

Recycling of Commingled Plastics by Cellulosic Reinforcement

CHANG-SIK HA, HAE-DONG PARK, WON-JEI CHO

Department of Polymer Science & Engineering, Pusan National University, Pusan, 609-735, Korea

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ABSTRACT: In this article, a model study was conducted on the effect of combining cellulose on the properties of virgin and/or recycled commingled plastics with a simulated waste-plastics fraction composed of high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), and poly(vinyl chloride) (PVC) (PE/PP/PS/PVC = 7/1/1/1 by weight ratio). The compatibilizing effect of maleic anhydride-grafted styrene-ethylene/butylene-styrene block copolymer (SEBS-*g*-MAH) for the cellulose-reinforced commingled blends was also investigated. Commingled blends were prepared in a table kneader internal mixer. Mechanical properties were measured by using a universal testing machine. Thermal stability was measured by a thermogravimetric analyzer. It was found that the addition of more than 12.5% cellulose into the commingled blends was effective to enhance the mechanical properties of the virgin and recycled blends. The thermal stability as well as the mechanical properties of the commingled blends were much improved by the reactive blending of cellulose with the commingled blends by peroxide and maleic anhydride. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1531–1538, 1999

Key words: commingled blend; recycling; cellulose; reactive blending

INTRODUCTION

The recycling of plastics waste is one method of reducing municipal solid waste (MSW).^{1–10} High-density polyethylene (HDPE), polypropylene (PP), and poly(vinyl chloride) (PVC), as well as polystyrene (PS), are primary constituents of plastics in MSW because they are the most frequently used commercial plastics in our daily lives as well as in industries.^{9,10} We can recycle mixed waste plastics as in the form of blends,^{11–15} because blending is a relatively easy and cost-effective way to produce a new combination of properties such as enhancement of impact strength, dimensional stability, stress cracking,

and improvement of processibility. This approach to reuse is attractive because it avoids the difficult task of separation. As a consequence, the academic and industrial interest in virgin and recycled polymer blends is rapidly expanding. However, the heterogeneous composition is one of the technical problems associated with plastic waste, and the lack of compatibility of different polymers, instead of one well-defined polymer, can give inferior properties when a compatibilizing agent was not added.¹⁶ In this vein, the processing of plastic mixtures for recycling was attempted with some success, but no commercial plant was built to use these raw materials because of poor mechanical properties and uncertain economic value.

A more promising way to recover the economic value of this mixture could be the manufacturing of plastics lumber combining cellulosic reinforcement by blending techniques without separa-

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tion.¹⁶ Cellulose materials offer several advantages, when combined with plastics, because of their low density, high modulus, and high strength.¹⁶ Extensive work was done by R. T. Woodhams in this area.^{17–19} Woodhams et al., for instance, investigated wood fibers as reinforcing fillers for polyolefins and confirmed that most wood pulp materials including Kraft pulp, mechanical pulp, newspaper reclaim, or recovered waste pulp from the Kraft process are equally effective as inexpensive reinforcing fillers for PE or PP.¹⁷ Recently, other authors with Woodhams reported on the X-ray photoelectron spectroscopic studies of lignocellulosic materials treated with maleated polypropylenes¹⁸ and on the influence of interfacial interactions on the properties of PVC cellulosic fiber composites.¹⁹ Plastic lumber is also viewed as a method to utilize tailing the miscellaneous plastics left after recyclable streams, which could not otherwise be collected in significant quantities to justify separation.²⁰

In this work, we report on the effect of combining cellulosic materials on the properties of the virgin and recycled commingled blends with a simulated waste plastics fraction composed of HDPE, PP, PS, and PVC waste polymers (7/1/1/1 HDPE/PP/PS/PVC by weight ratio).

EXPERIMENTAL

The materials used in this study were HDPE (MI = 0.89 at 190°C, M_w = 100,200) supplied by Korea Petrochemicals (Ulsan, Korea; M 830), PP (MI = 3.5 at 230°C, M_w = 60,000) supplied by Korea Petrochemicals (H 430), PS (M_w = 240,000) supplied by KumHo Chemicals (YeoCheon, Korea; GP 100), PVC (DP = 1000) supplied by LG Chemicals (YeoCheon, Korea; LS 100), and cellulose (DP = 1000) supplied by Rayonier Inc. (Gesup, GA; Rayonex-P). The virgin PVC was used in the form of a powder. To avoid thermal degradation, 3 phr of liquid thermal stabilizers based on tin complexes and 3 phr of epoxidized soybean oil plasticizers, supplied by Song Won Ind., were added to PVC by dry blending before the blend mixing. Maleic anhydride-grafted styrene–ethylene/butylene–styrene block copolymer [SEBS-*g*-MAH (MAH content = 0.89 wt %)] was obtained from Ashahi Chemical (Tuftec M1943). The recycled plastics used were postconsumer, mixed-color recycled HDPE, PP, PS, and PVC, which had been used in milk jugs, detergent containers, and beverage cups, etc., obtained from various recyclers.

