

Quantitative Characterization of Interfaces in Rubber–Rubber Blends by Means of Modulated-Temperature DSC

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ABSTRACT: Rubber–rubber blends are used widely in industry, for example, in tire manufacture. It is often difficult to characterize interfaces in such rubber–rubber blends quantitatively because of the similarity in the chemical structure of the component rubbers. Here, a new method was suggested for the measurement of the weight fraction of the interface in rubber–rubber blends using modulated-temperature differential scanning calorimetry (M-TDSC). Quantitative analysis using the differential of the heat capacity, dC_p/dT , versus the temperature signal from M-TDSC allows the weight fraction of the interface to be calculated. As examples, polybutadiene rubber (BR)–natural rubber (NR), BR–styrene-*co*-butadiene rubber (SBR), SBR–NR, and nitrile rubber (NBR)–NR blend systems were analyzed. The interfacial content in these blends was obtained. SBR is partially miscible with BR. The *cis*-structure content in BR has an obvious effect on the extent of mixing in the SBR–BR blends. With increasing styrene content in the SBR in the SBR–BR blends, the interface content decreases. NR is partially miscible with both BR and SBR. The NBR used in this research is essentially immiscible with NR. The maximum amount of interface was found to be at the 50:50 blend composition in BR–NR, SBR–BR, and SBR–NR systems. Quantitative analysis of interfaces in these blend systems is reported for the first time. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1791–1798, 2000

Key words: rubber blends; interface; modulated-temperature DSC; miscibility

INTRODUCTION

In recent years, the tire industry has been successful in reducing rolling resistance and increasing the traction of automobile tires by judiciously controlling the microstructure of polybutadiene rubber (BR).¹ BR, poly(styrene-*co*-butadiene) rubber (SBR), natural rubber (NR), nitrile rubber (NBR), and their blends are all important materials in the rubber industry. The morphologies of these blends control the glass transition behavior and their properties. Therefore, morphology and

miscibility represent important design factors in rubber compounding. Thus, it is important to be able to measure morphological parameters such as the domain size, domain connectivity, interfacial thickness, and weight fraction of the interface.

However, because the chemical structure is relatively similar for these rubbers, it is difficult to analyze their blend morphologies using electron microscopy or the small-angle X-ray scattering technique. Recently, experimental investigations on the morphology of polymer–polymer blends, core–shell latex films, and interpenetrating polymer networks were reported by us^{2–9} using modulated-temperature differential scanning calorimetry (M-TDSC). It has been shown that even

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Table I Characterization of the SBR Samples

Sample	Styrene Content (wt %)	Mooney Viscosity ML 1 + 4	Tensile Strength (MPa)	Elongation at Break (%)	Oil Extended
SBR1502	23.3	50.8	24.8	470	No
SBR1712	23.4	49.7	21.9	580	Yes
SBR401	33.0	51.5	21.3	640	Yes
SBR402	35.8	51.7	21.6	690	Yes
SBR1721	39.8	56.0	22.1	610	Yes
SBR6250	62.5	—	—	—	No

when the difference in glass transition temperatures, T_g 's, is as little as 10°C, the differential of the heat capacity with temperature, dC_p/dT , signal from M-TDSC may be used to characterize polymer–polymer miscibility. Weight fractions of less than 7% in multiphase polymeric materials can be determined by this technique.⁵ In this article, the application is extended to the rubber processing field to provide, hopefully, commercially valuable characterization parameters for such blends, especially the amount of interface present in rubber–rubber blends.

EXPERIMENTAL

Materials

NR and the series of SBR samples: SBR1502, SBR1712, SBR401, SBR402, SBR1721, and SBR6250, were kindly provided by EniChem Elastomers Ltd. (Southampton, UK). For the SBR6250 sample, M_w was 3.17×10^5 and M_n was 1.63×10^4 as determined by GPC calibration using standard polystyrene samples. Characterization details for all the SBR samples used are shown in Table I. The NBR series [NBR1 (19 wt % of acrylonitrile (AN)), NBR2 (30 wt % of AN), and NBR3 (42 wt % of AN)] and the BR1 and BR3 samples were obtained from Aldrich (Gillingham, UK). Molecular weight details for the NR, NBR, BR1, and BR3 samples are shown in Table II. These were determined by GPC, again calibrated using polystyrene standards.

