A Quantitative Estimation of the Extent of Compatibilization in Heterogeneous Polymer Blends Using Their Heat Capacity Increment at the Glass Transition

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ABSTRACT: In this paper a new method based on the determination of heat capacity increment at the glass transition (ΔCp) is presented to quantify the effectiveness of compatibilizers for immiscible polymer blends. In order to show the validity of the method, two immiscible blends, polypropylene–poly(ethylene terephthalate) (PP–PET) and PP–polyamide-6,6 (PP–PA66), and two compatibilizers, *N, N*-dihydroxyethyl monomaleic amide–grafted PP (g–PP) alone and together with a phenolic resin (PR), were investigated. Scanning electron microscopy (SEM) observations prove that the two compatibilizer systems are both effective for compatibilizing the blends, and the combined use of g–PP and PR is more effective than g–PP alone. Modulated-temperature differential-scanning calorimetry (M-TDSC) determinations reveal that the ΔCp varies with the extent of compatibilization. For the uncompatibilized blends, the ΔCp for the PET component in PP–PET or for the PA66 component in PP–PA66 was found to be almost unchanged. After compatibilization these quantities become smaller. Also, the combined use of g–PP and PR results in the smallest ΔCp values for both blends. This ΔCp change with different compatibilizers is in very good agreement with the corresponding morphological variation observed by SEM. Thus, ΔCp can be taken as a new parameter for quantifying the extent of compatibilization, since it is a direct measure of interfacial content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2868–2876, 1999

Key words: compatibilizing efficiency; heat capacity increment; heterogeneous polymer blends

INTRODUCTION

Polymer blends have certainly become a big family of organic materials and are still expanding rapidly because they may combine advantages of both the component polymers.[1] The properties of heterogeneous polymer blends are dominated by their morphologies and the extent of adhesion between the microphases.[2] In order to achieve a suitable morphology and acceptable interfacial adhesion, compatibilization is usually necessary because most polymer pairs are inherently immiscible.[3] During the past few decades a large number of papers have discussed the control of morphology and the improvement of interfacial adhesion through compatibilization.[4–12] It is now widely accepted that effective compatibilization usually leads to the reduction of interfacial ten-

sion and the strengthening of interfacial adhesion.[3] As a result, the blends show reduced dispersed-phase domain sizes and improved mechanical properties. Therefore, the changes of morphology and properties have been taken as both evidence and a qualitative description for compatibilizing effectiveness.[9,10] However, the morphology of a polymer blend is more or less dependent on the processing technology, and, in turn, the resulting morphology has an effect on the properties of the blend.[3,13] It is not enough to assess compatibilizing effectiveness merely by the changes in morphology and properties. Besides the morphology, it is believed that the improved interfacial adhesion caused by compatibilization contributes greatly to the ultimate properties of the blends.[3,9,13,14] Unfortunately, it is not easy to characterize quantitatively the interfacial adhesion by means of existing techniques. Barlow[14] previously used a lap shear test to measure macroscopically the degree of adhesion between blend components and found that the obtained lap shear strengths were proportional to the mechanical properties of the blends.

In this article a maleic anhydride derivative–grafted polypropylene and a phenolic resin were used to compatibilize polypropylene (PP) and poly(ethylene terephthalate) (PP–PET) and PP and polyamide-66 (PP–PA66) blends. A new method developed by Hourston and his coworkers[15–17] was used to monitor the changes in interface content induced by compatibilization. The main purpose was to relate the interface content to the morphology and physical properties of the blends and hence to present a method for quantitative assessment of the effectiveness of compatibilization of different compatibilizers.

EXPERIMENTAL

Materials

The polypropylene (grade: PP 1600; MFI was 7.5 g/10 min) used in this work was produced by the Yanshan Petroleum Chemical Group Corporation, China. Polyethylene terephthalate (intrinsic viscosity in *m*-dichlorobenzene was 0.68 g/dL) and the polyamide-66 were provided by FuRong Engineering Thermoplastics Company, China. The *N,N*-dihydroxyethyl monomaleic amide–grafted PP (g-PP) was prepared by reactive extrusion in our laboratory. (The fed maleic anhydride derivative was 8.0 phr based on PP, and the grafting level

was 6.4 phr determined by an extraction procedure. The g-PP was used, as prepared, without removal of the unreacted maleic anhydride derivative.) Phenolic resin (PR, trade name: Phenolic 2402) was purchased from the Guangzhou Chemical Materials Company, China.

