

# Renewable Elastomers Based on Blends of Maleated Polypropylene and Plasticized Starch

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**ABSTRACT:** Most recent developments in polymers from renewable resources have focused on thermoplastics, whereas there has been no comparable development of plastics with elastomeric properties. Here we evaluate the possibility of developing renewable elastomers based on starch. Potato starch plasticized with glycerol (called plasticized starch, or PLS) was melt-blended with small quantities (5 wt % or 15 wt%) of maleated polypropylene (MAPP). The maleic anhydride groups of the polypropylene are expected to react with the hydroxy groups of starch under melt blending conditions. The resulting blends of MAPP and PLS were characterized by mechanical testing, SEM, DMA, and DSC. SEM, solubility and adhesion tests indicate that the blends are two-phase materials, in which the continuous phase PLS is physically

crosslinked by polypropylene domains. The materials showed rubbery properties as judged by a low glass transition temperature ( $\sim -50^\circ\text{C}$  independent of polypropylene content), and a wide rubbery plateau in DMA experiments that extended from room temperature to as high as  $170^\circ\text{C}$ . The tensile properties are also characteristic of elastomers. However, slow aging due to starch crystallization, and extraction of glycerol upon water exposure remain two challenges that must be overcome before the materials can be used as practical elastomers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1775–1781, 2010

**Key words:** renewable polymers; plasticized starch; thermoplastic starch; elastomers; biodegradable polymers

## INTRODUCTION

There has been enormous progress in polymeric materials obtained from renewable resources to provide a more sustainable pathway to meet our current commercial needs.<sup>1</sup> Virtually all these developments have been in the thermoplastics family, and may be considered as renewable alternatives to materials such as polyolefins, polyvinyl chloride, or polyester terephthalate. There have been no comparable developments in the last few years in the elastomer family. Currently, natural rubber is the only commercially available renewable polymer with elastomeric properties. Poly-4-hydroxybutyrate (P4HB), a renewable polymer synthesized through bacterial fer-

mentation, is known to be elastomeric, but is used exclusively in medical devices, and is not available for routine elastomeric applications.<sup>2–5</sup> Applications such as shoe soles, gaskets, shock absorbers, etc. would benefit from the development of elastomers from renewable resources. In this article, we evaluate the potential of plasticized starch as a renewable elastomer.

Starch is a renewable polysaccharide and is produced by a variety of plants as a food source. Starch consists of sugar repeat units linked together by glycosidic bonds (see Fig. 1(a) for the monomer structure). Starch contains two types of molecules, the linear polysaccharide amylose and the branched polysaccharide amylopectin. In natural starch, these molecules are organized in a complex semicrystalline structure to form granules. Dry granular starch, by itself, cannot be processed like a plastic; however, it can be blended with small polar molecules (most commonly glycerol, but water or polar oligomers such as polyols may also be used), giving a thermoplastic material generally called Thermoplastic Starch (TPS) or Plasticized Starch (PLS).<sup>6,7</sup> PLS is a renewable, biodegradable, and economical thermoplastic that can be processed similarly to synthetic thermoplastics using standard polymer processing equipment. The mechanical properties of PLS are usually quite poor, however blends of PLS with