Blend Preparation

Mechanical blending of SBR with BR, SBR with NR, NR with BR, and NR with NBR was carried out using a Haake Rheochord. A total charge of 50 g was used. The rotor speed was 80 rpm and

the temperature was 138°C. For the SBR with BR and the SBR with NR blends, the SBR component was added first, and for NR with BR and the NR with NBR blends, the NR was added first and masticated for 30 s. The second component was then added and blended for a further 9 min before removal of the blend from the mixing chamber while still hot.

M-TDSC

A TA Instruments M-TDSC calorimeter (Model 2920) was used. The oscillation amplitude was 1.0°C, the oscillation period was 60 s, and the heating rate was 3°C/min. The calorimeter was calibrated, as for a conventional DSC, with a standard indium sample.

RESULTS AND DISCUSSION

Figure 1 shows the heat-capacity changes with temperature for BR1 blended with NR. Two distinct glass transitions were observed. It is difficult to obtain further detailed information about blend morphology from such heat-capacity versus temperature signals. However, Fig-

Table II Weight-Average Molecular Weight and Polydispersity Index for BR1, NR, and NBR

Sample	M_w (10^5)	M_w/M_n
NR	8.60	50.6
BR1	2.40	2.3
NBR1	0.95	4.4
NBR2	1.66	4.3
NBR3	1.17	4.6
BR3	4.23	10.3

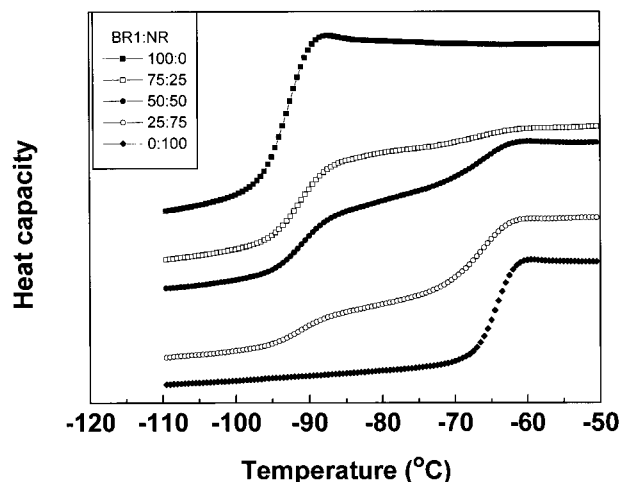


Figure 1 Heat capacity versus temperature plots (offset) for the BR1-NR blends.

Figure 2(a-c) shows the same data presented as dC_p/dT versus temperature signals and the corresponding physical blend (BR1 + NR) where

the components are simply placed in the appropriate mass ratio, but unmixed, in the DSC pans.

Figure 3 shows the dC_p/dT versus temperature signals for BR3 blended with SBR1502 (50 : 50 by weight) and the corresponding physical blend (BR3 + SBR1502). Figure 4 shows the dC_p/dT versus temperature signals for SBR1502 blended with NR (50 : 50 by weight) and again for the corresponding physical blend (SBR1502 + NR).

Comparing dC_p/dT signals of the blends with their equivalent physical blends, it was observed that the dC_p/dT signal of the blend systems was quite different from that of the equivalent physical blend. Between their glass transition temperatures, the values of the dC_p/dT signals of the blends are larger than those of the physical blends. This indicates that there is a transition in this temperature range, which can be related to the interfacial layer between the components.

