

# Soy Protein Isolate/Kraft Lignin Composites Compatibilized with Methylene Diphenyl Diisocyanate

Jin Huang, Lina Zhang, Hua Wei, Xiaodong Cao

Department of Chemistry, Wuhan University, Wuhan 430072, China

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**ABSTRACT:** Methylene diphenyl diisocyanate (MDI) was used to compatibilize kraft lignin (KL)/soy protein isolate (SPI) blends. The structure and properties of the resultant composite materials were investigated with wide-angle X-ray diffraction, differential scanning calorimetry, dynamical mechanical thermal analysis, scanning electron microscopy, and tensile and water absorption tests. The results indicated that graft copolymerization and a moderate degree of crosslinking between KL and SPI occurred in the composites because of the compatibilization of MDI, which favored the strengthening of the materials. Interestingly, the addition of 2 parts of MDI caused a simultaneous enhancement of the modulus, strength, and elongation of KL/SPI blends. The

structure with grafting and moderate crosslinks reduced the water absorption of the materials. However, the excess crosslinks hindered the interaction between KL and SPI, resulting in a reduction of the mechanical properties. Scanning electron microscopy showed that the domains of the graft copolymer and crosslinking enrichment existed in the blends. When the MDI content was relatively low, these domains became concentric points of stress, enhancing the mechanical properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 624–629, 2004

**Key words:** blends; compatibilization; proteins

## INTRODUCTION

The blending of polymers provides a powerful and convenient route to new materials with excellent properties of more than one existing polymer and improved property/cost performance.<sup>1</sup> Because most blended polymers are immiscible, compatibilization is required to obtain maximum synergy. Usually, the addition of some low-molecular-weight chemicals can form the actual compatibilizer of a branched, block, or graft copolymer during a reactive blending process. In addition, the introduction of a bifunctional chemical necessarily results in the formation of a crosslinked structure in the blend system.<sup>2</sup>

Methylene diphenyl diisocyanate (MDI), a low-molecular-weight chemical, is usually used to compatibilize blends containing natural polymers. Zhong and Sun added MDI to blends of soy protein isolate (SPI) and polycaprolactone (PCL)<sup>3</sup> and SPI and poly(ethylene-*co*-ethyl acrylate-*co*-maleic anhydride).<sup>4</sup> The com-

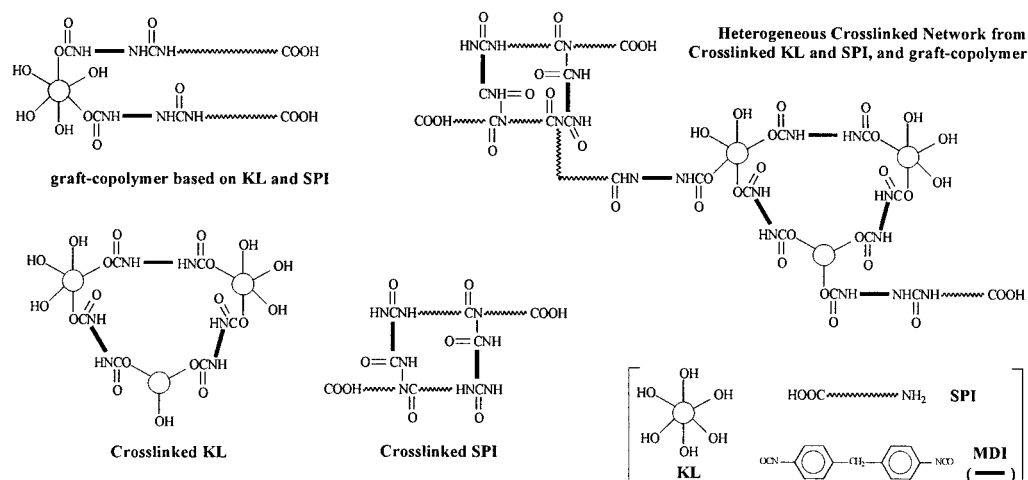
patibilized blends exhibited lower water absorption, and the SPI/PCL blend compatibilized with 2 wt % MDI exhibited the maximum values of the tensile strength ( $\sigma_b$ ), elongation at break ( $\epsilon_b$ ), Young's modulus ( $E$ ), and toughness. In addition, for blends of poly(lactic acid) (PLA) and starch with much lower mechanical properties and water resistance than those of pure PLA, the addition of MDI resulted in an enhancement of  $\sigma_b$ ,  $\epsilon_b$ , and  $E$  and a reduction of the water absorption.<sup>5,6</sup> The mechanical properties of the compatibilized PLA/starch blends were higher than those of pure PLA.