Extrusion Blending of PP–PET and PP–PA66

The blending of PP with PET or PA66 were carried out by extrusion, using a corotating twin-screw extruder with a screw diameter of 35 mm and a L/D ratio of 40. The screw rate was set at 30 rpm. The barrel of the extruder had eight temperature-control zones, and their temperatures were set at (from feeding section to die): 160, 260, 280, 290, 290, 290, 270, and 260°C. Before blending, the compositions were dried overnight in a vacuum oven at 120°C and then used immediately. The extrudates were cooled by passing through a water bath and were then pelletized. The pelletized blends were again dried in a vacuum oven at 120°C for 10 h. The dried-blend pellets were made into sheets of 4 mm thickness by compression moulding at 170°C and then cut into specimens according to the corresponding ASTM standards.

Characterization

Scanning Electron Microscopy (SEM)

The morphologies of PP–PET and PP–PA66 blends were observed using a Cambridge Instruments Stereoscan 360 scanning electron microscope.

Thermal Analysis

Analysis by modulated-temperature differential scanning calorimetry (M-TDSC) was performed using a model 2920 calorimeter from TA Instruments. The running conditions were: oscillation amplitude, 1.0°C; oscillation period, 60 s; heating rate, 3°C/min; and N_2 flow rate, 60 mL/min. All samples were first heated to 280°C and then quenched in liquid nitrogen so as to prevent the PET component from crystallizing and to ensure the same thermal history. M-TDSC data were processed using Graphware software from TA Instruments.

RESULTS AND DISCUSSION

Compatibilization Efficiency

It is well known that effective compatibilization leads to small phase sizes because the compatibi-

lizers at the interphase of a blend can reduce the interfacial tension and prevent the coalescence of the domains. Therefore, the morphological changes caused by compatibilization have been taken as an indication of compatibilizing efficiency. As shown in Figure 1, the morphologies of PP–PET blends have changed significantly by incorporating the two compatibilizers. Without compatibilizer, the blend shows an irregular PET phase, and a large fraction of the domains is fiberlike [Fig. 1(a)]. The addition of compatibilizers produces regular shapes and relative uniformity of size of the PET domains. Furthermore, there is also a big difference in PET domain sizes produced by different compatibilizers. By comparison of Figures 1(b) and 1(c), it is obvious that g-PP is not as effective as g-PP and PR together. For the g-PP compatibilized system, the reduction of PET domain size results from the improved interaction between the two phases. During blending the two hydroxyls of the g-PP may esterify with carboxyls at PET chain ends and transesterify with the main chain ester groups of the PET at the phase boundaries. Both reactions lead to formation of graft copolymers of PP and PET. The presence of the graft copolymers at the interfaces reduces interfacial tension and therefore PET domain size. For the g-PP and PR compatibilized blend, the PET domain size decreases further due to the addition of PR. This is because PR is a polar resin and has many phenolic hydroxyl and hydroxymethyl groups. These functional groups increase the possibilities of esterification and transesterification. Meanwhile, the hydroxymethyl groups in PR may also condense with the pendent hydroxyl groups on g-PP. In consequence, the formation of graft copolymers at the boundaries between the two phases is strongly enhanced, leading to a remarkable decrease in PET domain size.