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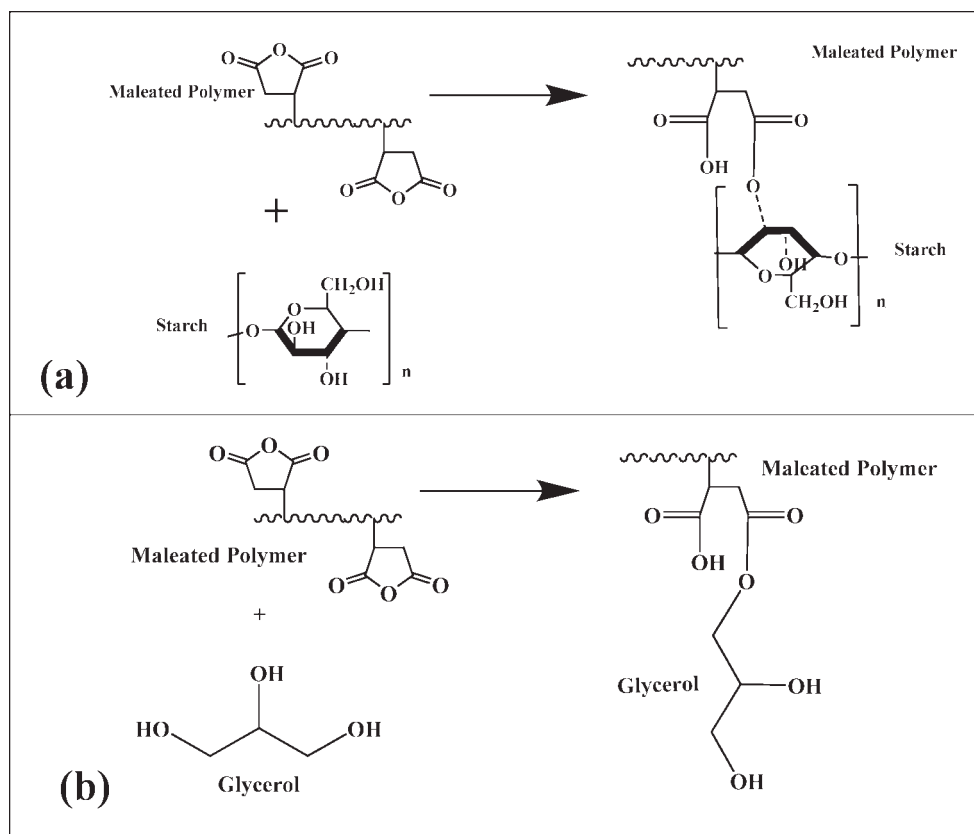
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**Figure 1** (a) Reaction of the MAPP and starch that results in crosslinking, (b) Competitive reaction between MAPP and glycerol.

other renewable or non-renewable thermoplastics can possess excellent mechanical properties.<sup>7–12</sup> Depending on the blend components, such blends may or may not be fully degradable, e.g. blends of PLS with polylactic acid are likely to be fully degradable, whereas those with polyethylene are not.

Past publications on the thermomechanical properties of glycerol-plasticized PLS suggests that the properties of PLS may be well-suited for elastomeric applications. Specifically, at sufficient glycerol content (>25%), the glass transition temperature of PLS is well below room temperature, which is of crucial importance to elastomers.<sup>13–17</sup> Due to its low  $T_g$ , such PLS is a soft, tacky material at room temperature and hence cannot be directly used as an elastomer. Natural rubber behaves similarly, and in that case, useful products can only be made upon crosslinking, either chemical crosslinking, e.g. in vulcanized rubber, or physical crosslinking, e.g. styrene-butadiene-styrene (SBS) copolymer elastomers. Analogously, it may be possible to crosslink PLS, while still retaining its elastomeric properties. Although there is much published research on crosslinking native starch for food applications,<sup>18,19</sup> the use of crosslinked starch as an elastomeric material has not been previously reported. In this article, we

will explore the possibility of physically crosslinking PLS with maleated polypropylene (MAPP). The goal is to create an elastomeric material with a micro-phase-separated morphology, where MAPP domains behave as physical crosslinks for the rubbery continuous phase PLS. We will evaluate the potential of such PLS/MAPP blends as elastomers. Finally, we note that while there have been several studies of blends of PLS with polyolefins,<sup>8,20,21</sup> to our knowledge, this is the first to explore PLS-polyolefin blends with a high PLS content.

## EXPERIMENTAL

### Materials

Potato starch was obtained from Honeyville Food Products (California, USA) and is approximately 79% amylopectin and 21% amylose. Glycerol, used as plasticizer, was obtained from TheChemistryStore.com (Pompano Beach, FL). Reagent grade dimethyl sulfoxide (DMSO) was obtained from Mallinckrodt Baker (Phillipsburgh, NJ). MAPP, was obtained from ExxonMobil (Houston, TX) and has a maleic anhydride content of 0.5–1% by weight, corresponding to approximately 16 reactive anhydride groups per chain (according to the manufacturer's estimated

**TABLE I**  
**Sample Compositions**

Sample	Starch	Glycerol	MAPP	MAPP <sup>a</sup>
S100	60 wt %	40 wt %	0 wt %	0 vol %
S95	57 wt %	38 wt %	5 wt %	7.5 vol %
S85	51 wt %	34 wt %	15 wt %	21.5 vol %

<sup>a</sup> Calculated assuming the following densities: MAPP = 0.9 g/cm<sup>3</sup>; glycerol = 1.26 g/cm<sup>3</sup>; and starch = 1.53 g/cm<sup>3</sup>, and assuming linear mixing rule for density.

molecular weight). The anhydride groups of the MAPP can react with the hydroxy groups of the starch as will be discussed later in this article.

