

Modulated differential scanning calorimetry: 4. Miscibility and glass transition behaviour in poly(methyl methacrylate) and poly(epichlorohydrin) blends

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(Received 8 November 1995; revised 20 March 1996)

The differential of heat capacity signal, dC_p/dT , from modulated-temperature differential scanning calorimetry (M-T d.s.c.) was used to elucidate the miscibility and glass transition behaviour of poly(methyl methacrylate) (PMMA) and poly(epichlorohydrin) (PECH) blends. The conclusion reached was the same as that reported by Higgins and co-workers (Clark, J.N., Higgins, J.S., Kim, C.K. and Paul, D.R. *Polymer* 1992, **33**, 3137) from small-angle neutron scattering, but different from that of Fernandes (Fernandes, A.C. Ph.D. Dissertation, University of Texas at Austin, 1986) from a d.s.c. study. This M-T d.s.c. study reveals that PECH/PMMA blends are not fully miscible. More detailed information was obtained from the dC_p/dT signal. In this blend system, there were PMMA-rich, PECH-rich phases and interfaces, indicating that the blend is partially miscible. The breadth of the glass transition region, ΔT_g , can be used to judge polymer–polymer miscibility. For polymer blends, ΔT_g as a miscibility criterion was considered to obey the following relation:

$$\Delta T_g = w_1 \Delta T_{g,1} + w_2 \Delta T_{g,2}$$

where w_1 and w_2 are the weight fractions for polymer 1 and polymer 2, and $\Delta T_{g,1}$ and $\Delta T_{g,2}$ are the glass transition widths for polymer 1 and polymer 2, respectively. Partial miscibility results in a broad transition region. The width of the transition may be indicative of the presence of microphase separation and of interfaces. The M-T d.s.c. dC_p/dT signal provides increased sensitivity and resolution for studying polymer–polymer miscibility and multiphase polymer materials. Copyright © 1996 Elsevier Science Ltd.

(Keywords: miscibility; modulated d.s.c.; glass transition)

INTRODUCTION

The most widespread method of determining polymer–polymer miscibility is by observing the glass transition temperature, T_g , behaviour. Miscible blends will have a single T_g at some intermediate value between the T_g s of the two components. The most common method for measuring T_g is by thermal analysis, particularly d.s.c. So far, many miscible polymer pairs have been found^{1–8}. However, in some reported miscible systems^{6–8}, the breadth of glass transition region, ΔT_g , which is the difference between the completion and onset temperatures, is quite broad. For some blend systems⁷, ΔT_g values approach 100°C. The transition region can also be

highly asymmetrical. Because d.s.c. does not have sufficient sensitivity and lacks resolution, overlapping thermal events, which include overlapping T_g s and signals from interfaces resulting from partial miscibility, cannot be separated. Consequently, we believe that some incorrect conclusions^{6,7} have been made. Some polymer blends which have quite broad ΔT_g s have been reported^{6,7} as miscible blends.

Recently, a new thermal analysis instrument, modulated-temperature d.s.c. (M-T d.s.c.)⁹, has been introduced. A review¹⁰ has already been published by Reading. One of the advantages of M-T d.s.c. is that overlapping thermal events can be separated¹⁰. The differential of heat capacity signal, dC_p/dT , from M-T d.s.c. is very sensitive to the glass transition process¹¹. In this paper, the miscibility and glass transition behaviour of

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poly(epichlorohydrin) (PECH) and poly(methyl methacrylate) (PMMA) blends were analysed by using the dC_p/dT signal. These results were compared with literature results from small-angle neutron scattering (SANS). ΔT_g as a miscibility criterion is also discussed.

EXPERIMENTAL

Materials

PECH and PMMA were obtained from Aldrich. The M_w value of PMMA was 1.98×10^5 and the M_w/M_n ratio was 2.03, and the M_w value of PECH was 1.95×10^5 and the M_w/M_n ratio was 2.5, as determined by gel permeation chromatography (Waters, model 510) calibrated with standard polystyrene (PS) samples. Other polymers used in this study were PS from B.P. Chemicals, poly(phenylene oxide) (PPO) from Aldrich and poly(vinyl chloride) (PVC) also from Aldrich. Their M_w values were 2.1×10^5 , 2.4×10^5 and 3.3×10^5 , respectively. The corresponding M_w/M_n ratios were 2.3, 3.2 and 2.8.

Sample preparation

The PECH/PMMA blends were cast from 5 wt% toluene solutions and dried under vacuum at 60°C for 20 days.

Instrumentation

An M-T d.s.c. calorimeter manufactured by TA Instruments was used. An amplitude of 1.0°C, an oscillation period of 60 s and a heating rate of 3°C min⁻¹ were used throughout this investigation.

