

# Biodegradable Polymers. III. Spectral, Thermal, Mechanical, and Morphological Properties of Cross-linked Furfural–Soy Protein Concentrate

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**ABSTRACT:** Soy protein concentrate, a potential alternative of petrochemical polymers, has been crosslinked with furfural at 0.5, 1, 2.5, 5, and 7.5% (w/w). The materials were then compression-molded into plastic tensile bars and tested for tensile and yield strength, percentage elongation, and water absorption. The infrared spectra of the crosslinked product have been studied. The degradation pattern of the crosslinked product has been monitored by TGA method. A

computerized LOTUS package method developed by us has been used for evaluating the kinetic parameters. The morphology as well as the biodegradability of the crosslinked product has also been investigated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2590–2596, 2004

**Key words:** biodegradable; crosslinked; furfural; soy protein

## INTRODUCTION

Today's plastics are designed with little consideration for their ultimate disposability or recyclability. This has resulted in mounting worldwide concerns over the environmental consequences of such materials when they enter the waste stream after their intended uses. The persistence of plastics in the environment, the shortage of landfill space, concerns over emissions during incineration, and entrapment and ingestion hazards from these materials have spurred efforts to develop biodegradable plastics. The challenge in replacing conventional plastics with biodegradable materials is to redesign materials that exhibit structural and functional stability during storage and use, yet are susceptible to microbial and environmental degradation upon disposal without any adverse environmental impact. These challenges often represent opposing considerations in polymer design. Therefore, the design of appropriate biodegradable materials will require a clear understanding of factors influencing material properties, performance, and biodegradability so that appropriate trade-offs can be made.<sup>1–3</sup>

Various renewable resources and agricultural products have been explored to make biodegradable plas-

tics to keep the environment cleaner and greener.<sup>3</sup> In the search for a replacement of petroleum-based plastics, soy-protein is identified to be a potential raw material because it is a widely available, renewable, cheap, and biodegradable agricultural product. Therefore, in recent years, soy-protein based plastics have received worldwide attention. Studies showed that unmodified soy-proteins are highly hydrophilic and plastics made from them are water-sensitive, resulting in poor mechanical properties.<sup>4,5</sup> Furthermore plastics made from unmodified soy-protein are very brittle<sup>6</sup> and difficult for processing. Therefore, attempts have been made to enhance the flexibility of soy-protein based plastics by plasticizing and crosslinking.<sup>4,7</sup> A number of polyhydric alcohols have been used as plasticizers to improve plastic elasticity. Glycerol, ethylene glycol, and propylene glycol are found to be better plasticizers than propanediol.<sup>4</sup> Soy-protein also is used as a major resin, which would be crosslinked with other chemicals. Mechanical strength and water resistance of soy protein could be improved by crosslinking with zinc sulfate<sup>5</sup> or formaldehyde,<sup>8</sup> or blending with poly phosphate<sup>9</sup> or anhydric group attached polyesters.<sup>10</sup>

The functional properties of soy-protein are highly related to its complex structure. Protein modification is designed to improve functional properties by tailoring protein structure through physical, chemical, and enzymatic methods. It is well known that protein modification including denaturation can improve functional properties of proteins such as solubility,

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foaming, emulsifying, gelation, and viscosity.<sup>11</sup> The denaturation of protein includes exposure of heat, acid, alkali, detergent, or organic solvent resulting in partially unfolded protein structures and flexible peptide chains.<sup>12</sup> Through acid treatment of soy-protein at pH 4.5, the water absorption of the final product could be lowered to about 30% within 26 hrs without having detrimental effect on the mechanical properties.<sup>13</sup> This was attributed to the minimal charge density of soy-protein at pH 4.5, the isoelectric point of the protein.

Soy-protein has many reactive groups (e.g.,  $-\text{NH}_2$ ,  $-\text{OH}$ , and  $-\text{SH}$ ) that are susceptible to crosslinking reactions in addition to naturally existing disulfide crosslinkage. Crosslinking of soy-protein leads to the formation of larger aggregates, accompanied by an increase in molecular weight, reduction of solubility, and reduced elasticity.<sup>14</sup>

Various researchers have used formaldehyde as a crosslinker for the modification of soy-protein.<sup>8</sup> Formaldehyde, however, is known to be hazardous, toxic, and carcinogenic; therefore, an alternative crosslinking agent has been explored to replace formaldehyde. In the present research program, soy-protein concentrate (SPC) has been crosslinked with a bio-based non-toxic aldehyde, that is, furfuraldehyde (furfural), with an aim of obtaining better processing material. The spectral, thermal, mechanical, morphological, and biodegradability properties of the crosslinked SPC have been investigated.

