ELSEVIER

Thermochimica Acta 337 (1999) 179–186

thermochimica acta

www.elsevier.com/locate/tca

Separation of glass transition and melting in polyethylene/poly(butyl-methacrylate-*co*-methyl-methacrylate) interpenetrating polymer networks in TMDSC and DSC curves

G. Pompe[a,*], U. Schulze[a], J. Hu[a], J. Pionteck[a], G.W.H. Höhne[b]

[a]*Institut für Polymerforschung Dresden e.V., Hohe Str. 6, D-01069 Dresden, Germany*
[b]*Universität Ulm, Sektion Kalorimetrie, Albert-Einsteinallee 11, D-89081 Ulm, Germany*

Received 5 May 1999; accepted 31 May 1999

Abstract

Temperature modulated DSC (TMDSC) was tested concerning the possibility to separate the glass transition of the copolymer (BMA-*co*-MMA) component from the melting effect of the polyethylene (PE) in PE/BMA-*co*-MMA interpenetrating polymer networks prepared by in situ polymerisation. It was shown that a direct separation of both effects using TMDSC is not possible. The influence of the (excess) specific heat capacity of PE on the measured curve in the range of the glass transition of the copolymer is not negligible. With the TMDSC results of pure cross-linked PE (and because of the high accuracy of TMDSC) a procedure was found to estimate both the step height $\Delta c_p(T_g)$ and the temperature T_g of the glass transition of the copolymer phase. Additionally, an estimation of the degree of cross-linking of the PE phase is possible.

The accuracy of standard DSC measurements is insufficient to apply successfully the procedure of data analysis developed for analysis of TMDSC results. In this case, the method of inflection point gives the chance to estimate the glass transition temperature of the copolymer phase. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: DSC; Temperature modulated DSC (TMDSC); Interpenetrating polymer networks; Cross-linking; Glass transition

---

1. Introduction

The formation of interpenetrating polymer networks (IPN) is practically the only way to combine two or more cross-linked polymers in a fine dispersion. This technology offers the possibility to obtain materials with combined properties of the components. IPN films based on polyethylene (PE) and poly(butyl-methacrylate-*co*-methyl-methacrylate) (BMA-*co*-MMA) were prepared by in situ polymerisation above the melting temperature of PE [1–4]. Since, besides cross-linking also grafting reactions between both phases occurred during the synthesis, the prepared films are IPN-like systems [2,4], abbreviated IPN in this paper.

A useful quantity for the characterisation of these processes is the glass transition temperature. The glass transition temperature T_g of the copolymer phase in the IPN should decrease after cross-linking and should increase after grafting to the PE phase. The exact determination of T_g (BMA-*co*-MMA) is not straightforward, because the glass transition of the methacrylic phase takes place in the same temperature range as the melting of PE. A separation of both effects is therefore necessary. Normally, dynamic

---

*Corresponding author. Fax: +49-0351-4658284
E-mail address: gpompe@argos.ipfdd.de (G. Pompe)

PII: S0040-6031(99)00164-1

mechanical analysis (DMA) is the preferred method for that purpose. However, the required sample geometry cannot always be realised.

The aim of this work was to test the TMDSC method for the characterisation of the thermal behaviour of the PE/BMA-*co*-MMA IPN. Using differential scanning calorimetry (DSC) and temperature modulated DSC (TMDSC) the problems concerning the separation of both processes will be discussed.

2. Experimental

2.1. Materials

The investigated interpenetrating polymer networks consist of 20 wt% PE and 80 wt% copolymer. The copolymer phase is cross-linked by addition of 1 mol% butanediol dimethacrylate cross-linker. The PE phase cross-links due to the added peroxide initiator. The synthesis of the IPN is described in [1]. The MMA content of the copolymer phase is 40, 50, or 60 mol%, respectively, which causes an increase of the glass transition temperature of the copolymer phase [3]. An overview to the IPN used in this work is given in Table 1. Additionally, samples of pure PE, unirradiated and electron beam irradiated with 400 and 800 kGy were measured. The results of irradiated PE give information about the influence of cross-linking on the PE melting behaviour [6]. The measurements were performed on films of about 5 mg (pure PE) or 10 mg (IPN) with a thickness of about 0.3 mm. Two states of the IPN samples were investigated: (i) the initial state and (ii) the recrystallised state obtained after melting followed by cooling at 10 K/min. For the analysis of experimental data the PE contribution in the IPN was described by the parameter n. The value $n = 5$ corresponds to the averaged PE content of 20 wt%.

