Reactive Extrusion of Polypropylene and Nylon Blends from Commingled Plastic Wastes

Gwang Ho Kim,[1] *Seung Sang Hwang,*[1] *Bong Gyoo Cho,*[2] *Soon Man Hong**[1]

Summary: Reactive extrusion for recycled PP/nylon blends from commingled plastic wastes was investigated through thermal, morphological, mechanical and rheological studies. From SEM investigation, we found improved surface morphologies with homogeneous domains in the recycled 75/25 PP/nylon blends compatibilized with copolymers containing maleic anhydride (MA) as a reactive functional group; SEBS-g-MA, PP-g-MA, PE-g-MA. Especially, SEBS-g-MA thermoplastic elastomer which is highly reactive with amine terminal group of nylon, resulted in a large increase of impact strength above nearly 200%. This compatibilization effect resulted from the increase of interfacial adhesion and the reduction of domain size of dispersed phase in PP/nylon blend system. To confirm the existence of this network structure, we measured a dynamic rheological properties.

Keywords: interfacial adhesion; reactive extrusion; recycling; rheology

Introduction

Multilayer films are widely used in packaging applications. However, most of commingled packaging film wastes are landfilled or incinerated without recycling, which cause a serious environmental pollution.[1–5] The main problem faced during recycling operations of multilayer films is degradation and delamination phenomena. These two aspects are common to all the recycled mixed polymers. Thus, suitable ways to recycle commingled packaging film wastes have been developed to protect the environment, and to utilize scarce resources efficiently. Among developed recycling ways, technology making new products using plastic wastes themselves as raw material, called 'material recycle' is being widely available due to its high economic value and energy efficiency, when compared to other recycling methods.[3–5] To recycle these mixed waste polymers without deteriorated mechanical properties, the compatibility between heterogeneous components must be enhanced by various methods, including both reactive and non-reactive processes. Commonly, compatibility is promoted by the addition of reactive graft or block copolymers which can enhance adhesion between heterogeneous components by reducing the interfacial tension.[6–11] Our intention was to convert the post-production multilayer films waste into thermoplastic polymers with high economical value using low-cost reactive extrusion.[4,5]

In this study, the relationships among morphology, mechanical properties and rheological properties by reactive extrusion based on commingled packaging film wastes containing polypropylene (PP) packaging films and Nylon packaging films were investigated to improve the compatibility and toughness of these wastes using various compatibilizers.

[1] Polymer Hybrids Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok Seongbuk, Seoul 136-791, Korea
Fax: (+82) 2 958 5309
E-mail: smhong@kist.re.kr
[2] Materials Processing Division, Korea Institute of Geoscience & Mineral Resources 30, Gajeong-dong, Yuseong-gu, Daejeon 305-350, Korea

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

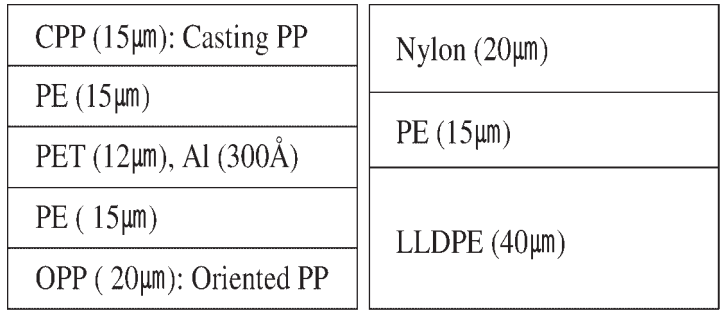

Figure 1.
Schematic diagram of waste packaging film layers; (a) recycled PP and (b) recycled nylon.

Experimental Part

Plastic wastes used in this study were commingled packaging film wastes containing polypropylene packaging film system [polypropylene (PP)/polyethylene (PE)/aluminum (Al)/polyethyleneterephthalate (PET)] and polyamide-6 packaging film system [polyamide-6 (Nylon)/polyethylene (PE)/linear low density polyethylene (LLDPE)] as represented in Figure 1. Blends of recycled PP and nylon 6 with the composition ratio of 75/25 by weight were prepared using a corotating twin screw extruder (PRISM TSE 16TC, L/D = 7.5, Thermo Electron Co., Woburn, MA, USA). In the temperature range of 180–250 °C, the extruder was processed at a screw speed of 50 rpm. Then, the prepared blends were dried under vacuum at 80 °C for 24 hr. During the process, various compatibilizers were added into the twin-screw extruder as shown in Table 1 and Table 2.