They were blended after proper washing and drying.

Blending was conducted in a table kneader internal mixer. The blending time, temperature, and rotating speed were 8 min, 180°C, and 60 rpm, respectively. The blend composition was fixed at 7/1/1/1 HDPE/PP/PS/PVC by weight ratio according to the data of Korea Curbside-Tailing Survey data in 1995. A measure of 5 phr of SEBS-*g*-MAH was used as a compatibilizer for the commingled blends, when necessary. The amount of cellulose was varied from 0 to 22.5 phr on the basis of the total amount of the blend mixture. To investigate the effect of the reactive compatibilization, 0.1 phr of *t*-butylhydroperoxide (HPO) (Aldrich) and 2.0 phr of MAH (Aldrich) based on the total amount of the blend mixture were added in the mixing chamber of the table kneader after commingled plastics were mixed and molten. During the experiment, torque was measured. Tensile and flexural strength were measured by using a tensile tester (Hounsfield, Model HM25) at room temperature. The crosshead speed used was 10 mm/min. To observe the morphology of the blends, the surface of compression-molded samples, cryogenically fractured under liquid nitrogen and then sputtered with gold in vacuum, was examined with a Jeol scanning electron microscope (SEM; Model 36CF). The thermal stability was measured by using a thermogravimetric analyzer (TGA; Shimatsu TGA) under nitrogen atmosphere and at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Effect of Cellulose Contents

Figure 1 shows the effect of cellulose on the tensile strength of the virgin commingled blends. The tensile strength was decreased up to 10 wt % of cellulose but was remarkably increased by further adding the cellulose above 12.5 wt %. Similar dependence of the tensile strength of the blends on the concentration of cellulose was observed when SEBS-*g*-MAH was used as a compatibilizer but more synergistic effect was observed when SEBS-*g*-MAH was used as a compatibilizer.

The effect of cellulose on the tensile strength of the recycled commingled blends is shown in Figure 2. The tensile strength was increased with increasing cellulose contents. The effect of SEBS-*g*-MAH was more remarkable.

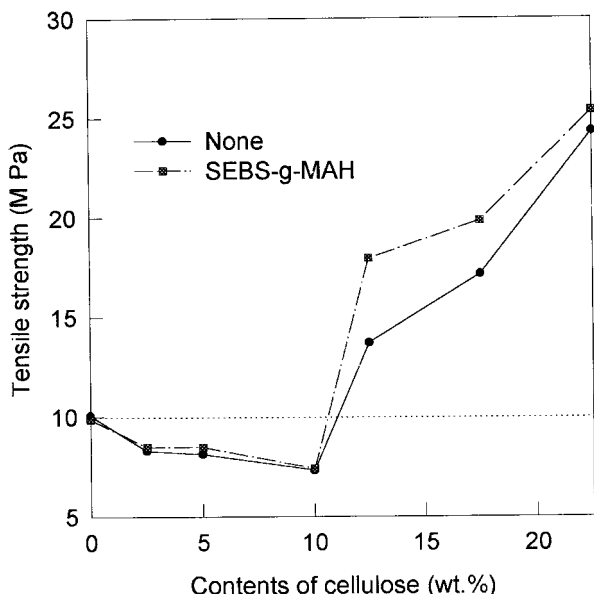


Figure 1 Tensile strength of virgin commingled blends with or without SEBS-*g*-MAH as a function of cellulose contents.

It was reported that the addition of a compatibilizer into a binary blend enhances the mechanical properties, such as impact strength, because of the additives located at the interface between the phases, which enhances the stress transfer and reduces particle size because of the emulsifying effect.^{21,22} As expected, the tensile strength of the blends prepared from both the virgin and the recycled plastics was enhanced when a compatibilizer was used. A comparison of Figures 1 and 2 indicates that the tensile strength of the recycled blend is much lower than that of the virgin commingled system, when cellulose is >10%, regardless of whether the system contains a compatibilizer or not. The result is due to the fact that the recycled polymer materials were mixed with various contaminants and exhibited more degraded mechanical properties than the virgin polymer material. Instead, for the virgin components, the following problems can be neglected: nonpolymeric contamination and degradation of the plastics. This may cause the larger property differences in between the virgin and recycled blends.