### Plasticization and processing

All blends had a starch: glycerol weight ratio of 60 : 40. Three blends were made with MAPP contents of 0, 5, and 15% by weight. Samples are designated as S<sub>x</sub>, where *x* is the weight percent of the starch/glycerol phase in the blend (and hence 100 - *x* is the weight percent of MAPP). Details of the blend compositions are given in Table I.

The three blends were prepared as follows. The starch and glycerol were first mixed together in a 60 : 40 weight ratio using a table top dough mixer at 350 RPM for 30 min and allowed to sit overnight to allow the diffusion of glycerol into the starch granules. The starch-glycerol mixture was then extruded using a single screw extruder (SSE) to obtain PLS, and the extruded strands of PLS were then cut into pellets. Mixtures of PLS pellets and MAPP pellets in the appropriate ratios were then extruded to obtain the blends of the compositions listed in Table I. These extrudates were pelletized and extruded twice more to promote adequate blending of MAPP and PLS (as single screw extruders are known to be relatively poor for dispersive blending), and to ensure the chemical reaction between the alcohol and anhydride groups. The S100 blend was also extruded two additional times to ensure that all blends have the same thermomechanical history. For all samples, a Brabender single screw extruder (0.75 inch diameter) was used at a temperature of 150°C, and a rotational speed of 45 RPM. The three blends were injection molded into tensile bars using a DeMag injection molding machine for mechanical testing. All samples were stored at room temperature in sealed plastic bags.

### Characterization

Scanning electron microscopy (SEM) was performed on cryofractured samples using a Philips XL-30 field emission scanning electron microscope at an acceleration voltage of 10 kV. The samples were briefly immersed in water to remove the glycerol close to the surface

(which may evaporate in the high vacuum of the SEM), and then fractured under liquid nitrogen. Samples were sputter coated with platinum before imaging.

Thermomechanical measurements were conducted using a TA Instruments Dynamic Mechanical Analyzer (DMA) Q800 in tensile mode. Before measurement, samples were heat pressed into ~1 mm thick films and cut into 5.3 mm wide strips. Dynamic mechanical temperature sweep measurements were conducted at a frequency of 1 Hz, amplitude of 1 μm (which corresponds to a strain of ~0.0074%) and a temperature ramp rate of 3°C/min from -120°C to 100°C or until the sample broke.

Calorimetric measurements were conducted using a TA Instruments DSC 2920 Modulated Differential Scanning Calorimeter, at heating or cooling rates of 10°C/min.

Tensile tests were performed at a rate of 0.2 in/min on an Instron 4400R tensile tester using a 200 lb load cell.

## RESULTS AND DISCUSSION

Due to the immiscibility of MAPP and PLS, the morphology of MAPP/PLS blends is expected to be composed of MAPP domains dispersed in the majority PLS matrix. Under the blending conditions, the anhydride groups are expected to react with the hydroxy groups of starch to form ester linkages [Fig. 1(a)]. The main hypothesis of this article is that because of starch-anhydride reactions, the MAPP domains can serve as physical crosslinking sites for PLS, and that such physically crosslinked PLS/MAPP blends will show good elastomeric properties. It should be noted that the term "physical crosslinking" does not necessarily imply reversible chemical associations as it does in materials such as ionomers or multiblock polyurethanes. The term is used only to draw the analogy to block copolymer elastomers, such as SBS, in which the glassy polystyrene domains serve as physical crosslinks for the elastomeric polybutadiene.<sup>22</sup>