2.2. Methods

A Perkin-Elmer DSC 7 with Pyris-Software was used in the standard as well as in the modulated mode. The standard measurements (heat–cool–heat ramps) were carried out at the scan rate of ± 10 K/min in the temperature range from $-60°C$ to $+150°C$.

The TMDSC measurements were realised from $-10°C$ to $+150°C$ with saw-tooth modulation. The parameters applied resulted in a temperature amplitude of 0.3 K, a time period of 24 s, and an underlying heating rate of 2 K/min, respectively.

Temperature and heat calibration were done with In and Pb standards at a heating rate of 10 K/min. To reduce the influence of heat transfer to and within the sample on the measured results, the samples were prepared as film and the Al pans containing the sample were pressed at about 50 MPa to obtain an as good as possible thermal contact. Nevertheless, a considerable change of phase shift of the modulated signal was observed in the PE melting region. Therefore, we preferred the magnitude of the complex specific heat capacity $|c_p|$ rather than the real part for further evaluation.

3. Results

3.1. TMDSC measurements

On starting our investigations we expected that the influence of the melting of the PE phase (i.e. 1/5 of the

Table 1
Data characterising the measured samples

Material	Sample	PE (feed, wt%) [1]	BMA : MMA (feed) mol ratio [1]	PE (wt%) [1]	PE (wt%)[b]	Gel content (wt%)
PE[a]	Virgin					0
	Irradiated with 400 kGy					83 [5]
	Irradiated with 800 kGy					90 [5]
IPN	M10–40	19.3	40:60	(30.4)	20	≈95 [1]
	M10–50	18.8	50:50	21.4	24	≈95 [1]
	M10–60	18.3	60:40	17.4	24	≈95 [1]

[a] LDPE: Bralen RA 2-19 (Slovnaft, Slovak Republic) with MFI = 2 g/10 min.

[b] Estimated using the transition heat (crystallisation and melting of the second heating).

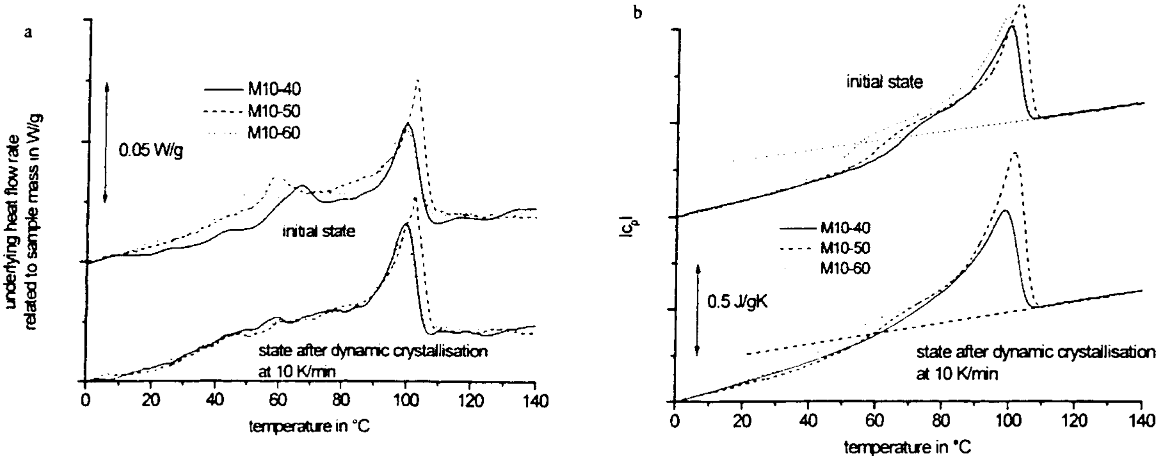

Fig. 1. TMDSC curves of IPN, measured in the initial and the recrystallised state (a) underlying heat flow rate normalised in relation to sample mass; (b) magnitude of specific heat capacity.

sample) should be negligible in the TMDSC signal and that $|c_p(T)|$ should be mainly determined by the copolymer phase. Unfortunately this is not the case, as can be seen in Fig. 1. The underlying heat flow rate curve (i.e. the conventional DSC curve) for the IPNs in the initial state and in the state after dynamic crystallisation at 10 K/min are plotted in Fig. 1(a). The pre-peak in the curves of the initial samples is assumed to be related to the enthalpy relaxation of the amorphous copolymer phase. The maximum temperature of this pre-peak increases with the increasing MMA content of copolymer. The comparison of peak temperature and height of the main peak, caused by PE phase melting, shows that the degree of cross-linking of PE seems to be smaller in M10–50 than in the samples M10–40 and M10–60 [2]. Probably, this is caused by differences in the synthesis conditions of the IPNs. The curves of the recrystallised samples do not show any remarkable differences in the region of the glass transition of the copolymer phase.

