

## Mechanical Properties of Acrylonitrile-Butadiene-Styrene Copolymer/Poly(L-lactic acid) Blends and Their Composites

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**ABSTRACT:** As the material properties of acrylonitrile-butadiene-styrene copolymer (ABS) have an excessively wide margin for applications in automobile console boxes, ABS partly replaced with poly(L-lactic acid) (PLA) may be used for the same purpose with improved ecofriendliness if the corresponding deterioration of the material properties is acceptable through the choice of appropriate additives. ABS composites with 30 wt % renewable components (PLA and cellulose pulp) were prepared by melt compounding, and the material properties were examined as a function of the additive content. The changes in the mechanical properties of the ABS/PLA blends were examined after the addition of cellulose pulp and two clays [Cloisite 25A (C25A) and sodium montmorillonite] as well as these two clays treated with bis(3-triethoxysilylpropyl)tetrasulfide (TESPT). The heat distortion temperatures of the composites were measured as a function of the content of the TESPT-treated C25A. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40329.

**KEYWORDS:** blends; clay; composites; fibers; mechanical properties

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### INTRODUCTION

Acrylonitrile-butadiene-styrene copolymer (ABS) is normally prepared by the compounding of the glassy acrylonitrile-styrene random copolymer (SAN) with rubbery polybutadiene-*g*-poly(styrene-*ran*-acrylonitrile) (*g*-ABS). The material properties depend strongly on the SAN/*g*-ABS ratio and on the final content of the butadiene (BD) units.<sup>1-5</sup>

ABS has excellent material properties, and ABS with a BD content of 12.8 wt % is normally used for car console boxes. On the other hand, the commonly used ABS with a BD content of 12.8 wt % displays material properties in considerable excess of the target values required for applications to car console boxes.<sup>6</sup>

Recent public concerns about global warming and the expected depletion of fossil resources in the near future has provided a great incentive for replacing fossil-resource-based materials with those derived from renewable resources. ABS is a good candidate for this purpose because it is one of the most frequently used plastics for car interior parts. Nevertheless, its replacement is not expected to increase production costs because ABS is relatively costly itself.<sup>7</sup>

The first target for car makers for making cars provisionally ecofriendly is to substitute at least 30 wt % of fossil-resource-based plastics in car interior parts with materials from renewable resources.<sup>6-9</sup> Poly(L-lactic acid) (PLA) is one of the most

spotlighted renewable plastics. Moreover, the recent upsurge in oil prices and the remarkable progress in fermentation/polymerization technologies for PLA have improved its price competitiveness compared to conventional commodity plastics.<sup>10</sup> On the other hand, PLA has grave shortcomings that impede its use in durable goods, such as an unacceptably low heat distortion temperature (HDT) and impact strength and a narrow processing window.<sup>11,12</sup>

Many researchers have evaluated ways of enhancing the material properties of PLA through copolymerization and compounding with other polymers, plasticizers, and fillers.<sup>13-15</sup>

Li and Shimizu<sup>3</sup> and Sun et al.<sup>16</sup> used ABS to toughen PLA. As PLA and ABS are thermodynamically immiscible with each other, they used SAN-*g*-glycidyl methacrylate (GMA) or ABS-*g*-GMA as a reactive compatibilizer for the blends. They showed experimental evidence of the chemical reaction between the epoxy groups of GMA and the end carboxyl and hydroxyl groups of PLA.

In this study, the replacement of part of ABS with PLA was attempted to improve the ecofriendliness of ABS-based car interior parts. When PLA was compounded with ABS that had a BD content of 25 wt % [ABS(BD25)] at a 50/50 weight ratio, the impact strength was as low as 22.0 J/m, which was far below the target impact strength value of 80 J/m required for the automobile console boxes. In our laboratory, ABS/PLA50/50

composites were developed with material properties that satisfied all of the target values, including the tensile strength and modulus, flexural strength and modulus, and impact strength, through an increase in the BD content of ABS to 28 wt % [ABS(BD28)] with *g*-ABS, whose BD content was 58 wt % and through the incorporation of 20-phr SAN-*g*-GMA as a compatibilizer.<sup>17</sup> The material properties of the ABS(BD28)/PLA50/50 composite were improved further by the addition of Songsorb-3270 as a heat stabilizer. The final PLA content in the ABS(BD28)/PLA50/50 composite was 40 wt % because 20-phr SAN-*g*-GMA and 4-phr of other additives were incorporated into the composite. However, a crucial problem still needs to be solved for the ABS(BD28)/PLA50/50 composite because its HDT was not high enough for it to be used in car console boxes.