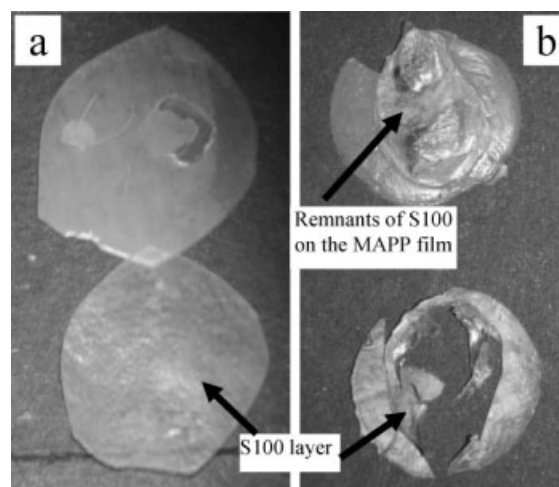
It is important to note that the MAPP domains can serve as effective crosslinks only if the hydroxy groups on the starch chains react with the anhydride groups on MAPP; if the reaction does not occur, the MAPP domains will merely act as rigid fillers. While the anhydride is expected to react with hydroxy groups under our extrusion conditions, in the present case, not all such reactions are between MAPP and starch. Specifically, as the glycerol used as plasticizer is itself a triol, it competes for the same anhydride groups [Fig. 1(b)]. At the 60 : 40 starch : glycerol ratio used here, there are 1.3 glycerol-hydroxy groups for every starch-hydroxy group. If it is assumed that the starch-hydroxy groups and the glycerol-hydroxy groups are equally reactive, only an estimated 43% of the anhydride groups that react are expected to react

with starch. Moreover, the anhydride may also react with residual levels of water, further reducing the number of anhydride groups that can react with starch. Accordingly, it is crucial to confirm that the starch reacts with MAPP under experimental conditions. Spectroscopic techniques such as FTIR are of only limited use as they cannot distinguish between MAPP–glycerol vs. MAPP–starch reactions. Therefore we used solubility tests and adhesion tests to verify the starch/MAPP reaction.

One simple test of the reaction is to test whether the MAPP/PLS blends are soluble in dimethyl sulfoxide (DMSO), which is a good solvent for PLS, but is unable to dissolve MAPP. Pellets of each blend were placed between two Teflon coated aluminum sheets and hot-pressed to form films. The films were placed in 10 mL of DMSO and gently shaken by hand upon immersion in the solvent. In less than 15 min, S100 completely dissolved in the DMSO, yielding a clear solution. In contrast, the S95 blend first became swollen, and then over a 1 h period broke into smaller fragments giving the solvent a cloudy, opaque appearance. This suggests that the physical crosslinking of S95 is not complete, although small regions may be locally crosslinked. Finally, the S85% sample remained intact even after 20 h, and did not show significant swelling or breakup, signifying that physical crosslinking is complete. These results strongly suggest that the MAPP can react with the starch under the extrusion conditions, and that the MAPP/PLS blend with 15% MAPP behaves as if it is physically crosslinked.

The second test is to examine the adhesion between PLS and MAPP; any reaction between MAPP and starch would sharply increase the adhesive strength.<sup>23</sup> Thus a comparison of the adhesion between MAPP and S100 vs. that between nonreactive PP and S100 will yield information about whether the starch–MAPP reaction has occurred or not. A crack propagation test was performed on pressed films of the samples. This test is the same as that used by Cole and Macosko<sup>24</sup> to obtain the interfacial fracture toughness. Films of S100, MAPP, and nonreactive polypropylene (i.e. not maleated) were heat pressed using 0.5 mm thick spacers to control the film thickness. Using these films, two bilayer laminates were made; one of S100 and MAPP, and the other of S100 and the nonreactive PP. The bilayer samples were placed in a vacuum oven at about 180°C for 30 min and then a razor blade was inserted at the interface. After several hours, the crack length ahead of the razor blade was measured and the fracture toughness was calculated according to:

$$G = \frac{3\Delta^2 E_1 E_2 h_1^2 h_2^2 (C_1 E_2 h_2^3 + C_2 E_1 h_1^3)}{8a^4 (C_1^3 E_2 h_2^3 + C_2^3 E_1 h_1^3)} \quad (1)$$



**Figure 2** Results of adhesion tests. (a) A bilayer laminate of S100 and PP delaminated readily into a PP layer (top disc) and S100 layer (bottom disc). (b) A bilayer laminate of S100 and MAPP did not delaminate completely.