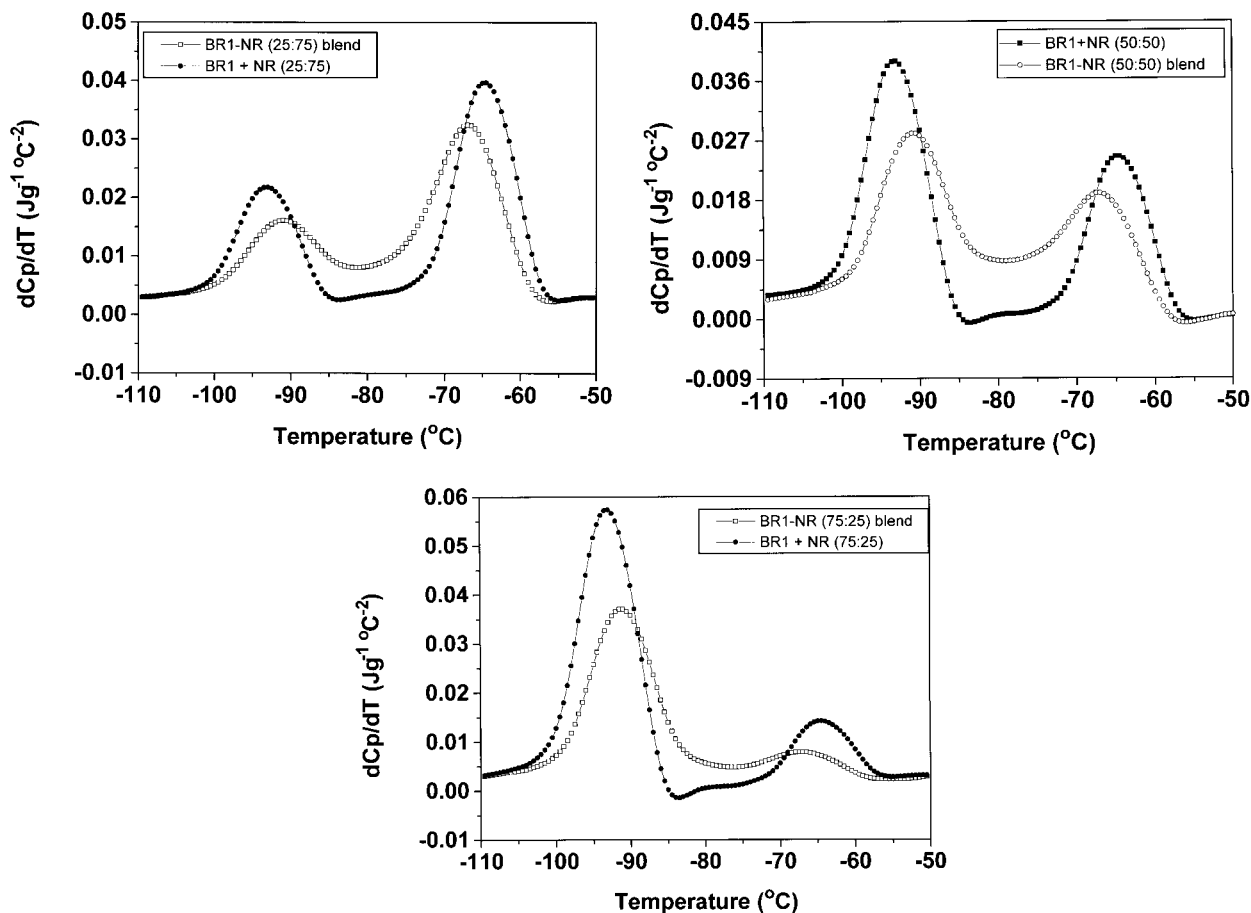


Figure 2 dC_p/dT versus temperature plots for the BR1-NR blends.

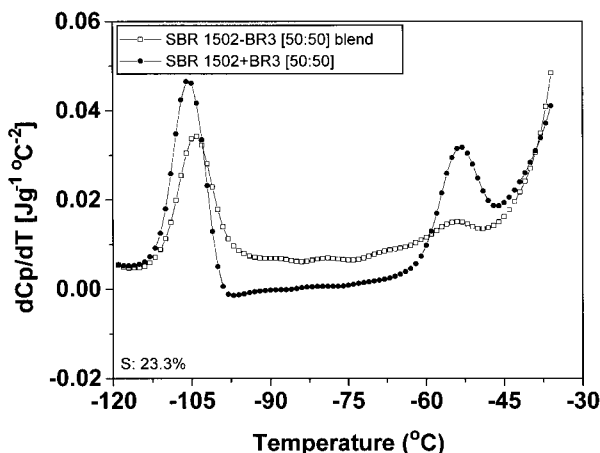


Figure 3 dCp/dT versus temperature plots for the SBR1502–BR3 (50 : 50 by weight) blend.