In this study, we reduced the content of PLA in the composite from 40 to 30 wt % because PLA was mainly responsible for the low HDT. Clay was also added to the composite because it has often been reported to be effective for the enhancement of HDT.<sup>18–20</sup> The decrease of the PLA content (and the increase of the ABS/PLA ratio) may have raised the impact strength of the composite and provided ample room for impact strength reduction due to the clay addition.

Cellulose pulp was also added to the ABS/PLA composite because it could reduce the weight and price of materials because of its low bulk density.<sup>21–23</sup> The content of the components from renewable resources, including PLA and cellulose pulp, was kept at 30 wt % because the polymeric materials for automobile interior parts are classified provisionally as eco-friendly in the automobile industry sector if they contain more than 30 wt % of renewable components. A range of organic/inorganic additives were added to ABS/PLA to minimize the deterioration of the material properties and meet the respective target values.

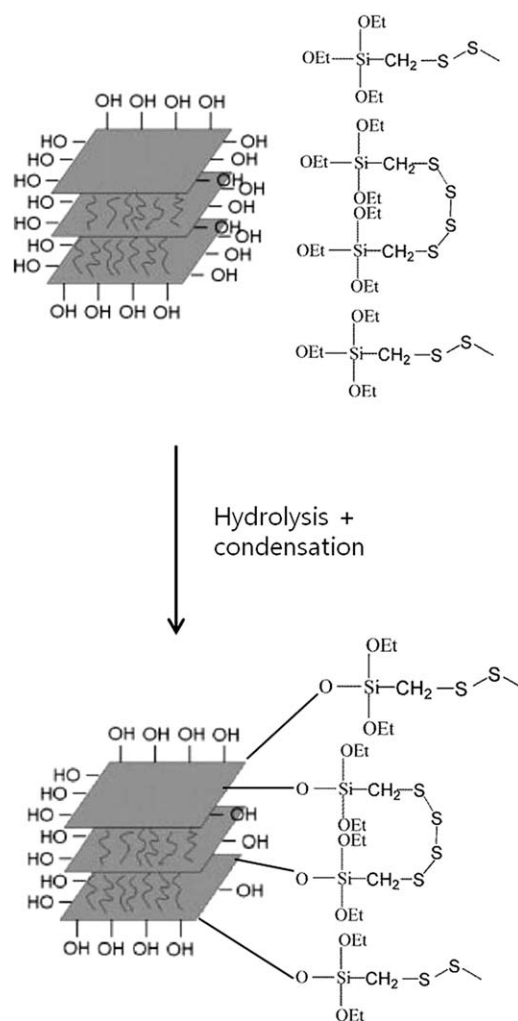
## EXPERIMENTAL

### Materials

ABS (SR0325-LTS, BD content = 12.8 wt %) and *g*-ABS (CHT, BD content = 58%) were used as received from Cheil Industries (Uiwang, Korea). The material properties of ABS depend not only on the BD content but also on the compounding conditions, including the compounding machine configuration. As the ABS (XR-409H, BD content = 25 wt %, LG Chem, Korea) and PLA (2002D, NatureWorks, Minnetonka, MN) used in our previous study<sup>17</sup> were not produced by the respective suppliers any more, ABS (SR0325-LTS, BD content = 12.8 wt %, Cheil Industries, Korea) and PLA (2003D, NatureWorks) were used in this study. ABS was prepared by compounding.

SAN-*g*-GMA (Cheil Industries) was used as a compatibilizer. PLA was purchased from NatureWorks (2003D).

2-(2'-Hydroxy-3',5'-di-*t*-butylphenyl)-5-chlorobenzotriazole (Songsorb-3270, Songwon Industries, Ulsan, Korea) was used as a heat stabilizer. Dicumyl peroxide (DCP) as an initiator was obtained from Sigma-Aldrich (St. Louis, MO). Cloisite 25A (C25A) and sodium montmorillonite (MMT) to be used as fillers were purchased from Southern Clay Products (Gonzales, TX). Bis(3-trie-