RESULTS AND DISCUSSION

Figure 1 shows the change of heat capacity with temperature for selected compositions determined by M-T d.s.c. The sets of thermograms appear to offer essentially the same interpretation as the results from Higgins¹² and Fernandes⁷. From these results, only a single and broad T_g transition is indicated for compositions up to 30 wt% of PECH. At 15 wt% of PECH there is evidence of two transitions. The conclusion seems to be for most compositions that the blend is miscible. However, SANS results reported by Higgins and co-workers¹² showed this blend system to possess two phases, indicating that it is essentially immiscible. The changes of dC_p/dT with temperature for PECH/PMMA blends at compositions of 100/0, 85/15, 70/30, 50/50, 30/70, 15/85 and 0/100 (wt/wt) were checked. The results are shown in Figure 2. The dC_p/dT signals give detailed and clear information about miscibility. For pure PECH and PMMA, the glass transition peaks are highly symmetrical. For the 85/15 PECH/PMMA blend, the glass transition peak shows the same behaviour as pure PMMA or PECH. This implies that this blend composition is miscible. For the 70/30 PECH/PMMA blend, the transition is obviously also symmetrical. However, there is a weak transition occurring between 40 and 100°C. For the 50/50 PECH/PMMA blend, the transition peak is asymmetrical, and exhibits a shoulder. For the 30/70 PECH/PMMA blend, there is obviously phase separation occurring. The dC_p/dT signal shows two transition peaks. Because the two components have very similar refractive indices¹², it is very difficult to

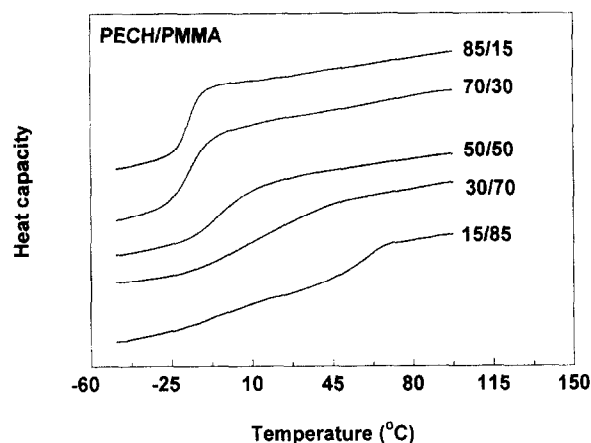


Figure 1 Heat capacity versus temperature for PECH/PMMA blends

check the phase behaviour using optical methods. For the 15/85 PECH/PMMA blend there are two well-separated transitions, indicating that the 15/85 PECH/PMMA blend is immiscible.

Table 1 shows the T_g and ΔT_g values for the PECH/PMMA blends. ΔT_g is defined as shown in Figure 2g. Clearly, ΔT_g values for the PECH/PMMA blends are quite large.

For the PMMA, the onset temperature was about 80°C. For the PECH, the completion temperature is about -18°C. Obviously, the large ΔT_g values do not arise because the completion of the lower transition and the onset of the higher transition cannot be resolved as has been suggested¹² by previous workers. The fact is that the blend systems exhibit a distribution of phases with continuously varying composition. The PECH/PMMA blends are partially miscible. The partial miscibility causes the large ΔT_g values. From Figure 1, it can be suggested that most of the PECH forms a mixed phase with PMMA for the 50/50 PECH/PMMA blend. However, for the 30/70 PECH/PMMA blend, there are PECH-rich and PMMA-rich phases.

PS blended with PPO and PVC blended with PMMA are miscible systems^{1,5}. Their ΔT_g changes with composition were also checked. These results are shown in Figures 3 and 4 for the PPO/PS and the PVC/PMMA blends, respectively. The following approximate relationship between ΔT_g , $\Delta T_{g,1}$ and $\Delta T_{g,2}$ may be suggested:

$$\Delta T_g \sim w_1 \Delta T_{g,1} + w_2 \Delta T_{g,2}$$

where w_1 and w_2 are the weight fractions of polymer 1 and polymer 2, respectively, and $\Delta T_{g,1}$ and $\Delta T_{g,2}$ are the widths of the glass transition regions for polymers 1 and 2, respectively. The deviation, δT_g ($\delta T_g = \Delta T_g - w_1 \Delta T_{g,1} - w_2 \Delta T_{g,2}$) is very small for fully miscible systems. Table 2 shows the change of δT_g with composition for the PECH/PMMA, PS/PPO and PVC/PMMA blends. Clearly, immiscible systems showed larger δT_g values.

