

Chapter 2

A Novel Reactive Compatibilization Strategy on Immiscible Polypropylene and Polystyrene Blend

Abstract

Polypropylene (PP) and polystyrene (PS) are immiscible and incompatible. Since both PP and PS components possess no reactive functional group, reactive compatibilization of PP/PS blend is impossible unless imparting certain reactive functional groups to either PP or PS. In this study, we provide a simple approach to reactively compatibilize the non-reactive PP/PS blend system by physically functionalize PP and PS with the addition of maleic anhydride grafted PP (PP-g-MA) and styrene maleic anhydride random copolymer (SMA), respectively. An epoxy monomer, serving as a coupler and possessing four epoxy groups able to react with the maleic anhydride of PP-g-MA and SMA was then added during melt blending. Observations of the finer PS domain sizes and improved mechanical properties support the plausibility of reactive compatibilization of this non reactive PP/PS blend by combining physically functionalized PP and PS with TGDDM in a one step extrusion process.

2.1 Introduction

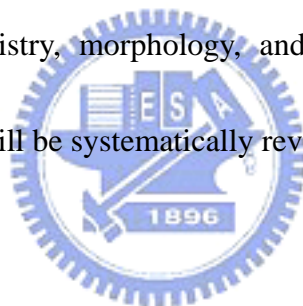
Polymer blends have attracted great attentions both industrially and academically because of their flexibility and versatility to create new materials with desired properties from existing polymers. However, it is nearly impossible to obtain a useful polymer blend material without compatibilization because most randomly selected polymer pairs are immiscible and incompatible, with only few exceptions. As a result, compatibilization of immiscible and incompatible polymer blends has become a critically important topic and research field for the past few decades [1.2].

Compatibilization of immiscible and incompatible polymer blends can be achieved by using various non-reactive and reactive compatibilizers. Non-reactive graft or block copolymers are successfully employed as efficient compatibilizers because they are able to locate at the interface and act as emulsifiers to lower the interfacial tension [2-4]. Due to their high molecule weight nature, however large portions of the block copolymers prefer to form micelles in either homopolymer phases, rather than residing along the interfaces. Moreover only a few block and graft copolymers suitable as compatibilizers are readily commercially available, most of them require separate synthesis process and are costly. Those shortcomings make reactive compatibilization become an alternative and more practical way to produce useful polymer blends [5-8]. Instead of premade block or graft copolymers, reactive

compatibilization forms copolymers in situ during melt blending process if the constituent polymers contain certain functional groups. Since the reaction of functional groups occurs at the interfaces, the in situ formed copolymers tend to stay at the interface, providing better compatibilization effect.

Polypropylene(PP) and polystyrene(PS) represent two of the largest commodity polymers in the world. Polymer blends of PP and PS have always been an interesting topic for resin suppliers and compounders because of the potential to recycling the large volume wastes. PP and PS are immiscible, and lots of work on compatibilizing PP/PS blend have been done by using SBS, SEBS, SEP and SIS block copolymers as non-reactive compatibilizers[9-11]. However, relatively few studies on reactive compatibilization of PP/PS blend have been reported because lacking of functional groups in both PP and PS. Dicumyl peroxide was employed by Xie [12] and Zheng to generate in situ PP-g-PS graft copolymer in a one step extrusion process and the dispersed particle size was greatly reduced. Kim [13] et al. found the molecular architecture and functional group inhomogeneity of in situ compatibilizers strongly affects the compatibilizing efficiency, rheology as well as the morphology. Sun et. al. [14] reported that an in situ compatibilization of PP/PS blend was achieved by using Friedel-Crafts benzene ring alkylation of PS through reactive extrusion and resulted in improved tensile elongation.

It is known that PP-g-MA [15-17] and SMA [6] with low MA content are miscible with PP and PS, respectively. In this study, we attempt to physically functionalize both PP and PS by adding a small quantity of commercially available PP-g-MA and SMA, respectively. By doing so, the reactive compatibilization of the non-reactive blend becomes possible. A multi-functional epoxy, which was proven to be an effective coupler in reactive compatibilization [7-8] is then introduced into the blend and is capable of reacting with the maleic anhydride of SMA and PP-g-MA simultaneously at the interface to form various PS-co-epoxy-co-PP copolymers during the melt blending process. The chemistry, morphology, and mechanical properties of the compatibilized PP/PS blend will be systematically revealed and discussed.



2.2 Experimental

2.2.1 Materials

Homopolymer polypropylene (PP), a general purpose grade PC-366-5, was obtained from Taiwan Polypropylene Company. Polystyrene (PS), PG-33, was purchased from the Chi Mei Co., Taiwan. PP-g-MA with MA content 0.8wt% was supplied by the UniRoyal Chemical Co. SMA copolymer containing 8 wt% maleic anhydride, Dylark 232, was purchased from ARCO Chemical Co. The epoxy resin, tetra-glycidyl ether of diphenyl diamino methane (TGDDM), with the trademark of NPEH-434, was purchased from the Nan Yea Plastics Co. of Taiwan. Table 2-1 and Table 2-2 list the properties and the chemical structures of materials used in this work, respectively.



2.2.2 Extrusion and injection molding

All blends were dry mixed first and the melt blending process was carried out with a 30-mm corotating intermeshing twin-screw extruder (L/D=36 Sino Alloy Machinery Inc. of Taiwan) with a rotational speed 180 rpm. The standard ASTM test specimens were prepared by an Arburg 3 oz injection-molding machine. Prior to melt blending and injection molding, all pellets were dried in an oven at 80°C for 4 hours. The detailed processing conditions for extrusion and injection molding are summarized in Table 2-3.

2.2.3 Infrared spectroscopy

All infrared spectra were obtained at a resolution of 1cm^{-1} on a Nicolet AVATAR 320 FTIR Spectrometer at 25°C .

2.2.4 Torque versus time measurement

To verify potential chemical reaction among PP-g-MA, SMA, and TGDDM based on the viscosity increase (torque versus time), 45g of the selected composition was tested at 200°C and 40 rpm in a Brabender Plasti-Corder, type PLD 651.