Fractured surface morphologies were investigated using scanning electron microscope(SEM) with various magnification at 15kV. In addition, to measure the rheological properties, we used a rotational rheometer (MCR 300, Physica, Stuttgart, Germany) equipped with a parallel-plate geometry of 1.1 mm thickness and 25 mm diameter at 190 °C. Furthermore, sample for the tensile (Modle 420, Instron) and impact (ITR-2000, RADMANA) tests were prepared using Baby Plast 6/10 under 120 bar at 250 °C. The tensile and impact properties for prepared samples were measured at a crosshead speed of 10 mm/min and averaged.

Results and discussion

As shown in Figure 1, various compositions of each recycled multilayer films can be confirmed from its DSC thermograms shown in Figure 2.

The thermogram of recycled PP indicates its composition of LDPE (Tm = 110C), LLDPE (Tm = 125C), PP (Tm = 165C) and a tiny amount of PET

Table 1.
Types and Properties of Compatibilizer.

Compatibilizer	Company	Grade	
SEBS-g-MA	Kraton	Kraton FG-1901X	Maleic anhydride (2wt%)
SEBS	Kraton	Kraton G-1651	Polystyrene (2wt%)
PP-g-MA	Honam Petrochemical	CM-1120	MI(230) = 50g/10 min
PE-g-MA	Honam Petrochemical	EM-520M	MI(190) = 1.5g/10 min

SEBS-g-MA: styrene-(ethylene/butylenes)-styrene-graft-maleic anhydride copolymer. MA: maleic anhydride.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 2.
Composition of PP/Nylon blend.

PP/Nylon	Compatibilizer	Content
100/0	None	
75/25	SEBS, SEBS-g-MA, PP-g-A,PE-g-MA	5phr
50/50	None	
25/75	None	
0/100	None	

(Tm = 250C). Furthermore, we can also confirm the composition of recycled nylon with LDPE (Tm = 110C), LLDPE (Tm = 165C) and nylon 6 (Tm = 225C). The impact strength and tensile strength measurements for the commingled packaging film wastes were performed, as shown in Figure 3.

With increase in the content of Nylon, the impact strength is increased, however, the tensile strength is decreased. On the other hand, the binary blend gives impact strength and the tensile strength falling below those predicted by the additivity rule of mixing in the whole range. This suggests that the incompatibility between heterogeneous PP and nylon phases exhists. Based on these binary blends, the fractured surface morphologies of 75/25 PP/nylon blend compatibilized with various reactive copolymers were investigated to examine their compatibility effect in the 75/25 PP/nylon blend as shown in Figure 4.

The uncompatibilized 75/25 PP/nylon blend possesses a morphology composed of irregular and coarse particles. By adding reactive copolymers, it was expected that 75/25 PP/nylon blend shows more regular and finer dispersion of small domains due to the enhancement of miscibility between recycled PP and nylon. However, apparent compatible outcome seemed to be achieved only in the case of copolymers containing maleic anhydride (MA); SEBS-g-MA and PP-g-MA, showing the efficiency in reducing the domain size and refining the coarsening of the morphology. This is due to the formation of strong interfacial adhesion through the chemical reaction taking place between maleic anhydride (MA) group and the amine end group of nylon as shown in Figure 5.

