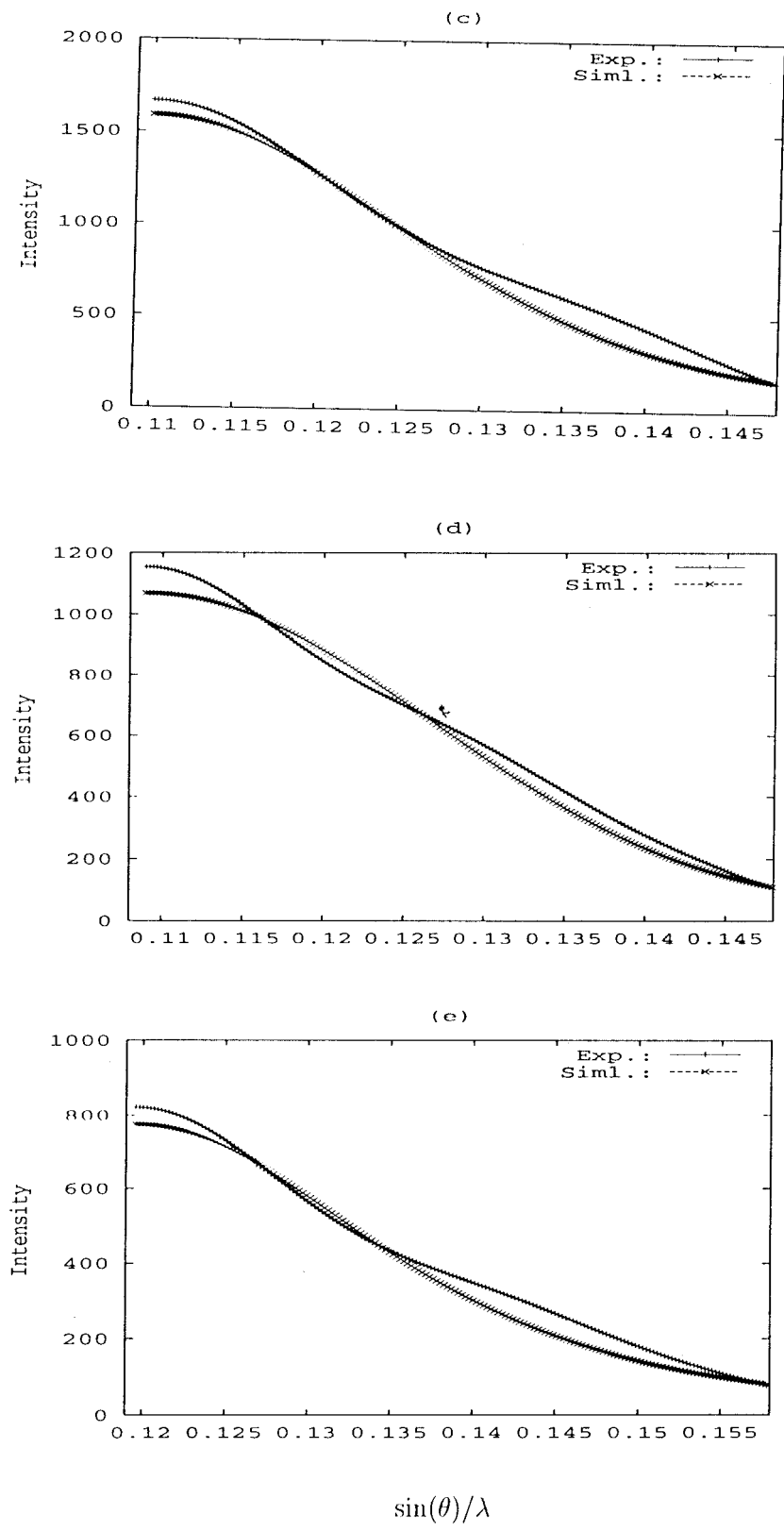


Figure 4 (Continued from previous page)

The decrease in percentage elongation at break when starch content is increased above 15% is due to the fact that the excess of starch forms a separate phase and gets dispersed. This indicates that unreacted particles may act as the origin of cracking rather than as reinforcing filler in this PU system.

Surface hardness reflects the resistance to local deformation, which is a complex property, related to crosslink density, modulus, strength, elasticity, plasticity, and porosity of the polymer matrix. The surface hardness values of all PU/starch systems lie in the range of 91–97 Shore A and 57–68 Shore D. From Table I it was noticed that surface hardness values increases with an increase in starch content.²⁰ That means the incorporation of starch improves dimensional stability of the chain-extended PU. This result clearly supports the reinforcing behavior of starch in the PU matrix.