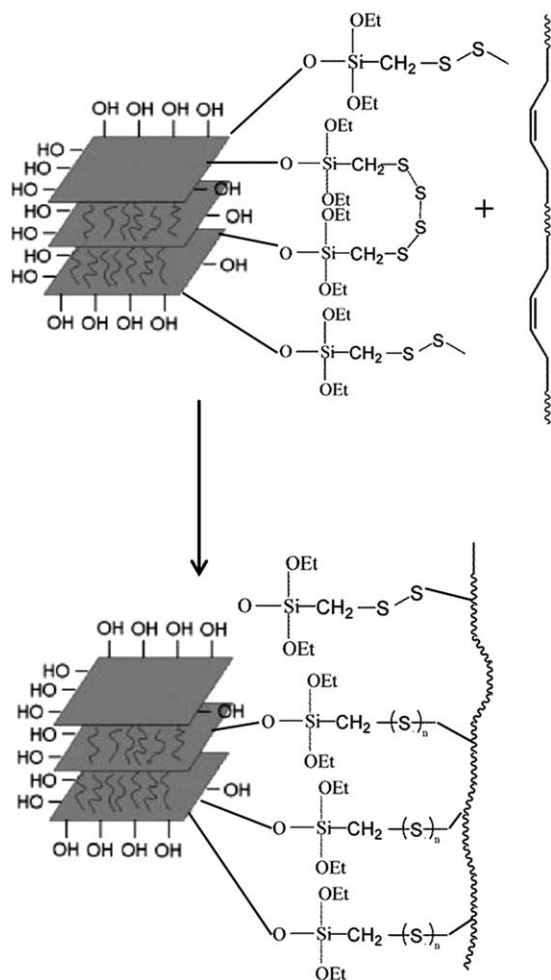


**Scheme 1.** Introduction of  $S_4$  groups to the clay surface.

thoxysilylpropyl)tetrasulfide (TESPT), supplied by Shin Etsu Chemical (Tokyo, Japan), was used to modify the clays. Cellulose pulp (TC750) to be used as porous filler was donated from Creaffil (Chestertown, MD). The average length of cellulose pulp was about 0.7 mm, with average aspect ratio of 35.

### Modification of Clay

MMT and C25A were treated with TESPT to introduce tetrasulfide ( $S_4$ ) groups to the clays, as shown in Scheme 1. The clays were predried in a convection oven at 60°C for 24 h. An ethanol/deionized water 9/1 mixture at pH 4 was prepared with hydrochloric acid, where 9 g of TESPT was added and hydrolyzed for 2 h. The predried clay (90 g) was added to 1800 g of the prepared ethanol/deionized water/TESPT mixture and stirred at 70°C for 14 h. The modified product was filtered and washed several times with ethanol at room temperature and then dried in a vacuum oven at 60°C for at least 48 h. The final product obtained was ground to a 50- $\mu$ m-sized powder. The TESPT-treated clays (C25A- $S_4$  and MMT- $S_4$  from C25A and MMT, respectively) could increase the interaction with ABS because the  $S_4$  attached to C25A- $S_4$  and MMT- $S_4$  could react with the unsaturated groups of ABS, as shown in Scheme 2.



**Scheme 2.** Plausible reaction between the  $S_4$  groups and unsaturated groups of ABS.

### Preparation of ABS/PLA Composites

ABS, *g*-ABS, PLA, and SAN-*g*-GMA were dried in a convection oven at 60°C for at least 4 h. The clays, modified clays, and cellulose pulp also were dried in a vacuum oven at 60°C for 6 h. The ABS/PLA/clay and ABS/PLA/pulp composites were prepared by melt compounding at 200–230°C with a twin-screw extruder (screw diameter = 19 mm, length/diameter ratio = 40, BauTechnology, Uijeongbu, Korea). The contents of the components (in weight percentage) are listed in Table I. The additives in Table I were composed of heat stabilizers, processing aids, and impact modifiers, and their composition is shown in Table II. The BD content of the base ABS/*g*-ABS blend (ABS blend) was controlled either at 20 or 30 wt % by the ABS/*g*-ABS weight ratios.

The extruded products were dried in a vacuum oven at 60°C for 24 h. The dried products were molded at 230°C with an injection molder (screw diameter = 22 mm, clamping force = 50t, VDC-II, JinHwa GloTech, Cheonan, Korea) to prepare the test specimens.

### Characterization

The mechanical properties of the composites were tested with a universal testing machine (Hounsfield, H10KS-0061, Surrey,

England). The tensile strength was measured according to ASTM D 638. The crosshead speed was 50 mm/min. The flexural properties were also measured with a universal testing machine according to ASTM D 790 at a crosshead speed of 2.8 mm/min. The notched Izod impact strength was measured with an impact testing machine (Custom Scientific Instruments, CSI-137C, Easton, PA) according to ASTM D 256. The results of at least seven measurements were averaged.

HDT was measured with a HDT tester (HDT, Qmesys, QM950H, Gwangmyeong, Korea) according to ASTM D 648. The load was applied to its center to give a maximum stress of 0.455 MPa.

The morphological aspects of the blend were examined by scanning electron microscopy (SEM; Hitachi High-Technologies, S-4300SE, Tokyo, Japan) to observe the internal morphology. The injection-molded test specimens were further subjected to hot pressing at 230°C to make them thinner. The surface morphology of the thinner specimens was cleaner and free from any marks such as plastic flow or shear yielding when fractured in liquid nitrogen. The fracture surface was then etched with tetrahydrofuran (THF).