where:

$$C_i = 1 + 0.64 \left( \frac{h_i}{a} \right)$$

$\Delta$  = wedge thickness

$E$  = elastic modulus

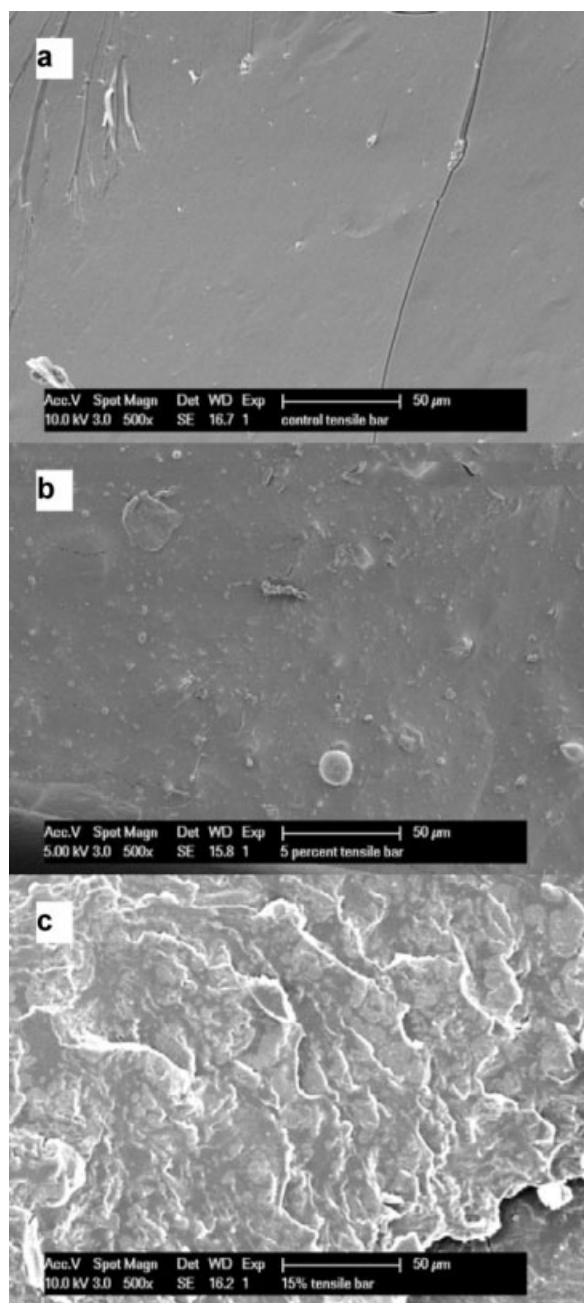
$h$  = layer thickness

$a$  = crack length ahead of wedge.

Upon application of the razor blade, the PP/S100 bilayer completely delaminated [Fig. 2(a)], and hence the fracture toughness could not be measured; as expected, this pair of materials has poor adhesion. For the MAPP/S100 bilayer laminate, the crack length ahead of the razor blade was measured and the resulting fracture toughness was calculated to be  $2.45 \pm 0.66 \text{ J/m}^2$ . After the completion of the fracture toughness test, an attempt was made to force the MAPP and S100 layers apart. Even after scraping the S100 layer away from the MAPP with a razor blade, the two layers did not delaminate completely as pictured in Figure 2(b). The contrast between the complete delamination of the nonreactive bilayer versus the pieces of S100 that remain adhered to the MAPP film support the solubility results, suggesting that an interfacial reaction between MAPP and plasticized starch does indeed occur.

Having confirmed that the MAPP can react with starch, and hence that the MAPP domains can act as physical crosslinking agents, we examined the morphology of the blends. The S100 blend [Fig. 3(a)] displays a smooth continuous fracture surface under SEM. There are no starch granules visible in the micrograph, suggesting that the granular structure has been completely disrupted and the glycerol has gelatinized the starch. For the S95 blend [Fig. 3(b)],