2.2.5 Thermal properties

Thermal properties of pure components and blends were investigated on a TA instrument DSC 2010 with a sample weight of 5-10 mg. All samples were heated to 220°C and subsequently annealed for 3 minutes, then cooling to 80°C to determine the crystallization temperature (T_c) of the polypropylene. After the cooling process, the sample was reheated to 220°C to determine the melting temperature (T_m) of the polypropylene. Both heating and cooling rate are $10^{\circ}\text{C}/\text{min}$.



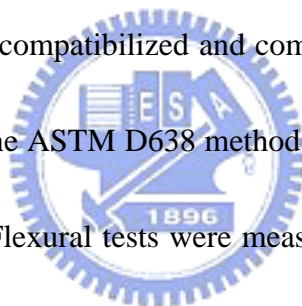
2.2.6 Scanning electron microscopies

The morphologies were examined by a Scanning Electron Microscopy (SEM) at

accelerating voltage 20 kV, Model S-570, Hitachi Co. of Japan from cryogenically fractured specimens in the plane perpendicular to flow direction of injection molding. Samples were etched with tetrahydrofuran (THF) to dissolve the PS phase out of the blends. The fractured surfaces of specimens were coated with thin film of gold to prevent charging.

2.2.7 Mechanical properties

An Instron Universal Testing Machine model 4201 was used to measure the mechanical properties of the incompatibilized and compatibilized blends. Tensile tests were measured according to the ASTM D638 method with crosshead speed 5mm/min using at ambient conditions. Flexural tests were measured according to ASTM D790 method with 50mm span and 5mm/min test speed at ambient condition.



2.3 Results and Discussion

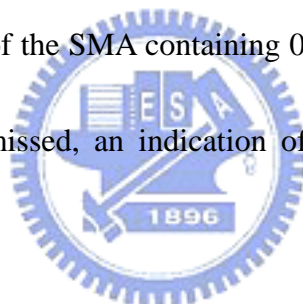
2.3.1 Chemistry

In reactive compatibilization, the chemical reactions between the functional groups of the reactive copolymers and the coupler are expected to occur and to form various desired in situ formed compatibilizers during the melt blending process. The formation of the in situ compatibilizers is critically depended on the relative reactivities between functional groups of the reactive polymers with the coupler, processing temp, time and mixing efficiency. The main reaction involved in this study is the reactions of the anhydride groups of SMA and PP-g- MA with the epoxy groups of the TGDDM. As illustrated in Scheme 2-1(a), the reaction can be initiated by steam of the atmosphere or the residual moisture content in the feeding materials, proceeding the ring-opening reaction. The ring opened anhydride group will then react with the epoxy group of TGDDM as shown in Scheme 2-1(b). The reaction will basically take place along the interfaces, thus, the in situ formed PP-g-MA-co-TGDDM-co-SMA copolymers tend to stay at the interface as interfacial emulsifiers. As a result, the compatibilization is more efficient than a non-reactive block or graft copolymer.

2.3.2 FT-IR spectroscopy

The FT-IR spectroscopy is a powerful tool for observing the reactions between the

functional groups of anhydride of SMA and PP-g-MA and the epoxy group of TGDDM. Figure 2-1 shows the superimposed FT-IR spectra of mixtures of SMA containing various amount of TGDDM after melt blending. The peak in the 1780 cm^{-1} is assigned to carbonyl stretching mode of the maleic anhydride group of SMA. The intensity of the characteristic peak of the maleic anhydride decreases with increasing the quantity of the TGDDM, due to the reaction between TGDDM and SMA as would be expected. With the addition of 0.32phr TGDDM, the peak at 1780 cm^{-1} is nearly disappeared, implying that nearly all MA groups are consumed during melt blending process. The FTIR spectrum of the SMA containing 0.48 phr TGDDM shows that the peak at 1780 cm^{-1} is totally missed, an indication of total consumption of the MA groups.



The FTIR spectra of PP-g- MA, TGDDM and melt blended mixture of PP-g-MA with 3 phr TGDDM are shown in Figure 2-2. The characteristic peak at 1770 cm^{-1} of the anhydride group from the PP-g MA decreases significantly with the presence of TGDDM, comparing to that of the pure PP-g-MA. The intensity decrease of the characteristic peak can be attributed to the partial reaction of TGDDM and PP-g-MA during the melt blending process. Based on the FTIR findings, it is expected that TGDDM will react simultaneously with SMA and PP-g-MA during melt blending and form various PP-g-MA-co-TGDDM-co-SMA copolymers along the interfaces to

serve as the compatibilizers of the immiscible PP/PS blend.

2.3.3 Torque versus time

Torque measurement was utilized to obtain the qualitative information on the chemical reactivity in this study. Figure 2-3 plots the torque versus time curves for various PP-g-MA/SMA/TGDDM blends at the processing condition of chamber temperature of 200°C at rotational speed of 40 rpm. PP-g-MA and SMA pellets were dry blended and fed into the mixer. TGDDM was then added at time t=180 seconds, where the torque value reached steady and ensured at melt state. The torque value of PP/PP-g-MA/SMA/PS/TGDDM = 55/20/3/22/0.48phr [Figure 2-3(a)] and PP/PP-g-MA/SMA/PS/TGDDM = 75/0/3/22/0.48phr [Figure 2-3(b)] suddenly dropped to nearly close to zero with addition of TGDDM because of the low molecule weight nature of TGDDM, by functioning as a lubricant before reacting with maleic anhydride. After certain reaction time the torque value of PP/PP-g-MA/SMA/PS/TGDDM = 55/20/3/22/0.48phr [Figure 2-3(a)] increases only slightly while the torque of PP/PP-g-MA/SMA/PS/TGDDM = 75/0/3/22/0.48phr [Figure 2-3(b)] rises sharply. It indicates that the reaction rate of SMA and TGDDM is significantly faster than that of PP-g-MA and TGDDM during melt blending. The sharper increased torque value also implies the degree of molecular weight increase of

SMA is higher than that of PP-g-MA with the addition of the multifunctional TGDDM. The torque value of PP/PP-g-MA/SMA/PS/TGDDM = 55/20/3/22/0phr [Figure 2-3(c)] is close to zero, implying that no reaction or interaction between PP-g-MA and SMA. However, the torque value of PP/PP-g-MA/SMA/PS/TGDDM = 55/20/3/22/0.48phr [Figure 2-3(d)] shows higher torque value, which can be attributed to the formation of various PP-g-MA-co-TGDDM-co-SMA copolymers in the blend, as well as the molecular weight increase of SMA and PP-g-MA, respectively.