The change in the interlayer distance of the clay layers in the composites was analyzed by X-ray diffraction (XRD; Rigaku, DMAX 2200V, Tokyo, Japan). Cu  $K\alpha$  radiation was operated at 60 kV and 60 mA. The patterns were recorded within the range of scattering angles of 2–6° diffraction angle ( $2\theta$ ) with a scanning rate of 1°/min.

## RESULTS AND DISCUSSION

The mechanical properties of the ABS/PLA composites are summarized in Table III. As SAN-*g*-GMA was added in the range of 0–24 wt % to ABS/PLA as a compatibilizer, the amount of ABS and *g*-ABS was adjusted correspondingly to maintain the PLA content in the composite at 30 wt %.

SG0 exhibited an impact strength of 240 J/m, which was far superior in comparison to that of ABS(BD28)/PLA50/50, that is, 97.8 J/m, as reported in our previous article,<sup>17</sup> because the PLA content had been reduced from 40 to 30 wt %. A huge difference in the impact strength was also attributed to the change in the raw materials, that is, ABS and PLA (due to the hiatus of commercial production).

As the SAN-*g*-GMA content was increased from 0 to 24 wt %, the tensile and flexural strength increased from 36.1 to 46.2 and 44.0 MPa to 54.6 MPa, respectively. The flexural modulus was also enhanced from 1490 to 1830 MPa. The impact strength was increased from 240 to 407 J/m with increasing SAN-*g*-GMA content from 0 to 16 wt %. On the other hand, a further increase in the SAN-*g*-GMA content did not affect the impact strength significantly. An increase in the SAN-*g*-GMA content in the blends may have increased the impact strength because of the compatibilizing effect, but at the same time, the replacement of part of the ABS with SAN-*g*-GMA may have affected the impact strength adversely because SAN-*g*-GMA was more rigid and less flexible than ABS. That may explain the reason why the impact strength of the blend was increased when the

**Table I.** Compositions (wt %) of the ABS/PLA Composites

Composite	PLA	ABS Blend		SAN-g-GMA	DCP	Clay	Pulp	Additive
		ABS	g-ABS					
SG0	30	41.7	25.5	0				2.8
SG4	30	39.2	24	4				2.8
SG8	30	36.7	22.5	8				2.8
SG12	30	34.2	21	12				2.8
SG16	30	31.7	19.5	16				2.8
SG20	30	29.2	18	20				2.8
SG24	30	26.7	16.5	24				2.8
SG20/DCP	30	29.1	17.8	20	0.24			2.8
SG24/DCP	30	26.6	16.3	24	0.24			2.8
Clay 0	30	39.4	7.5	20	0.24	0		2.8
C25A 1	30	38.6	7.3	20	0.24	1		2.8
C25A 2	30	37.7	7.2	20	0.24	2		2.8
C25A 3	30	36.9	7	20	0.24	3		2.8
C25A-S <sub>4</sub> 1	30	38.6	7.3	20	0.24	1		2.8
C25A-S <sub>4</sub> 2	30	37.7	7.2	20	0.24	2		2.8
C25A-S <sub>4</sub> 3	30	36.9	7	20	0.24	3		2.8
MMT 1	30	38.6	7.3	20	0.24	1		2.8
MMT 2	30	37.7	7.2	20	0.24	2		2.8
MMT 3	30	36.9	7	20	0.24	3		2.8
MMT-S <sub>4</sub> 1	30	38.6	7.3	20	0.24	1		2.8
MMT-S <sub>4</sub> 2	30	37.7	7.2	20	0.24	2		2.8
MMT-S <sub>4</sub> 3	30	36.9	7	20	0.24	3		2.8
Pulp 0	30	39.4	7.5	20	0.24		0	2.8
Pulp 1	29	39.4	7.5	20	0.24		1	2.8
Pulp 2	28	39.4	7.5	20	0.24		2	2.8
Pulp 3	27	39.4	7.5	20	0.24		3	2.8

SAN-g-GMA content rose to 16 wt %, but thereafter, the positive effect of the addition of SAN-g-GMA on the impact strength faded out.

The tensile strength and impact strength of SG12–SG24 met the respective target values, whereas their flexural strength and modulus fell short of the respective target values.