In previous work,<sup>7,8</sup> lignosulfonate (LS) and alkyl lignin (AL) were each blended with SPI to obtain modified materials with improved mechanical properties. For example, LS interacted with soy protein molecules to form networks with physical crosslinks, and this resulted in a simultaneous enhancement of the strength and elongation of soy-protein-based materials, whereas the addition of AL enhanced the water resistivity and strength of materials because of the hydrophobicity and rigidity of AL. The results of structural characterization showed that there existed a certain degree of microphase separation in the lignin/SPI blends. Furthermore, MDI was used to compatibilize kraft lignin (KL)/SPI blends in this work, and sheets were obtained through blending in an intensive mixer and compression molding. The effects of MDI on the structure and properties of the blend materials were investigated with wide-angle X-ray diffraction

Correspondence to: L. Zhang (lnzhang@public.wh.hb.cn).  
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**Scheme 1** Possible molecular structures in the compatibilized system after the addition of MDI.

(WAXD), differential scanning calorimetry (DSC), dynamical mechanical thermal analysis, scanning electron microscopy (SEM), and tensile and water absorption testing.

## EXPERIMENTAL

### Materials

SPI with a moisture content of 6.8% was provided by Dupont Yunmeng Protein Technologies, Ltd. (Hubei, China) and was vacuum-dried for 72 h to remove the moisture before use. KL was supplied by South China University of Technology (Guangzhou, China). MDI (98%) was purchased from Aldrich Chemical Co. (United States). Glycerol (GL; analytical-grade) was purchased from Shanghai Chemical Co. (Shanghai, China).

### Preparation of the samples

Mixtures of SPI and KL (100 parts) in a weight ratio of 7:3 without and with the addition of 0.5, 1, 2, 3, 5, and 8 parts of MDI as a compatibilizer were mechanically mixed at room temperature; this was followed by melt blending with an intensive mixer (Brabender Instruments Co., Germany) at 140°C and 30 rpm for 5 min. Subsequently, 50 parts of GL as a plasticizer were directly added to the intensive mixer containing SPI, KL, and MDI, and then blending was carried out at 140°C and 30 rpm for 10 min.

The resultant blend was placed in a mold covered with two polished stainless steel plates and then was compression-molded with a hot press. The sheets were molded at 160°C and 20 MPa for 5 min and then wind-cooled to about 50°C for 0.5 h under constant pressure before removal from the mold. The sheets were coded SK-M0, SK-M1, SK-M2, SK-M3, SK-M4,

SK-M5, and SK-M6, which corresponded to 0, 0.5, 1, 2, 3, 5, and 8 parts of MDI.

The MDI molecules exhibited two functional —NCO groups, which could react with —OH in KL and —NH in SPI. As shown in Scheme 1, the addition of MDI could form the KL–SPI graft copolymer or chemical crosslinks, including the components of KL and SPI. Obviously, the crosslinked structure increased with an increase in the MDI content.

### Characterization

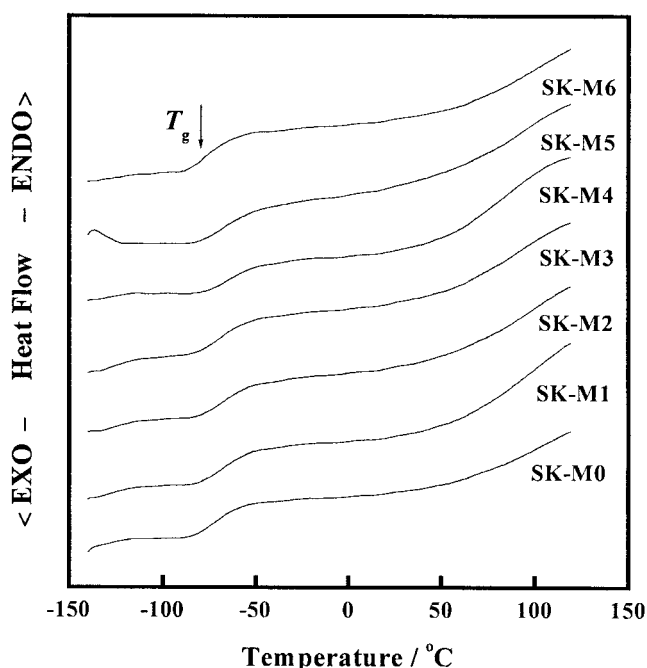
WAXD patterns of the sheets were recorded on a D/max-1200 X-ray diffractometer (Rigaku Denki, Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5405 \times 10^{-10}$  m), and the sheets were examined with  $2\theta$  ranging from 6 to 40° at a scanning rate of 10° min<sup>-1</sup>.