## EXPERIMENTAL

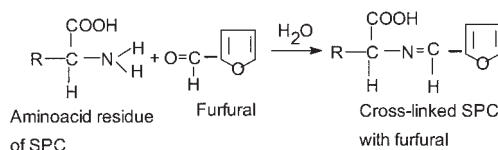
### Materials

SPC with a reported protein content of 70% was a gift of Archer Daniel Midland (Decatur, IL). Propionic acid, acetic acid, citric acid, adipic acid, and furfural were reagent grade (GR) chemicals and were used without further purification.

### Crosslinking of spc with furfural

SPC was mixed with distilled water at a ratio of 1 : 10. The slurry was continuously stirred with a mechanical stirrer and then furfural was added drop by drop (0.5, 1, 2.5, 5, or 7.5% dry base of SPC). The mixture was allowed to stand for 18–24 h. The pH of the solution was adjusted to 4.5 by adding propionic acid and others respectively, while the mixture was continuously stirred. The slurry was centrifuged to remove excess water (Sorvall Superspeed RC2-B; 4541g, 10 min; USA) and the precipitated residue was dried in a convection oven at  $\leq 50^\circ\text{C}$  until a moisture content of  $\leq 10\%$  was reached. The dried and modified SPC was then milled (Cyclone Sample Mill/UDY Corp./Fort Collins, CO) to pass through a 35-mesh sieve. The

mechanism of the reaction between SPC and furfural is furnished below.



The reaction between the  $\text{NH}_2$  group of SPC and CHO group of furfural is ascertained from IR spectral data.

### Specimen preparation

The crosslinked SPC powder was molded into a tensile bar specimen (Type-1V) according to standard method ASTM D 638–91.<sup>15</sup> SPC powder (5g) was molded into a dog bone shaped mold and compression molded into a hot press (Model 3890 Auto “M” Carver Inc., Wabash, IN) at 20 Mpa and at temperature ranging from 80 to 160°C for 5 min. The specimen was then cooled to 50°C at 30°C/min before removal from the mold. Flash was removed by sanding the edges of specimen with grade 180 abrasive sandpaper.

### Instrumentation and analysis

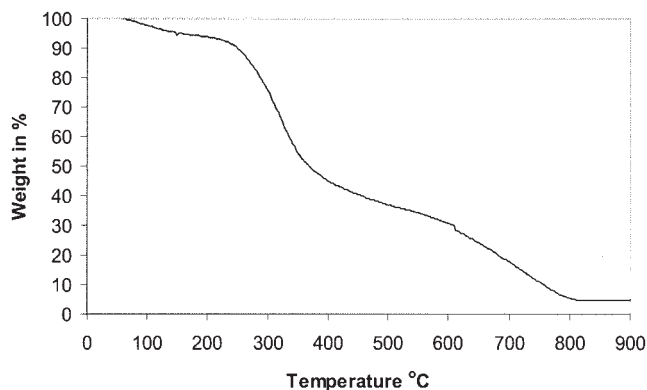
Infrared spectra were recorded using Perkin–Elmer 1720 spectrophotometer. Thermal transition of the polymers was assessed using a Perkin–Elmer DSC-7 (Norwalk, CT) differential scanning calorimeter. Thermal degradation patterns of the polymers were studied using TA Instruments TGA-2950 (USA) thermogravimetric analyzer. The SEM was monitored using Hitachi 5–3500N; Hitachi Science System, Ltd. Tokyo, Japan.

### Tensile testing

Mechanical properties were measured using Instron (Model 4465; Canton, MA) according to the Standard Test Method, ASTM D638–91.<sup>15</sup> The SPC plastics were preconditioned at 23°C and 50% humidity for 48h before testing. The cross-head speed was 5 mm/min. Stress at maximum load, strain (%) at break, and Young’s modulus were calculated. The reported results are averages of five samples.