Figure 2 shows the morphologies of PP–PA66 blends. All three samples are cocontinuous along the direction of extrusion, while in the transverse direction the PA66 is the dispersed phase. Once again, incorporating the same two compatibilizers produces significant differences in morphology. This can be clearly seen both in cross-sectional and longitudinal surfaces (Fig. 2). As shown in Figures 2(a) and 2(aa), without compatibilizer, the PA66 cylinders in the PP matrix exhibit large cross sections with irregular shapes and diameters. Even gaps at the interfaces are obvious in the pelletized cross-sectional surfaces [Fig. 2(a)]. After compatibilization with g-PP, the PA66 phase becomes more regular in shape and
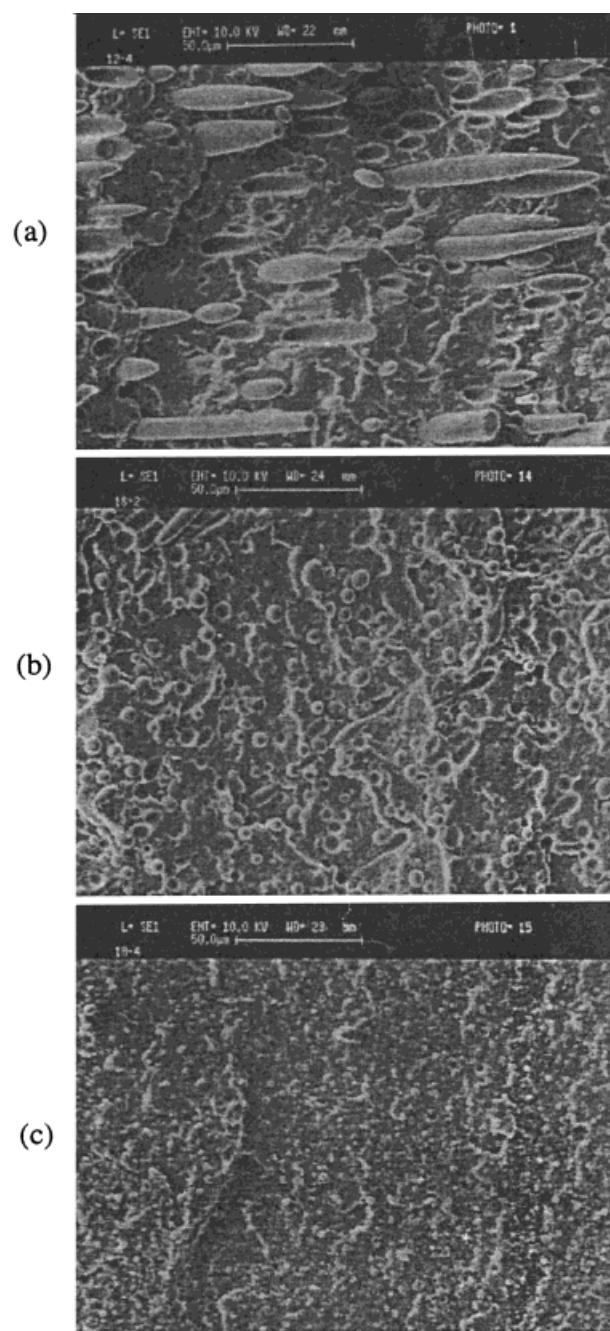

Figure 1 SEM micrographs of impact fracture surfaces of PP–PET blends (blend composition: PP/Compatibilizer/PET = 80/5/20 weight ratio): (a) without compatibilizer; (b) g-PP 5.0 wt %; (c) g-PP 3.0 wt % and PR 2.0 wt %.