Figure 6 represents the mechanical properties of 75/25 PP/nylon blends with or without reactive copolymers at room temperature. As expected from the SEM analysis, the addition of SEBS-g-MA, grafting a maleic anhydride (MA) as a functional group to induce the chemical reaction with amine end group of nylon, causes a remarkable improvement of mechanical properties as an indicator of effective compatibilization. Although ten-

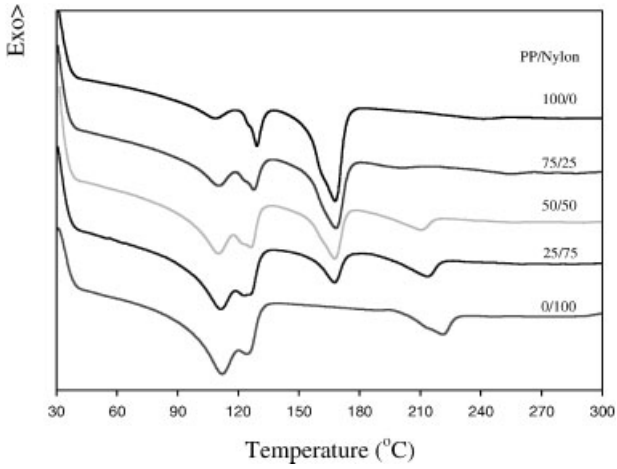

Figure 2.
DSC thermograms of recycled PP/nylon blends.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

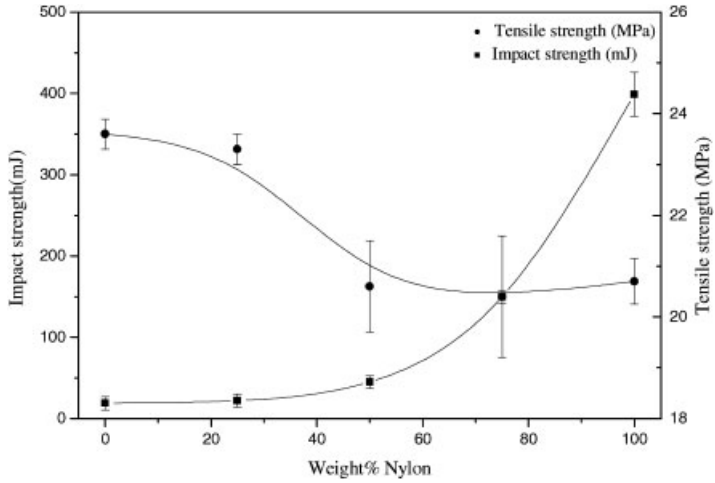

Figure 3.
Mechanical properties of 75/25 PP/nylon blends with or without various compatibilizers (5phr); ● ; impact strength, ■ ; tensile strength.

sile strength does not increase remarkably, a large increase of impact strength above nearly 200% was observed, when compared to the uncompatibilized 75/25 PP/nylon blend system. This large increase can be explained in conjunction with somewhat homogeneous morphological characteristics observed in the SEM.

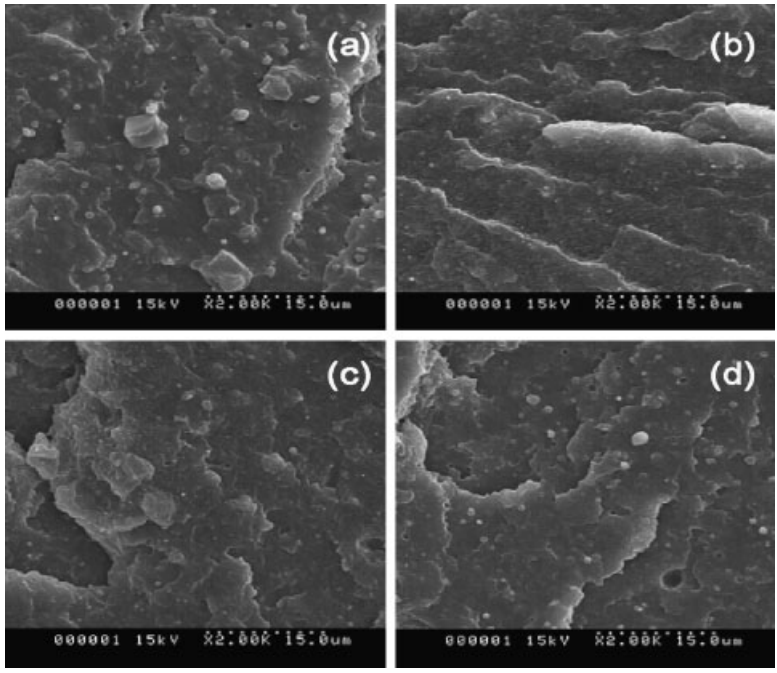

Figure 4.
Scanning electron micrographs (SEM) of 75/25 PP/nylon blends with or without various compatibilizers (5phr); (a) none, (b) SEBS-g-MA, (c) PP-g-MA and (d) PE-g-MA.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