### Water absorption measurement

Water absorption was measured following ASTM standard methods, ASTM D570–81.<sup>16</sup> The SPC plastic samples were preconditioned at 50°C for 24 h and then cooled in a desiccator before being weighed. The preconditioned SPC plastics were submerged in distilled water at 25°C for 2 and 24 h. They were removed and dried with a paper towel before weighing. Water ab-



**Figure 1** TG-Thermogram of sample 3 (SN3) soy-protein concentrate (SPC) cross-linked with 5% furfural in air at 3°C/min.

sorption was calculated as the percentage of initial weight. The soluble material loss was checked by weighing the specimens after drying them in an oven at 50°C for another 24 h. The total water absorption for 24 h was calculated including the soluble material loss.  $\{(w_2 + w_3) - w_1\} / w_1 \times 100\%$ , where  $w_1$  = initial sample weight,  $w_2$  = sample weight after 24 h, and  $w_3$  = soluble material weight.

## RESULTS AND DISCUSSION

### Infrared spectra

The FTIR spectra of the neat SPC along with the crosslinked SPC have been taken. The absorption at  $3338\text{ cm}^{-1}$  indicates the presence of primary amino group in case of neat SPC. The free primary amino group of the SPC has been reacted with the aldehyde group of the furfural to form a Schiff's base like cross-linked product. A perusal of the FTIR spectra of the crosslinked soy-protein indicates the absence of the peak around  $3300\text{ cm}^{-1}$ – $3500\text{ cm}^{-1}$ , indicating the absence of the primary amino group in the crosslinked product.

Further, a new peak has been observed around  $619\text{ cm}^{-1}$ , indicating the presence of the furanyl ring in the crosslinked product. Further, a peak around  $1650\text{ cm}^{-1}$  confirms the  $\text{-C}=\text{N-}$  group in the crosslinked product, confirming that the furfural aldehyde group

has been reacted with the primary amino group of the SPC resulting in a crosslinked product.

### Thermal properties

The thermogravimetric analysis of the furfural crosslinked SPC has been studied (Fig. 1). The degradation pattern of the compounds has been furnished in Table I.

The thermogram of the furfural modified SPC can be dissected into five parts. The first break takes place around 241°C having weight loss of about 10%, the second break takes place around 395°C having weight loss of about 56%, the third break takes place around 667°C having weight loss of about 91%. This can be explained by considering the structure of soy-protein. It is well known that the three-dimensional structure of soy-protein is governed by its primary structure, that is, the sequence of amino acids. Two kinds of covalent bonds are mainly found in the proteins; one is the peptide bond between the amino acid residue, and the other is the disulfide bonds. The other noncovalent bonds present in the protein are electrostatic and hydrophobic interactions and the hydrogen bonding.<sup>17</sup>

The first break, between 65°C–241°C, is attributed to elimination of water and the dissociation of quaternary structure of proteins. Further, it is known that beyond 100°C the protein denatures their subunits and promotes the formation of protein aggregate via electrostatic, hydrophobic, and disulfide interchange bonding mechanisms. This has been recently substantiated by Kilara and Sharkasi.<sup>18</sup> It is generally accepted that hydrophobic and disulfide bonding is involved and responsible for protein–protein aggregation caused by heating to temperatures above 100°C. Further, during this period the electrostatic and hydrogen bonding is also affected.

The second break, between 244°C–395°C, is mainly due to breakage of the covalent bonding between the peptide bonds of amino acid residues. During this period, 60% of phenyl-alanine and tryptophan residues and 80% of the tyrosine residue remain buried. Further heating also causes simultaneous reactions in the structure of soy-protein. First, the dissociation of 7S and 11S protein subunits; second, the unfolding of

**TABLE I**  
Thermal Decomposition Data of Cross-Linked Soy-Protein Concentrate with Furfural

Sample	Medium	% weight loss at various temperatures							
		100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C
SN3	Propionic acid	2	6	25	55	63	69	82	95
SN5	Acetic acid	4	7	25	53	62	69	84	—
SN7	Adipic acid	4	6	23	52	61	71	86	—
SN8	Citric acid	2	5	23	53	62	69	83	94