smaller in diameter, as can be seen in Figure 2(bb). A shear flow morphology is still observed, and the interfacial separation cannot now be seen in the cross-sectional surfaces [Fig. 2(b)]. This means that the g-PP has the ability to some ex-
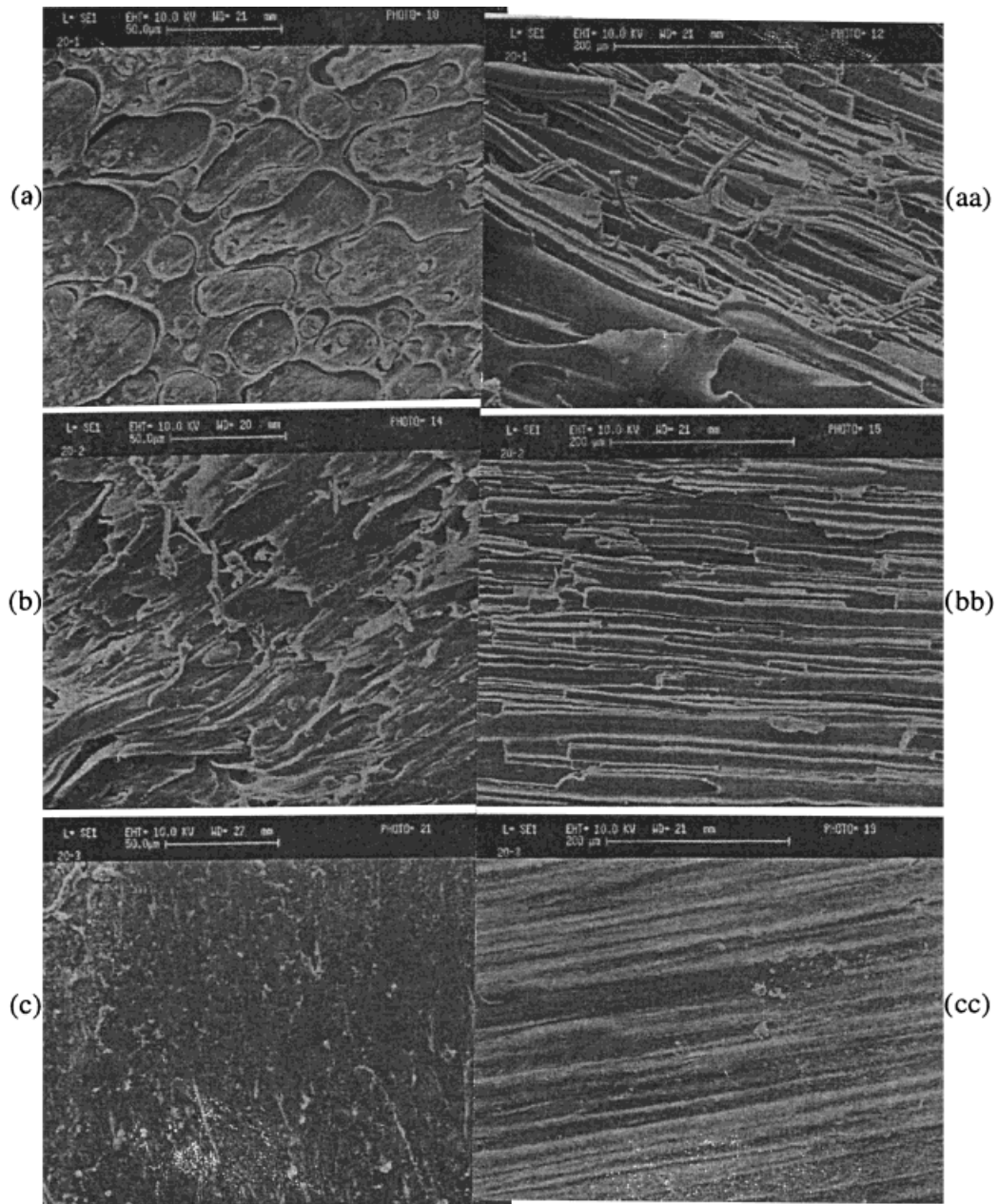
Figure 2 SEM micrographs of the PP–PA66 blends (blend composition: PP/compatibilizer/PA66 = 60/4/40 weight ratio): (a) and (aa) without compatibilizer; (b) and (bb) g-PP 4.0 wt %; (c) and (cc) g-PP 2.0 wt % and PR 2.0 wt %. Left column: cross sections of the pellets; Right column: longitudinal sections fractured after cooling with liquid nitrogen.

tent to stabilize the morphology and improve interfacial adhesion. For the blend compatibilized with g-PP and PR, the two-phase morphology cannot be distinguished in the cross-sectional surfaces [Fig. 2(c)]. Although the PA66 cylinders can be observed in the longitudinal sections [Fig. 2(cc)], it is difficult to distinguish the interfaces.

This morphology suggests good interfacial adhesion in the blend. The better compatibilizing effectiveness of the g-PP and PR together may be due to hexamethylenetetramine, the curing agent for PR, grafting onto the PA66 main chains through reaction with the hydrogens on the amide groups. This reaction, as well as the ones

discussed above, raises the possibility of formation of graft copolymers at the interfaces.

The above morphological analyses prove that both compatibilizing systems are effective for PP–PET and PP–PA66 blends. The effectiveness of compatibilization of g-PP and PR together is higher than g-PP alone.

The Influence of Compatibilization on Thermal Properties

The significant changes in morphology discussed above suggest the increase of interfacial areas in the two kinds of blends after compatibilization. This implies that the interfacial compositions of the blends are also a function of compatibilization.

In this experiment, M-TDSC was used to characterize the interfacial contents of both kinds of blends with different compatibilizing extents. Figures 3 and 4 show the melting peaks of the PP components in the PP–PET and PP–PA66 blends, respectively. It is seen that although the melting temperatures (T_m) for PP components remain unchanged, their melting enthalpies (ΔH_m) change with compatibilization and are all lower than that of pure PP (Tables I and II). With reference to morphology, it is clear that enhanced compatibilization leads to lower ΔH_m values. This may be due to the increase in interfacial content and the consequent decrease in weight fraction of bulk PP.