The  $\sigma_b$ ,  $\epsilon_b$ , and  $E$  values of the sheets were measured on a CMT6503 universal testing machine (Shenzhen SANS Test Machine Co., Ltd., China) at a tensile rate of 10 mm min<sup>-1</sup> according to ISO 6239-1986 (E).

SEM images were taken on a Hitachi S-570 microscope (Japan). The fracture surfaces of the sheets at break after tensile testing were coated with gold for SEM observations.

DSC was performed on a DSC-204 apparatus (Netzsch Co., Germany) under a nitrogen atmosphere at a rate of 10°C min<sup>-1</sup> from -150 to 100°C. Before the testing, the samples were heated from room temperature to 100°C; they were then cooled to -150°C at a rate of 20°C min<sup>-1</sup>.

Dynamic mechanical thermal analysis (DMTA) was carried out with a DMTA-V dynamic mechanical analyzer (Rheometric Scientific Co., United States) at a frequency of 1 Hz. The temperature ranged from -100 to 100°C at a heating rate of 5°C min<sup>-1</sup>.



**Figure 1** DSC thermograms of SK-M sheets with various MDI contents.

### Water absorption

Water absorption was measured according to ASTM D 570-81 with minor modifications. The sheets were vacuum-dried for 72 h and then dried at 50°C for 24 h in an oven. Subsequently, they were cooled in a desiccator for a few minutes, weighed, and submerged in distilled water at room temperature for 26 h. The extra water on the surface of the sheet after water soaking was removed with a paper towel, and then the sheet was weighed again. The container with the distilled water containing the sheet was placed in an air oven at 50°C for 72 h to evaporate the water, and the water-soluble content of the sheet was equal to the increase in the container weight. The water absorption ( $A_b$ ) was calculated as follows:

$$A_b = (W_1 - W_0 + W_{\text{sol}}) / W_0$$

where  $W_1$ ,  $W_0$ , and  $W_{\text{sol}}$  are the weight of the sheet containing water, the weight of the dried sheet, and the weight of the water-soluble residuals from the sheet, respectively.

## RESULTS AND DISCUSSION

### Thermal properties

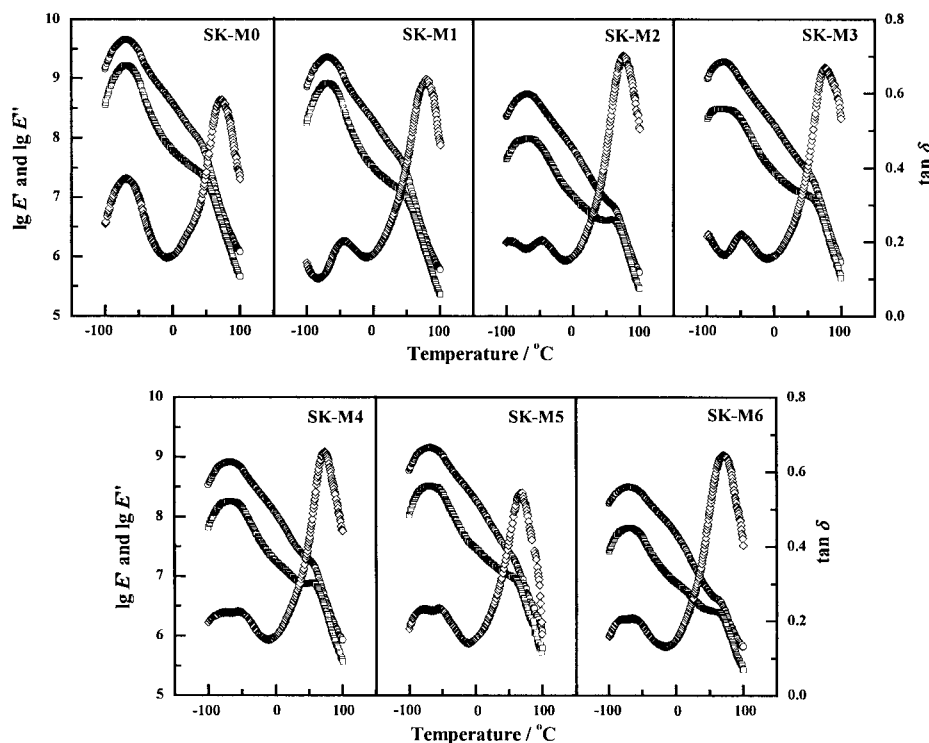
DSC thermograms of the SK-M sheets with various MDI contents are shown in Figure 1. The endothermal peaks in the low temperature range of  $-88$  to  $-77^\circ\text{C}$  were assigned to the glass-transition temperature of