**TABLE II**  
Kinetic Parameters of the Cross-Linked Soy-Protein Concentrate With Furfural

Sample no.	Steps	Temperature range		Model	R-squared	Slope	Intercept	Activation energy E(kj/mole)	Frequency factor
		Start	End						
SN3	1	64.42	238.51	B1	0.97166	-733.066	6.945	13.427	2.32E + 03
SN3	2	244.53	395.6	B1	0.97928	-1744.503	8.439	31.952	2.46E + 04
SN3	3	401.6	667.78	B1	0.97746	-1601.665	7.740	29.336	1.12E + 04
SN3	4	673.66	760.04	H3	0.96432	-41758.788	46.913	764.843	3.02E + 22
SN3	5	765.92	825.54	H3	0.98055	-78187.260	78.870	1432.058	4.27E + 36
SN5	1	59.21	238.31	H2	0.95860	-775.926	7.361	14.212	3.73E + 03
SN5	2	244.33	389.4	B1	0.98011	-1791.475	8.528	32.812	2.76E + 04
SN5	3	395.4	617.73	B1	0.97324	-1664.221	7.875	30.481	1.34E + 04
SN5	4	623.77	741.75	B1	0.96576	-4100.679	10.196	75.107	3.35E + 05
SN5	5	747.65	788.65	H3	0.98079	-94965.525	96.754	1739.364	3.03E + 44
SN7	1	59.75	238.92	B1	0.95256	-632.426	6.745	11.583	1.64E + 03
SN7	2	244.92	384	B1	0.98108	-1824.034	8.590	33.409	2.99E + 04
SN7	3	389.99	600.93	B1	0.97216	-1692.080	7.928	30.992	1.43E + 04
SN7	4	606.97	739.64	B1	0.96804	-3701.269	9.806	67.791	2.05E + 05
SN7	5	745.44	765.33	H3	0.98918	-149087.179	150.286	2730.642	8.44E + 67
SN8	1	66.33	239.31	B1	0.96266	-654.452	6.769	11.987	1.74E + 03
SN8	2	245.32	390.24	B1	0.97966	-1795.618	8.532	32.888	2.78E + 04
SN8	3	396.24	621.35	B1	0.97261	-1655.948	7.862	30.330	1.31E + 04
SN8	4	627.29	748.43	B1	0.96525	-4068.071	10.142	74.510	3.15E + 05
SN8	5	754.39	802.73	H3	0.97787	-83032.818	84.387	1520.808	1.13E + 39

Where SN3, SN5, SN7, and SN8 are sample code numbers.

the subunit secondary structure; and third, the reassociation of denatured subunits via disulfide hydrophobic, electrostatic, and other important bonding forces. The third break, between 401°C–667°C, is due to cleavage of S-S, O-N, and O-O linkages of the protein molecule. The fourth break, between 673°C–760°C, may be due to complete decomposition of protein molecule forming various gases like CO, CO<sub>2</sub>,

NH<sub>3</sub>, H<sub>2</sub>S, and other gases. Beyond 760°C, only the char residue remains.

A computerized LOTUS package method developed by us has been used for assigning the degradation mechanism. The kinetic parameters have been given in Table II using 30 kinetic mechanisms.<sup>19–25</sup>

The DSC thermogram of neat SPC and 5% furfural crosslinked SPC is shown in Figure 2 and Figure 3,

