

# The Mechanical and Rheological Behavior of the PA/TPU Blend with POE-g-MA Modifier

Hsien-Tang Chiu, Chao-Yin Chuang

Graduate School of Polymer Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, Republic of China

Received 3 June 2008; accepted 24 September 2008

DOI 10.1002/app.30944

Published online 23 September 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this research, we attempt to improve the impact strength and the viscosity of PA (polyamide) by blending two elastomers, TPU (thermoplastic polyurethane) and POE-g-MA (maleic anhydride-grafted polyethylene-octene elastomer), in PA matrix with twin screw extruder. The ratio of blending is 80PA/20TPU and 80PA/20TPU/20POE-g-MA (66.66PA/16.67TPU/16.67POE-g-MA). Results indicate that POE-g-MA improves the low viscosity of PA and TPU during the blending process, and also

their compatibility. Thus, the 80PA/20TPU/20POE-g-MA blend has better tensile stress and elongation than 80PA/20TPU blend, and furthermore POE-g-MA significantly improves the impact strength of PA, even to super-toughness grade. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1278–1282, 2010

**Key words:** blends; elastomers; mechanical properties; polyamides; rheology

## INTRODUCTION

Polymer blends can create compounds that meet diverse product demands; an extrusion process is often used to blend the materials.<sup>1–3</sup> Polyamide (PA), as an engineering plastic, has excellent mechanical properties, elasticity, and abrasion resistance, but its drawback is its lack of impact strength. Previous researches<sup>4,5</sup> used TPU and other materials to improve the material's impact strength. Zhang et al. blended PA and thermoplastic polyurethane (TPU) with a twin screw extruder. They found that the impact strength is maximized when TPU is at 20 weight percent (wt %) of the blend. The research pointed out that TPU at 20 wt % represented an optimal dispersion of about 3  $\mu\text{m}$ . Further addition of TPU, however, resulted in larger dispersion size and lower impact strength. Genovese and Shanks<sup>6</sup> used simulation method to discuss the specific interactions between PA and TPU. Some researchers<sup>7,8</sup> have attempted to use functionalized polyethylene-octene elastomer (POE) to improve PA's impact strength.

The researchers mentioned earlier used a single elastomer to improve PA's toughness. The 80PA/20TPU saturated in terms of impact strength, but still low for the industrial used. We expected that maleic anhydride-grafted polyethylene-octene elasto-

mer (POE-g-MA) can improve the processing viscosity and mechanical properties of 80PA/20TPU. No research has yet been published on using two or more elastomers to improve PA's toughness. Our research thus focuses on this point, especially in the research of 80PA/20TPU and its rheology behavior, mechanical properties, and morphology after introducing POE-g-MA.

## EXPERIMENTS

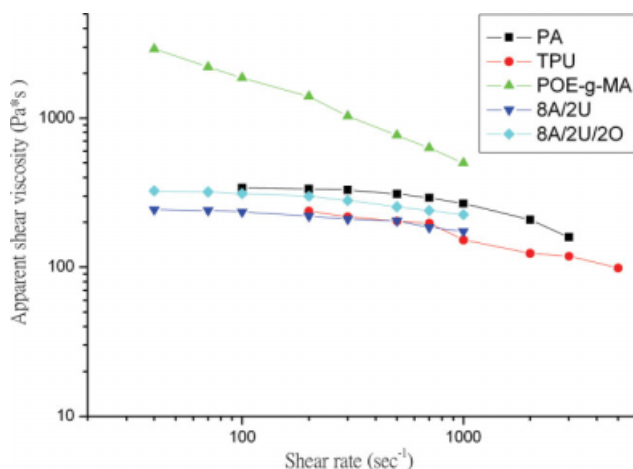
### Materials

The Polyamide 6 used in this study is manufactured by Li Peng Enterprise under the name Libolon. The material has low relative viscosity (2.45), and is a semi-dull, fiber grade product. The TPU is manufactured by Great Eastern Resins Industrial, as a general grade polyether TPU, product serial number 3075A, with a hardness of 73 Shore A. POE-g-MA is Dow Chemical's Engage 8445, octene content 9.5%, melting index 3.5 g/10 min, MA graft rate 1%.<sup>9,10</sup>

### Blending and sample preparation

The materials were dried for 4 h at 80°C with a dehumidifier before processing. The 80PA/20TPU and 80PA/20TPU/20POE-g-MA were then prepared with a twin screw extruder (Kobe Steel, model KTX-30). The screw speed was 100 rpm, and the barrel temperatures were set to 200, 215, 220, 220, 220, 220, 225, 225, 220°C. The plastic pellets after blending and extrusion were again dried for 4 h at 80°C

Correspondence to: H.-T. Chiu (hchiu@mail.ntust.edu.tw).