SANS is able to distinguish between microphase separation and concentration fluctuations¹². For PECH/PMMA blends, SANS results¹² showed the data for four blend compositions (PECH/PMMA = 70/30, 50/50, 30/70 and 15/85) were very similar (see Figure 9 in Clark *et al.*¹²). There was no obvious trend in scattered intensity with composition. These data were fitted by

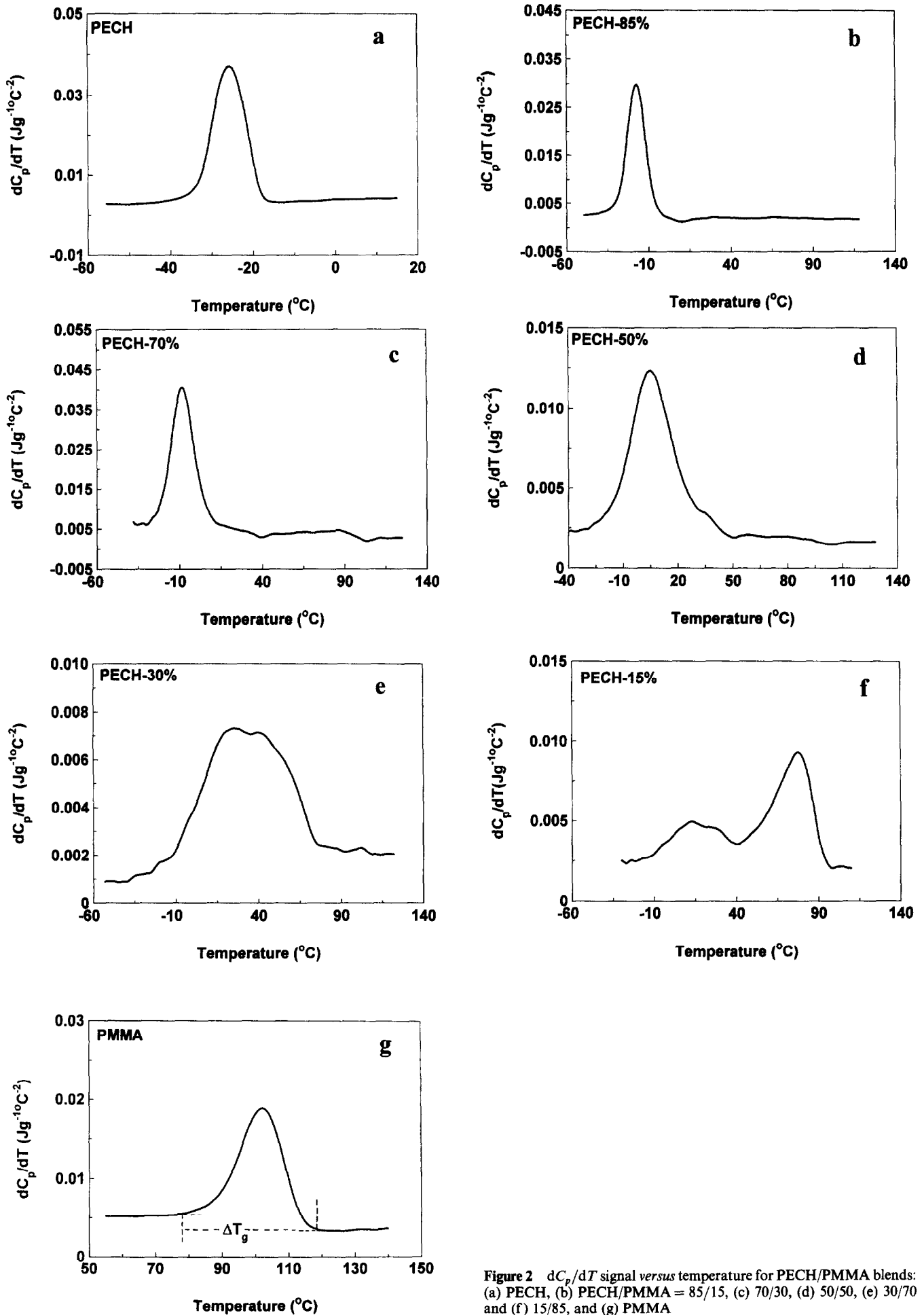


Figure 2 dC_p/dT signal versus temperature for PECH/PMMA blends: (a) PECH, (b) PECH/PMMA = 85/15, (c) 70/30, (d) 50/50, (e) 30/70 and (f) 15/85, and (g) PMMA

Table 1 T_g and ΔT_g for the PMMA/PECH blends

PECH/PMMA	T_g (°C)	ΔT_g (°C)	Correlation length (Å) ^a
100/0	-26	20	—
85/15	-17	26	—
70/30	—	65	140
50/50	—	80	370
30/70	—	100	470
15/85	Two phase transitions observed		
0/100	102	40	—