Figure 5 shows the change of dCp/dT with temperature for NBR3 blended with NR, again with the corresponding physical blends also shown. It can be seen clearly that the dCp/dT versus temperature signals of the blends are very similar to those of the physical blends. This indicates that there is little interface in these blends.

For blends showing some significant degree of interface development, a characteristic behavior was found in that there was a decrease in the increment of the heat capacity, ΔCp , at the glass transition temperature for both polymers. The ΔCp value is proportional to the weight fraction of the components in the transition concerned. Therefore, the weight fraction of this interfacial layer can be calculated from the experimentally determined “missing” amounts of each component.

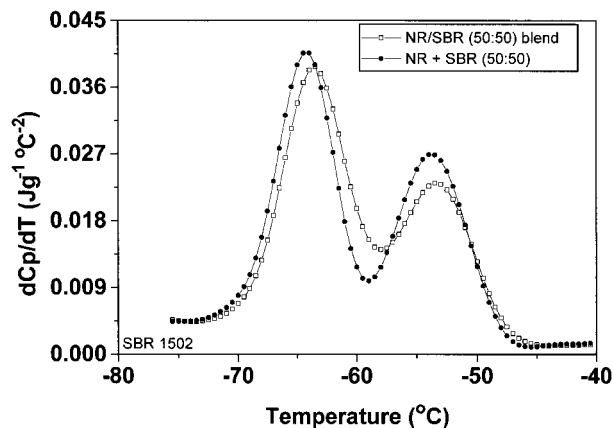


Figure 4 dCp/dT versus temperature plots for the NR–SBR1502 (50 : 50 by weight) blend.

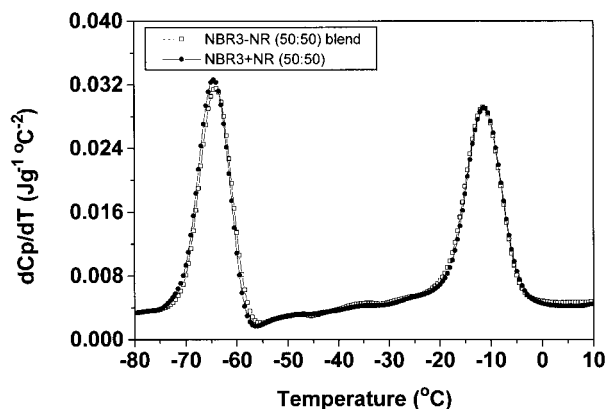


Figure 5 dCp/dT versus temperature plots for the NBR3–NR (50 : 50 by weight) blend.

For an immiscible polymer blend, the total ΔCp is the linear sum of the ΔCp values of the two constituent polymers⁶:

$$\Delta Cp = \omega_{10}\Delta Cp_{10} + \omega_{20}\Delta Cp_{20} \quad (1)$$

ΔCp_{10} and ΔCp_{20} are the increments of heat capacity at T_{g1} and T_{g2} , respectively, before mixing. ω_{10} and ω_{20} are the weight fractions of polymers 1 and 2, respectively. For rubber–rubber blends, the morphology can be considered, in general, as a three-phase structure: pure polymer 1 and pure polymer 2 phases plus the interface. When the system exhibits an interphase, the following equations apply:

$$\Delta Cp = \Delta Cp_1 + \Delta Cp_2 + \Delta Cp_i \quad (2)$$

$$\Delta Cp_1 = \omega_1\Delta Cp_{10} \quad (3)$$

$$\Delta Cp_2 = \omega_2\Delta Cp_{20} \quad (4)$$

ΔCp_1 and ΔCp_2 are the increments of heat capacity at T_{g1} and T_{g2} , respectively, after mixing. ΔCp_i is the increment of the heat capacity of the interphase. ω_1 and ω_2 are the weight fractions of pure polymer 1 and polymer 2 phases, respectively, after mixing. The weight fractions, δ_1 and δ_2 , for polymers 1 and 2 in interfacial regions can be obtained⁵ as follows:

$$\delta_1 = \omega_{10} - \Delta Cp_1/\Delta Cp_{10} \quad (5)$$

$$\delta_2 = \omega_{20} - \Delta Cp_2/\Delta Cp_{20} \quad (6)$$

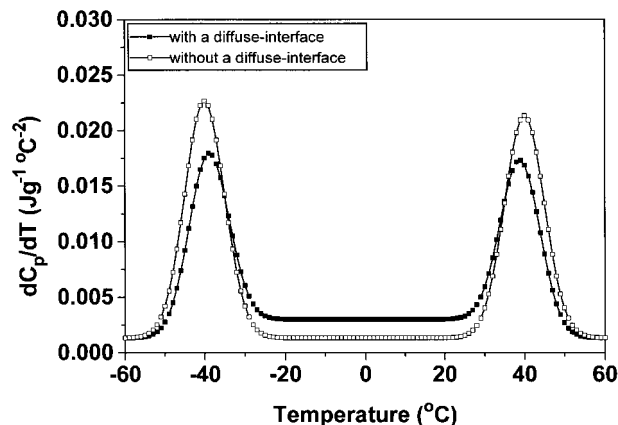


Figure 6 dC_p/dT versus temperature plots for a blend with a diffuse interface and for one without a diffuse interface.

For pure polymers and miscible polymer blends, the dC_p/dT versus temperature signal can be described^{2,7,9} by a Gaussian function $\{dC_p/dT = \Delta C_p / [\omega_d (\pi/2)^{1/2}] \exp[-2(T - T_g)^2 / \omega_d^2]$; ω_d is the half-width of the glass transition}. For a multiphase polymer system, the dC_p/dT versus temperature signal can be described by a multiple Gaussian function.^{2,7,9} Thus, for a three-phase system, eq. (7) holds:

$$dC_p/dT = [dC_p/dT]_1 + [dC_p/dT]_2 + \Psi \quad (7)$$

$[dC_p/dT]_1$ and $[dC_p/dT]_2$ are related to the pure polymer 1 and polymer 2 phases, respectively. Ψ is the differential of the heat capacity versus the temperature signal for the interfacial phase.

The glass transition temperature as a function of distance from a discrete phase boundary between polystyrene and poly(bisphenol A carbonate) was studied theoretically.¹⁰ Consider that the interfacial phase is divided into N subsystems. Each subsystem has an average concentration, $\langle \phi^1 \rangle, \langle \phi^2 \rangle, \dots, \langle \phi^n \rangle$. For the N subsystems, there is a glass transition temperature spectrum, $T_g^1, T_g^2, T_g^3, \dots, T_g^n$. Assume that the differential of the heat capacity versus the temperature signal, Ψ_i , for i th subsystem can also be described by such a Gaussian function. For the glass transition temperature spectrum, Ψ is as follows:

$$\begin{aligned} \Psi &= \sum \Psi_i \\ &= \sum \Delta C_{p_i} / [\omega_{di} (\pi/2)^{1/2}] \exp[-2(T - T_{gi})^2 / (\omega_{di})^2] \end{aligned} \quad (8)$$

ΔC_{p_i} is the increment of the heat capacity; T_{gi} , the glass transition temperature, and ω_{di} , the half-width for i th subsystem.

Figure 6 shows the dC_p/dT signal versus temperature for a three-phase system calculated using eq. (8). Here, it is assumed that the difference of the glass transition temperatures between polymers 1 and 2 is 80°C. The interphase was divided into seven subsystems. Assume that the weight fraction of the interphase is 20% and $\Delta C_{p_{10}}$ and $\Delta C_{p_{20}}$ are 0.4 and 0.38 J g⁻¹ °C⁻¹ for polymers 1 and 2, respectively. Figure 7 shows the calculated interfacial signal.