Thermogravimetric analysis (TGA)

The thermal stability of starch-filled PU systems were evaluated by TGA. A typical TGA and derivative thermogram (DTG) curve is shown in Figure 1 for PU+10% starch system. TGA thermograms for all PU/starch systems are shown in Figure 2.

TGA scans of PU systems shows two-step degradation in the temperature range of 254–391°C and 391–528°C for first and second step, respectively. Figure 2 shows that after the incorporation of starch, PU/Starch systems undergo three-step thermal degradation processes. The temperature range and percent weight loss for different thermal degradation steps for all PU/starch composites are given Table II. The weight loss occurs in the first step in the temperature range of 235–382°C. The weight loss in the first step increases from 32 to 39.2% with the increase in starch content. This result clearly indicates that the weight loss in the first step is due to the loss of starch content along with moisture. The weight loss that occurs in the temperature range of 367–491°C is called a second-stage thermal decomposition with the weight loss in the range of 20–35%. The weight loss in this step may be assigned to the thermal degradation or decrosslinking²⁹ of chain-extended PUs under investigation. In the final step the weight loss occurs in the temperature range of 480–582°C with a weight loss in the range of 30.7–35.8%. The weight loss in this step is due to the complete decomposition of starch and crosslinked chain-extended PUs. From Table II it was observed that the percent ash content increased from 0.6 to 2.6, with an increase in starch from 5 to 25%. It may be due to the fact that the starch is a carbohydrate, which yields high charred (ash) products. The weight loss in the second and third steps are not following any systematic order with an increase in starch content in the

PUs. Generally, chain-extended PUs under observation do not break down in a simple manner, and there is a change in the morphological structure of the PUs at each and every instant of pyrolysis, and that effects the rate of decomposition. From Table III it was noticed that the incorporation of starch in PU matrix has not significantly affected the thermal degradation temperature. This is because degradation temperature range of starch is about 260–400°C.

The thermograms obtained during TGA scans were analysed to give the percent weight loss as a function of temperature, T_0 (temperature of onset decomposition) T_{10} , T_{20} , T_{30} , T_{50} , and T_{max} (temperature for 10, 20, 30, 50%, and maximum weight loss) are the main criteria to indicate the thermal stability of the PUs.

The IPDT values lie in the range of 406–506°C. A slight improvement in IPDT value was observed for PUs after incorporation of starch. Oxidation indices (OI) values lie in the range of 0.062–0.186, which increases with an increase in the starch content, because the OI value depends upon the starch content. These values are very low, and hence, starch-filled PUs are not good flame-retardant polymers.

X-ray analysis

X-ray diffractograms for all PU/starch systems are given in Figure 3(a)–(e). It is evident from these figures that there is one intense broad reflection at 19.57° (2θ), which suggests that the diffraction is mostly by an amorphous polymer region. All these samples belong to the orthorhombic system. The broadening which arises in X-ray diffractograms of polymers is due to two main factors. According to Warren,³⁰ these are due to a decrease in (1) crystal size ($\langle N \rangle$) and an increase in (2) strain or lattice disorder (g in %) present in the samples. Here the crystal size ($\langle N \rangle$) has been estimated by considering the lattice distortion effect of the second kind on the basis of Hosemann's paracrystalline model.³¹ We have estimated microcrystalline parameters by simulating the experimental profile by employing the procedure described in the earlier article³² and using a Bragg reflection observed at $2\theta = 19.57^\circ$. For the sake of completeness we have produced the simulated and experimental profile of all PU/starch systems [Fig. 4(a)–(e)]. In fact, the goodness of the fit was less than 2% in all PU/starch systems. Table IV gives various microcrystalline parameters like crystal size ($\langle N \rangle$), smallest crystal unit (p), crystal size distribution width (α), lattice strain (g in %), the enthalphy (α^*) and surface weighted (D_s) crystal size. From Table IV, no systematic variation in these microcrystalline parameters with the starch concentration has been observed.