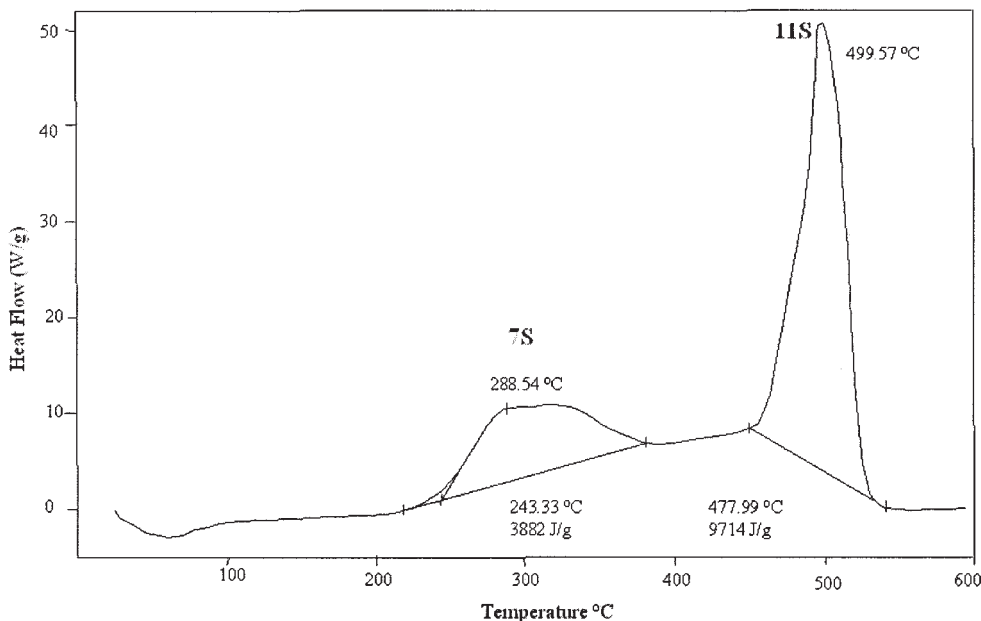


Figure 2 DSC thermogram of neat SPC.

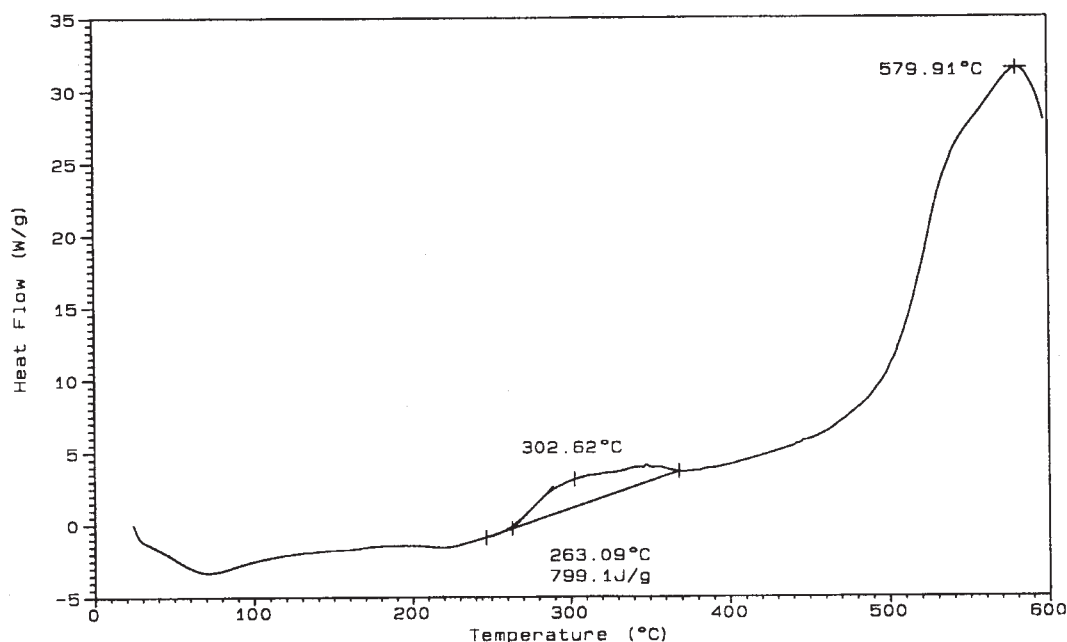


Figure 3 DSC thermogram of Sample 3 (SN3) SPC cross-linked with 5% furfural.

respectively. Heating converts soy-protein from its native state to its denatured state accompanied by unfolding and disruption of the intramolecular bonding<sup>26</sup>, which is observed as an endothermic peak. A typical denaturation of neat SPC (Fig. 2) and crosslinked SPC (Fig. 3) gave two peaks, one at 288.54°C and 499.57°C and the other at 302.62°C and 579.91°C, respectively. Hence, SPC and crosslinked SPC showed two endothermic peaks corresponding to two major components of the storage soy-protein, that is, conglycinin (7S) and glycinin (11S), respectively. The denaturation of 7S globulins and 11S globulins for crosslinked SPC powder were higher than the neat SPC. The enthalpy of denaturation ( $H = J/g$ ) value also decreased from 3882J/g to 799 J/g.

### Water absorption

The water absorption of the SPC plastics crosslinked with furfural has been investigated and presented in

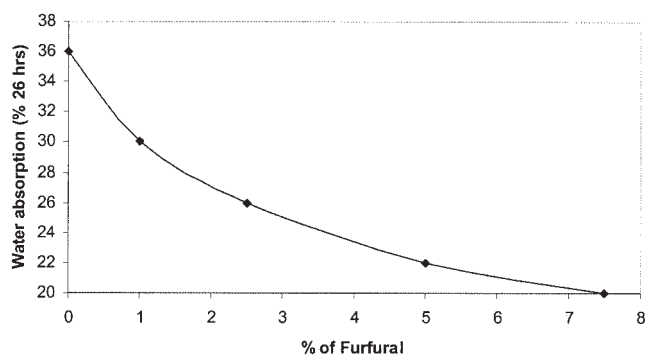


Figure 4 Effect of cross-linking by furfural on the water absorption of SPC plastics.