SPI plasticized with GL ( $T_{g1}$ ), that is, the GL-rich domain in SPI; the glass-transition temperature of pure SPI was about  $100^\circ\text{C}$ .<sup>9</sup> The  $T_{g1}$  values and heat capacity changes ( $\Delta C_p$ ) of all the sheets containing SPI are listed in Table I. In comparison with the SK-M0 sheet without MDI,  $T_{g1}$  at the onset, middle, and end points of the SK-M1–SK-M5 sheets shifted to higher temperatures. It was suggested that the formation of graft copolymers and crosslinked structures due to the reactivity of MDI increased the entanglements among components and hence improved the miscibility; this restricted the motion of soy protein molecules and segments. The SK-M6 sheet containing 8 parts of MDI exhibited a lower  $T_{g1}$  than the SK-M0 sheet; that is, the soy protein molecules and segments moved more freely. This may have resulted from the increase in microphase separation caused by the high crosslinking degree of one component when the MDI content was relatively high.

DMTA curves of the SK-M sheets with various MDI contents are shown in Figure 2, and the data are summarized in Table II. The  $\tan \delta$ - $T$  curves can usually be used to determine the different chemical environments concerning molecular and/or segmental motions in polymers. The relaxation peaks at the low temperature range of  $-79$  to  $-43^\circ\text{C}$  corresponded to the glass transition of SPI plasticized with GL. The SK-M1–SK-M3 sheets exhibited a higher  $\alpha$ -relaxation temperature ( $T_{\alpha 1}$ ) at  $-48$  to  $-43^\circ\text{C}$ , which was assigned to the soy protein in the sheets, than the SK-M0 sheet ( $-68.95^\circ\text{C}$ ), and this suggested that the grafting and crosslinks caused by MDI restricted the motion of soy protein molecules and segments. Interestingly, as the MDI content further increased, the  $\alpha$  relaxation for the SK-M4 and SK-M5 sheets showed two peaks at  $-79$  to  $-74^\circ\text{C}$  and at  $-55$  to  $-53^\circ\text{C}$ , indicating that there existed two different chemical environments. At the same time, the temperatures for the two peaks were lower than that for the SK-M0 sheet and that for other compatibilized sheets with relatively low MDI contents, demonstrating, similarly to DSC results, that too much MDI reduced the interaction between KL and SPI. However, DSC reflected this result only when

**TABLE I**  
DSC Results for SK-M Sheets with Various MDI Contents

Sample	$T_{g1,\text{onset}}$ ( $^\circ\text{C}$ )	$T_{g1,\text{mid}}$ ( $^\circ\text{C}$ )	$T_{g1,\text{end}}$ ( $^\circ\text{C}$ )	$\Delta C_p$ ( $\text{J g}^{-1} \text{K}^{-1}$ )
SK-M0	-83.4	-71.3	-59.2	0.390
SK-M1	-80.8	-65.8	-50.8	0.447
SK-M2	-80.0	-66.0	-52.1	0.408
SK-M3	-80.9	-67.5	-54.0	0.426
SK-M4	-77.8	-62.7	-47.6	0.374
SK-M5	-79.8	-64.6	-49.5	0.421
SK-M6	-87.2	-75.1	-62.9	0.440