2.3.4 Morphologies

One of the key objectives in reactive compatibilization is to control the domain size of the minor phase. Factors influencing the polymer blend morphology development include the viscosity ratio of the blend constituents, composition, processing conditions, elasticity ratio and interfacial modification [17]. Generally, immiscible and incompatible blends possess high interfacial tension and results in coarser morphology than corresponding adequately compatibilized blends. Figure 2-4(a) shows the SEM micrograph of the cryogenic-fracture surface of the PP/PS = 75/25 blend where the PS phase was etched out by the solvent. Large and irregular PS domains can be easily identified in this incompatibilized PP/PS blend. The interface is also quite sharp, indicating poor interfacial adhesion and high interfacial tension of PP



and PS. The SEM micrographs of the PP/PS=75/25 series blends with various amounts of PP-g-MA and SMA were given in Figures 2-4(b), 2-4(c) and 2-4(d). Comparing to figure 2-4(a), no obvious reduction in PS domain was observed, implying that without a coupler, PP-g-MA and SMA alone are unable to effectively compatibilize the incompatible PP/PS blend. Significant reduction of the PS domain sizes was found with the presence of TGDDM in these PP/PP-g-MA/SMA/PS blends as seen in Figures 2-5(a), 2-5(b) and 2-5(c). As mentioned earlier, an efficient compatibilizer functions as an emulsifier to reduce the interfacial tension of the immisible blend, leading to finer domain sizes and broad interface thickness. During the melt blending process, the multi functional TGDDM can react simultaneously with PP-g-MA and SMA to form various in situ PP-g-MA-co-TGDDM-co-SMA copolymers at the interfaces and results in finer PS domains. Better compatibilization can be achieved by using higher TGDDM content, as the PS domains are finer in Figures 2-5(b) and 2-5(c). These morphological findings further provide evidence to explain the observed trend of the mechanical properties.

2.3.5 Thermal properties

Table 2-4 summarizes the DSC results of the pure components, uncompatibilized and compatibilized blends. Here we only present the data of T_m and T_c to discuss the

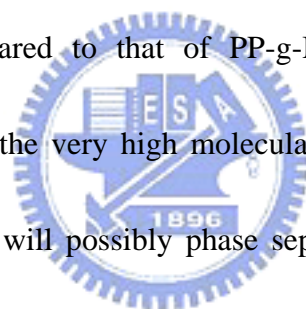
effect of compatibilizer on the crystalline phase behavior. The effect of compatibilizer on the amorphous phase is not explored because the T_g of PP and PP-g-MA is difficult to observe due to their high crystallinity. For SMA, which is the minor component that made the T_g not easily detected by DSC. Duvall et al [15] demonstrated that PP-g-MA with low MA content is capable to cocrystallize with PP and no phase separation between PP-g-MA crystal and PP crystal was observed by DSC and hot stage microscopy. The cocrystallization behavior between bulk PP and PP segment of PP-g-MA was also proven by WAXD analysis by Ma et al [16]. In Table 2-4, the T_m values of the PP phase in the blends are almost the same as that of pure PP, regardless of the quantity of the TGDDM. This result suggests that in our blend systems, PP-g-MA cocrystallizes with PP and are miscible in the crystal form. The crystallization temperature (T_c) can be used as an indicator of the crystallization rate. In Table 2-4 it is shown that for various blend compositions, the T_c of the PP component in blends is increased with increasing TGDDM quantity. The highest T_c of the PP component in the compatibilized blend is about 19°C higher than pure PP (131.9°C vs 113.1°C). The significant change in T_c can be attributed to the finer PS domains in the compatibilized blends observed in the morphology section, which function as effective nucleating agents and further enhance the crystallization rate of PP. From the polymer processing point of view, the T_c increase of the crystalline

component in polymer blends is quite beneficial for injection molding because of the dramatic cycle time reduction. Higher T_c means the product in the mold solidify faster and can be ejected at shorter time. As a result, the processing cycle time can be decreased and the overall productivity will be improved.

2.3.6 Mechanical properties

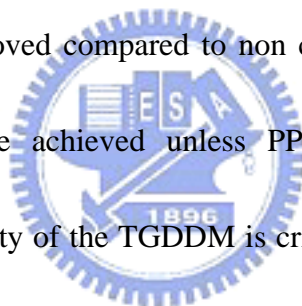
The mechanical properties can be served as an indicator for the effectiveness of a compatibilizer in immiscible or incompatible blends. Generally it is expected that the mechanical properties of the compatibilized polymer blends will be improved compared to the corresponding incompatibilized ones because of the lower interfacial tension and enhanced interfacial adhesion of the compatibilized blends, making stress transfer more efficiently between phases during fracture. Figure 2-6 and Figure 2-7 show the tensile strength at break and flexural modulus of various incompatibilized and compatibilized PP/PS blends. With the addition of the TGDDM coupler, both tensile strength and flexural modulus are improved for all physically functionalized PP/PS blends [Figures 2-6(a) ~ 6(c), Figures 2-7(a) ~ 7(c)]. The observed mechanical property improvements imply that those in situ formed PP-g-MA-co-TGDDM-co-SMA copolymers tend to anchor along the interface and broaden the interface region, resulting in finer domain and better stress transfer.

Blends of which only PP component was physical functionalized [Figure 2-6(d) and Figure 2-7(d)] also exhibit better mechanical properties with addition of TGDDM. The mechanical properties increase is mainly due to the molecular weight increase of PP-g-MA, as the PS phase was not physically functionalized and formation of the in situ copolymer is impossible. However, for the PP/PS/PP-g-MA/SMA=75/22/0/3 series blends [Figures 2-6(e) and Figures 2-7(e)], the presence of TGDDM is detrimental to tensile strength as well as flexural modulus. As discussed in the torque versus time section, the molecular weight increase of SMA is very significant with the addition of TGDDM, compared to that of PP-g-MA. Without the presence of PP-g-MA in the blend, only the very high molecular weight i.e. lightly cross-linked SMA will be formed, which will possibly phase separate from the PS domain and resulted in poorer mechanical properties.