**Table II.** Ingredients in the Additives Listed in Table I

Additive	Purpose	Composition (wt %)
Irganox 1010	Antioxidant	0.08
Irganox 1076	Antioxidant	0.08
Irgafos 168	Antioxidant	0.08
Antioxidant	Antioxidant	0.08
Lubricant	Processing aid	0.08
Wax (502N)	Processing aid	0.24
Songsorb 3270	Heat stabilizer	0.24
Biomax 120	Impact modifier	2.00

According to Greszta and Matyjaszewski,<sup>24</sup> the incorporation of DCP helps improve the mechanical properties of ABS/PLA. The radicals formed from DCP can induce a polymer reaction between ABS and PLA *in situ* to produce an ABS-g-PLA copolymer, which should help enhance the compatibility between ABS and PLA.<sup>25–28</sup>

SG20/DCP and SG24/DCP, which contained ABS blend/PLA with 20 and 24 wt % SAN-g-GMA, respectively, together with 0.24 wt % DCP, exhibited improved tensile strength, flexural strength and modulus, and impact strength compared to SG20 and SG24, respectively. This confirmed the positive effect of DCP on the mechanical properties of ABS/PLA. The ABS and g-ABS contents in SG20/DCP and SG24/DCP were slightly lower than those in SG20 and SG24 because of the addition of DCP when the PLA content in the composite was kept at 30 wt %, as cited before. The tensile strength and flexural strength and modulus of SG24/DCP were not significantly higher than those of SG20/DCP, and the impact strength of the former was even lower than that of the latter. This might have been due to the lower ABS and g-ABS contents in the former composite compared to that in the latter.

**Table III.** Mechanical Properties of the ABS/PLA Composites

Composite	Tensile strength (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
Target value	40	60	2000	80
ABS (BD: 12.8 wt %)	53.0 ± 0.7	71.9 ± 1.0	2227 ± 63	324 ± 7
SG0	36.1 ± 0.3	44.0 ± 0.6	1490 ± 11	240 ± 1
SG4	37.7 ± 0.7	46.3 ± 0.2	1570 ± 19	276 ± 4
SG8	39.6 ± 0.4	48.2 ± 0.4	1640 ± 11	314 ± 11
SG12	41.7 ± 0.3	50.1 ± 0.5	1690 ± 43	353 ± 9
SG16	42.2 ± 0.2	51.5 ± 0.7	1720 ± 20	407 ± 6
SG20	44.9 ± 0.2	53.4 ± 0.4	1830 ± 20	402 ± 12
SG24	46.2 ± 0.3	54.6 ± 0.6	1830 ± 80	402 ± 22
SG20/DCP	45.5 ± 0.3	58.6 ± 0.6	1770 ± 55	508 ± 20
SG24/DCP	47.0 ± 0.5	59.4 ± 0.3	1890 ± 14	476 ± 21
Clay 0	50.9 ± 0.2	66.5 ± 1.2	2180 ± 19	148 ± 6
C25A 1	49.9 ± 0.9	61.3 ± 0.7	2240 ± 21	82 ± 7
C25A 2	50.1 ± 0.4	61.0 ± 1.8	2280 ± 10	67 ± 7
C25A 3	49.4 ± 0.7	60.8 ± 1.3	2400 ± 37	36 ± 4
C25A-S <sub>4</sub> 1	51.8 ± 0.5	65.7 ± 0.5	2310 ± 8	134 ± 10
C25A-S <sub>4</sub> 2	51.3 ± 0.5	64.8 ± 0.4	2330 ± 73	73 ± 3
C25A-S <sub>4</sub> 3	51.9 ± 0.1	65.0 ± 0.6	2410 ± 6	70 ± 6
MMT 1	47.0 ± 0.4	60.6 ± 0.3	2210 ± 35	79 ± 10
MMT 2	46.8 ± 0.4	60.2 ± 0.6	2270 ± 10	70 ± 7
MMT 3	47.2 ± 0.2	60.0 ± 0.4	2370 ± 11	72 ± 4
MMT-S <sub>4</sub> 1	50.1 ± 0.9	61.4 ± 0.9	2240 ± 33	99 ± 5
MMT-S <sub>4</sub> 2	50.0 ± 0.4	63.5 ± 0.7	2250 ± 23	79 ± 6
MMT-S <sub>4</sub> 3	49.9 ± 0.3	64.2 ± 0.7	2290 ± 24	73 ± 1
Pulp 0	50.9 ± 0.2	66.5 ± 1.2	2180 ± 19	148 ± 6
Pulp 1	50.5 ± 0.3	64.3 ± 0.3	2230 ± 7	81 ± 9
Pulp 2	49.5 ± 0.3	64.0 ± 0.6	2240 ± 22	76 ± 4
Pulp 3	49.2 ± 0.2	64.0 ± 0.3	2240 ± 2	63 ± 4

Figure 1 shows the cryofractured surface of SG20 and SG20/DCP etched with THF. The droplets in Figure 1(a) are the THF insoluble components in SG20, whereas the holes are the sites where the THF soluble fraction was located. The sizes of the holes shown in Figure 1(a) were much larger than those shown in Figure 1(b); this confirmed the positive effect of DCP on the compatibility between ABS and PLA.