**Figure 2** Storage modulus ( $E'$ ), loss modulus ( $E''$ ), and  $\tan \delta$  as functions of temperature for SK-M sheets with various MDI contents.

the MDI concentration reached 8 parts, and this suggested that DMTA testing for characterizing the motions of chains and segments exhibited more microscale and higher sensitivity. Different from sheets SK-M4 and SK-M5, SK-M6 exhibited a broad peak for  $\alpha$  relaxation, and its  $T_{\alpha 1}$  was slightly higher than that of the SK-M0 sheet. This indicated that higher chemical crosslinks resulted in a relatively homogeneous microstructure for SK-M6. In addition, the loss peak  $T_{\alpha 2}$  at a high temperature (ca. 70°C) for all the sheets could be assigned to SPI in SPI-rich domains; it should have been about 100°C. In this case, the reduction of  $T_{\alpha 2}$  resulted from the induction of GL and KL.

### Crystallinity and morphology

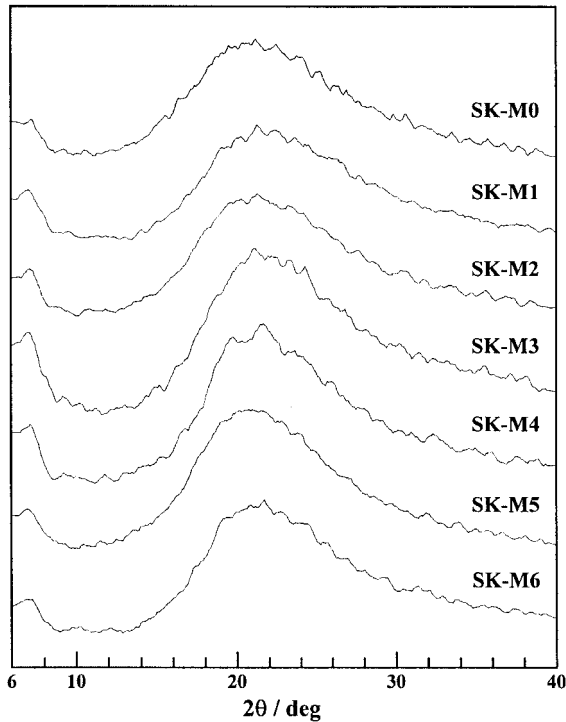
WAXD patterns of SK-M sheets with different MDI contents are depicted in Figure 3, and two diffraction

peaks located at about 7 and 21° ( $2\theta$ ) suggest that certain ordered structures occurred on different scales in the blends; this was different from blends of lignosulfonate calcium and SPI<sup>7</sup> and alkaline lignin and SPI.<sup>8</sup> The SK-M1 and SK-M2 sheets exhibited WAXD patterns similar to that of the SK-M0 sheet, indicating that the addition of MDI at a lower concentration had no influence on the ordered structure in the SPI/KL blend. The diffraction peaks for SK-M3–SK-M6 were sharpened and heightened because of the crosslinks caused by MDI.

SEM images of the fracture surfaces for SK-M sheets are shown in Figure 4. The fracture surface of the SK-M0 sheet without MDI was a homogeneous plane with many white grains. However, adding MDI to the blends resulted in an inhomogeneous fracture surface containing many fuscous domains, and the numbers of the domain increased with an increase in the MDI

**TABLE II**  
DMTA Results for SK-M Sheets with Various MDI Contents

Sample	$\alpha$ transition				Peaks	Loss peak	
	$T_{\alpha 1}$ (°C)		$\tan \delta$			$T_{\alpha 2}$ (°C)	$\tan \delta$
SK-M0	-68.95	—	0.370	—	Single	74.15	0.582
SK-M1	-43.24	—	0.201	—	Single	79.34	0.638
SK-M2	-45.88	—	0.204	—	Single	75.89	0.702
SK-M3	-47.71	—	0.219	—	Single	76.36	0.669
SK-M4	-74.33	-55.82	0.223	0.224	Double	74.42	0.653
SK-M5	-78.85	-54.40	0.231	0.234	Double	70.51	0.543
SK-M6	-64.98	—	0.206	—	Broad	71.09	0.645