For the PET components in the PP–PET blends, the T_m and ΔH_m values are all lower than those for pure PET, as shown in Figure 5 and

Figure 3 M-TDSC thermograms of the melting peaks for the PP component in the PP–PET blends. The same samples as in Figure 1. The signal for neat PP is scaled to 0.8 times its original value.
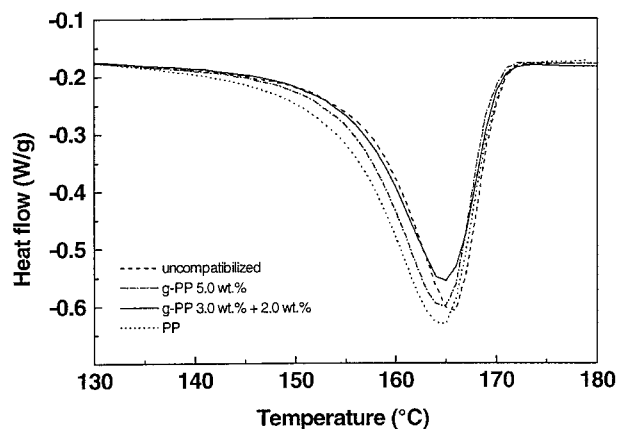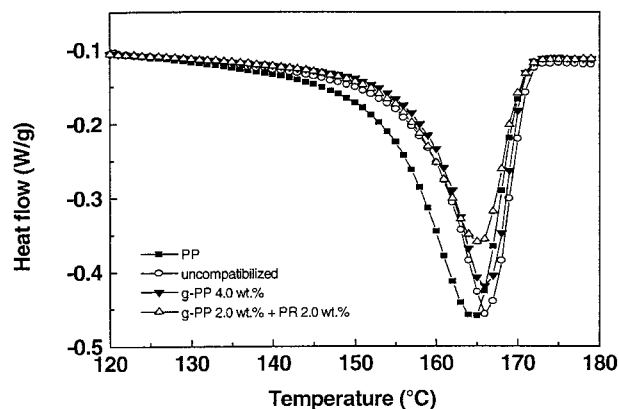

Figure 4 M-TDSC thermograms of the melting peaks for the PP components in the PP–PA66 blends. The same samples as in Figure 2. The signal for neat PP is scaled to 0.6 times its original value.

Table I. The blends, uncompatibilized (blend 1) and compatibilized by g-PP (blend 2), have similar T_m and ΔH_m values, while the blend compatibilized with g-PP and PR (blend 3) shows much lower T_m and ΔH_m values. This change in ΔH_m conforms to that of the PP component and therefore can be explained as a result of a decrease in the amount of bulk PET. It can also be observed that the change in T_m is related to the PET domain size: the smaller the PET domain size, the lower the T_m value. This result may originate from the effect of interfacial tension between the two phases.

Figure 6 shows the melting regions of the PA66 component in the PP–PA66 blends and the pure PA66. The variations of the T_m and ΔH_m values for PA66 components with compatibilization (Table II) exhibit a similar trend to the PET components in the PP–PET blends, but the change in T_m for the PA66 component is not as much as for the PET component. This is because the weight fraction of PA66 in the PP–PA66 blends is larger than that of PET in the PP–PET blends.

Figure 7 shows the crystallization process of the PET component in the PP–PET blends and that of the pure PET. The temperatures of crystallization (T_c) for the blends drop to much lower values than that of the pure PET. As listed in Table II, the uncompatibilized blend gives the lowest T_c (101°C), which is 24°C lower than that of the pure PET (125°C). The compatibilized blends show T_c values about 6°C higher. The dramatic decrease in T_c values may result from a PET nucleating effect by the PP component. Bourland[18] reported a similar observation in a

Table I   M-TDSC Data for the PP–PET Blends (PP/compatibilizer/PET = 75/5/20 weight ratio)

Sample	Compatibilizer	PP Component				PET Component					
		T_g (°C)	ΔCp (mJ/g/°C)	T_m (°C)	ΔH_m (J/g)	T_g (°C)	ΔCp (mJ/g/°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PET	—	—	—	—	—	77	69.8[b]	125	7.5[b]	257	13.5[b]
PP	—	5	46.6[a]	165	104.1[a]	—	—	—	—	—	—
Blend 1	—	3	44.4	166	95.0	68	66.2	101	5.8	254	11.5
Blend 2	g-PP 5.0 wt %	5	49.4	165	96.3	67	58.6	106	6.0	253	11.6
Blend 3	g-PP 3.0 wt % + PR 2.0 wt %	4	42.7	165	85.5	66	35.8	107	2.7	250	5.7