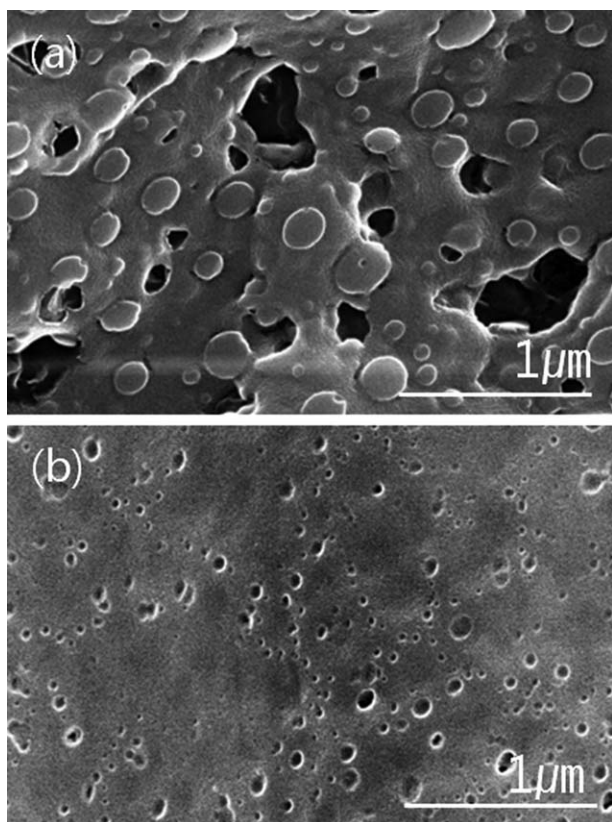
The tensile and impact strengths of SG20/DCP and SG24/DCP were well over the respective target values, whereas their flexural strength and modulus were far below the respective target values. Therefore, the BD content of the ABS blend was reduced from 30 to 20 wt % with the adjustment of the ABS/g-ABS ratio. This increased the flexural strength and modulus at the cost of the tensile and impact strengths. The mechanical properties of SG24/DCP were similar to those of SG20/DCP. Therefore, SG20/DCP was used instead of SG24/DCP for further study because g-ABS and SAN-g-GMA are much more expensive than ABS.

According to Table I, the amount of the ABS blend in SG20 was similar to that in Clay 0, but the ABS/g-ABS ratio of the ABS

blend added to SG20 was different from that of the ABS blend added to Clay 0 (the BD content of the ABS Blend in SG20 was 30 wt %, whereas that in Clay 0 was 20 wt %). The slight difference between the amount of ABS blend in SG20 and that in Clay 0 was due to the addition of DCP to the latter to maintain the PLA content at 30 wt %. The tensile strength and flexural strength and modulus of Clay 0 were higher than those of SG20, but the impact strength was lower. This could be explained by the lower BD content of the ABS blend in Clay 0 compared to that in SG20.

We observed that Clay 0 exhibited mechanical properties that satisfied all of the target values.

The addition of clay often has a positive effect on enhancing the HDT of many polymers.<sup>29–31</sup> The mechanical and thermal properties of the clay-incorporated composites depended strongly on the degree of exfoliation and the interaction of the clay layers within the polymer matrix. C25A and MMT were modified with TESPT to introduce sulfide groups (S<sub>4</sub>) to the respective clays. The incorporation of C25A-S<sub>4</sub> and MMT-S<sub>4</sub> into the ABS/PLA composites instead of C25A and MMT

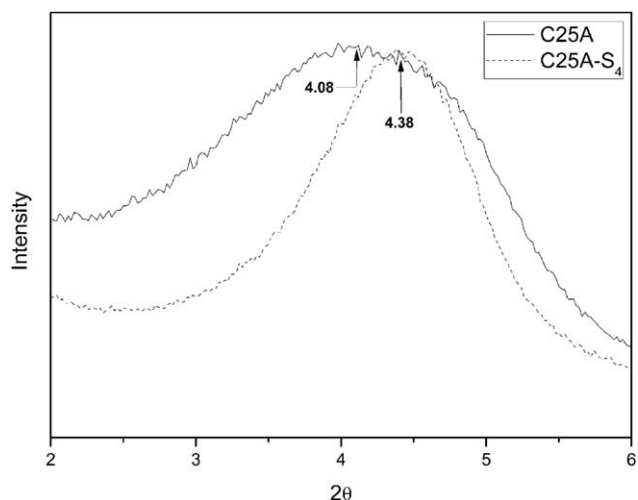


**Figure 1.** SEM images of the cryofractured surfaces of the (a) SG20 and (b) SG20/DCP composites.

increased the interaction between the clay and ABS because the  $S_4$  attached to C25A- $S_4$  and MMT- $S_4$  may have reacted with the unsaturated groups of ABS, as shown in Scheme 2.