The corresponding specific heat capacity magnitudes $|c_p(T)|$ are plotted in Fig. 1(b). The $|c_p(T)|$ curves of all IPNs are rather identical in the melt. This confirms the high reproducibility of c_p measurements with TMDSC, one of the advantages of this method! However, the $|c_p(T)|$ curves contain, nevertheless, contributions of the melting of the PE phase, even in the temperature region of the glass transition of the copolymer phase. This effect appears to be less significant for the initial samples than for the recrystallised ones. For accurate evaluation of the glass transition a further analysis of the experimental data is necessary, in particular for the results of measurements obtained from IPNs after recrystallisation of the PE phase.

In what follows, the influence of cross-linking on the melting behaviour of PE will be discussed using the results of unirradiated and irradiated PE shown in Fig. 2. The decreasing melting temperature and the decreasing heat of melting are correlated to increasing cross-linking by increasing irradiation [2,6]. For a

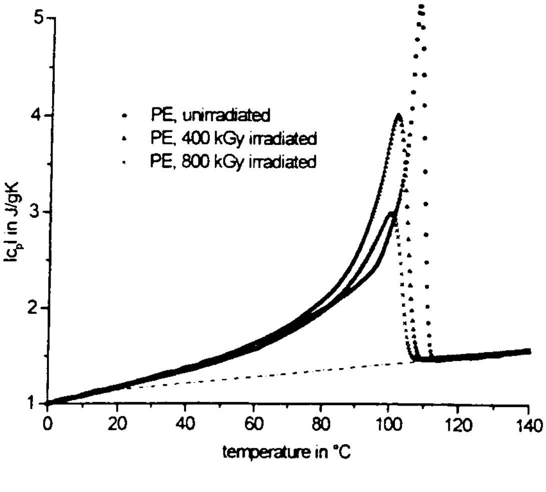

Fig. 2. TMDSC curves of magnitude of specific heat capacity $|c_p(T)|$ for PE, unirradiated and irradiated, measured in the recrystallised state.

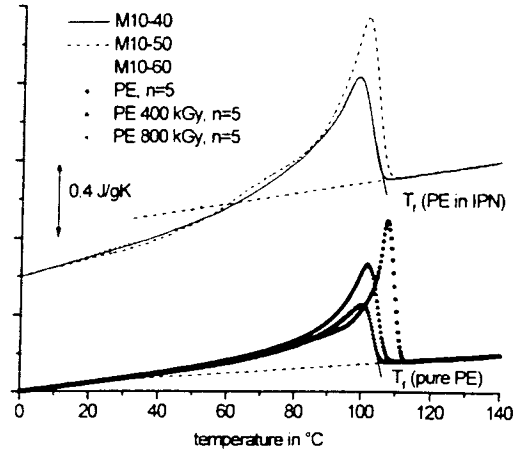

Fig. 3. TMDSC curves of magnitude of specific heat capacity $|c_p(T)|$ for IPN in the recrystallised state and for the contribution of the PE-phase calculated with $n = 5$ from PE sample runs.

direct comparison of the melting behaviour of the PE phase in IPN and that of pure PE, the measured curves of unirradiated and irradiated PE were adapted to the real mass fraction of PE in the IPN by division with 5 (Fig. 3). The PE melting curve of the IPN seems similar to that of cross-linked PE. Comparing the extrapolated offset temperature T_f of the PE melting peak (marked in Fig. 3) an assignment can be given: the melting behaviour of PE in IPN M10–40 and M10–60, which are more cross-linked, is similar to that of PE irradiated with 800 kGy, while the melting behaviour of M10–50 is similar to that of PE irradiated with 400 kGy. However, the degree of crystallinity of PE in the IPN is higher than that of pure PE, this follows from comparing the peak areas in relation to mass fraction.