[a] 0.8 times the values determined with neat PP.
[b] 0.2 times the values determined with neat PET.

study of PET crystallization containing various nucleating agents, including PP. The somewhat higher T_c values for compatibilized blends may be due to the change in the interfacial state. The occurrence of an interfacial layer may restrict the nucleating effect by the PP component to some extent. With respect to the heat of crystallization (ΔH_c) for the PET component, the blends, both uncompatibilized and compatibilized with g-PP, have nearly the same values, which are slightly smaller than that of the pure PET. On the other hand, the ΔH_c value for blend 3 is much lower than that of the others. The variation of ΔH_c for the PET component shows an analogous profile to that of ΔH_m, though ΔH_c values are about half the magnitude of the ΔH_m values. The lower ΔH_c values suggest that the same cold crystallization of the PET components had occurred before the DSC determination. Xanthos[19] reported similar results.

M-TDSC is superior to conventional DSC in determining the glass transition.[20] In M-TDSC

thermograms, the glass transition is displayed as a peak when the differential signal of heat capacity versus temperature is plotted (see Fig. 8). This means the peak plus the onset and final temperatures of the glass transition can be precisely determined. Hence, the increment of heat capacity at the glass transition (ΔCp) can also be obtained precisely from the following integration, since ΔCp is the peak area of the glass transition region:

$$\Delta Cp = \int_{T_1}^{T_2} (dCp/dT)\ dT = \int_{T_1}^{T_2} dCp \qquad (1)$$

T_1 and T_2 are the onset and final temperatures of the glass transition region, respectively.

It is well known that the heat capacity of matter is a characteristic constant at a given temperature and pressure. The ΔCp of a pure material is also a specific constant under fixed conditions of

Table II   M-TDSC Data for the PP–PA66 Blends (PP/compatibilizer/PA66 = 60/4/40 weight ratio)

Sample	Compatibilizer	PP Component				PA66 Component			
		T_g (°C)	ΔCp (mJ/g/°C)	T_m (°C)	ΔH_m (J/g)	T_g (°C)	ΔCp (mJ/g/°C)	T_m (°C)	ΔH_m (J/g)
PA66	—	—	—	—	—	44	63.1[b]	261	41.3[b]
PP	—	5	35.0[a]	165	78.1[a]	—	—	—	—
Blend 4	—	−2	23.0	166	72.1	43	64.5	261	39.9
Blend 5	g-PP 4.0 wt %	−2	16.8	166	68.0	41	53.3	261	36.3
Blend 6	g-PP 2.0 wt % + PR 2.0 wt %	−2	13.8	166	60.6	38	48.6	257	27.1

[a] 0.6 times the values determined with neat PP.
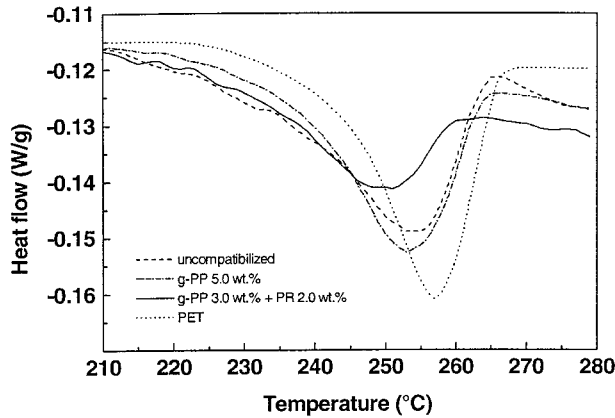[b] 0.4 times the values determined with neat PA66.

Figure 5 M-TDSC thermograms of the melting peaks for the PET component in the PP–PET blends. The same samples as in Figure 3. The neat PET signal is scaled to 0.2 times its original value.
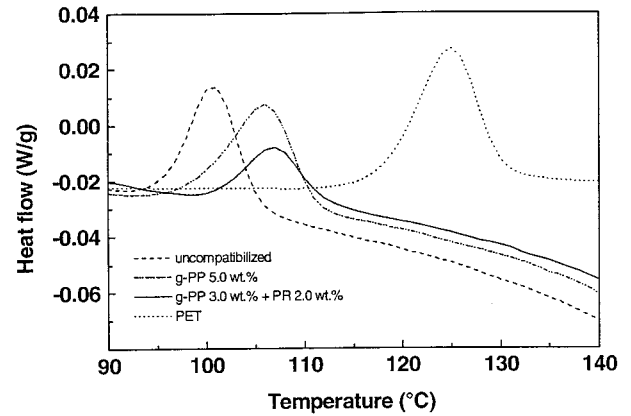