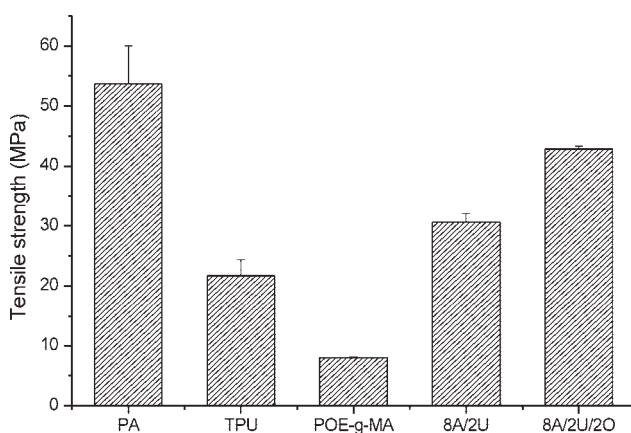


**Figure 1** Rheological curves at 245°C of pure PA, TPU, POE-g-MA, 80PA/20TPU(8A/2U), and 80PA/20TPU/20POE-g-MA(8A/2U/2O) blends. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

with a dehumidifier. The pellets were injection-molded using a Battenfeld BA750CD injection molding machine, at barrel temperatures of 230, 235, 235, 240°C and a mold temperature of 100°C, to produce various specimens conforming to ASTM standards.

### Mechanical testing

Before mechanical testing, the various specimens were placed in a regulated environment set at 23°C and relative humidity of 50% for 48 h, according to ASTM rules. We used a universal mechanical tester (Instron 5567) to perform experiments on tensile stress, elongation, and flexural stress, according to ASTM D638 and ASTM D790 standards. Notched Izod impact strength was tested with an Atlas Cs 137-25 impact tester according to ASTM D256, at room temperature (23°C).



**Figure 2** The tensile stress of pure PA, TPU, POE-g-MA, 80PA/20TPU (8A/2U), and 80PA/20TPU/20POE-g-MA (8A/2U/2O) blends.

### Rheology

We used a Gottfert 1501 Rheo-tester to examine the melt viscosity at variable shearing speeds at 245°C. The die radius used was 0.5 mm,  $L/D$  30 (length-to-diameter ratio of 30).

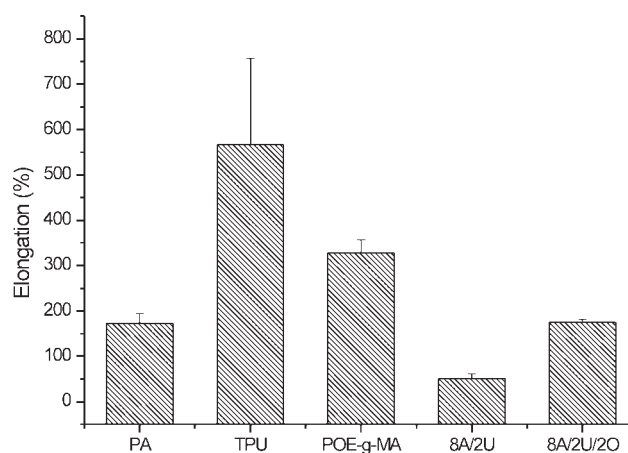
### Morphology

The specimens were rapidly frozen by immersion in liquid nitrogen, and then fractured with the Izod impact tester. The cross-sections of the broken specimens were then gold-electroplated and viewed with a Topcon ABT-150S scanning electron microscopy EM at 15 kV.