The dC_p/dT versus temperature signal can be described by a Gaussian function for polymers and miscible polymer blends over the glass transition.^{2,7,9} However, the dC_p/dT versus the temperature signal for polymer 1 + polymer 2 cannot be described well by the sum of two Gaussian functions because of the shift of the baseline between the glass transition temperatures. Therefore, the dC_p/dT versus temperature signal includes a nonconstant baseline for multiphase systems. Because, in this article, the Gaussian function was used for the quantitative analysis of interphases in the multiphase systems, this nonconstant baseline has to be corrected. The values of the dC_p/dT versus temperature signal for polymer 1 + polymer 2 above and below the two glass transition temperatures are considered as the baseline for the dC_p/dT signal of multiphase systems. Such a baseline, which is linear with temperature, was chosen.¹¹

Figure 8 shows the corrected differential of the heat capacity versus temperature data, $[dC_p/dT]_c$, for the BR1-NR (50:50) blend system. Figure 9 is the interfacial signal, which is obtained

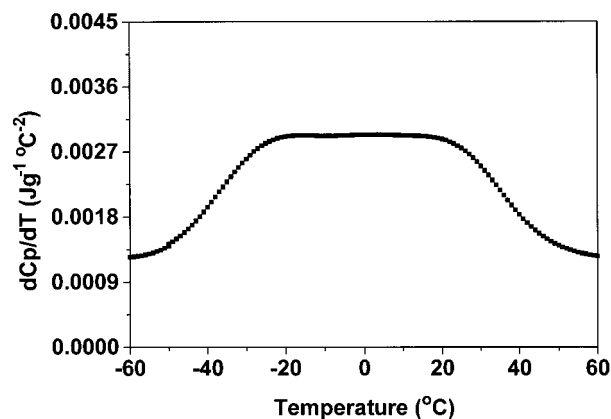


Figure 7 Model prediction of the dC_p/dT versus temperature plot for the interface signal.

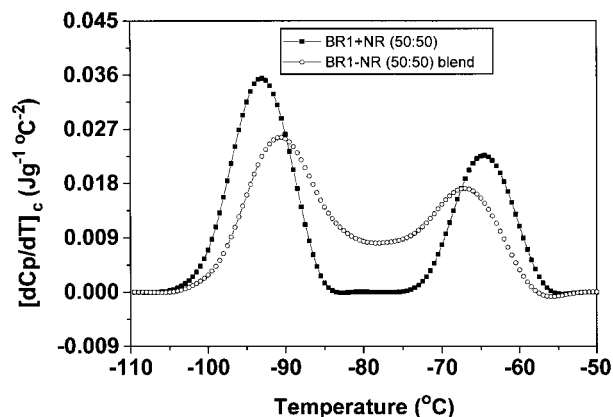


Figure 8 Corrected dCp/dT versus temperature plots, $[dCp/dT]_c$, for the BR1–NR (50 : 50 by weight) system.

by a peak resolution technique,^{3,7,8,12} which was discussed in detail in ref. 12. The model prediction is in good agreement with the experimental data for the interfacial signal. The interfacial phase does not show a single glass transition temperature, but is a continuous glass transition spectrum. According to eqs. (5) and (6) and the peak-resolution method,^{3,7,8,12} the interface weight fraction in rubber–rubber blends can be obtained. Figure 10 shows the change of the weight fraction of the interphase with composition in the BR1–NR blends. The maximum amount of interface was found, reasonably, to be in the 50 : 50 BR1–NR blend.

However, it is not easy to obtain the value of ΔCp for the pure SBR phase in the SBR–BR3 blends. This is because the dCp/dT signal for the pure SBR phase is affected by recrystallization in the BR3 component. The difference of dCp/dT

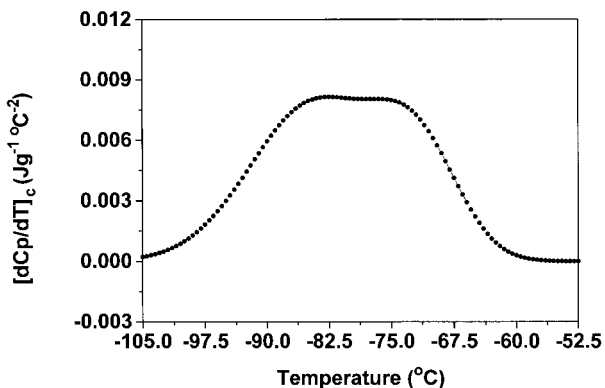


Figure 9 Interfacial plot for the BR–NR (50 : 50 by weight) blend.