**Figure 3** WAXD patterns of SK-M sheets with various MDI contents.

content. This indicated that the internal structure of the compatibilized materials was inhomogeneous to a certain degree, and the fuscous domain might be the aggregated region of graft copolymers and crosslinked polymers formed by the addition of MDI. When the volume fraction of these domains was relatively low, they became the concentric points of stress in tensile tests, and this favored the enhancement of the mechanical properties. However, once the volume fraction of the domains was too high, another region might become the dotted regions of the mechanical properties. The SK-M6 sheet containing 8 parts of MDI exhibited a homogeneous fracture surface. This suggested that relatively high MDI contents resulted in homogeneous crosslinked structures in the blends, and this was consistent with the results of DSC and DMTA.

### Mechanical properties

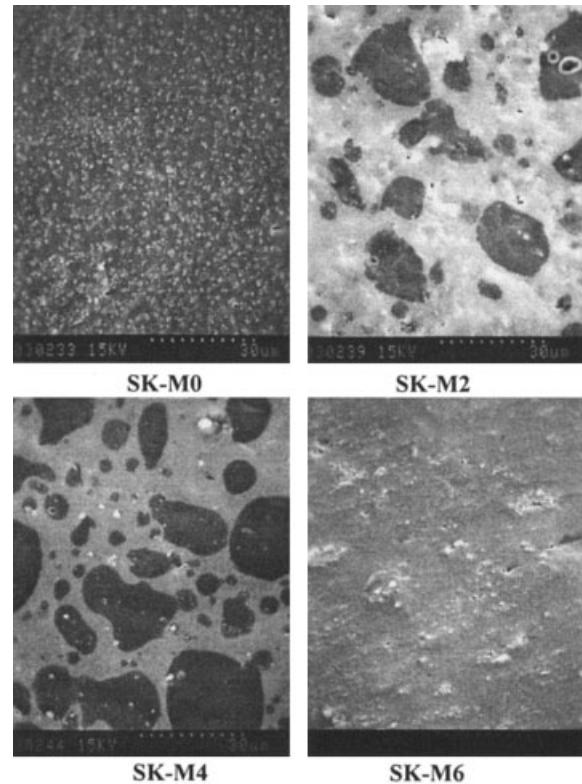
The effects of the MDI contents on  $\sigma_b$ ,  $\epsilon_b$ , and  $E$  for the SK-M sheets are shown in Figure 5. The  $\sigma_b$  and  $E$  values of the compatibilized materials first decreased with an increase in the MDI content up to 1 part and then obviously increased up to 2 parts of MDI. Subsequently, the  $\sigma_b$  and  $E$  values gradually decreased with an increase in the MDI content, but when the MDI concentration was 8 parts, the  $\sigma_b$  and  $E$  values sharply increased. At the same time,  $\epsilon_b$  increased with

an increase in the MDI content up to 1 part and then gradually decreased. Interestingly, the compatibilized materials containing 1 part of MDI exhibited the highest  $\epsilon_b$  values, and that containing 2 parts of MDI exhibited the highest  $\sigma_b$  values and  $\epsilon_b$  values higher than those of the SK-M0 sheet without MDI.

The addition of MDI led to the graft copolymer and crosslinking to a moderate degree between KL and SPI, resulting in an enhancement of  $\epsilon_b$ . At the same time, the graft copolymer and crosslinked polymer tended to aggregate as domains, which became the concentric points of stress and enhanced  $\sigma_b$ . The  $\sigma_b$  and  $\epsilon_b$  values of SK-M3 with a moderate degree of crosslinking simultaneously increased. However, with an increase in the MDI content, the interaction between SPI and KL, hindered by the relatively high degree of crosslinking, was accompanied by an increase in the aggregate domains, which resulted in a decrease in the elongation and strength (e.g., SK-M4 and SK-M5). With respect to SK-M6 containing 8 parts, the homogeneous crosslinked networks in the blends caused sharp increases in  $\sigma_b$  and the maximum value of  $E$ .