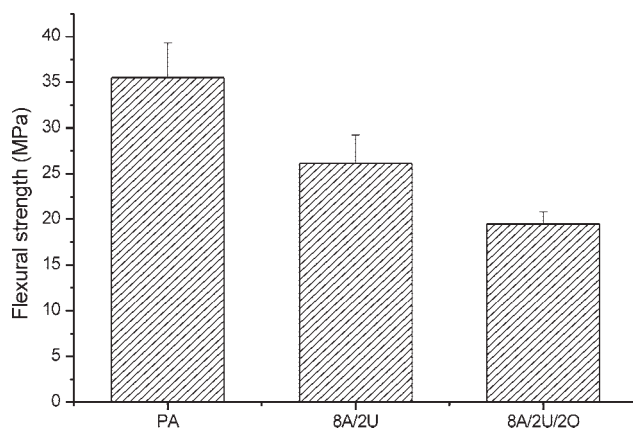
## RESULTS AND DISCUSSION

### Rheology behavior

Polymer's melt viscosity behavior determines whether the input material can be mixed evenly in the blending process, and is closely linked to injection molding, extrusion, or spinning. The blending and processing of the input material should in principle be carried out at as close to identical viscosity as possible, to get better blending results. Figure 1 shows the relationship between shearing speed and viscosity at 245°C for PA, TPU, POE-g-MA, and blended 80PA/20TPU and 80PA/20TPU/20POE-g-MA blends. The figure shows that regardless of shearing speed, viscosity relationships could be listed as POE-g-MA, PA, 80PA/20TPU/20POE-g-MA, TPU, and 80PA/20TPU. POE-g-MA has a high melt viscosity and displays significant shear thinning at lower shear speeds ( $100 \text{ s}^{-1}$ ) in an order of magnitude greater than PA and TPU materials; POE-g-MA's viscosity only approaches PA's viscosity at high shear speeds. PA and TPU show low melt



**Figure 3** The elongation of pure PA, TPU, POE-g-MA, 80PA/20TPU (8A/2U), and 80PA/20TPU/20POE-g-MA (8A/2U/2O) blends.

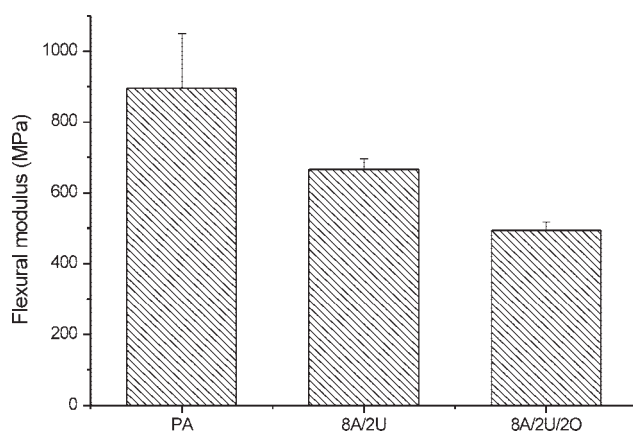


**Figure 4** The flexural stress of pure PA, 80PA/20TPU (8A/2U), and 80PA/20TPU/20POE-g-MA (8A/2U/2O) blends.

viscosity, with shear thinning linearly increasing with shearing speed. 80PA/20TPU also has low viscosity because its raw materials have low viscosity, but when 20 phr (parts per hundred resin) of POE-g-MA is introduced into the 80PA/20TPU mixture, viscosity can be increased to improve the efficiency of the blending. Di et al.<sup>11</sup> examined the effect of the increase in the viscosity on the distribution of additives, using the melt intercalation method, polycaprolactone (PCL), and organoclay. They found that a low processing temperature could produce high shear stress, allowing the clay to delaminate inside the PCL.

### Mechanical analysis

Usually a blend will show one of the three results: no effect, sum effect, or a multiplying effect. The compatibility between the base material and the modifier governs what results will be seen. Figures 2



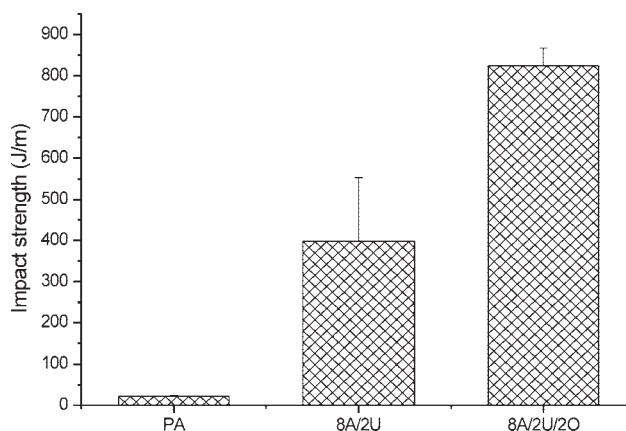
**Figure 5** The flexural modulus of pure PA, 80PA/20TPU (8A/2U), and 80PA/20TPU/20POE-g-MA (8A/2U/2O) blends.

and 3 are tensile stress and elongation of the base materials PA, TPU, POE-g-MA, as well as blends 80PA/20TPU and 80PA/20TPU/20POE-g-MA. PA is an engineering plastic, having high-tensile stress; TPU and POE-g-MA are elastomers having low-tensile stress but high elongation. Further, TPU outperforms POE-g-MA in tensile stress and elongation. Blend 80PA/20TPU shows a large drop in stress and extension, thus the blend has no multiplicative effect.