It was already reported that SEBS-*g*-MAH can be used as a compatibilizer for binary blends of PS with PE, regardless of whether it is high-density or low density PE (LDPE), because the copolymer possesses the same monomer units as its parent polymers (i.e., ST and ethylene).²³⁻²⁵ Gatenholm et al. reported¹⁶ that blends of LDPE and PS (70/30 composition by weight percent) is success-

fully compatibilized by SEBS-*g*-MAH even after they are reinforced with cellulose. (They used chemithermomechanical pulp fibers as a cellulose.) Gatenholm et al. reported¹⁶ that maleic anhydride grafted on SEBS chain is highly reactive toward hydroxyl groups at the cellulose surface and, when compounding at elevated temperature, both covalent and hydrogen bonds develop between the functionalized compatibilizer and the cellulose fiber. To the best of our knowledge, however, no work has been reported to reveal the compatibilizing effect of the SEBS-*g*-MAH in commingled blends consisting of more than three components. It is noteworthy, therefore, that the compatibilizer, SEBS-*g*-MAH, works well even for the recycled blend system as well as the virgin commingled system, although the system contains four different polymers.

Effect of Reactive Compatibilization

Figure 3 shows the effect of 12.5 phr of cellulose on the tensile strength of the virgin and recycled commingled blends with and without SEBS-*g*-MAH. In this figure, we fixed the content of cellulose at 12.5 phr on the basis of the results of Figures 1 and 2. In Figure 3, MAH + HPO denotes that MAH was added to the commingled blends compatibilized in the presence of HPO, where the possibility of the reactive compatibili-

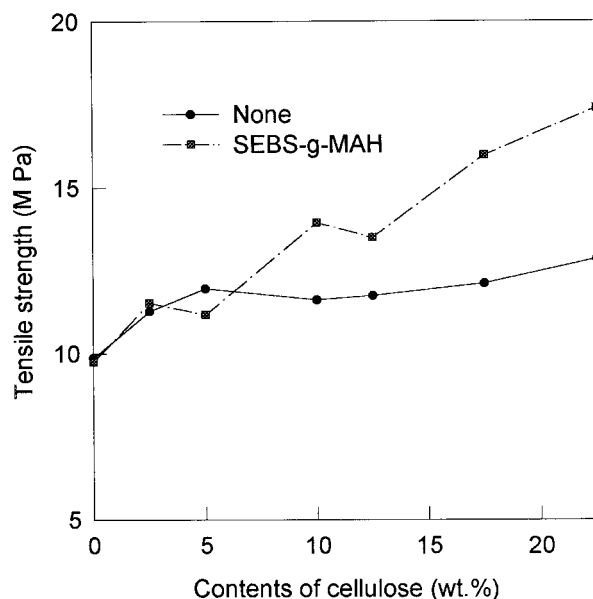


Figure 2 Tensile strength of recycled commingled blends with or without SEBS-*g*-MAH as a function of cellulose contents.

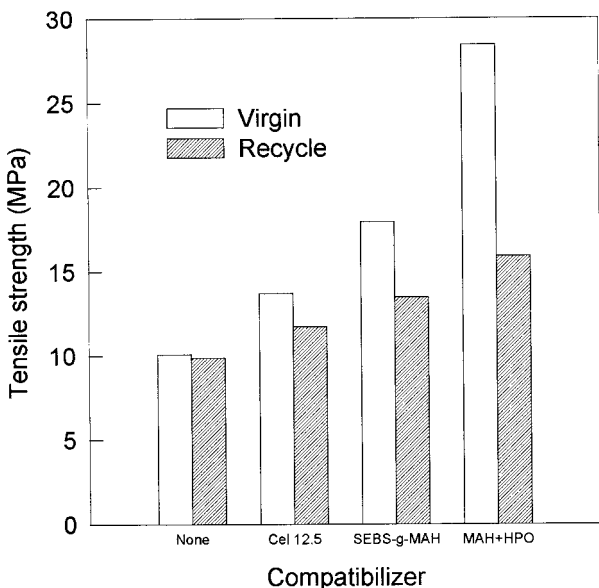


Figure 3 Tensile strength of virgin and recycled commingled blends. The notations are as follows. NONE, blends without cellulose; Cel 12.5, blends with 12.5 phr of cellulose; SEBS-*g*-MAH, blends with 12.5 phr of cellulose and SEBS-*g*-MAH; MAH + HPO, reactive compatibilized blends with 12.5 phr of cellulose by MAH and HPO.

zation would be tested by the torque record later. The tensile strength of the virgin commingled blends was greatly enhanced with the addition of cellulose and SEBS-*g*-MAH. When MAH was added to the system in the presence of HPO, the tensile strength was more significantly enhanced, maybe due to the grafting of cellulose onto some polymer backbone in our blend system by MAH, which improves the interfacial adhesion between component polymers and cellulose in the commingled blends. It may be assumed that the grafting reaction is similar as for 70/30 LDPE/PS blends compatibilized with SEBS-*g*-MAH in the presence of cellulose, which was already reported by Gateholm et al.¹⁶ The result of Figure 3 strongly suggests that the reactive compatibilization is more effective to compatibilize the blend systems than to use an external compatibilizer such as SEBS-*g*-MAH even for multicomponent commingled blend systems.