Figure 4. As the percentage of furfural increases, the water absorption decreases. Crosslinking leads to the formation of larger aggregates accompanied by increases in molecular mass, thereby reducing the water absorption.

### Effect of temperature on mechanical properties

The mechanical properties such as tensile strength, % of elongation, yield strength, and Young's modulus of the crosslinked SPC have been carried at different temperatures ranging from 80 to 160°C. The results have been furnished in Table III and Figure 5. The tensile strength increases from 26 MPa as the temperature increases from 80 to 140°C, and then a decreasing trend is noticed. The % of elongation, yield strength, and Young's modulus increases with increasing of temperature. These results may be attributed to the fact that high molding temperatures increase the mobility of the polymer chains, which in

TABLE III  
Effect of Molding Temperature on Mechanical Properties of Soy-Protein Concentrate Cross-Linked with Furfural (Sample SN3)

Molding temp °C	Tensile strength (MPa)	% elongation	Yield strength (MPa)	Young's modulus (MPa)
80	26	2.8	4.1	1570
100	30	3.3	4.4	1590
120	38	4	4.8	1620
140	42	4.3	5.4	1625
160	40	4.4	5.5	1678

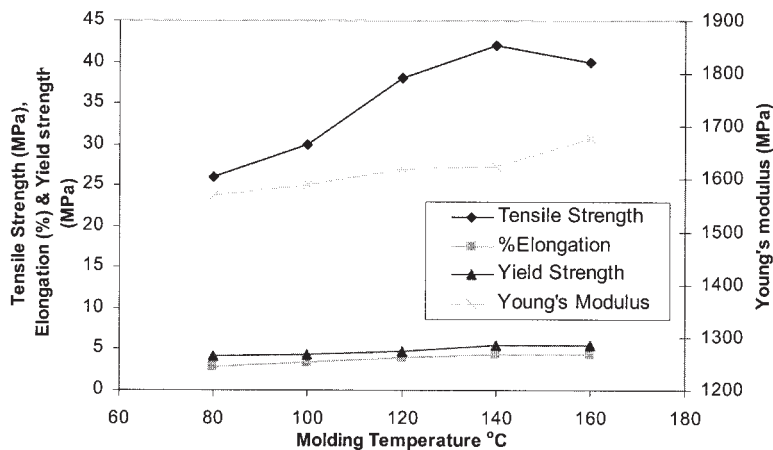


Figure 5 Effect of molding temperature on the mechanical properties of SPC plastics cross-linked by furfural.

turn enhance the flow properties of the material and improve the alignment and interaction of the chains.<sup>27</sup> High temperature processing probably contributes to

a closer packing of polymer chains and is likely to exclude water.

**Morphology**

The morphology of crosslinked SPC was studied using scanning electronic microscope. The micrographs are illustrated in Figure 6. The morphology of Figure 6a represents crosslinked SPC with furfural (0.5%) and Figure 6b represents crosslinked SPC with furfural (1%). Soy-protein is composed of 20 amino acids with various side groups such as carboxyl, amino, and sulfhydryl groups, which are relatively very active. Crosslinks take place mainly with the amino group. Figure 6a where % of furfural is low, the morphology indicates a brittle fracture shape with voids all around. As the % of furfural increases, the brittleness gradually disappears and the surface becomes very tough and tightened. Hence, as the % of crosslinking agent increases, the structure of protein molecule becomes tougher.