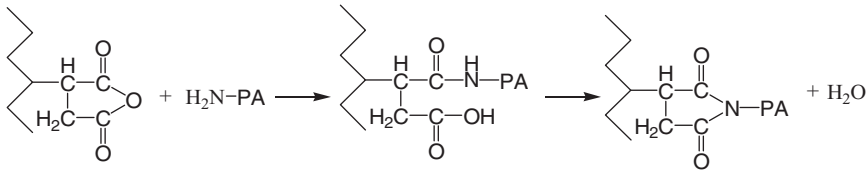

Figure 5.
Reaction between maleic anhydride groups and the amine end groups of nylon.

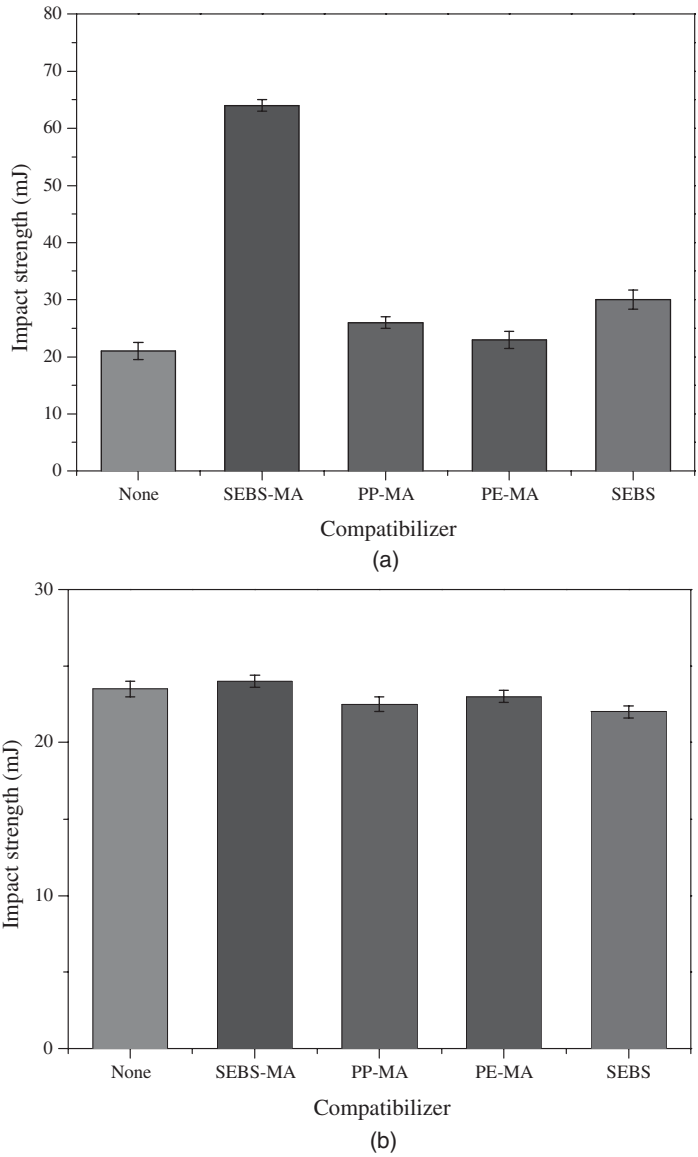

Figure 6.
Mechanical properties of 75/25 PP/nylon blends with or without various compatibilizers (5phr); (a) impact strength, (b) tensile strength.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