Figure 4 shows the effect of MAH + HPO as well as cellulose and SEBS-*g*-MAH on the flexural strength of virgin and recycled commingled blends. The flexural strength of the virgin cellulose-reinforced commingled blend was highest when *in situ* compatibilization was made by using MAH with HPO. Similar results were observed for recycled commingled blends. The use of SEBS-

g-MAH as an external compatibilizer was not effective to improve the flexural strength of both the virgin and the recycled commingled blends, even though the exact reason is not clear at present. As for tensile strength, the flexural strength of the virgin commingled blends was much higher than that of the recycled blends, regardless of whether the *in situ* (MAH + HPO) or the external compatibilizer (SEBS-*g*-MAH) is present or not. The low flexural strength of the recycled commingled blends are due to large gross-phase separation between components and the presence of various undefined fillers and so on, as discussed above.

The SEM micrographs of the fractured surfaces of virgin blends with or without an *in situ* or external compatibilizer are shown in Figure 5. Because the direct visual confirmation of the presence of different phases preliminarily indicates the degree of miscibility in blends, microscopic investigations can help in clarifying some aspects of the mechanical properties. As compared to the uncompatibilized blend, the dispersed domain size of the compatibilized system is much smaller with more compacted structure. The SEM micrographs of the fractured surfaces of the commingled blends with cellulose show that the gross-phase separation was observed but the domain sizes were greatly reduced by adding a small amount of the *in situ* or external compati-

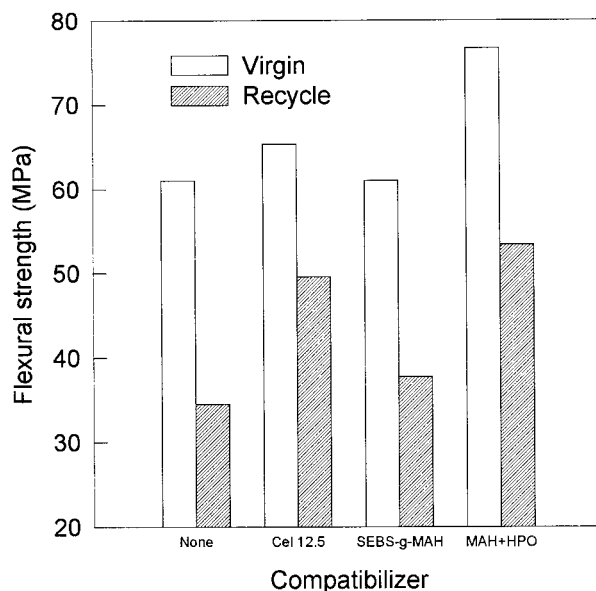


Figure 4 Flexural strength of virgin and recycled commingled blends. The notations are the same as for Figure 3.