The X-ray studies do not explain the observed improvement in physico-mechanical properties of

TABLE IV
The Microcrystalline Parameters for Starch-filled CO+MDI+DDS Systems Obtained from WAXS Studies

Blend composition (% wt/wt)	2θ	$\langle N \rangle^a$	g in ^a %	p^a	α^a	α^*	D_s^a in Å	d_{hkl}	R^1
CO+MDI+DDS+5% Starch	19.71	2.36 ± 0.17	0.50 ± 0.04	1.70	1.51	0.01	10.69	2.284	2.544
CO+MDI+DDS+10% Starch	20.96	2.39 ± 0.19	1.00 ± 0.08	1.42	1.04	0.02	10.53	2.153	2.399
CO+MDI+DDS+15% Starch	20.00	2.33 ± 0.18	0.50 ± 0.04	1.75	1.62	0.01	10.59	2.252	2.509
CO+MDI+DDS+20% Starch	19.52	2.38 ± 0.19	0.50 ± 0.04	1.95	2.99	0.02	10.92	2.305	2.568
CO+MDI+DDS+25% Starch	20.79	2.56 ± 0.26	1.00 ± 0.10	1.66	1.11	0.10	10.70	2.170	2.417

^a All these parameters calculated at 19.57 (2θ).

CO—castor oil.

starch-filled PUs. This is not a powerful tool to indicate the hydrogen bond formation in the polymer network. The hydrogen bonds formed by the addition of starch in PU form the back bone, and hence, result in the improvement of mechanical properties without much change in the crystal size.

There is no systematic variation of crystal size distribution (P) for PU/starch systems with an increase in starch content. Phase stabilization, which is consequence of the minimum value of enthalpy, α^* (0.01–0.10) is observed for all PU/starch composition.³³ The interplanar distance (R^1) and interplanar spacing (d_{hkl}) are also calculated and are given in Table IV. d_{hkl} and R^1 values lie in the range of 2.153–2.305 Å and 2.399–

2.568 Å, respectively. These values are almost identical for all the systems. On a macroscopic scale these do effect on the physical properties such as tensile strength and percentage elongation at break [Fig. 5(a)–(b)]. In fact, Figure 5 shows a slight increase in tensile strength and a reduction in percentage elongation with increase in crystal size.

CONCLUSIONS

It was observed that the incorporation of starch component into chain-extended PUs improves physico-mechanical properties of the resulting systems. This is due to the multifunctional component (starch) present in the filled chain-extended PUs and the formation of extensive hydrogen bonds between PU and starch. From the physico-mechanical properties it was concluded that 95/5 PU/starch is the optimized composition to achieve high performance composite. TGA thermograms of PU/starch show that the thermal decomposition occurs in three different stages. The phase stabilisation occurs for all PU/starch systems. This conclusion has been drawn on the basis of the minimum value of α^* (0.015 ± 0.005), the enthalpy that is a measure of the energy required for the formation of net plane structure. Addition of starch to the material does not alter the crystalline region or the extent of crystallinity. But the chain conformation in the amorphous region may change, which is not indicated in the present study.

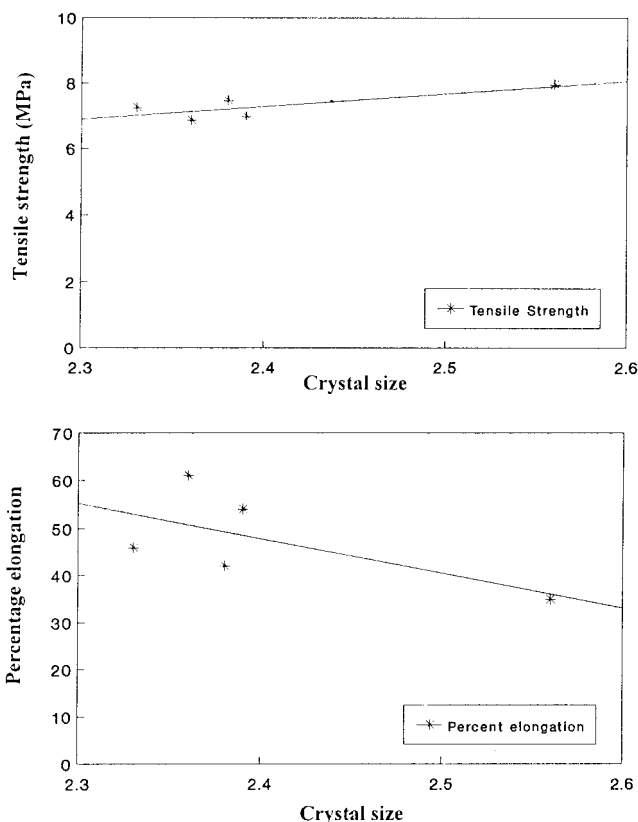


Figure 5 Variation of: (a) tensile strength with crystal size; (b) percentage elongation with crystal size.

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