To separate the glass transition of copolymer phase in the $|c_p(T)|$ curve of IPN from the contribution of PE melting we divided the respective curves of pure PE by a number n, which was chosen to give the best fit of the $|c_p(T)|$ curve of the cross-linked pure PE to that of the IPN in the melting region. For IPN M10–40 and M10–60 this was achieved with $n = 3$ and PE irradiated with 800 kGy and for IPN M10–50 with $n = 3.5$ and PE irradiated with 400 kGy, respectively (see Fig. 4(a)). Obviously, the cross-linking in the IPN results in a higher crystallinity than the cross-linking by irradiation in pure PE, although the maximum temperature T_m and the extrapolated offset-temperature T_f of the PE melting peak characterising also the degree of cross-linking, are very similar. Apparently, the character of cross-linking caused by irradiation and by in situ synthesised IPN are not directly comparable. In addition, $|c_p(T)|$ of the PE contribution plotted in Fig. 4(a) was shifted and sloped that way to get an identical curve with $|c_p(T)|$ of IPN in the temperature region from 110°C to 150°C (i.e. the melt).

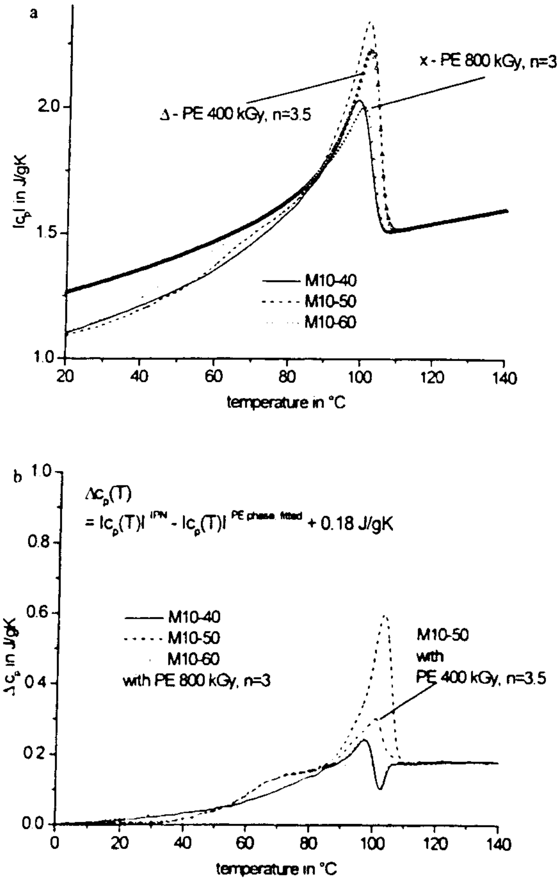

Fig. 4. (a) TMDSC curves of magnitude of specific heat capacity $|c_p(T)|$ for IPN in the recrystallised state and for the contribution of the PE-phase calculated with $n = 3$ for PE irradiated with 800 kGy and with $n = 3.5$ for PE irradiated with 400 kGy; (b) Differences $\Delta c_p(T)$ of $|c_p(T)|^{\mathrm{IPN}}$ and $|c_p(T)|^{\mathrm{PE\ phase,\ fitted}}$ measured in the recrystallised state (for details see text).

The high precision of the experimental values enables a very exact fit. As a result $|c_p(T = 20°\mathrm{C})|$ of the PE phase curve, fitted this way, is about 0.18 J/g K higher than $|c_p(T = 20°\mathrm{C})|$ of the IPN. This difference of 0.18 J/g K is the same for all investigated states within 0.1 J/g K. This finding can be explained as follows: the mass fraction of the copolymer phase to the IPN is 0.8 (Table 1) and the glass transition step height of the specific heat capacity of pure copolymer amounts to 0.23 J/g K [3,7]. From these data the step height of the copolymer phase in the IPN should be 0.184 J/g K. This value is in good agreement with the observed difference of 0.18 J/g K. The difference $\Delta c_p(T)$, shown in Fig. 4(b), can be calculated:

$$\Delta c_p(T) = |c_p(T)|^{\mathrm{IPN}} - |c_p(T)|^{\mathrm{PE\,phase,fitted}} + 0.18\,\mathrm{J/g\,K}.$$

On the whole, the result represents $|c_p(T)|$ of the copolymer phase content of IPN. In the temperature region from 85°C to 110°C there are, of course, some discrepancies which are attributed to the insufficient fit of the contribution of the PE phase in the IPN by pure irradiated PE. The reason, on the one hand, comes from a higher endothermic effect in the PE melting range of M10–50 (compared to M10–40 and M10–60) if we use PE irradiated with 800 kGy and $n = 3$ for the fit. Obviously there is a lower degree of cross-linking of the PE phase in M10–50 than in the other IPNs. This is supported by the finding, that the fit becomes better if we use PE irradiated with 400 kGy and $n = 3.5$ in this case. On the other hand, there is a difference in the degree of crystallinity of PE in irradiated and IPN samples which cannot be compensated totally by our fit procedure. Nevertheless, a satisfactory estimation of the glass transition temperature T_g of the copolymer phase in the IPN is possible this way (see Section 4).