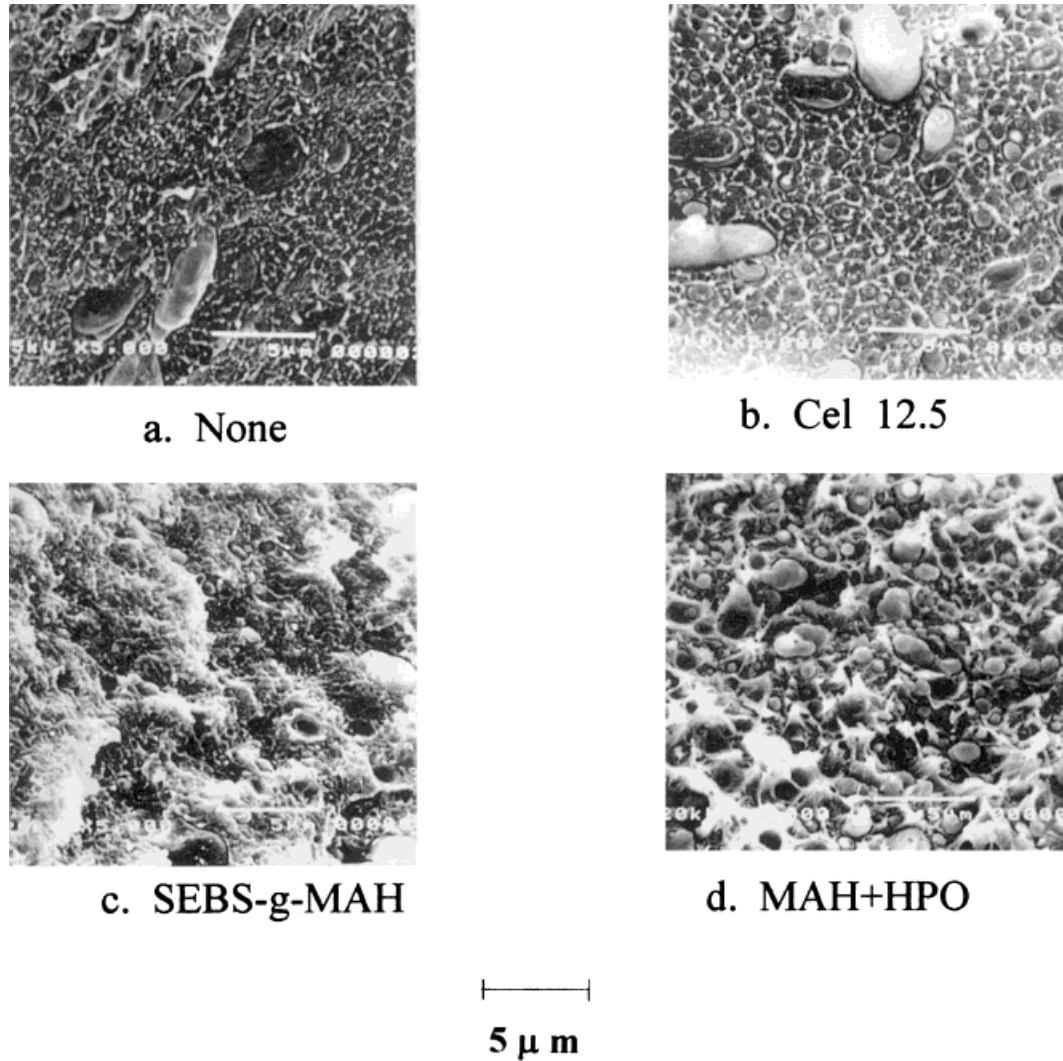


Figure 5 SEM micrographs of the fractured surfaces of virgin commingled blends. The notations are the same as for Figure 3.

bilizer, SEBS-g-MAH, meaning that compatibilization was achieved for the commingled blend in the presence of the compatibilizers. On the basis of the above results, one can conclude that the SEBS-g-MAH works well as a compatibilizer in the commingled blend of HDPE/PP/PS/PVC (7/1/1/1). Figure 5 also shows well that the compatibilization effect of *in situ* MAH + HPO is larger than the external compatibilizer, SEBS-g-MAH. The same morphological features were observed for the recycled blends (Fig. 6).

Thermal Stability

Figure 7 shows the TGA curves of the virgin commingled blends with or without cellulose and with

cellulose/SEBS-g-MAH or cellulose/MAH + HPO. In the previous section, cellulose was revealed to reinforce the mechanical strength of the commingled blend but the TGA curve in Figure 7 shows that the thermal stability was greatly reduced by the addition of cellulose. The commingled blends with cellulose only was degraded at low temperature in comparison with the blends without cellulose. Cellulose is labile to be degraded at high temperature during mixing. The decrease of thermal stability for the commingled blends is not desirable for the reuse of those commingled blends, even though their mechanical properties were enhanced with reinforcing cellulose addition.