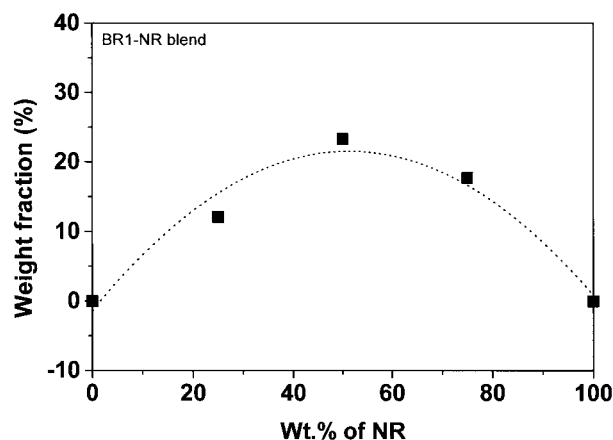


Figure 10 Weight fraction of interface versus composition in BR1–NR blends.

signals of the SBR–BR3 blends and their corresponding physical blends between the endpoint of the glass transition of BR3 and the onset point of the SBR glass transition was used to calculate the increment of the heat capacity for the interfacial phase. Figure 11 gives an example of the calculation. The weight fraction of the interface, δ , was obtained using the following equation:

$$\delta = \Delta Cp_i / (\omega_{10}\Delta Cp_{10} + \omega_{20}\Delta Cp_{20}) \quad (9)$$

Figure 12 shows the change of the weight fraction of the interface in SBR–BR3 blends with changing styrene content in the SBR. It is clear that with increasing styrene content, the interfacial content decreases. Comparing SBR1502 and SBR1712, the difference between their interfacial weight fractions is small. It is therefore clear that

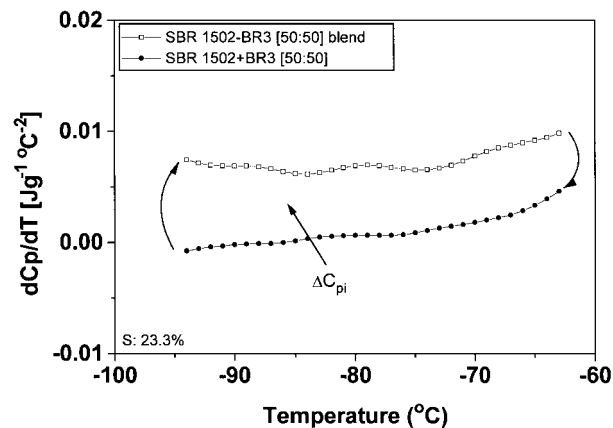


Figure 11 ΔCp_i calculation method for the SBR–BR3 blends.

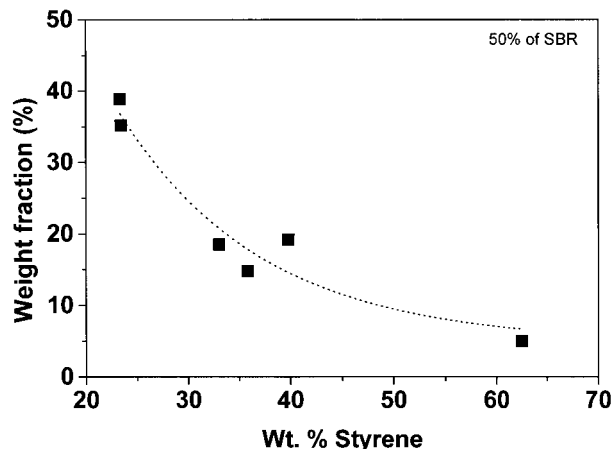


Figure 12 Weight fraction of interface versus SBR styrene content for the 50 : 50 BR3 : SBR blend.

the oil extension in the SBR1712 samples does not influence the interface content to any significant extent.

Figure 13 shows how the weight fraction of the interface changes with the SBR composition in the SBR1502-BR3 blends. The maximum amount of the interface was also found to be at the 50 : 50 composition.