2.4 Conclusions

FTIR analysis provides direct evidence of reactions of TGDDM with PP-g-MA and SMA during melt blending. The torque v.s. time plot shows the reactivity of TGDDM with SMA is significantly higher than that of TGDDM with PP-g-MA. The PS domain size is significantly reduced for those compatibilized PP/PS blends from the SEM graphs. The crystallization temperature of PP in the compatibilized blends increases with decreasing PS domain size, whereas the melting temperature remains close to that of pure PP. Tensile strength and flexural modulus of the compatibilized blends are substantially improved compared to non compatibilized blends. Reactive compatibilization can not be achieved unless PP and PS are both physically functionalized. A small quantity of the TGDDM is critical to function as a coupler in the PP/PS blend during melt blending.



References

1. L. A. Utracki, "Commercial Polymer Blends", Chapman & Hall, London, 1998
2. D. R. Paul and C. B. Bucknall, "Polymer Blends", John Wiley & Sons, New York, 2000.
3. J. W. Barlow and D.R. Paul, *Polym. Engng. Sci.*, **24**, 525 (1984).
4. Y. Lyatskaya and A. C. Balazs, *Macromolecules*, **29**, 7581 (1996).
5. W.E. Baker, C. E. Scott and G. H. Hu, "Reactive Polymer Blending", Hanser Publishers, Munich, 2001.
6. M. Y. Ju and F. C. Chang, *Polymer*, **41**, 1719 (2000).
7. K. C. Chiou and F. C. Chang, *J. Polym. Sci., part B Polym. Phy.*, **38**, 23 (2000).
8. M. Y. Chu, M. Y. Chen and F. C. Chang, *Macromol. Chem. Phy.*, **201**, 2298 (2000).
9. G. Radonjic, V. Musil and I. Smit, *J. Appl. Polym. Sci.*, **69**, 2625 (1998).
10. D. Hlavata, Z Horak and J. Hromadkova, *J. Polym. Sci., part B Polym. Phy.*, **37**, 1647 (1999).
11. P. Raghu, C. K. Nere and R. N. Jagtap, *J. Appl. Polym. Sci.*, **88**, 266 (2003).
12. X. M. Xie and X. Zheng, *Mater. Design*, **22**, 11 (2001).
13. S. H. Kim, J. K. Kim, C. E. Park, *Polymer*, **38**, 1809 (1997).
14. Y. Sun, R. Willemse, T. Liu, and W. Baker, *Polymer*, **39**, 2201 (1998).

15. A. Gonzalez-Montiel, H. Keskkula and D. R. Paul, *J. Polym. Sci., part B Polym. Phy.*, **33**, 1751 (1995).
16. I. Duvall, C. Sellitti, C. Myers, A. Hiltner and E. Bear, *J. Appl. Polym. Sci.*, **52**, 207 (1994).
17. Z. L. Ma, J. G. Gao, H. J. Niu, H. T. Ding and J. Zhang, *J. Appl. Polym. Sci.*, **85**, 257 (2002).
18. D. R. Paul and C. B. Bucknall, "Polymer Blends", John Wiley & Sons, New York, 2000, Chap. 16.



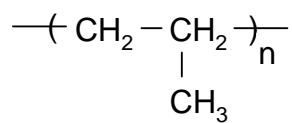
Table 2-1. Properties of Materials Used in this Study

	MA (wt%)	Tg(°C)	Tm(°C)	Tc(°C)	Melt index (g/10min)
PP	0	--	165.6	113.1	7.9
PS	0	92.9	--	--	8.7
PP-g-MA	0.8	--	160.9	127.9	17.3
SMA	8	118.7	--	--	5.3

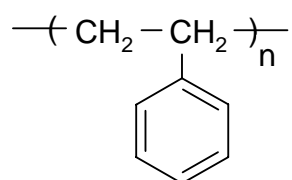


Table 2-2. Chemical Structure of Materials Used in this Study

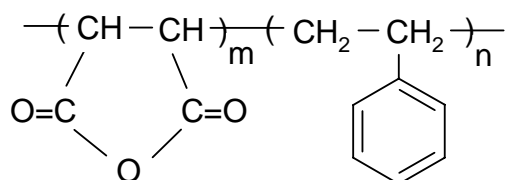
PP



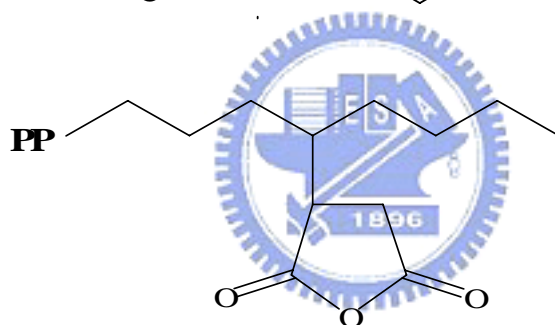
PS



SMA



PP-g-MA



TGDDM

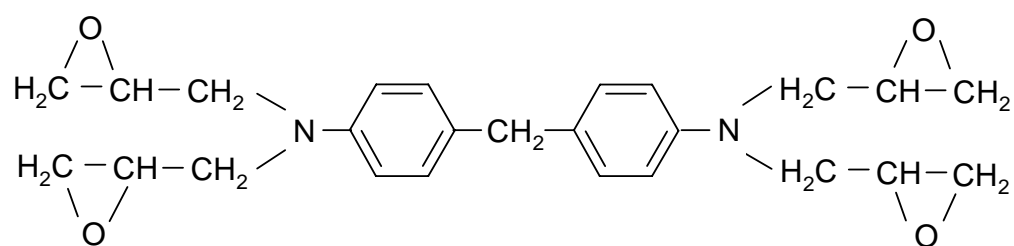


Table 2-3. Processing Conditions of Extrusion and Injection Molding

Stage	Temp (°C)									Die	Nozzle	Mold
	1	2	3	4	5	6	7	8	9			
<i>Extrusion</i>	150	180	190	200	220	230	230	240	240	245	-	-
<i>Injection</i>	225	230	235	-	-	-	-	-	-	-	240	70