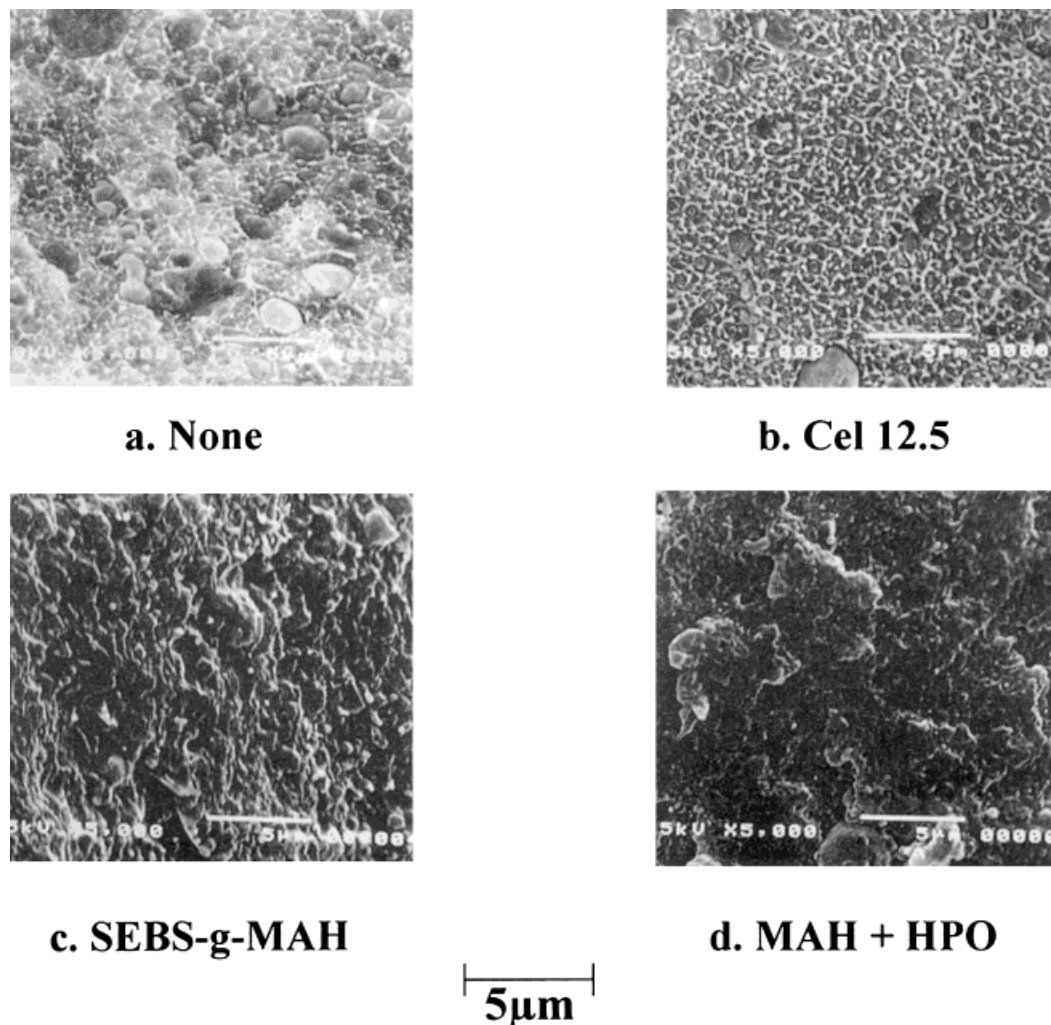


Figure 6 SEM micrographs of the fractured surfaces of recycled commingled blends. The notations are the same as for Figure 3.

It was found that the use of SEBS-*g*-MAH increased the thermal stability of the commingled blends reinforced with cellulose, which must be another reason why the compatibilizer should be used together with cellulose in the commingled blends, notwithstanding the compatibilizing effect for the system. The *in situ* compatibilization of the cellulose-reinforced commingled blends using MAH and HPO shows slightly better thermal stability than the application of the external compatibilizer, SEBS-*g*-MAH.

Figure 8 shows the effect of the thermal aging on the mechanical properties of the virgin commingled blends reinforced with cellulose to test the thermal stability of the commingled blends at elevated temperature in the practical point of view. The samples had been exposed in a heating

oven at 100°C for 6 months before measurement. The oven was frequently purged with nitrogen gas to remove latent moisture inside. Even though the thermal stability of the cellulose-reinforced commingled blend was poor at high temperatures of mixing, no significant degradation of mechanical strength was observed at 100°C after 6 months' aging, regardless of the cellulose contents. Similar results were observed, as in Figure 9, when *in situ* or external compatibilizer was used.

Of great interest is, however, that the tensile strength of the commingled blends compatibilized with MAH + HPO is higher than any other samples after thermal aging. The result implies *in situ* grafting reaction between component polymers and cellulose by MAH, which partially took

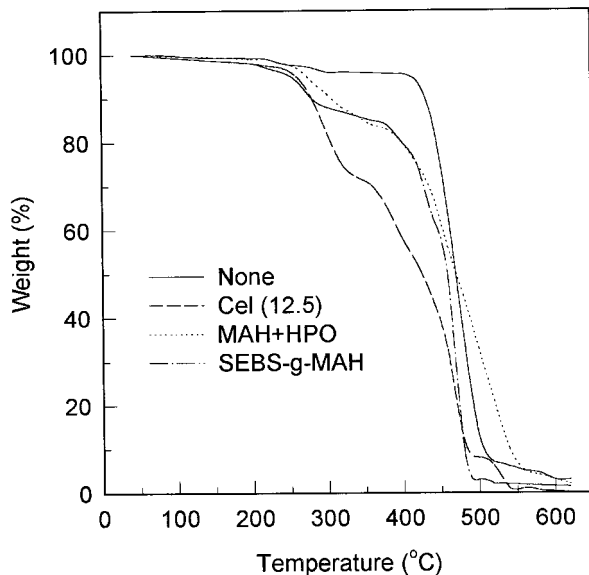


Figure 7 TGA curves for virgin commingled blends. The notations are same as for Figure 3.

place during mixing, may continue when the blends are kept at high temperature for long times and enhances the mechanical strength of the commingled blends.