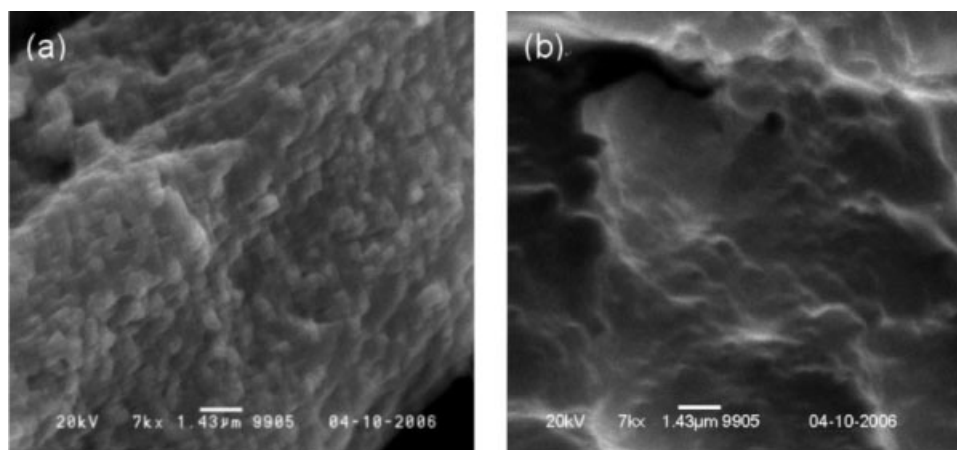
However, 80PA/20TPU/20POE-g-MA clearly shows a multiplicative effect for tensile stress, while its elongation approaches pure PA. This shows the compatibility of PA, TPU, and POE-g-MA. In research by Pesetskii et al.,<sup>12</sup> it was shown that PA and TPU have partial compatibility and hydrogen bond forces through dynamic mechanical analysis, solubility parameter, and IR spectroscopy. Other researchers showed<sup>13-16</sup> that the NH<sub>2</sub> groups of PA and modifier which had maleic anhydride may generate ring closure or ring opening copolymers. Furthermore, the mechanical properties of PA blends, where the modifier had maleic anhydride, were better than ungrafted one. Research by Wu et al.<sup>17</sup> shows that maleic acid has functional groups, that is, C=O and OH, that result in hydrogen bonding with the urethane. This suggests the possibility of PA, TPU, and POE-g-MA being compatible.

In Zhang et al.'s<sup>4</sup> research on PA/TPU blends, when TPU ratio is 70PA/30TPU, impact strength was seen to fall because in the 80PA/20TPU blend, TPU dispersion within PA was about 3  $\mu\text{m}$ , while in 70PA/30TPU, dispersion was around 11  $\mu\text{m}$ . 80PA/20TPU/20POE-g-MA in our research had an elastomer of 33.3 wt %, and the increase in impact and tensile stress came from improving the distribution of elastomer and compatibility of the base materials.

Figures 4 and 5 show the flexural stress and flexural modulus of PA, 80PA/20TPU, and 80PA/



**Figure 6** The Izod impact strength of pure PA, 80PA/20TPU (8A/2U), and 80PA/20TPU/20POE-g-MA (8A/2U/2O) blends.



**Figure 7** SEM micrographs of freeze fracture surfaces under liquid nitrogen of the (a) 80PA/20TPU (b) 80PA/20TPU/20POE-g-MA blend (magnification,  $\times 7000$ ).

20TPU/20POE-g-MA. As elastomers are flexible and soft by definition, TPU and POE-g-MA neither have flexural stress nor flexural modulus. When PA is introduced into an elastomer, both the blends 80PA/20TPU and 80PA/20TPU/20POE-g-MA show a decrease in flexural stress and modulus, with the material with more elastomers showing greater decline. Figure 6 is the impact strength of PA, 80PA/20TPU, and 80PA/20TPU/20POE-g-MA. As elastomers do not break under impact, the energy absorbed cannot be measured. 80PA/20TPU can absorb 18 times the impact energy of pure PA, while 80PA/20TPU/20POE-g-MA outperforms PA by a multiple of 38, reaching 824.9 J/m. In industrial use, plastics with impact strength of 800 J/m or more are termed “super tough” plastics; 80PA/20TPU/20POE-g-MA can be defined as a super tough plastic.