3.2. DSC measurements

The heating curves of the IPN in the initial as well as in the recrystallised state are plotted in Fig. 5. The pre-peak visible in the curves of the initial samples may be assigned to the enthalpy relaxation, its maximum temperature should refer to the glass transition temperature.

The measurements of the recrystallised state have been added to show the difficulties with the overlapping PE melting on the determination of T_g for the copolymer phase if we use the common half-step method. Using the straight line obtained by extrapolation of the heat flow rate curve at $T > 110$°C to lower temperatures (dotted in Fig. 5) T_g of the copolymer phase can be formally estimated. Nevertheless, Fig. 5 shows that the contribution of the PE melting process in the T_g region makes an exact determination difficult.

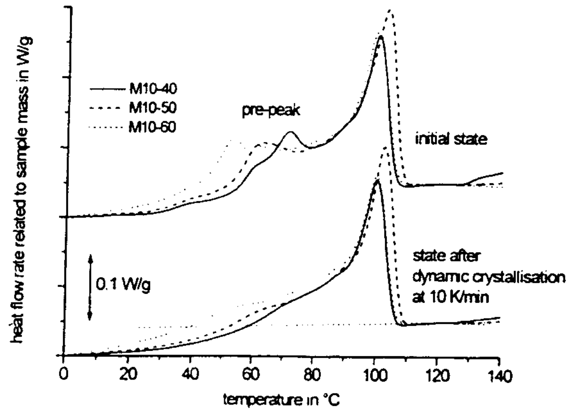

Fig. 5. DSC heat flow rate normalised in relation to the sample mass of IPN, measured in the initial and the recrystallised state.

Another common method to determine the glass transition temperature is the inflection point method. The inflection point is normally determined from the maximum of the derivative of the measured heat flow rate curve. In Fig. 6 those curves are plotted for the recrystallised IPN samples. The peak maximum correlates to the MMA-content of the copolymer phase. To see the influence of the PE phase, the respective

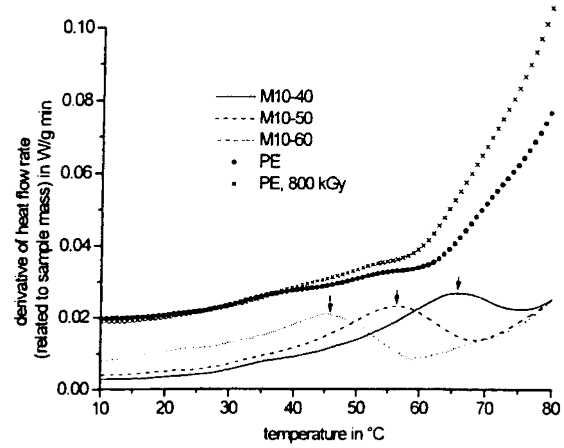

Fig. 6. Derivative of DSC heat flow rate normalised in relation to the sample mass of IPN, unirradiated PE and PE irradiated with 800 kGy.