MMT, C25A, C25A- $S_4$ , and MMT- $S_4$  were added to Clay 0. The narrower peak of C25A- $S_4$  shifted to a higher  $2\theta$ s ( $2\theta = 4.38$ ) in comparison to the more diffuse peak of the parent C25A ( $2\theta = 4.08$ ) indicated better ordering of silicate layers with a lower clay layer spacing of C25A- $S_4$  compared to that of the pristine C25A (Figure 2). This could be ascribed to lateral interactions with TESPT attached to the clay layers.<sup>32,33</sup> The release of some surfactant out of the clay layers during the modification of C25A with TESPT may be another reason for the decreased interlayer spacing.

According to Table III, the incorporation of the clays reduced the impact strength of Clay 0. On the other hand, the decrease in the impact strength of C25A- $S_4$  was the lowest among the four clays, and C25A- $S_4$  1 (Clay 0 added with 1 wt % of C25A- $S_4$ ) showed an impact strength acceptable for automobile console boxes. Moreover, the other mechanical properties, that



**Figure 2.** XRD patterns of the C25A and modified C25A.

is, tensile strength and flexural strength and modulus, of C25A- $S_4$  1 satisfied the respective target values.

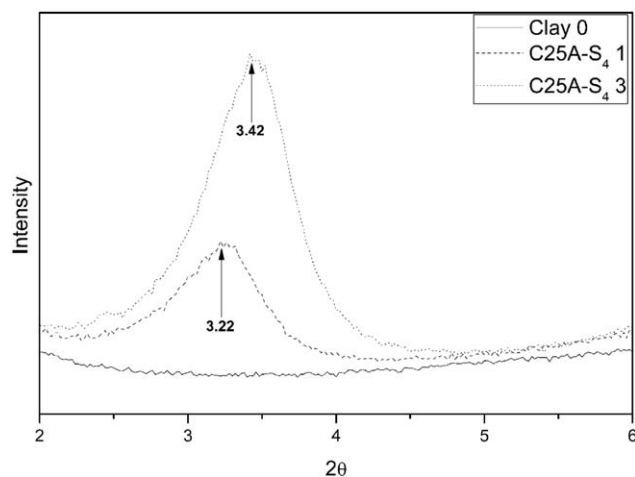
Table IV lists the HDT values of the ABS/PLA/C25A- $S_4$  composites at different clay loadings. The HDTs are the average values of at least seven specimens. The HDT of C25A- $S_4$  was the highest and about 7°C higher than that of Clay 0. On the other hand, it was unclear why the HDT showed a maximum at 1 wt % C25A- $S_4$  and then decreased with further increases in the clay content. The decrease in the amount of ABS blend in the composite with increasing clay loading was partly responsible for the HDT reduction because the HDT of ABS was higher than that of PLA. The slightly larger interlayer spacing of C25A- $S_4$  of C25A- $S_4$  1 ( $2\theta = 3.22$ ) compared to that of C25A- $S_4$  3 ( $2\theta = 3.42$ ), as shown in Figure 3, could also help explain the higher HDT of the former compared to the latter.

It is worth noting that C25A 1 exhibited a slightly lower impact strength compared to C25A- $S_4$  1 but still met all the target values. Therefore, when HDT was not crucially required, C25A may be more recommendable as a filler in the composites than C25A- $S_4$  because the former clay does not need surface-treatment steps, and thus, it is economically more feasible than the latter clay.

Cellulose pulp is also made from renewable resources and is much less expensive than PLA. Pulp 1, 2, and 3 were Clay 0 containing 1, 2, and 3 wt % cellulose pulp, respectively. The amount of PLA in the composites was adjusted to keep the sum of PLA and cellulose pulp at 30 wt %. SEM images of the cryofractured surface of the composites incorporated with cellulose pulp are shown in Figure 4. We observed that blending of the composite components with cellulose pulp before twin-screw

**Table IV.** HDT Values of C25A- $S_4$  Composites with Different Clay Loadings

	Composite				
	Clay 0	C25A 1	C25A- $S_4$ 1	C25A- $S_4$ 2	C25A- $S_4$ 3
HDT under 0.455 MPa (°C)	82.2 ± 4.2	81.7 ± 5.3	89.5 ± 2.9	85.8 ± 3.3	86.3 ± 2.8