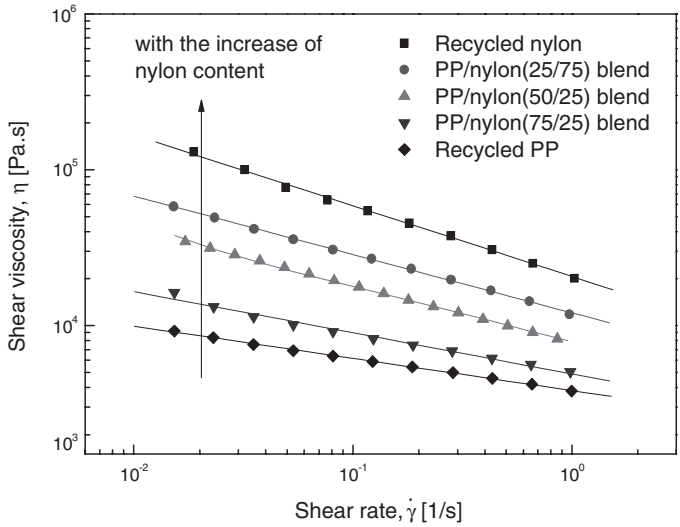

Figure 7.
Steady shear viscosity (η) behaviors of PP/nylon (75/25) blends.

The steady shear viscosities of the pure components and its blend are shown in Figure 7. In a shear rate range explored, both the steady shear viscosity and the degree of shear thinning for PP/nylon blends are more enhanced with the nylon content. These rheological parameters, which represent flow behavior of polymer blends at a fixed temperature, can be used to optimize their processing conditions.[12,13] On the other hand, the addition of copolymer containing a maleic anhydride (MA); SEBS-g-MA, PP-g-MA makes the blend more resistant to flow as represented in Figure 8 in the case of 75/25 PP/nylon, suggesting strong interfacial adhesion at the interface through the chemical reaction taking place between maleic anhydride (MA) group and the amine end group of nylon.[7,9]

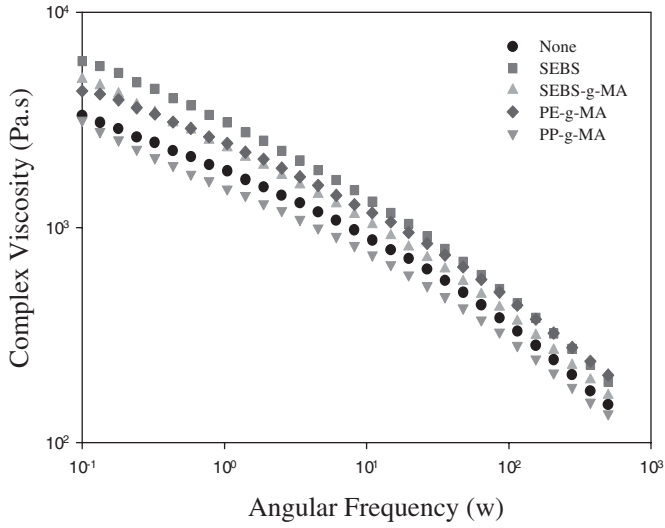

Figure 8.
Complex viscosity (η^*) behaviors of 75/25 PP/nylon blends with or without various compatibilizers (5phr).

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

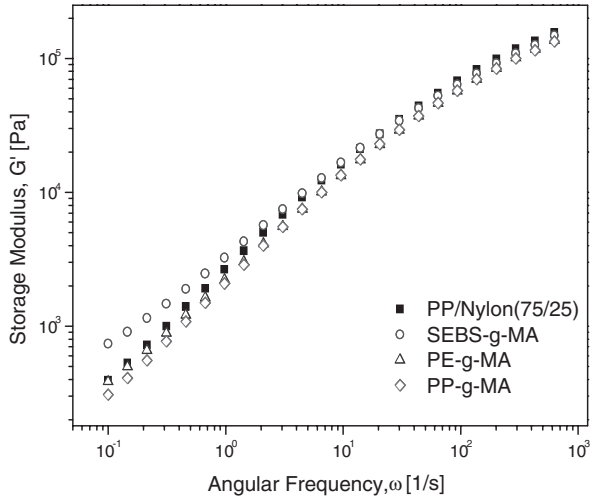

Figure 9.
Storage modulus (G′) behaviors of 75/25 PP/nylon blends with or without various compatibilizers (5phr).