**Figure 3** SEM micrographs of (a) S100, (b) S95, and (c) S85 blends. Note the domains of light gray in (c).

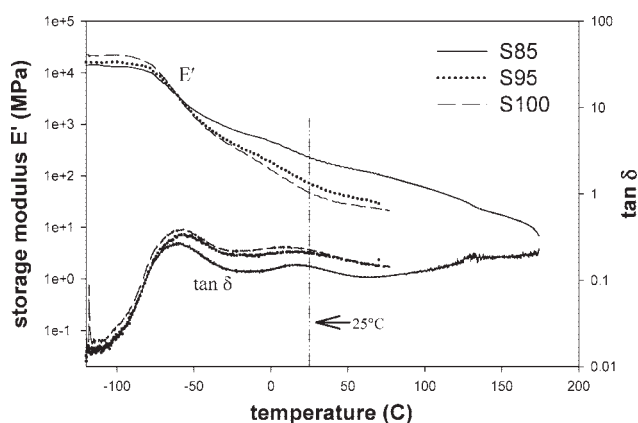
the fracture surface appears mostly smooth, but now numerous features (light gray domains) of size smaller than 5  $\mu\text{m}$  appear throughout the image. Upon further increasing the MAPP content to 15 wt %, irregular gray domains are much more clearly evident [Fig. 3(c)]; in S85, they occupy a larger fraction of the cross sectional area, and also appear to be significantly larger, with some being more than 10  $\mu\text{m}$  in size. These domains, which we believe are polypropylene domains, indicate that in both S95 and S85 samples, (1) the morphology is two-phase with MAPP being the dispersed phase, and

(2) the MAPP domain size increases significantly with increasing MAPP content. DSC data support the conclusion that the samples have a two-phase morphology, specifically, a polypropylene melting endotherm is clearly evident (described later).

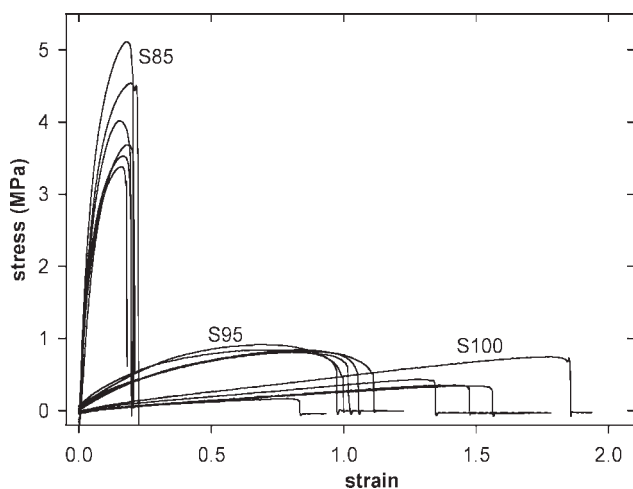
As mentioned in the Introduction, the goal is to show that MAPP/PLS blends have properties that make them potentially-useful as elastomers. To test this, DMA experiments were performed to probe the thermomechanical behavior (Fig. 4). All three samples appear glassy at  $-100^\circ\text{C}$  with a modulus on the order of  $10^4$  MPa. Between about  $-70^\circ\text{C}$  and  $-40^\circ\text{C}$ , the S100 sample shows a significant relaxation process, which is indicated by the maximum in  $\tan \delta$  and a decrease in the storage modulus by more than one order of magnitude. This temperature agrees well with the glass transition temperature of PLS measured by DSC<sup>13,25,26</sup> and the corresponding relaxation process has been identified as the  $\alpha$  relaxation of the glycerol plasticizer.<sup>27</sup> At higher temperatures, a second broad relaxation centered around  $10^\circ\text{C}$  is evident in the  $\tan \delta$  curve, but the  $E'$  is nearly a plateau until the sample breaks at about  $70^\circ\text{C}$ .

The DMA data for the S95 sample are virtually identical to that of the S100. However, S85 shows a much wider rubbery plateau that extends far above room temperature; this sample did not break until  $170^\circ\text{C}$ , which is close to the melting temperature of the MAPP. It is also noteworthy that the low temperature relaxation occurs at about  $-50^\circ\text{C}$  regardless of the MAPP content. These DMA data – specifically the low  $T_g$  and the wide rubbery plateau – are the best indicator of the elastomeric nature of PLS/MAPP blends.

The results of the tensile tests for all three samples are presented in Figure 5, and the tensile strength, Young's modulus, and ultimate elongation obtained from these data are presented in Table II. The ultimate elongation of the S100 blends is about 150%, which is comparable to that measured previously at comparable glycerol contents.<sup>13,14</sup> With increasing



**Figure 4** DMA results. The vertical line is drawn at  $25^\circ\text{C}$  (room temperature).



**Figure 5** Tensile properties of PLS/MAPP blends.

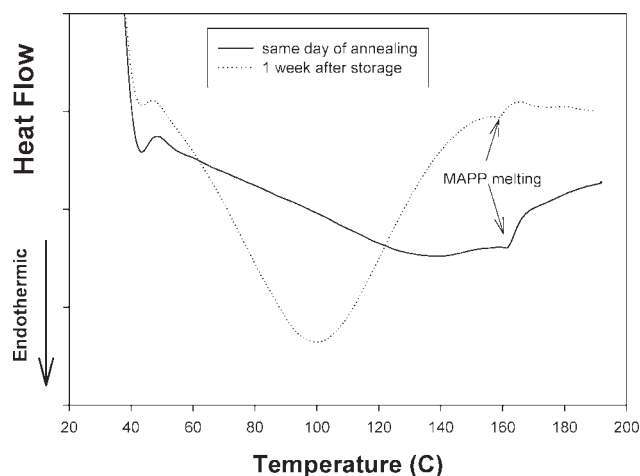
MAPP content, the ultimate elongation decreases, whereas the ultimate strength and modulus increases. These effects are likely attributable to both the filler effect of the rigid MAPP domains, as well as their physical crosslinking effect. The moduli of the blends range from about 0.75 MPa to about 40 MPa, i.e. MAPP/PLS blends can cover the modulus range of typical elastomers. The ultimate elongation of S85, about 20%, is somewhat low from an elastomeric viewpoint, but ultimate elongation is highly sensitive to glycerol content<sup>28,29</sup> and hence can be increased.

Finally, it is important to note two challenges that must be overcome before PLS/MAPP blends become viable elastomers. The first is the susceptibility of such materials to water as the glycerol plasticizer can be extracted by water. For example, upon immersion in water, the S85 blend remained physically intact, however, upon recovering this sample from water and drying it, a weight loss corresponding to the weight of glycerol was noted, and the sample was found to be brittle due to lack of plasticizer. This water susceptibility must be addressed for most potential applications as elastomers.

The second challenge is slow aging of the materials at room temperature. After 3 weeks of storage, the modulus of all three samples increased, and their ultimate elongation decreased. We believe that

**TABLE II**  
Summary of Tensile Data, Presented as the Arithmetic Average of Several Specimens of Each Sample

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Ultimate elongation
S100	0.38	0.77	154%
S95	0.84	2.53	111%
S85	4.04	43.64	20%



**Figure 6** DSC data to illustrate effect of room-temperature aging.

such aging is attributable to slow recrystallization of starch, as has also been noted previously.<sup>30</sup> To test whether such recrystallization had indeed occurred in our samples, we conducted DSC experiments: a sample of S95 was annealed at 200°F ( $\sim 93^\circ\text{C}$ ), allowed to cool to room temperature, and a DSC scan was conducted the same day. The sample was then stored at room temperature for one week, and another scan was conducted. Results are presented in Figure 6. Both samples show a small endotherm at about 160°C that corresponds to melting of polypropylene; this is consistent with the two-phase morphology suggested by SEM. However, the scan after storage for one week also shows a large and broad endotherm at lower temperatures suggesting crystallization of starch at room temperature. This same trend of slow recrystallization, also known as retrogradation, has been observed by previous researchers.<sup>13,15,27,30</sup> Slow aging is a complication that must be addressed before starch-based elastomers can be used in practical applications.

## SUMMARY

We have evaluated the potential for physically crosslinking glycerol-plasticized starch with MAPP so as to make renewable elastomers. PLS/MAPP blends were prepared by single screw extrusion, and injection-molded specimens were tested. Solubility and adhesion tests show that the MAPP is successful in physically crosslinking the starch, and DSC, DMA, and SEM indicate a two-phase morphology consisting of MAPP domains surrounded by the PLS continuous phase. The MAPP/PLS blends have potential for elastomeric applications, as judged by the low  $T_g$  of about  $-50^\circ\text{C}$ , a rubbery plateau extending from room temperature up to as much as 170°C, and tensile properties within the range of many elastomers.

Water susceptibility and slow aging due to starch recrystallization are significant challenges that must be overcome before viable elastomers can be realized.

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