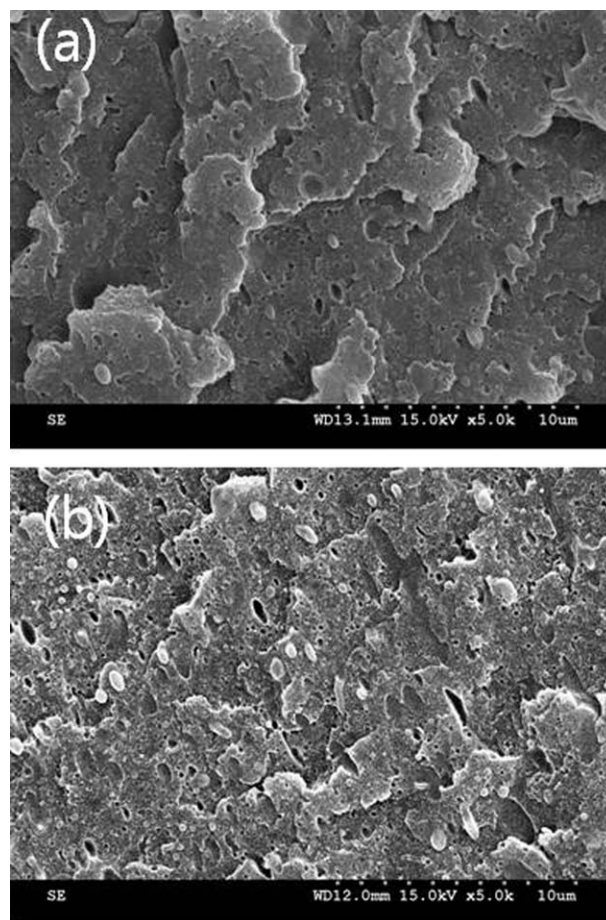
**Figure 3.** XRD patterns of the ABS/PLA/C25A and ABS/PLA/C25A- $S_4$  composites.

extrusion was effective for yielding composites with well-distributed cellulose pulp. During cryofracturing, the cellulose pulp fibers were either broken or pulled out and left holes behind. The cellulose pulp fibers seemed to be fibrillated during compounding because the diameter of the intact cellulose pulp fibers was about 20  $\mu\text{m}$ .

Table III shows that the impact strength decreased suddenly as a result of the addition of a small amount of pulp. Poor adhesion of the cellulose pulp fibers to the polymer matrix, as confirmed by the clean holes in Figure 4, should have been responsible for the reduced impact strength. Only the composite containing 1 wt % pulp satisfied all of the target values, including the impact strength. The more phase-separated morphology of the blend with 3 wt % pulp [Figure 4(b)] as compared to the morphology of the blend with 1% pulp [Figure 4(a)] may explain the worse mechanical properties of the former composite compared to those of the latter one. Porous cellulose pulp has a low bulk density, and the addition of pulp, even in as small quantity as 1 wt %, to the ABS/PLA composites contributed to the weight saving of the material and to the production cost more than a little.

## CONCLUSIONS

ABS was melt compounded with 30 wt % of renewable materials, such as PLA and cellulose pulp. SAN-*g*-GMA random copolymer was an effective compatibilizer for the ABS/PLA composites. The incorporation of DCP helped to improve the mechanical properties of the ABS/PLA because of the ABS-*g*-PLA produced *in situ* from the reaction between ABS and PLA. When the BD content of the ABS/*g*-ABS blend was 30 wt %, the tensile and impact strengths of the ABS/PLA composites met the respective target values, whereas the flexural strength and modulus were far below the respective target values. Decreasing the BD content of the ABS blend from 30 to 20 wt % increased the flexural strength and modulus and tensile strength of the ABS blend/PLA. The impact strength decreased with decreasing BD content. On the other hand, all of the material properties met the respective target values. The incorpora-



**Figure 4.** SEM images of the cryofractured surfaces of (a) pulp 1 and (b) pulp 3.

tion of clay resulted in a decrease in the impact strength, but the decrease was lowest when C25A- $S_4$  was used among MMT, C25A, C25A- $S_4$ , and MMT- $S_4$ . C25A- $S_4$  1 showed an acceptable impact strength, tensile strength, flexural strength, and modulus for automobile console boxes. The HDT of C25A- $S_4$  1 was about 7°C higher than that of Clay 0 (ABS blend/PLA/DCP without C25A- $S_4$ ). The impact strength decreased precipitously after the addition of a small amount of pulp. Only a composite with less than 1 wt % pulp satisfied all of the target values, including the impact strength. Taking into consideration the mechanical properties and the HDT value, we suggest C25A- $S_4$  1 as the most appropriate composite system for automobile console boxes.

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