### Water absorption

As shown in Figure 6, the addition of MDI (0.5–2 and 8 parts) could slightly lower the water absorption of



**Figure 4** SEM images of cross sections of sheets SK-M0, SK-M2, SK-M4, and SK-M6.

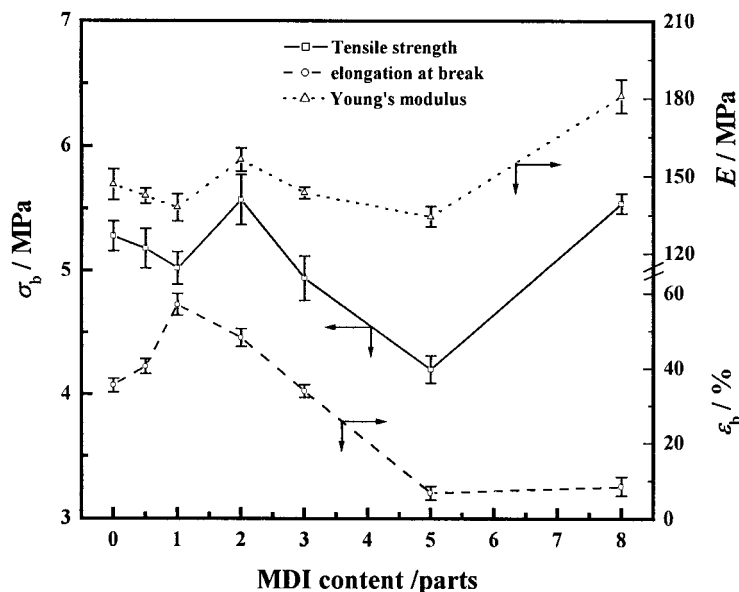


Figure 5 Effects of the MDI content on  $\sigma_b$ ,  $\epsilon_b$ , and  $E$  of SK-M sheets.

KL/SPI blends. When MDI was added to KL/SPI blends, the formation of graft copolymers and moderate crosslinking restricted the swelling of the sheets. Moreover, the SK-M6 sheet containing 8 parts of MDI exhibited low water absorption because of its internal high crosslinking density. With respect to the SK-M sheets containing 3–5 parts of MDI, the water absorption was higher than that of the SK-M0 sheet without the compatibilizer. It might be explained that the increase in the chemical crosslinks destroyed the interaction between SPI and KL, and at this time, integrated crosslinked networks such as the SK-M6 sheet did not form.

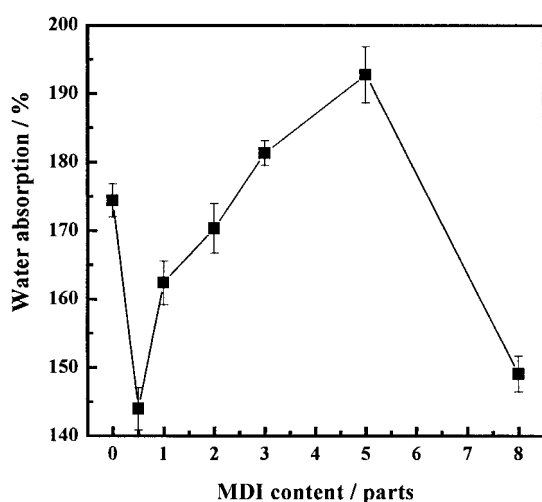


Figure 6 Effects of the MDI content on the water absorption of SK-M sheets immersed in water for 26 h.

## CONCLUSIONS

The formation of a moderately grafted and crosslinked structure and aggregate domains caused by reactive MDI favored the enhancement of  $\sigma_b$  and  $\epsilon_b$  and lowered the water absorption of the compatibilized materials. In particular, the addition of 2 parts of MDI resulted in a simultaneous enhancement of  $E$ ,  $\sigma_b$ , and  $\epsilon_b$  of KL/SPI blends. However, excess crosslinks hindered the interaction between SPI and KL because of the relatively high MDI content, whereas the region of aggregate domains also increased with an increase in the MDI content, which did not favor the improvement of the properties of the composite materials. Although the SK-M6 sheet containing the highest MDI content exhibited higher  $\sigma_b$  values because of its highly crosslinked structure, it was very brittle. Therefore, the addition of MDI in a moderate concentration could improve the water resistivity and mechanical properties.

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