Table 2-4. DSC Results of Pure Component and Corresponding Blends

PP/PP-g-MA/SMA/PS/TGDDM(phr)	T _m (°C)	T _c (°C)
PP	166.6	113.1
PP-g-MA	160.9	127.9
PP/PS (75/25)	166.8	114.2
55/20/1/24/0	167.1	124
55/20/1/24/0.16	166.7	127.6
55/20/1/24/0.32	167.2	129.6
55/20/1/24/0.48	167.4	131.2
55/20/2/23/0	166.5	122.5
55/20/2/23/0.16	166.5	128
55/20/2/23/0.32	167.2	129.7
55/20/2/23/0.48	167	131.8
55/20/3/22/0	167.2	121.7
55/20/3/22/0.16	166.7	127.5
55/20/3/22/0.32	167	129.5
55/20/3/22/0.48	167.3	131.9



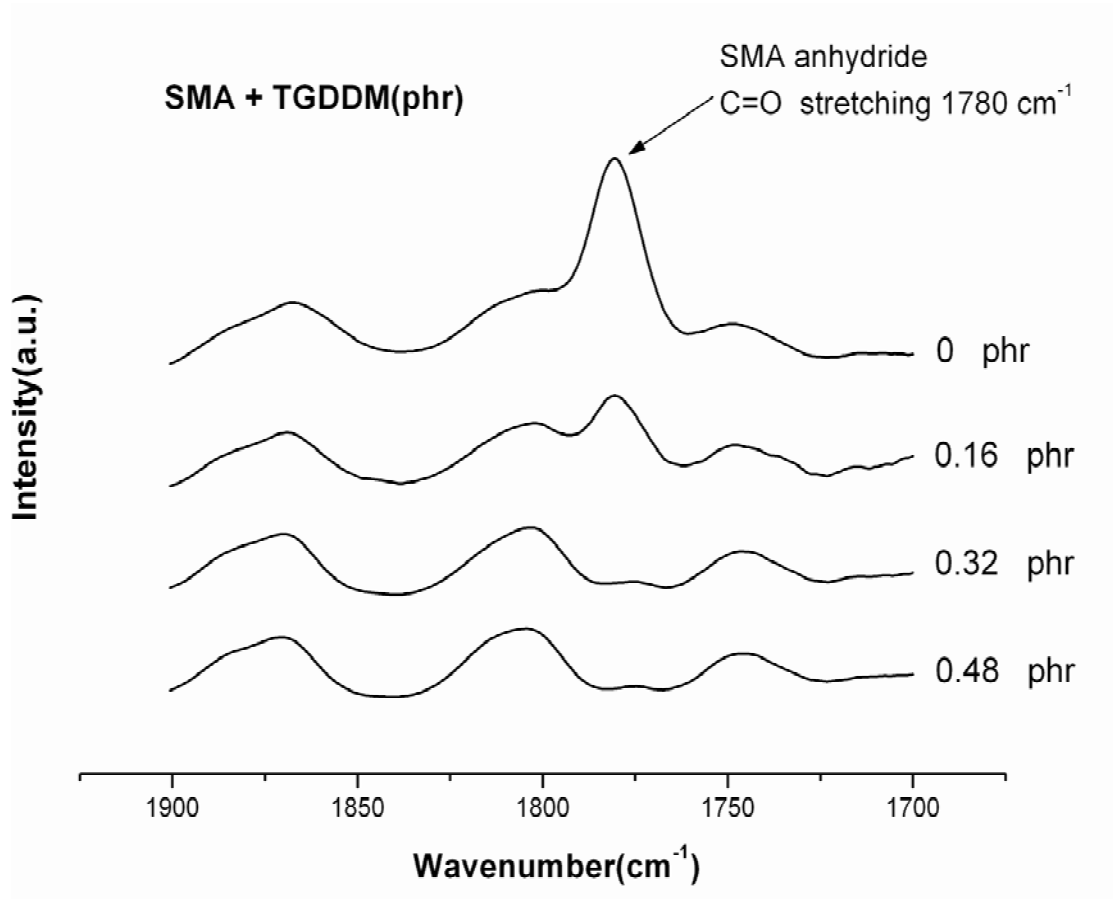


Figure 2-1. FTIR spectrum for SMA melt blended with various amount of TGDDM in 1900-1700cm⁻¹ region.



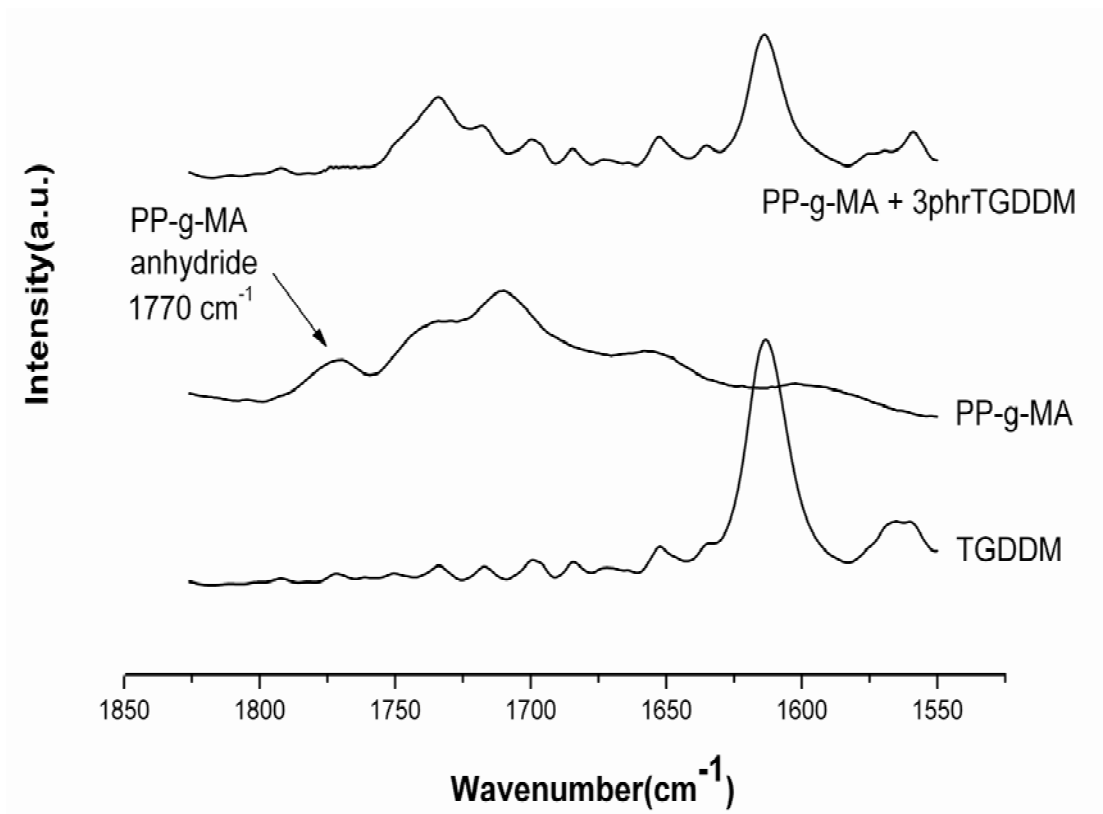


Figure 2-2. FTIR spectrum for PP-g-MA melt blended with 3phr TGDDM in 1900-1700cm⁻¹ region.



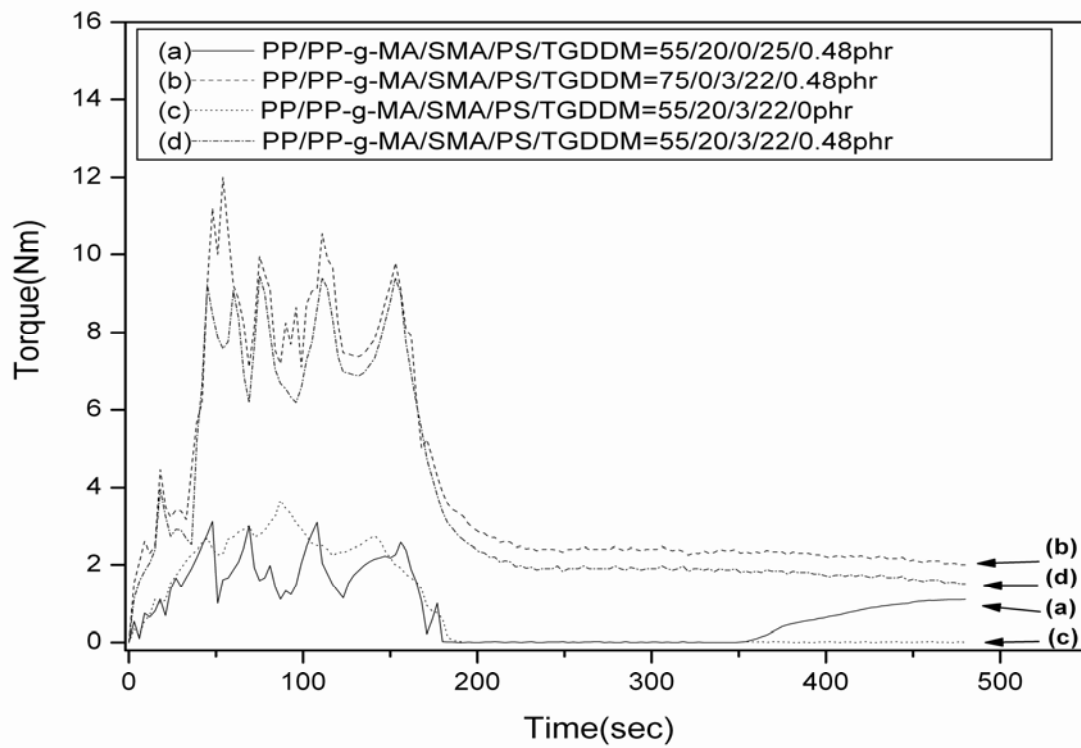
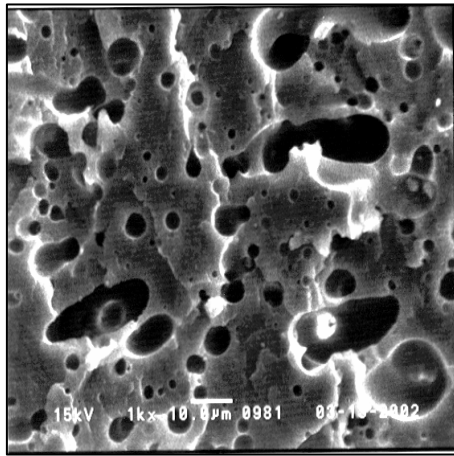
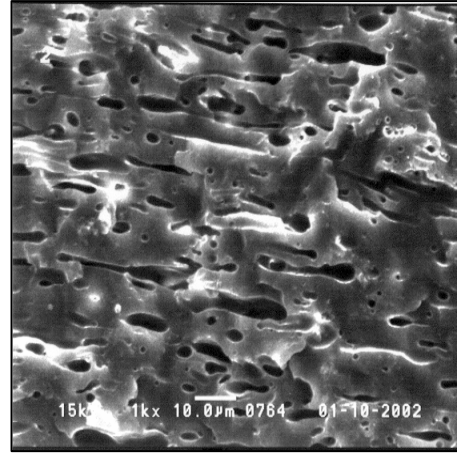


Figure 2-3. Plot of torque versus time for various PP-g-MA/SMA/TGDDM blends. Blends were prepared at 240°C and 40rpm in a Brabender mixer.

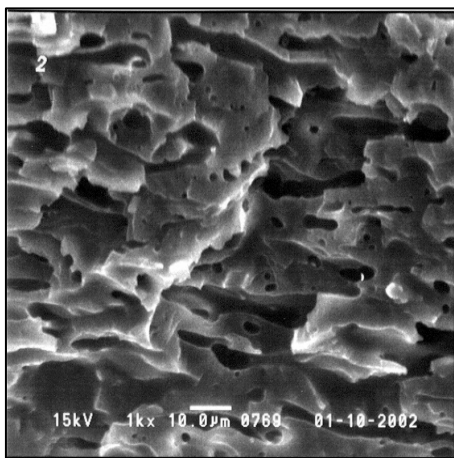




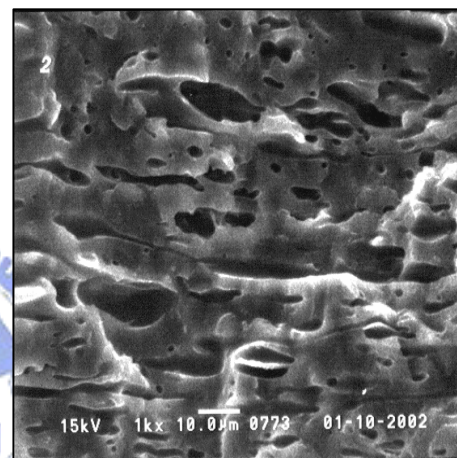
(a)



(b)

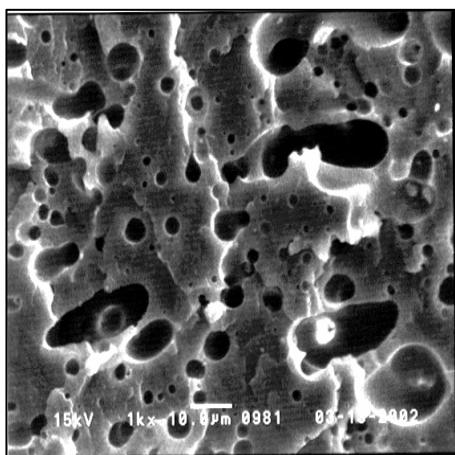


(c)

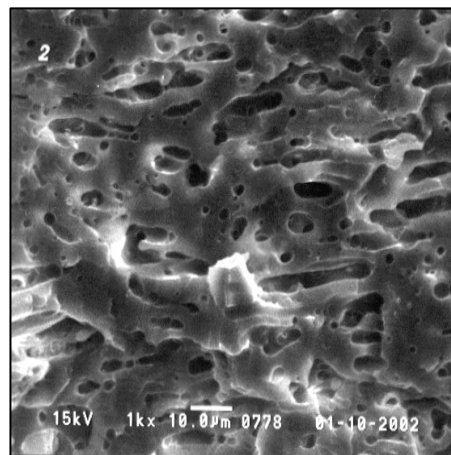


(d)

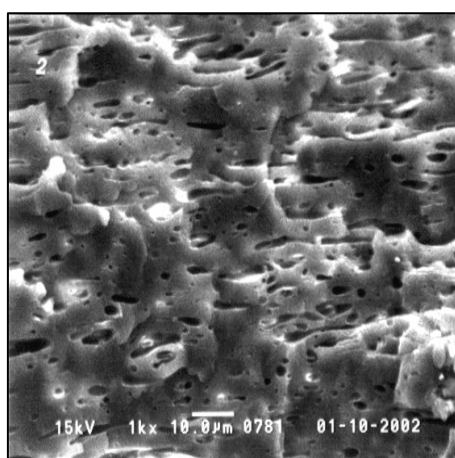
Figure 2-4. SEM micrographs of cryogenic fractured surfaces for PP/PS and various physically functionalized PP/PS blends ($\times 1000$): (a) PP/PS=75/25; (b) PP/PP-g-MA/SMA/PS=55/20/1/24; (c) PP/PP-g-MA/SMA/PS=55/20/2/23; (d) PP/PP-g-MA/SMA/PS=55/20/3/22.



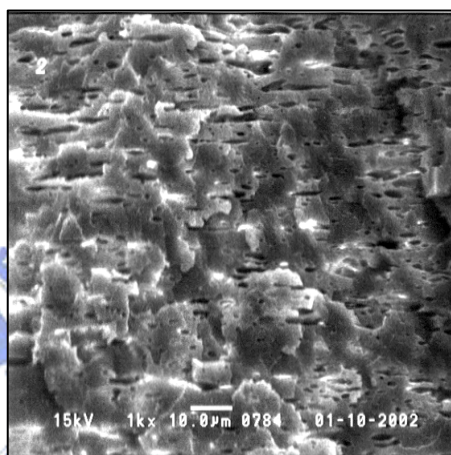
PP/PS=75/25



(a)



(b)



(c)

Figure 2-5. SEM micrographs of PP/PP-g-MA/SMA/PS=70/20/1/24 blends containing (a) PP/PS-75/25, (b) 0.16phr; (c) 0.32phr; (d) 0.48phr of TGDDM

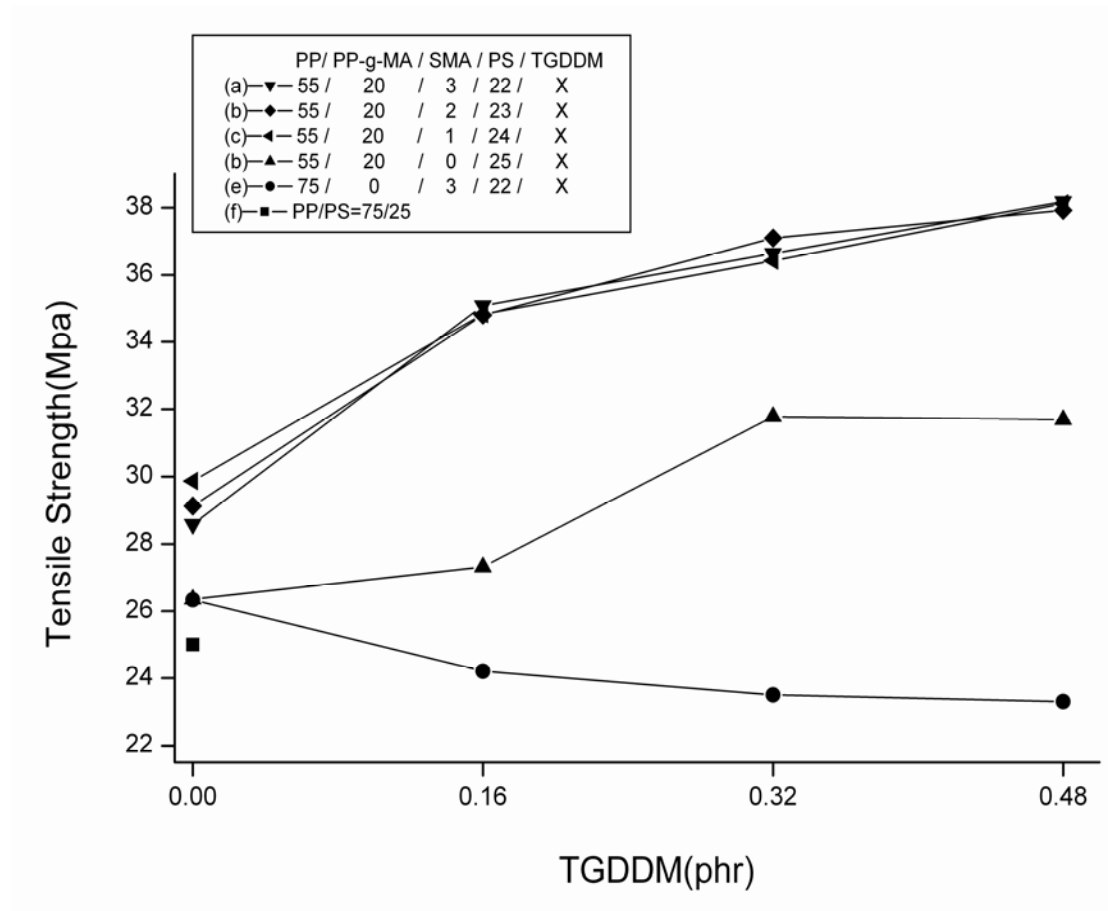


Figure 2-6. Effect of TGDDM amount on the tensile strength of various PP/PP-g-MA/SMA/PS blends.

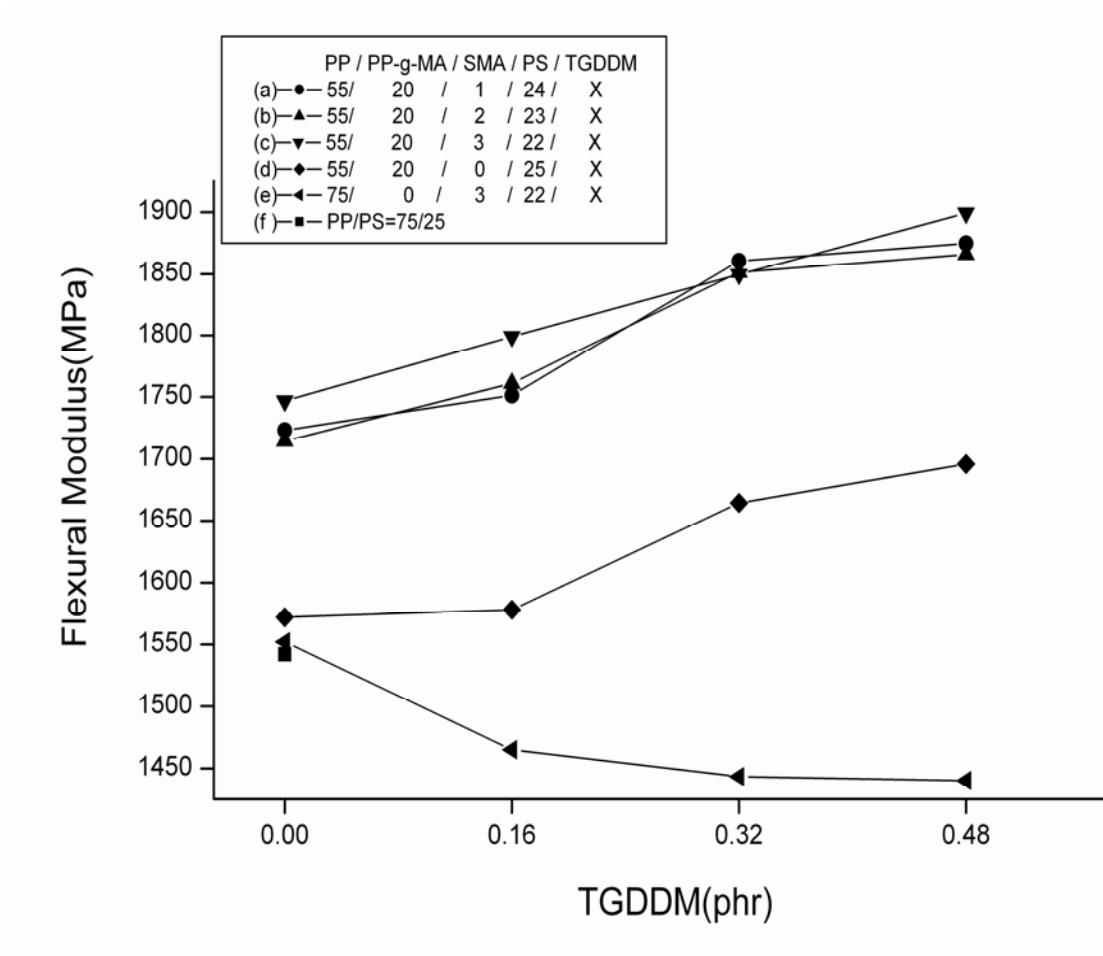
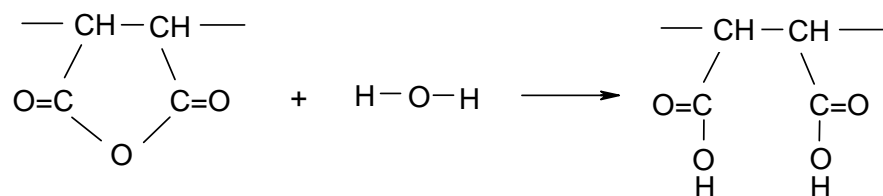


Figure 2-7. Effect of TGDDM amount on the flexural modulus of various PP/PP-g-MA/SMA/PS blends.

Scheme 2-1. The simplified reaction mechanism between anhydride and epoxy. (a) ring opening reaction of anhydride by vapor water. (b) reaction of ring opened anhydride with epoxy.

(a)



(b)