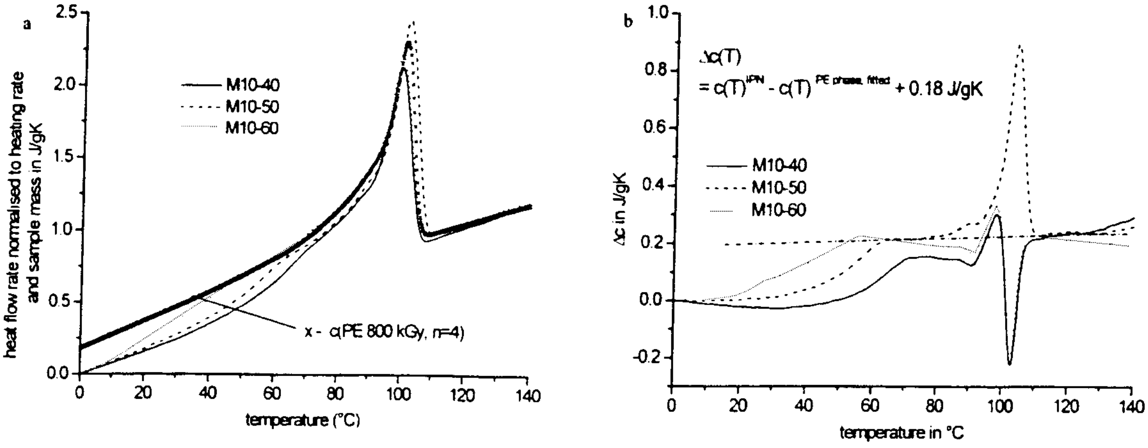

Fig. 7. (a) DSC heat flow rate normalised in relation to the sample mass of IPN and to the PE-phase content, measured in the recrystallised state. The contribution of the PE-phase was calculated with $n = 4$ from PE, irradiated with 800 kGy; (b) Differences $\Delta c(T)$ of $|c(T)|^{\mathrm{IPN}}$ and $|c(T)|^{\mathrm{PE\ phase,\ fitted}}$ in the recrystallised state (for details see text).

curves of 800 kGy irradiated samples are included. There is a remarkable increase of the PE curves in the interesting temperature range of the copolymer glass transition which causes a systematic error for the T_g determined this way. In spite of this error, the method gives acceptable results for T_g of the copolymer phase in IPNs.

The procedure developed for the analysis of the $|c_p(T)|$ curves of TMDSC (see Section 3.1) was also applied to the curves measured with common DSC. From Fig. 7(a) and (b) (which give the results corresponding to those of Fig. 4(a) and (b)) the insufficient accuracy of the DSC measurements is obvious. It is not possible to obtain an unambiguous fit for the PE content in the melt. The plotted results, using PE irradiated with 800 kGy, were obtained with the assumption that $\Delta c(T_g)$ of the copolymer phase is 0.18 J/g K. The calculated differences $\Delta c(T)$:

$$\Delta c(T) = (\beta m)^{-1}\,(\mathrm{d}Q/\mathrm{d}t^{\mathrm{IPN}} - \mathrm{d}Q/\mathrm{d}t^{\mathrm{PE\ phase,fitted}}) + 0.18\,\mathrm{J/g\,K}$$

are shown in Fig. 7(b) with β: heating rate (10 K/min) and m: sample mass. The uncertainty of $\Delta c(T)$ in the melt ($T > 110°\mathrm{C}$) does not allow an exact extrapolation of $\Delta c(T)$ to lower temperatures. Consequently, the determination of the glass transition temperature using the half-step method is inaccurate in this case.

4. Discussion

The values of T_g of the copolymer phase of the IPNs determined by the different methods discussed in Section 3 are summarised in Table 2 and are represented in Fig. 8 as a function of the MMA content of the copolymer phase. The expected tendency of increase of T_g with increasing MMA content was found in every case.

From DSC results we get a linear relation both for $T_{\max}$ of the enthalpy relaxation peak of the initial samples and for the T_g values of the recrystallised samples determined with the inflection method. Of course, the maximum temperature of the enthalpy relaxation peak is always

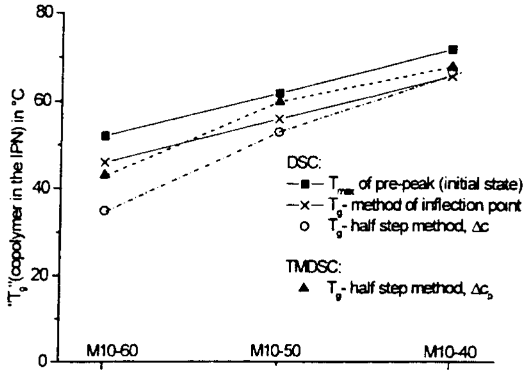

Fig. 8. Temperatures characterising the glass transition temperatures of the copolymer phase in the IPNs using different methods as a function of composition of the copolymer.