Figure 7 Crystalline peaks for the PET components in the PP–PET blends. The same samples as in Figure 3. The neat PET signal is scaled to 0.2 times its original value.

determination, whether it is in the bulk state or dispersed in another medium. This feature provides a effective way to investigate interfacial contents of polymer blends. That is, the ΔCp of the ith component in a fully phase-separated blend must be exactly the product of that in its pure state multiplied by its weight fraction in the blend. In a compatibilized or partially miscible blend, however, a portion of the ith component is not in the equivalent phase but mixes with a portion of other components to form interfaces. So, the ΔCp of the ith component becomes smaller because of this net reduction of the component in the blend. Thus the change of ΔCp values before and after blending provides a criterion to estimate compatibility of the blend.

$$\delta\Delta Cp = \omega\Delta Cp^0 - \Delta Cp$$

$$\begin{cases} = 0, \text{ the blend is fully incompatible} \\ = \omega\Delta Cp^0, \text{ the blend is fully compatible} \\ > 0 < \omega\Delta Cp^0, \text{ the blend is partially compatible} \end{cases}$$

ΔCp and ΔCp^0 are heat capacity increments in the blend and pure state, respectively, and ω is the weight fraction of the ith component in the blend.

In addition to being merely a qualitative description, $\delta\Delta Cp$ can also be applied as a quantitative estimation of the extent of compatibilization, since its magnitude is a direct measure of any change in interfacial content of the blend.
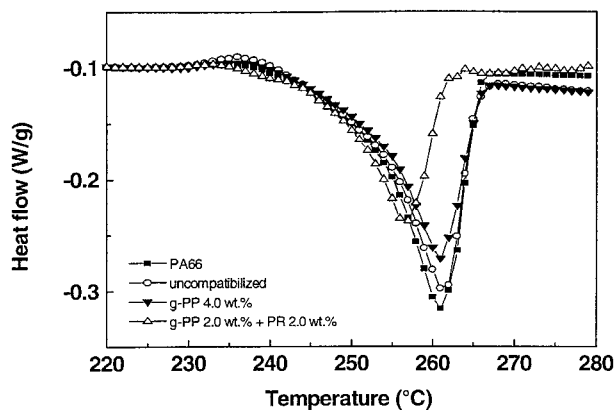

Figure 6 M-TDSC thermograms of the melting peaks for the PA66 component in the PP–PA66 blends. The same samples as in Figure 4. The neat PA66 signal is scaled to 0.4 times its original value.
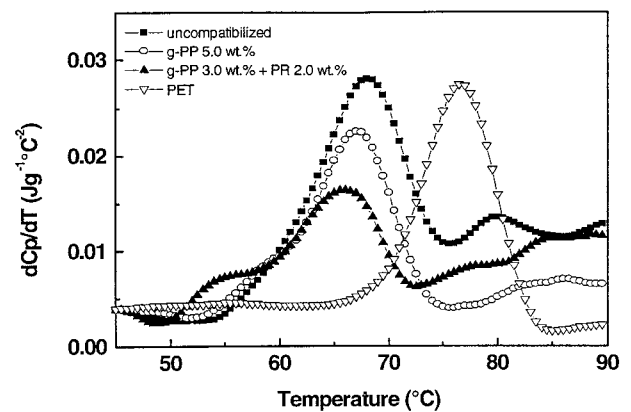

Figure 8 The glass transition of the PET component in the PP–PET blends. The same samples as in Figure 3. The neat PET and PP signals are scaled to 0.2 and 0.8 times their original values.