^a Values were obtained from Clark *et al.*¹²

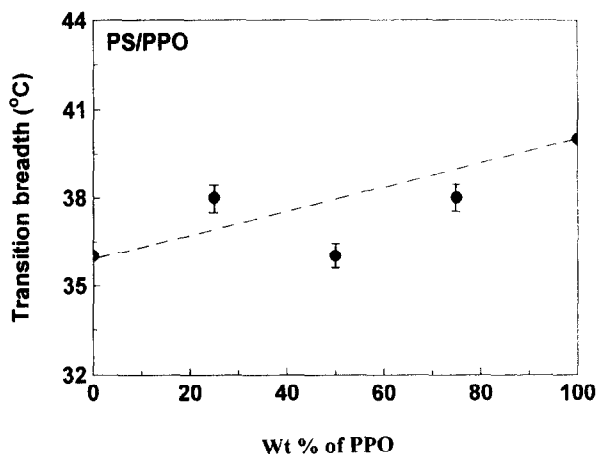


Figure 3 Transition width *versus* composition for PS/PPO blends

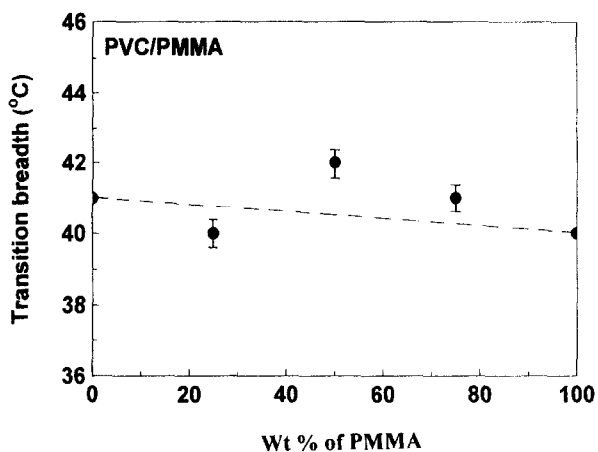


Figure 4 Transition width *versus* composition for PVC/PMMA blends

a two-function scattering law, indicating that the sample was phase separated, but within the domains, single-phase scattering laws prevail. These results¹² showed that it is more probable that the very large concentration fluctuations which give rise to the Debye-Bueche neutron scattering are also responsible for the extraordinarily large ΔT_g values found in this blend. Obviously, because the curves for the four blend compositions¹² are very similar, it is difficult to obtain more detailed information about morphology and concentration distribution in domains from the SANS results. From the dC_p/dT *versus* temperature signal for the four PECH/PMMA blend compositions, it can be

Table 2 Increment of transition width for the PECH/PMMA, PS/PPO and PMMA/PVC blends

Blend	δT_g (°C)
PECH/PMMA	
100/0	0
85/15	5
70/30	39
50/50	50
30/70	66
0/100	0
PS/PPO	
100/0	0
75/25	1
50/50	-2
25/75	-1
0/100	0
PMMA/PVC	
100/0	0
75/25	1
50/50	2
25/75	-1
0/100	0

seen that the four dC_p/dT signals with temperature are very different.

From above discussion, it is concluded that the dC_p/dT signal from M-T d.s.c. can readily yield very useful information about polymer-polymer miscibility.

Figure 5 suggests for PECH/PMMA blends that there is some correlation between the δT_g measured by M-T d.s.c. and the correlation lengths measured by SANS¹². Obviously, more detailed work is needed in this area.

CONCLUSIONS

It has been shown that the dC_p/dT signal from M-T d.s.c. is a useful tool in studying polymer-polymer miscibility. Comparing the heat capacity and the dC_p/dT signals of PECH/PMMA blends, the dC_p/dT signal shows higher sensitivity and resolution than does the heat capacity signal. The dC_p/dT signal from M-T d.s.c. showed that PECH/PMMA blends are partially miscible. From conventional d.s.c., a dC_p/dT signal is only obtained with considerable difficulty because the

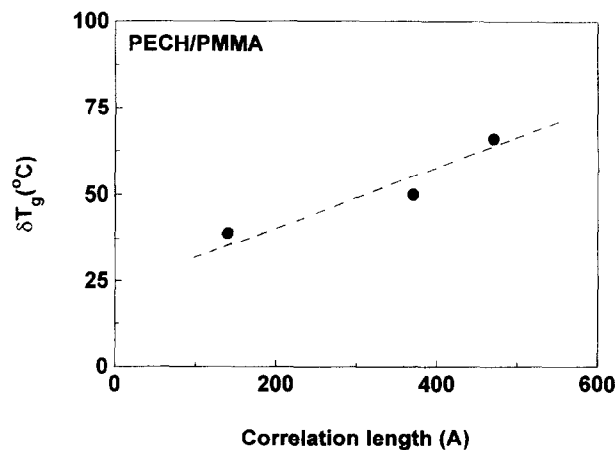


Figure 5 Increment of transition width *versus* correlation length for PECH/PMMA blends

relaxation part of the signal cannot be separated from the total heat flow as it can in M-T d.s.c.

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