To obtain the evidence of the reaction indirectly, the torque during mixing of the commingled blends was recorded. Figure 10 shows the

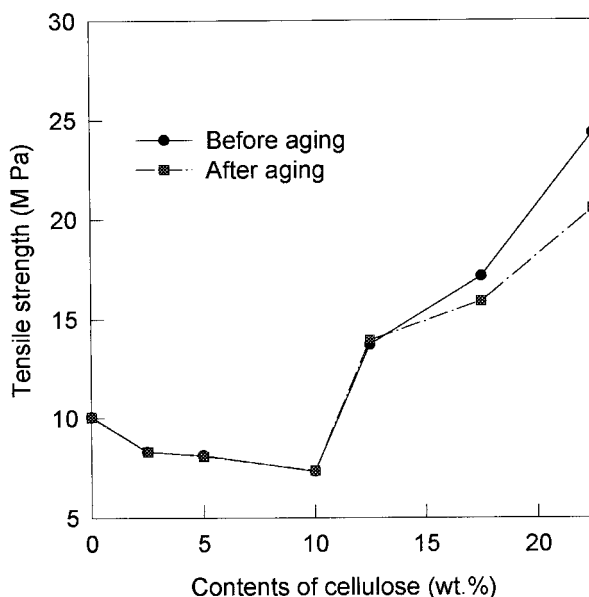


Figure 8 Tensile strength of virgin commingled blends with different contents of cellulose before and after aging at 100°C for 6 months.

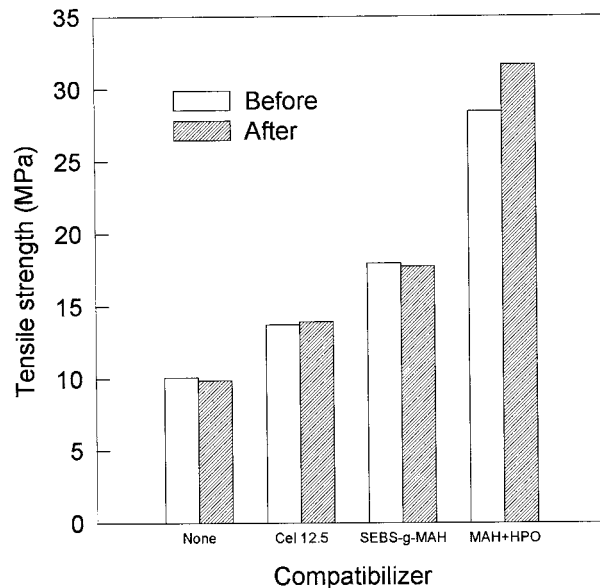


Figure 9 Tensile strength of virgin commingled blends before and after aging at 100°C for 6 months. The notations are the same as for Figure 3.

result. There was no appreciable change in the torque for the commingled blends with cellulose and SEBS-g-MAH. However, a little increase in the torque was observed at longer mixing times for the blends in the presence of MAH and HPO. The increasing torque might imply the plausible

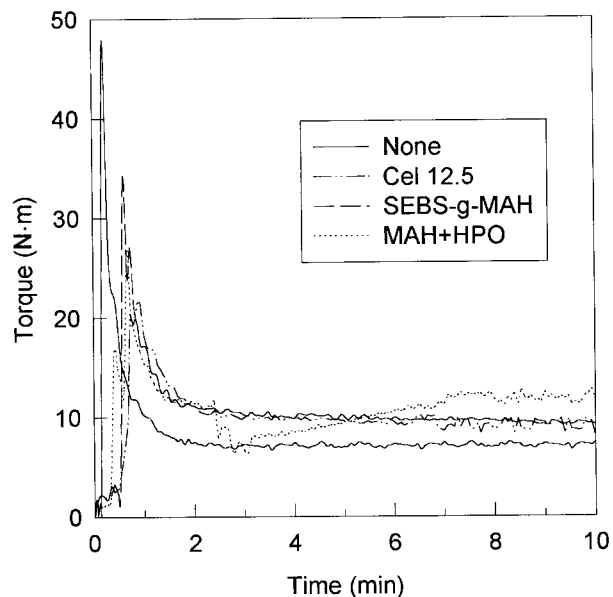


Figure 10 Torque during mixing of the virgin commingled blends. The notations in the inset are the same as for Figure 3.

in situ grafting reaction between component polymers and cellulose by MAH at the interface, although more direct evidence of the grafting is not given here and the time scale of Figures 9 and 10 are not the same.