In this article, M-TDSC was used to estimate the compatibilizing efficiency of two compatibilizers for both PP–PET and PP–PA66 blends. Figure 8 shows the differential of heat capacity (dCp/dT) for the PET component versus temperature signals over the glass transition region. It is clear that the base lines for the blends drift with temperature. This is typically encountered in M-TDSC determinations involving semicrystalline polymers. The theoretical solution for this problem has not been achieved yet. However, in this case it is certain that the baseline drift is due to the presence of the crystalline PP component because there is no baseline drift for the amorphous PET, as shown in Figure 8. Therefore, the signal response to the PP component was subtracted before performance of the integration of eq. (1). There may still be some variation from the true value of ΔCp, but it is believed that the method should give a result much closer to the true value than merely using a straight line drawn between the onset and final points of the glass transition region.[21] The obtained ΔCp values and the peak temperatures, T_g, are listed in Table I. It is clearly seen that the ΔCp becomes smaller after compatibilization, and its magnitude varies with the compatibilizer used. For the uncompatibilized blend, the ΔCp value is very close to the product of $\omega \Delta Cp^0$, indicating that the blend is essentially immiscible. After being compatibilized with g-PP (blend 2), the ΔCp decreases. According to the loss of ΔCp listed in Table I, about 16 wt % of the PET component in blend 2 has been removed from its equivalent bulk phase. This fraction of the PET mixes with a portion of PP to form the interfaces. For blend 3 the ΔCp value is only half of $\omega \Delta Cp^0$, implying that nearly half the PET in blend 3 exists in the interfaces. It is important to note that the ΔCp trend with compatibilization strongly agrees with the morphological variations: a larger PET domain size gives a larger ΔCp value, and vice versa. As discussed above, a larger ΔCp means a lower $\delta \Delta Cp$ and therefore a lower interface content.

Figure 9 shows the glass transitions of PA66 components displayed as dCp/dT versus temperature signals. The treatment of the baseline is the same as in Figure 8. The ΔCp values and T_g obtained are listed in Table II. These results are actually analogous to Figure 8. The uncompatibilized blend shows a ΔCp value of nearly the same as the product of $\omega \Delta Cp^0$, while the compatibilized blends give lower ΔCp values. For blend 5 the PA66 component lost to the interface, calculated
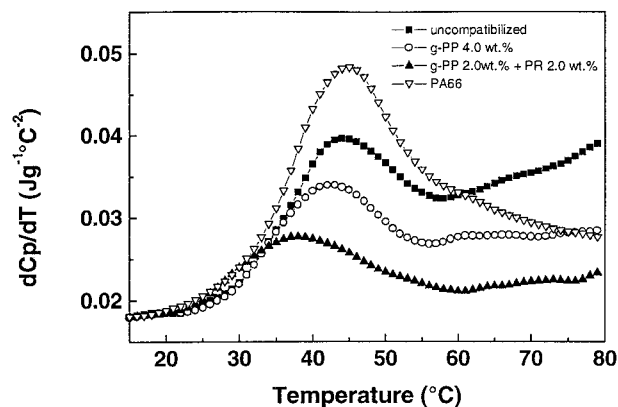

Figure 9 The glass transition of the PA66 component in the PP–PA66 blends. The same samples as in Figure 4. The neat PA66 and PP signals are scaled to 0.4 and 0.6 times their original values.

from its ΔCp, is 16 wt %, and for blend 6 this quantity is 23 wt %. This result once again shows the difference in compatibilizing efficiency of the two compatibilizers. Again, the ΔCp trend is consistent with the morphological variations shown in Figure 2. Smaller ΔCp values indicate good interfacial adhesion because of the increase in interfacial content.

The above discussion confirms that ΔCp is a very useful parameter to describe the compatibility of multicomponent blends. This is because ΔCp is directly related to the interfacial contents in the blends. Therefore, the relative magnitude of the ΔCp values shows the variation of the extent of compatibilization and can be taken as a quantitative measure of the effectiveness of compatibilizers.

CONCLUSIONS

The SEM analysis proves that the PET domain sizes and PA66 cylinder diameters in the blends become smaller and more uniform after the addition of compatibilizer. The combined use of g-PP and PR results in the smallest PET domain sizes in the PP–PET and PP–PA66 blends. This means that the two compatibilizing systems are both effective for the PP–PET and PP–PA66 blends and that the combined use of g-PP and PR is more effective than g-PP alone.

The M-TDSC studies show that T_m, ΔH_m, T_g, and ΔCp for the PET and for the PA66 components in the blends all decrease after compatibilization. The variation in extent is dependent on

the compatibilizer used, indicating the change in interfacial interaction between the two phases in the blends. The increase in T_c and the decrease in ΔH_c for the PET component caused by compatibilization is also evidence of enhanced interfacial interaction. However, the most sensitive and important parameter for quantitative characterization of the degree of compatibilization is found to be ΔCp. This is because the change of ΔCp is actually a measure of interfacial content. The trends of ΔCp with compatibilization for the PET and PA66 components in the blends show the same profile as the morphological changes. Thus, the magnitude of ΔCp values provide a quantitative measure of the degree of compatibilization.

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