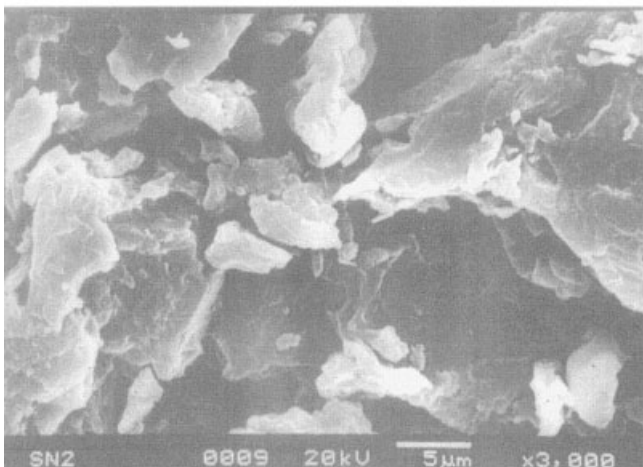
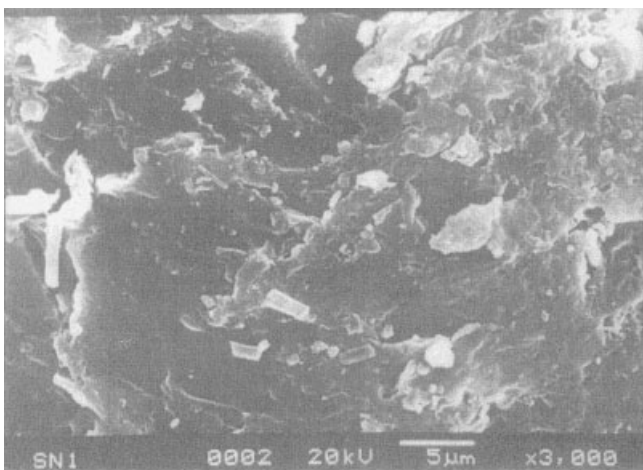


Figure 6 (a) Surface morphology SPC plastic cross-linked with 0.5% furfural. (b) Surface morphology SPC plastic cross-linked with 1% furfural.

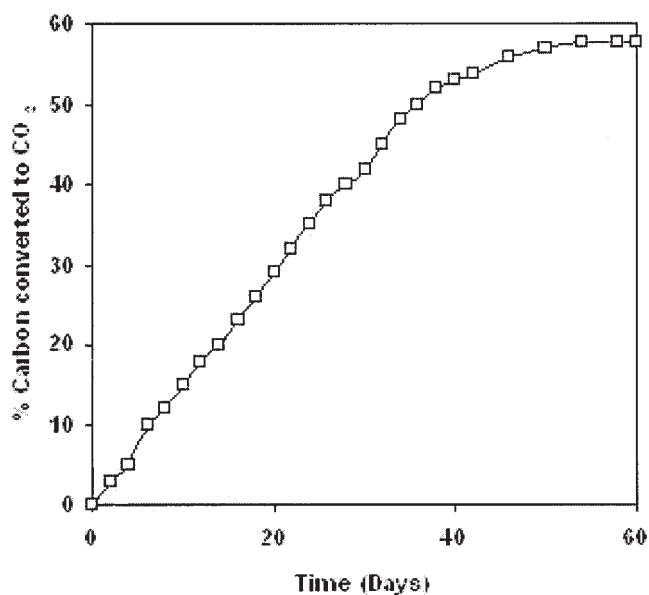
**Biodegradability**

The biodegradability of crosslinked SPC was investigated using aerobic biodegradability procedure (ASTM D 5209-92). Compression molded (samples 25.45 dia and 3.3 mm thickness) were broken into smaller pieces and placed in a respirometer devised by us containing the compost. Within a short period of time, the sample displayed excellent growth of bacteria on the surface. After about 60 days, the amount of carbon dioxide generated was almost negligible, indicating complete degradation of crosslinked SPC. The carbon dioxide generated as a function of time is shown in Figure 7. The percentage of carbon dioxide evolved is calculated as shown below:

$$\begin{aligned}
 &C + O_2 \rightarrow CO_2 \\
 &12g \text{ C yield } 44g \text{ CO}_2 \\
 &y \text{ mg C yield } 44/12 \times y \text{ mg CO}_2 \\
 &= \frac{\text{mgCO}_2 \text{ produced}}{\text{mgCO}_2 \text{ theoretical}} \times 100 \\
 &= \frac{Z \times \text{mlHCl} \times 12}{44 \times Y}
 \end{aligned}$$

Where Y = mg of carbon charged to respirometer and Z = strength of HCL used for titration of absorbed CO<sub>2</sub> by 1N NaOH in the post trap.

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**Figure 7** CO<sub>2</sub> evolution of SPC (cross-linked with furfural) plastic from composted manure respirometer in aerobic biodegradation process.

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