CONCLUSIONS

In this article, commingled blends were prepared in a table kneader internal mixer. The virgin and recycled commingled blends consist of a simulated waste plastics fraction composed of HDPE, PP, PS, and PVC (PE/PP/PS/PVC = 7/1/1/1 by weight ratio). Mechanical properties were measured using a universal testing machine. Thermal stability was measured by a thermogravimetric analyzer.

It was found that the addition of cellulose > 12.5% into the commingled blends was very effective in enhancing their mechanical properties for both the virgin and the recycled blends except thermal stability. The SEBS-*g*-MAH worked well as a compatibilizer to improve tensile properties and thermal stability in both virgin and recycled commingled blend systems. The *in situ* reactive compatibilization by MAH and HPO showed most prominently enhanced mechanical properties for the cellulose-reinforced commingled blends.

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REFERENCES

- Ehrig, R. J. "Plastics Recycling," Hanser Publishers: New York, 1992.
- Andrews, G. D.; Subramanian, P. M. ACS Symp Ser 1992, 513.
- Hites, R. A.; Czuczwa, J. M. Environ Sci Technol 1984, 18, 444.
- Marklund, S.; Rappe, C.; Tsklind, M. Chemosphere 1987, 16, 29.
- Leaversuch, R. Modern Plastics 1989, 66(11), 19.
- Kreisher, K. R. Modern Plastics 1990, 67(1), 60.
- Ajji, A. Polym Eng Sci 1995, 35, 64.
- Akkapeddi, M. K.; Mason, C. D.; Van Buskirk, B. Polym Prepr 1993, 34, 848.
- Paul, D. R.; Vinson, C. E.; Locke, C. E. Polym Eng Sci 1972, 12,3,157.
- Jody, B. J.; Daniels, E. J.; Brockmeier, N. F. Chemtech 1994, 11, 41.
- Paul, D. R.; Newman, S. "Polymer Blends," Academic Press: New York, 1978.
- Kim, Y.; Ha, C. S.; Kang, T.; Cho, W. J. J Appl Polym Sci 1994, 51, 1453.
- Park, H. D.; Park, K. O.; Cho, W. J.; Ha, C. S.; Kwon, S. K. Polym Recycl 1996, 2, 4, 277.
- Park, H. D.; Cho, W. J.; Ha, C. S.; Kwon, S. K. Polym Recycl 1996, 2, 4, 283.
- Ha, C. S.; Park, H. D.; Kim, Y.; Cho, W. J.; Kwon, S. K. Polym Adv Tech 1996, 7, 483.
- Gatenholm, P.; Hedenberg, P.; Klason, C. in "Plastics and Rubber Recycling—A Pragmatic Approach," Rader, C. P.; Baldwin, S. D.; Cornell, D. D.; Sadler, G. D.; Stockel, R. F., Eds.; ACS Symp Series 609; American Chemical Society: Washington, DC, 1995, pp 367–377.
- Woodhams, R. T.; Thomas, G.; Rodgers, D. K. Polym Eng Sci 1984, 24, 15.
- Kazayawoko, M.; Balatinecz, J. J.; Woodhams, R. T.; Sodhi, R. N. S., J Wood Chem Technol 1998, 18, 1.
- Matuana, L. M.; Woodhams, R. T.; Balatinecz, J. J.; Park, C. B. Polym Comp 1998, 19, 4, 446.
- Saba, B. G.; Person, W. E. In "Plastics and Rubber Recycling—A Pragmatic Approach," Rader, C. P.; Baldwin, S. D.; Cornell, D. D.; Sadler, G. D.; Stockel, R. F., Eds.; ACS Symposium Series 609; American Chemical Society: Washington, DC, 1995, pp 11–15.
- Galli, P.; Danesi, S.; Simonazzi, T. Polym Eng Sci 1984, 248, 544.
- Yang, D.; Zhang, B.; Yang, Y.; Fang, Z.; Sun, G. Polym Eng Sci 1984, 248, 612.
- Lindsey, C. R.; Paul, D. R.; Barlow, J. W. J Appl Polym Sci 1981, 26, 1.
- Vermeire, H. F. Kunststoffe 1988, 43, 11, 90.
- Fayt, F.; Hadjiandreou, P.; Teyssie, Ph. J Polym Sci, Polym Chem Ed 1985, 23, 337.