Table 2
Glass transition temperatures of the copolymer phase in the IPN determined by different methods

Sample	DSC initial state	DSC recrystallisation state		TMDSC recrystallisation state
	$T_{\max}$ (°C) of pre-peak (Fig. 5)	T_g (°C) inflection point (Fig. 6)	T_g (°C) half-step method $\Delta c(T)$ (Fig. 7(b))	T_g (°C) half-step method $\Delta c_p(T)$ (Fig. 4(b))
M10–60	52	46	≈35	≈43
M10–50	62	56	≈53	≈60
M10–40	72	66	(≈67)	(≈68)

higher than the real glass temperature of that material. Nevertheless, it is an interesting finding that the difference in the T_g of the recrystallised sample, measured with the inflection point method, $\Delta T = T_{\max} - T_g$ (=6 K) is independent of the MMA content. A detailed discussion of that finding is not useful because the condition of preparation and the thermal history of the IPN samples influence the enthalpy relaxation peak and the glass temperature distinctly [8].

It can further be seen that the glass transition temperatures determined with the half-step method differ from the former findings: (i) the slope is different and (ii) there is no linear behaviour, the values for the M10–50 sample seem to be higher than expected. The former result points to systematic error sources in the different T_g determination methods. The latter result is interesting in connection with the finding that the cross-linking of PE in M10–50 is lower than in M10–40 and M10–60 which implies a smaller influence of the network in M10–50 than in the two other IPN and a smaller decrease of the glass transition temperature of the pure copolymer than in a stronger cross-linked IPN. In this respect, the results of the half-step method appear more meaningful than those which yield a linear relation.

The values of T_g obtained by the analysis of TMDSC data are in between the results from DSC analysis. The tendency is similar to the values obtained by the half-step method from DSC measurements but higher than those. This seems reasonable and supports the statement that the applied evaluation method is more accurate in the case of TMDSC measurements and thus the method which should be preferred to obtain temperature and the step height of the glass transition of the copolymer phase in the IPN. The reliability of the results could even be improved if the real degree of cross-linking of the PE phase and its melting behaviour in the IPN would be known better than from irradiated samples.

The T_gs, determined by the different methods, seem to differ non-uniform with the different IPNs, but this result should not be overestimated because of the imponderabilities of the evaluation, specially for M10–60 (Fig. 4(b), Fig. 7(b)).

5. Conclusions

The determination of the glass transition temperature of the copolymer phase in the IPN using the half-step method is not possible from the raw data either in the case of conventional DSC nor TMDSC. The subtraction of the contribution of the PE phase melting from the measured data is necessary to obtain the contribution of the copolymer phase. Nevertheless, there are differences between both methods which should be considered:

TMDSC. The TMDSC method gives more accurate results and allows, thus, a better separation of the melting influence in the glass transition region. The values of the step height $\Delta c_p(T_g)$ and temperature T_g of the glass transition of the copolymer phase in the IPN are more reliable. Although the influences of the PE melting cannot be excluded totally, the curves of the calculated difference $\Delta c_p(T)$ correspond more or less to $|c_p(T)|$ of the copolymer phase. The result would be even more correct if the exact PE content and its real degree of cross-linking and crystallinity would be known.

DSC. The accuracy of common DSC measurements is insufficient to obtain acceptable results for the glass transition temperature of the copolymer content by using the half-step method after subtraction of the PE melting influence.

An estimation of the glass transition temperatures T_g was only possible using the inflection point method. Nevertheless, there are systematic sources of error in this determination.

Acknowledgements

We are grateful for the financial support of the Sächsisches Ministerium für Wissenschaft und Kunst.

References

[1] J. Hu, G. Pompe, U. Schulze, J. Pionteck, Polym. Adv. Technol. 9 (1998) 1.

[2] U. Schulze, G. Pompe, E. Meyer, A. Janke, J. Pionteck, A. Fiedlerova, E. Borsig, Polymer 36 (1995) 3393.

[3] U. Schulze, A. Fiedlerova, G. Pompe, E. Meyer, A. Janke, J. Pionteck, E. Borsig, Polymer 39 (1998) 1289.

[4] E. Borsig, A. Fiedlerova, K.G. Häusler, R.M. Sambatra, G.H. Michler, Polymer 34 (1993) 4787.

[5] J. Hu, U. Schulze, J. Pionteck, E. Borsig, J. Mater. Sci.-Pure Appl. Chem. A 35 (1998) 1285.

[6] G. Bolder, M. Meier Kautschuk+Gummi, Kunststoffe 39 (1986) 715.

[7] G. Pompe, unpublished results.

[8] A. Agrawal, J. Polym. Sci., Polym. Phys. 27 (1989) 1449.