However, 75/25 PP/nylon blend compatibilized with PP-g-MA exhibits the lower viscosity than other 75/25 PP/nylon blend in an overall shear rate region. It means that graft chains formed at the interface between recycled PP and nylon by the chemical reaction break easily under shear force as anticipated from the mechanical test. In addition, this result comes from PP-g-MA containing a low molecular weight (melt index = 50g/10min) compared with other compatibilizers. Based on these results, we can conclude that the overall compatibility effect is mainly originated from not the surface morphology but the degree of interfacial adhesion. In an oscillatory test mode, we also could get storage modulus (G′) as a function of angular frequency. Compared to the uncompatibilized 75/25 PP/nylon blend, the addition of SEBS-g-MA showed the remarkable increase in storage modulus (G′) at a low frequency, while the addition of other copolymers shows no significant change, as shown in Figure 9.

In the case of 75/25 PP/nylon blend compatibilized with SEBS-g-MA, curve has two steep portions, separated by a ''plateau'' region of smaller slope. The high-frequency steep portion is due to the viscoelasticity of the polymer blend itself and low-frequency steep portion is due to the interfacial contribution.[14] Thus, we can conclude that this increased storage modulus (G′) at a low frequency is indicative of a strong adhesion between recycled PP and nylon, showing the formation of a specific structure at the interface.

Conclusions

The relationships among morphology, mechanical properties and rheological properties by reactive extrusion based on commingled plastic packaging film wastes containing PP packaging films and Nylon plastic were investigated to improve the compatibility and toughness of these wastes using various compatibilizers. We found improved surface morphologies with regular and fine domains in recycled 75/25 PP/nylon blend compatibilized with copolymers containing maleic anhydride (MA) as a reactive functional group; SEBS-g-MA, PP-g-MA. Such morphological characteristics were further analyzed with the results of mechanical and rheological test. This means that SEBS-g-MA can be used as a reactive compatibilizer and impact modifier to improve the interfacial adhesion between incompatible commingled PP/Nylon packaging film wastes.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Acknowledgements: This study was supported by the 21C Frontier R&D Program, Industrial Waste Recycling R&D Center.

[1] K. T. Shin, J. H. Kim, H. J. Choi, M. S. John, *J. Appl. Polym. Sci.* **2000**, *77*, 1348.
[2] B. H. Jeon, H. G. Yoon, S. S. Hwang, J. A. Kim, S. M. Hong, *Polymer(Korea)* **2005**, *29*, 1.
[3] I. S. Arvanitoynnis, L. A. Bosnea, *Food Rev. Int.* **2001**, *17*, 291.
[4] A. Pawlak, J. Morawiec, F. Pazzagli, M. Pracella, A. Galeski, *J. Appl. Polym. Sci.* **2002**, *86*, 1473.
[5] I. Fortelny, D. Michálková, Z. Kruliś, *Polym. Degrad Stabil* **2004**, *85*, 975.
[6] M. Pracella, L. Rolla, D. Chionna, A. Galeski, *Macromo.l Chem. Phys.* **2002**, *203*, 1473.
[7] C. S. Ha, H. D. Park, W. J. Cho, *J. Appl. Polym. Sci.* **2000**, *76*, 1048.
[8] M. Iza, M. Bousmina, R. Jerome, *Rheol. Acta* **2001**, *40*, 10.
[9] R. Krache, D. Benachour, P. Pőtschke, *J. Appl. Polym. Sci.* **2004**, *94*, 1976.
[10] F. Pazzagli, M. Pracella, *Macromol. Symp.* **2000**, *149*, 225.
[11] H. J. Choi, S. H. Park, J. K. Kim, J. I. Jun, *J. Appl. Polym. Sci.* **2000**, *75*, 417.
[12] T. H. Kim, L. W. Jang, D. C. Lee, H. J. Choi, M. S. Jhon, *Macromol. Rapid Commun.* **2002**, *23*, 191.
[13] Z. K. Zhong, S. X. Zheng, K. J. Yang, Q. P. Guo, *J. Appl. Polym. Sci.* **1998**, *69*, 995.
[14] O. Meincke, B. Hoffmann, C. Dietrich, C. Friedrich, *Macromol. Chem. Phys.* **2003**, *204*, 823.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim