

Chapter 4

Reactive compatibilized Polypropylene and Modified Poly (2,6-dimethyl-1,4-phenyl ether) Blend

Abstract

In order to extend the engineering application limit of polypropylene (PP), blending modified poly (2,6-dimethyl-1,4-phenyl ether) (mPPO) with PP to increase the heat resistance and stiffness is an economical and attractive approach. However, due to the incompatibility between PP and mPPO, compatibilization is needed to obtain useful blends. Since PP contains no functional groups and mPPO has little functionality, reactive compatibilization can be achieved by physically imparting functionality to both PP and mPPO with the addition of PP grafted maleic anhydride copolymer (PP-g-MA) and low molecular weight poly (2,6-dimethyl-1,4-phenyl ether) (lmw PPE), respectively. Epoxy monomers, serving as a coupler and able to react with the maleic anhydride of PP-g-MA and phenolic OH of lmw PPE, was then added during melt blending. Observations of the finer domain sizes and improved mechanical properties support the plausibility of reactive compatibilization of this non reactive PP/mPPO blend by combining physically functionalized PP and mPPO with epoxy in a one step extrusion process.

4.1 Introduction

PPE is an extremely useful class of high performance engineering thermoplastics by reason of their hydrolytic stability, high dimensional stability, toughness, heat resistance and dielectric properties. It also exhibits high glass transition temperature values, typically 210° C., and good mechanical performance. This unique combination of properties renders PPE based formulations suitable for a broad range of applications which are well known in the art. To avoid the degradation of PPE during high processing temperature, commercially available PPE are usually blended with polystyrene (PS) in various ratios to lower the glass transition temperature, i.e. the processing temperature. Such miscible PPE/PS blends are called modified PPO (mPPO). Polymer alloy comprised of mPPO and PP is an ideal engineering thermoplastic polyolefin (TPO) that combines the flowability and chemical resistance of PP with PPE's high-temperature performance, surface hardness and rigidity [1-6]. In addition, the good compatibility of the PPE/PP blends with TPO based materials makes adhesion easier in the secondary processing. It also attracts the automotive makers' interest in materials compatibility for recycling because it can be reground together with other PP-based resins or with standard mPPO.

PP and PPE are immiscible, and must be appropriately compatibilized to obtain useful blends. However, only a few discussions can be found in the patents or related

research journals [3-6]. In most of the patents, various copolymers such as polypropylene grafted polystyrene copolymer [7], polyolefin-poly(arylene ether) graft copolymers [8-10] and polyolefin-poly(arylene ether) block copolymers [11,12] were utilized as compatibilizers, and the resulting blends have higher temperature resistance and better mechanical properties. For example, compare with TPOs used in bumper fascias, the compatibilized PP/PPE blend offers both higher heat resistance and 30-50% greater stiffness for the same level of toughness. High stiffness and high flow of the compatibilized PP/PPE also allow parts with thinner walls and faster molding cycles.

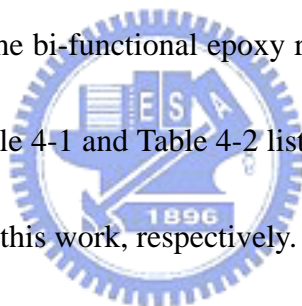


In this study, we intend to reactively compatibilized the PP and PPE blends. In our previously report [13], it is proved that PP and PS can be successfully reactively compatibilized with the addition of a multifunctional coupler and functionalized PP and PS. Same method will be applied here except the functionalized PS been replaced by a low molecular weight PPE (lmw PPE), which possess much higher phenolic end group contents than high molecular weight PPE. The effect of compatibilization on the morphology, modulus-temperature relationship and mechanical properties of the resulting blends will be discussed.

4.2 Experimental

4.2.1 Materials

Homopolymer polypropylene (PP), a general purpose grade PC-366-5, was obtained from Taiwan Polypropylene Company. PP-g-MA with MA content 0.8wt% was supplied by the UniRoyal Chemical Co. Modified poly (2,6-dimethyl-1,4-phenyl ether) , Noryl N300 and a low molecular weight PPE, Noryl PPO SA120 was purchased from GE Plastics. The epoxy resin, tetra-glycidyl ether of diphenyl diamino methane (TGDDM), with the trademark of NPEH-434, was received from the Nan Yea Plastics Co. of Taiwan. The bi-functional epoxy resin, Epon 828 was supplied by Shell Chemical Company. Table 4-1 and Table 4-2 list the properties and the chemical structures of materials used in this work, respectively.



4.2.2 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 4-3.

4.2.3 Dynamic mechanical analysis (DMA)

DMA measurements were carried out in order to analyze the phase behavior of the blends. The DMA measurements were done in the bending mode with a frequency of 1 Hz and a heating rate of 2°C/min by Perkin Elmer DMA 7. The ASTM standard Izod impact test specimens were used to perform the DMA measurements.

4.2.4 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 chloroform to dissolve the PPE phase out of the blends. The fractured surfaces of specimens were coated with thin film of gold to prevent charging.

4.2.5 Mechanical properties

An Instron Universal Testing Machine model 4201 was used to measure the mechanical properties of the uncompatibilized and compatibilized blends. Tensile tests were measured according to the ASTM D638 method with crosshead speed 5mm/min

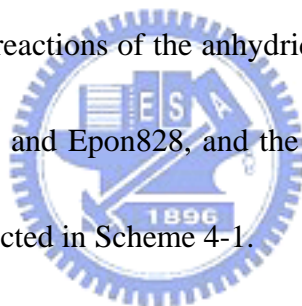
using at ambient conditions. Flexural tests were measured according to ASTM D790 method with 50mm span and 5mm/min test speed at ambient condition.



4.3 Results and Discussion

4.3.1 Chemistry

In reactive compatibilization, the chemical reactions between the functional groups of the polymers and the coupler are expected to occur in the interfacial layer 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 temperature, time and mixing efficiency. The main reactions involved in this study are the reactions of the anhydride groups of PP-g- MA with the epoxy groups of the TGDDM and Epon828, and the phenolic OH end group of low molecular weight PPE, as depicted in Scheme 4-1.



4.3.2 Dynamic mechanical analysis

4.3.2.1 Storage modulus

Except studying the molecular levels thermal transitions in polymeric materials, Dynamic mechanical analysis (DMA) is also useful in providing elastic modulus as a function of temperature in a wide temperature range [14]. The DMA plot of neat mPPO, PP and various PP/mPPO blends is shown in Figure 4-1, and is divided into three regions, except for that of the neat amorphous mPPO resin. The first region is

from -20 to 30 °C, representing the glassy transition of pure PP. The second region is the rubbery state of pure PP, ranging from 30 to 120 °C. In the third region, from 120 to 160 °C, the melting of pure PP and the glassy transition of pure mPPO take place.

It is interesting to note that in region II, the slope of storage modulus of neat PP,

PP/mPPO=70/30, PP/PP-g-MA/mPPO/lmw PPE = 60/10/20/20,

PP/PP-g-MA/mPPO/lmw PPE/Epon828 = 60/10/20/20/0.5phr and

PP/PP-g-MA/mPPO/lmw PPE/TGDDM = 60/10/20/20/0.5phr is almost the same and

quite steep. On the other hand, PP/PP-g-MA/mPPO/lmw PPE/Epon828 =

60/10/20/20/2phr and PP/PP-g-MA/mPPO/lmw PPE/TGDDM = 60/10/20/20/2phr

show a rather flatter slope of the storage modulus. In general, reactive compatibilized

blends have a broader interface than uncompatibilized ones, due to the lower

interfacial tension, caused by the in situ formed copolymers. A broader interface

means there will be more PP chains entangle with the mPPO chains. In region II

(rubbery state of PP) the mPPO is still in the glassy state, so only the amorphous PP

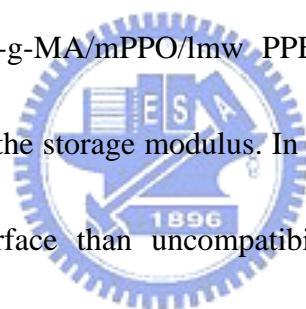
segments are able to do Brownian motion. If the PP/mPPO blend is well

compatibilized, i.e. broader interface and more mutual chain entanglements, the

Brownian motion of the PP segments might be restricted by the glassy mPPO

segments. As a result, compatibilized PP/mPPO blends will exhibit slope somewhere

between that of neat PP and neat mPPO. For uncompatibilized blends, due to the sharp



interface and few chain entanglements, the slope will be similar or close to that of neat PP. The DMA result indicate that PP/PP-g-MA/mPPO/lmw PPE/Epon828 = 60/10/20/20/2phr and PP/PP-g-MA/mPPO/lmw PPE/TGDDM = 60/10/20/20/2phr were better compatibilized than the others in the study.

4.3.2.2 Heat distortion temperature (HDT) VS storage modulus

One of the key performances of engineering plastics is the ability to withstand loads at elevated temperatures. HDT has been widely used as an indicator on the heat resistance of polymeric materials by the plastics industry. The detailed procedure on conducting HDT measurements can be found from the ASTM or ISO standard. The relationship between the modulus and HDT has been reported by Takemori [15]. Scobbo et al. [16,17] further utilized the storage-modulus plot obtained by DMA to predict the HDT. The loadings used in HDT, 264 psi and 66psi, for unreinforced and reinforced materials, respectively, have been converted to the modulus in the DMA test, when the failure deflection depth reaches 0.25mm. The conversion is based on a number of models and equations with the creep and thermal expansion effects been negligible. The calculated modulus is approximately 0.75 GPa and 0.1875 GPa, for 264 psi and 66 psi, respectively. Since in DMA test the modulus is usually represented on a logarithmic scale in units of Pa, the calculated modulus thus become 8.9 and 8.3, respectively. Scheme 4-2 shows how to use modulus-temperature plot to predict HDT.

The measured HDT will fall in the temperature vicinity where the storage modulus hit the value of 8.3. Applying this concept to the PP/mPPO blends in this study, it can be predicted that the better compatibilized blends will exhibit higher HDT, as shown in Figure 4-1. Therefore, the modulus-temperature relationship obtained by DMA can be adopted to judge the compatibilization efficiency and heat resistance prediction, before further characterizations and tests on the polymer blends.

4.3.3 Morphologies

In reactive compatibilized immiscible polymer blends, the in situ formed copolymers is expected to act as emulsifier and reduce the interfacial tension, resulting in finer domain size than uncompatibilized ones. SEM has been widely used as a powerful and convenient tool for qualitatively study on the dispersed phase size of immiscible polymer blends. The SEM pictures of various cryogenically fractured surfaces of PP/mPPO blends were given in Figure 4-2. A coarse morphology is found in the PP/mPPO = 70/30 blend [Figure 4-2(a)]. In comparison with PP/mPPO = 70/30 blend, a smaller domain size is observed for PP/PP-g-MA/mPPO/lmwPPO = 60/10/20/10 blend, as shown in Figure 4-2(b). As discussed in the previous chapter, the viscosity ratio is a key factor influencing the size of the dispersed phase. Addition of PP-g-MA and lmw PPE to the PP matrix and the mPPO phase, respectively, may change the viscosity ratio between the domain and matrix. Therefore, the observed

domain size reduction can be related to the changes in viscosity ratio. Further domain size reduction is achieved with the addition of both Epon828 and TGDDM [Figure 4-2(c) ~ (f)]. With increasing amount of both type of epoxy couplers, the size of the dispersed phase gradually reduced. However, the finest domain size is obtained with 2 phr TGDDM added [Figure 4-2(f)]. The TGDDM seems to be a more effective coupler than Epon828 in view of the size domain reduction. A similar trend was also found previously in the reactive compatibilized PET/PPE blends by Chang et al. [18]. As a result, the epoxy couplers, especially TGDDM can be considered as effective and economical additives for the reactive compatibilization of PPE based blends.



4.3.4 Mechanical properties

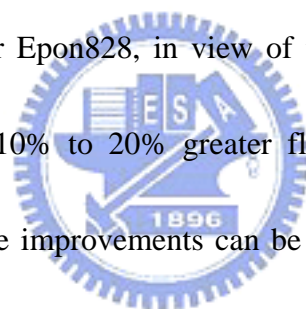
Figure 4-3 shows the tensile strength at break and flexural modulus of various uncompatibilized and compatibilized PP/mPPO blends. Due to the sharp interface and high interfacial tension, the mechanical properties of uncompatibilized PP/mPPO = 70/30 blend is poor. However, the worst mechanical properties falls in the PP/PP-g-MA/mPPO/lmwPPE = 60/10/20/10. Without a suitable coupler, the presence of PP-g-MA and lmwPPE are detrimental to the blends, due to the low molecular weight of both additives. With the addition of a coupler, the mechanical properties were improved with increasing amount of both Epon828 and TGDDM. The results

indicate that the epoxy couplers can react with both PP-g-MA and lmwPPE during the melt extrusion. The in situ formed PP-g-MA-co-epoxy-co-lmwPPE is able to act as effective compatibilizers and reduce the interfacial tension as well as strengthening the interface through chain penetration, resulting in better mechanical properties upon failure.



4.4 Conclusions

Immiscible PP/mPPO blends has been successfully reactively compatibilized. The stress modulus data obtained from DMA measurements shows the onset of the drop of the flexural modulus to failure in compatibilized blends can be extended. In other words, the HDT of the compatibilized blends are higher than the uncompatibilized ones. From the SEM pictures, the compatibilized blends also possess finer domain size, implying lower interfacial tension and broader interface between the blend components. The multifunctional epoxy monomer TGDDM is better than the bi-functional epoxy monomer Epon828, in view of the domain size reduction. The compatibilized blends have 10% to 20% greater flexural modulus and increased tensile strength. All the above improvements can be attributed to the in situ formed PP-g-MA-g-epoxy-g-lmw PPE copolymers, which are able to anchor along the interface and reduce the interfacial tension.



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. U.S. Patent 5166264
4. U.S. Patent 6495630
5. U.S. Patent 6855767
6. U.S. Patent 7022765
7. U.S. Patent 4990558
8. U.S. Patent 3522326
9. U.S. Patent 5124410
10. U.S. Patent 4876310
11. U.S. Patent 5262477
12. Japan Patent 06-287367
13. C. J. Hung, H. Y. Chuang and F. C. Chang, *J. Appl. Polym. Sci*, to appear.
14. T. Murayama, "Dynamic Mechanical Analysis of Polymeric Material", Elsevier, New York, 1978.
15. M. Takemori, SPE ANTEC, **24**, 216 (1994).
16. J. J. Scobbo and P. L. Cometti, SPE ANTEC, **40**, 3326 (1994)



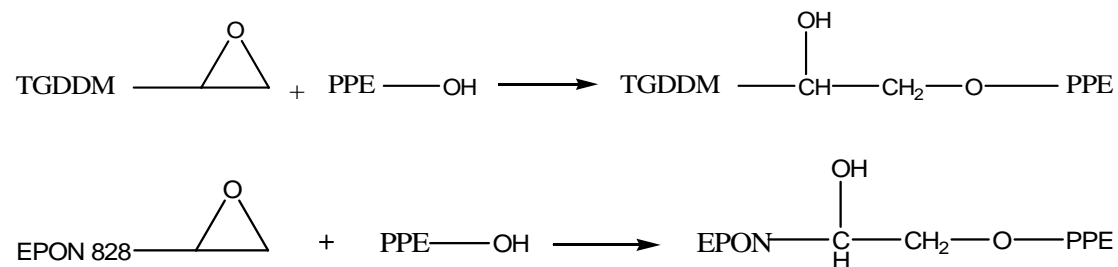
17. J. J. Scobbo, P. L. Cometti and P. J. Strom, SPE ANTEC, **40**, 3326 (1994)

18. D. W. Lo, C. R. Chiang and F. C. Chang, *J. Appl. Polym. Sci.*, 65, 739, 1997



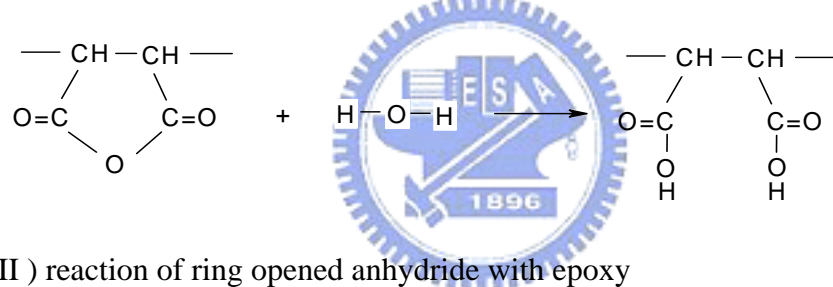
Scheme 4-1. Chemical Reactions Involved in the Study

(A) reaction of the epoxide of TGDDM and Epon828 with the phenolic OH of PPE

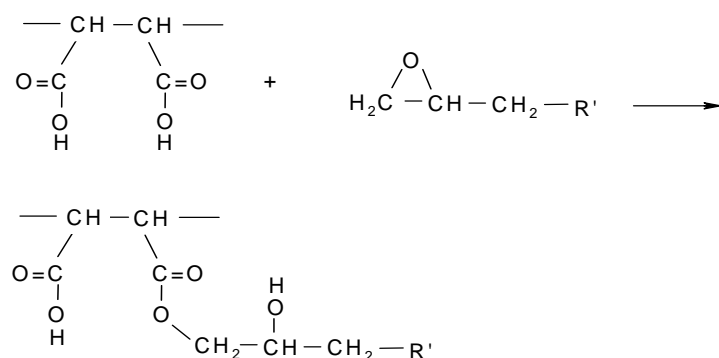


(B) reaction of maleic anhydride of PP-g-MA with the epoxide of TGDDM and Epon828

(I) ring opening reaction of anhydride by vapor water



(II) reaction of ring opened anhydride with epoxy



Scheme 4-2. Schematic Diagram Showing How to Use the Modulus Temperature Plot to Predict HDT.

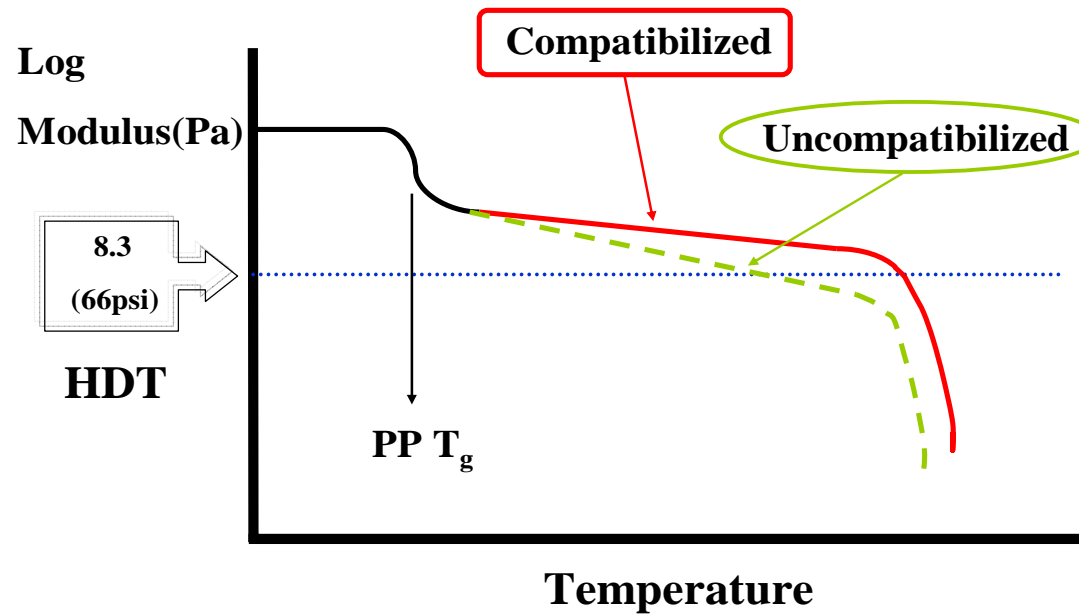


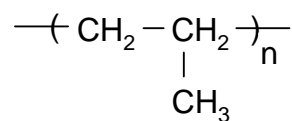
Table 4-1. Properties of Materials Used in this Study

Grade	Noryl N300	PPO SA120	PP 366-5	PP-g-MA	Epon828	TGDDM
Appearance	Pellet	Granule	Pellet	Pellet	Liquid	Liquid
Density (g/cm ³)	1.02	1.02	0.9	0.9	1.16	
T _g (°C)	215	160				
T _m (°C)			160	158		
Decomposition Temp (°C), TGA, N ₂	460	440				
Dielectric Constant	2.5	2.5				
Melt Viscosity (Pa.S) ^a	100,000 ^a	32 ^a			11~15 ^c	
Melt Index (g/10min) ^b				5.5 ^b	22 ^b	
M _w , GPC	60,000	6,300				
M _n , GPC	25,000	2,350				
Polydispersity Index	2.4	2.7				
Phenolic End Groups(μ mol/g), FTIR	< 80	425				
Epoxy Equivalency (g/eq)					185~192	110~130
MA content (wt%)				0.8		

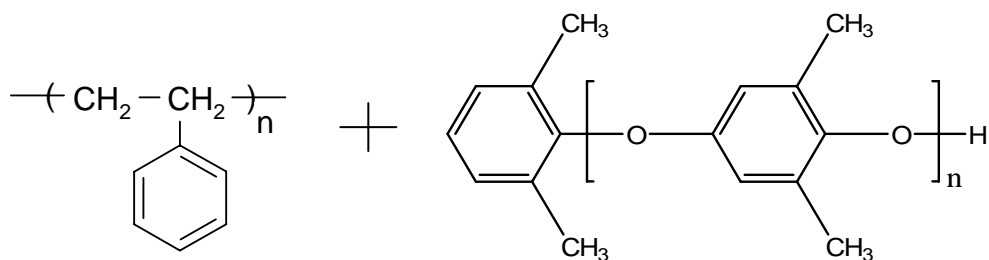
(a) @260°C, 1 rad/sec, (b) @230°C, 2.16Kg (c) @25°C

Table 4-2. Chemical Structure of Materials Used in this Study.

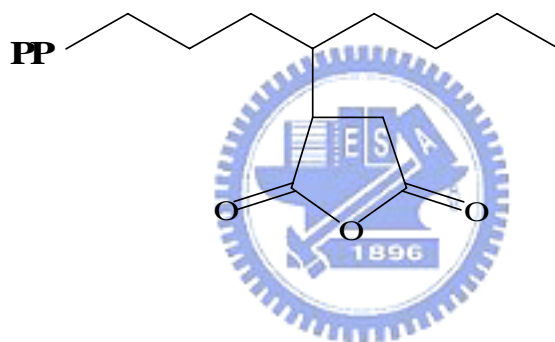
PP



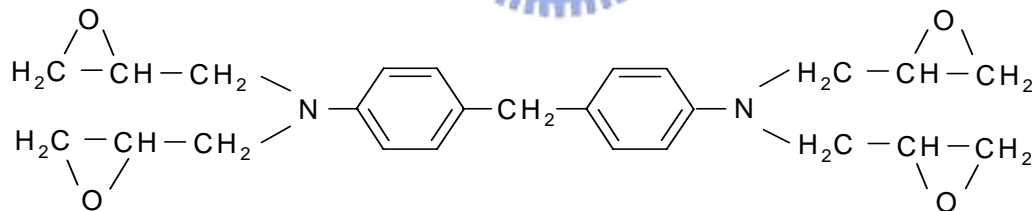
mPPO



PP-g-MA



TGDDM



Epon828

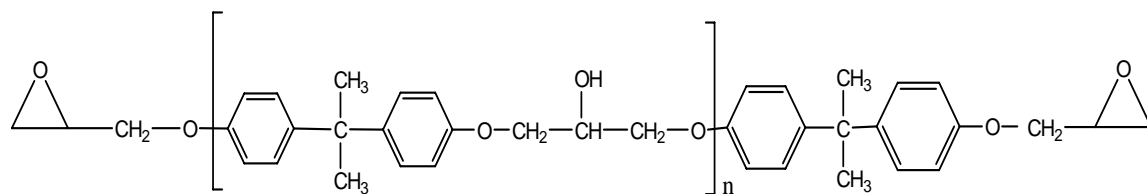


Table 4-3. Processing Conditions of Extrusion and Injection Molding

Stage	Temp (°C)									Die	Nozzle	Mold
	1	2	3	4	5	6	7	8	9			
<i>Extrusion</i>	150	180	200	220	240	260	260	255	255	260	-	-
<i>Injection</i>	245	260	255	-	-	-	-	-	-	-	260	70



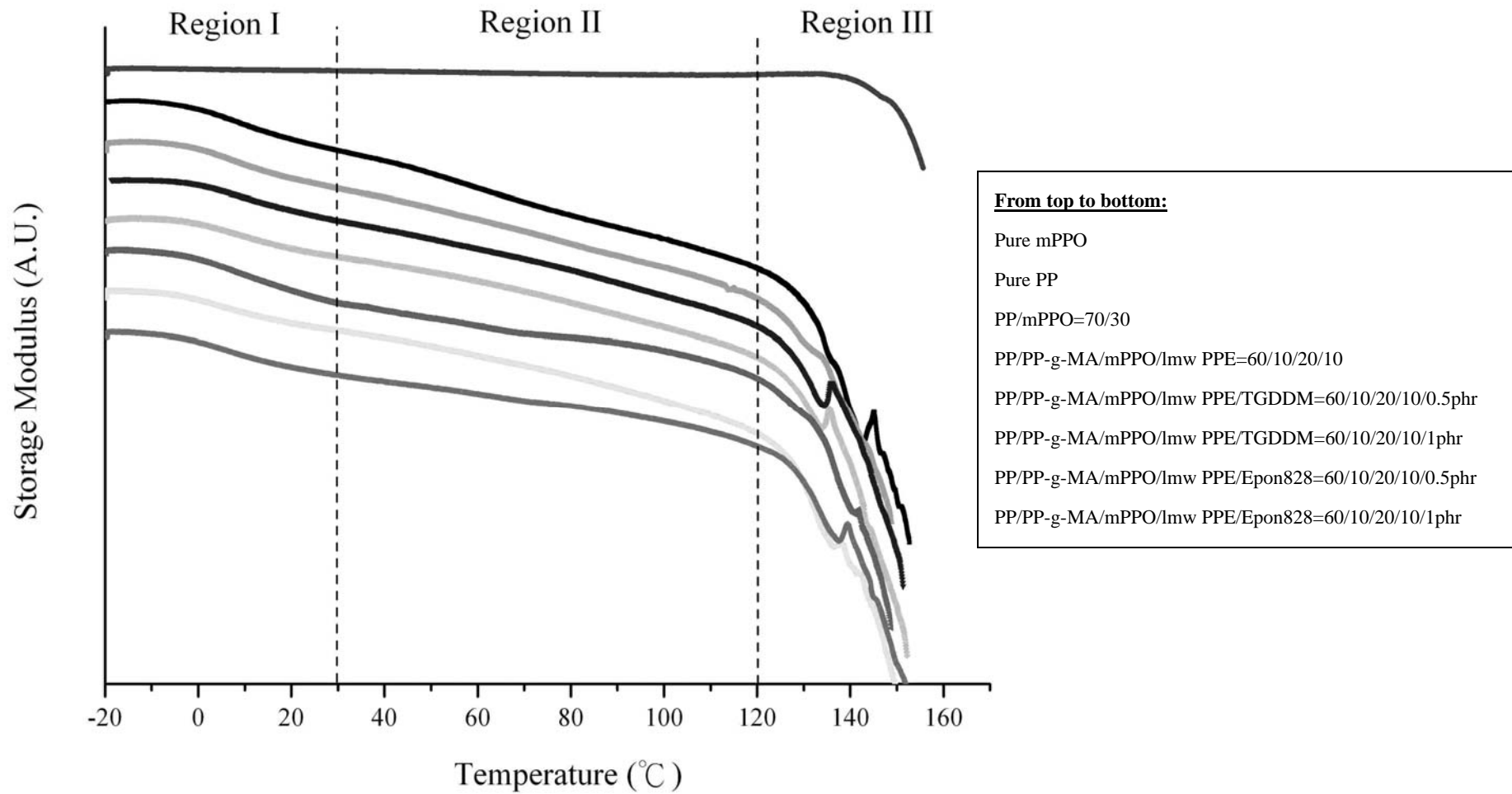


Figure 4-1. Modulus temperature plot of various PP/mPPO blends.

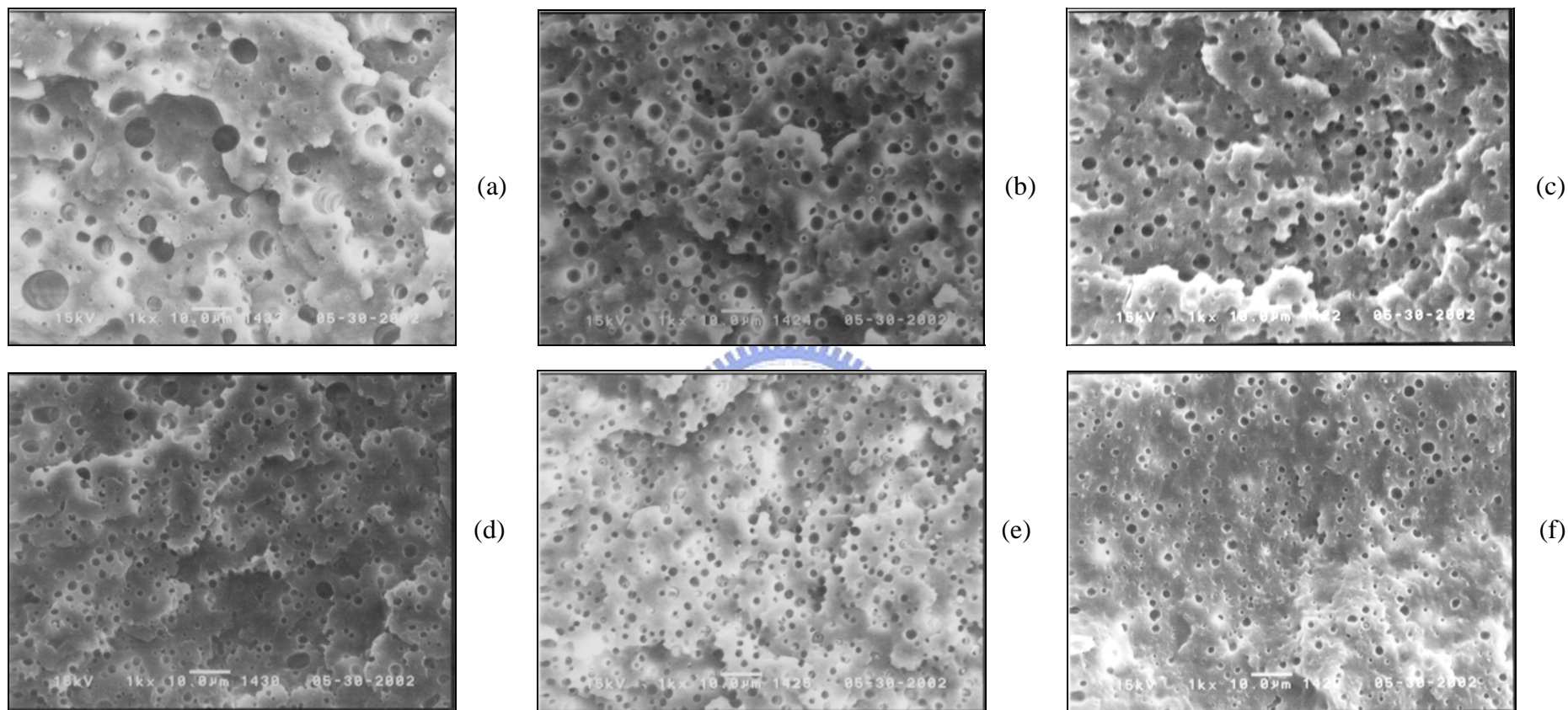


Figure 4-2. SEM micrographs of cryogenic fractured surfaces for various PP/mPPO blends ($\times 1K$): (a) PP/mPPO=70/30, (b) PP/PP-g-MA/mPPO/lmw PPE=60/10/20/10, (c) PP/PP-g-MA/mPPO/lmw PPE/Epon828=60/10/20/10/0.5phr, (d) PP/PP-g-MA/mPPO/lmw PPE/Epon828=60/10/20/10/2phr, (e) PP/PP-g-MA/mPPO/lmw PPE/TGDDM=60/10/20/10/0.5phr, (f) PP/PP-g-MA/mPPO/lmw PPE/Epon828=60/10/20/10/2phr.

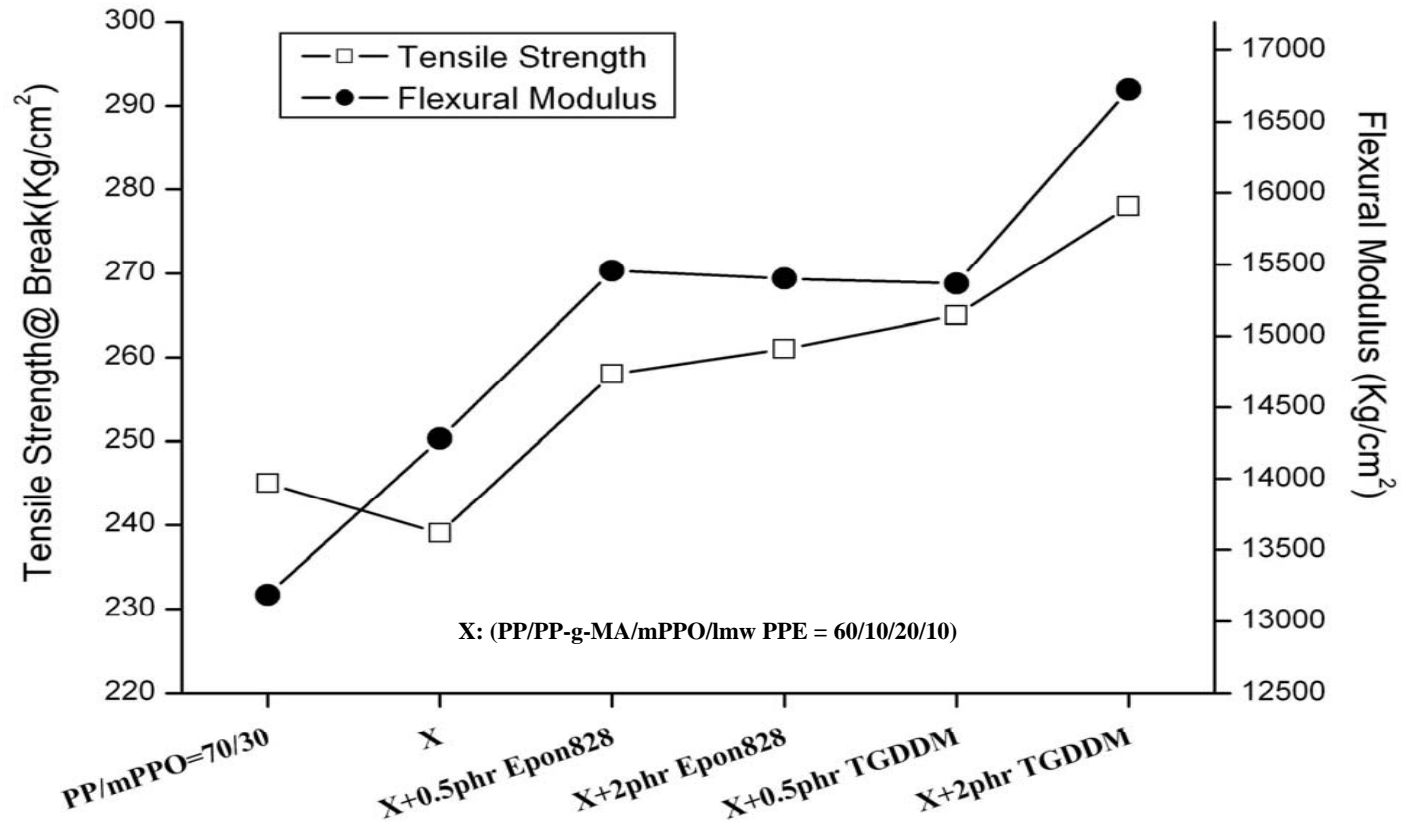


Figure 4-3. Tensile strength at break and flexural modulus of various PP/mPPO blends.