### Morphology

To better clarify the distribution of TPU and POE-g-MA within the PA, we used an SEM to observe directly. Figure 7 is an SEM analysis of (a) 80PA/20TPU and (b) 80PA/20TPU/20POE-g-MA. At  $7000\times$  magnification, it can be noted that TPU is dispersed within the PA at  $0.5\ \mu\text{m}$ , while the cross-section also showed small holes of about  $0.1\ \mu\text{m}$  in size. To increase the toughness of the plastic, the uses of modifiers with lower  $T_g$ , smaller particles and better compatibility with the base materials have to be used. Although PA and TPU both have polar groups and thus could be compatible, the small holes present in 80PA/20TPU do not allow tensile stress to multiply by adding the modifier. Under the same conditions, 80PA/20TPU/20POE-g-MA shows some holes but at lesser extent than in the 80PA/20TPU.

This shows that POE-g-MA can greatly improve the compatibility of PA and TPU. Thus, 80PA/20TPU/20POE-g-MA has higher tensile stress than 80PA/20TPU.

### CONCLUSIONS

From the above results some conclusions can be reached:

1. The ranking of shearing viscosity is POE-g-MA, PA, and TPU; 20 phr of POE-g-MA can greatly assist in increasing the melt viscosity of 80PA/20TPU and increasing compatibility.
2. 80PA/20TPU/20POE-g-MA has higher tensile stress than 80PA/20TPU, and a multiplying effect; compatibility of 80PA/20TPU/20POE-g-MA is thus shown.
3. 80PA/20TPU/20POE-g-MA has impact strength above 800 J/m, making it a super tough plastic.
4. 80PA/20TPU shows TPU existing as  $0.5\ \mu\text{m}$  particles within the PA base, and small holes  $0.1\ \mu\text{m}$  in size. 80PA/20TPU/20POE-g-MA shows some holes but at lesser extent than in the 80PA/20TPU.

### References

1. Chiu, H. T.; Hsiao, Y. K. *J Polym Res* 2005, 12, 355.
2. Chiu, H. T.; Hwung, D. S. *Eur Polym J* 1994, 30, 1191.
3. Chiu, H. T.; Hsiao, Y. K. *J Polym Res* 2006, 13, 153.
4. Zhang, S. L.; Wang, G. B.; Jiang, Z. H.; Wang, D.; Ma, R. T.; Wu, Z. U. *J Polym Sci Part B: Polym Phys* 2005, 43, 1177.
5. Zhang, S. L.; Wang, D.; Guan, S. W.; Jiang, Z. H.; Wu, Z. W.; Wang, G. B. *Mater Lett* 2007, 61, 267.
6. Genonese, A.; Shanks, R. A. *Comput Theor Polym Sci* 2001, 11, 57.

7. Chen, H.; Yang, B.; Zhang, H. *J Appl Polym Sci* 2000, 77, 928.
8. Chiu, F. C.; Lai, S. M.; Chen, Y. L.; Lee, T. H. *Polymer* 2005, 46, 11600.
9. Aróstegui, A.; Gaztelumendi, M.; Nazábal, J. *Polymer* 2001, 42, 9565.
10. Wu, C. S.; Liao, H. T.; Lai, S. M. *Polym Plast Technol* 2002, 41, 645.
11. Di, Y.; Iannace, S.; Di Maio, E.; Nicolais, L. *J Polym Sci Part B: Polym Phys* 2003, 41, 670.
12. Pesetskii, S. S.; Fedvarov, V. D.; Jurkowski, B.; Polosmak, N. D. *J Appl Polym Sci* 1999, 74, 1054.
13. Chow, W. S.; Abu Bakar, A.; Mohd Iskak, Z. A.; Karger-Kocsis, J.; Ishiaku, U. S. *Eur Polym J* 2005, 41, 687.
14. Takahashi, T. *Sen-I Gakkaishi* 2002, 58, 238.
15. Jing, B.; Dai, W. L.; Liu, P. S.; Zhang, P. *Polym Int* 2007, 56, 1240.
16. Wang, Q.; Liu, C.; Chen, Z. *Polym J* 2001, 33, 522.
17. Wu, H. L.; Wang, C. H.; Ma, C. C.; Chiu, Y. C.; Chiang, M. T.; Chiang, C. L. *Compos Sci Technol* 2006, 67, 1854.