Now, we wish to consider the Paul et al.¹¹ theory with regard to interface development in rubber-rubber blends. BR may be considered to be a copolymer because of the *cis* and *trans* structures. The binary interaction model developed by Paul et al.¹¹ can be extended to the BR and SBR blend system in which BR (A) is a copolymer of one (*trans*) and two (*cis*) structures and SBR (B) is a copolymer of one (*trans*) and three (styrene). The heat of mixing¹¹ in this case is given by eq. (10):

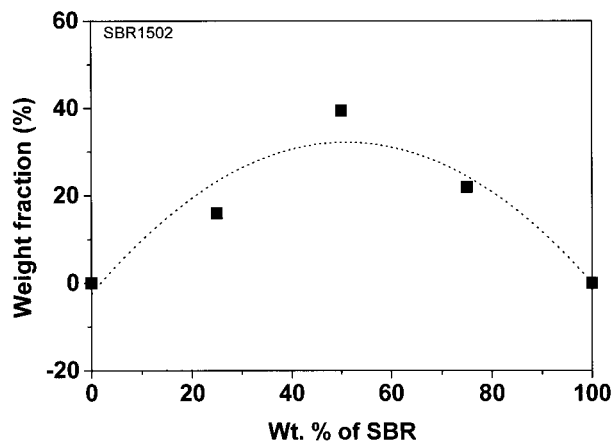


Figure 13 Weight fraction of interface versus composition for the SBR1502-BR3 blends.

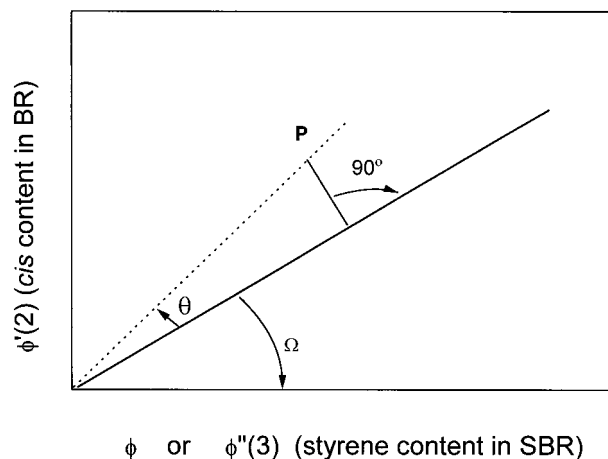


Figure 14 Schematic illustration of the effect of interaction on miscibility (after D. R. Paul et al.¹¹).

$$\Delta H_m = \sum_{i>j} [V(A) + V(B)]B(i,j)\phi(i)\phi(j) - V(A)B(1,2)(\phi'(1)\phi'(2) - V(B)B(1,3)\phi''(1)\phi''(2)) \quad (10)$$

The first term on the right gives the heat of mixing for the blend composed of the three homopolymers and the other two terms are the “heats of mixing” of the two copolymers, BR and SBR, on the same basis. The difference is the heat of mixing of the two copolymers. $\phi'(i)$ gives the composition of BR and $\phi''(i)$ gives the composition of SBR. Then, the effective interaction parameter, $\Delta H_m/\phi(A)\phi(B)V$, for mixing of BR and SBR is as follows¹¹:

$$\Delta H_m/\phi(A)\phi(B)V = B = B(1,2)\phi'(2)[\phi'(2) - \phi''(3)] + B(1,3)\phi''(3)[\phi''(3) - \phi'(2)] + B(2,3)\phi'(2)\phi''(3) \quad (11)$$

Following work by Paul et al.,¹¹ if we make the assumption of symmetry, that is, $B(1,2)$ is equal to $B(1,3)$, and define new coordinates θ and ϕ (ref. 11) as shown in Figure 14, point P is described as follows¹¹:

$$\begin{aligned} \phi'(2) &= \phi(1 + \tan \theta) \\ \phi''(3) &= \phi(1 - \tan \theta) \end{aligned} \quad (12)$$

Using these new coordinates and the symmetry assumption, eq. (11) can be rewritten¹¹ as follows:

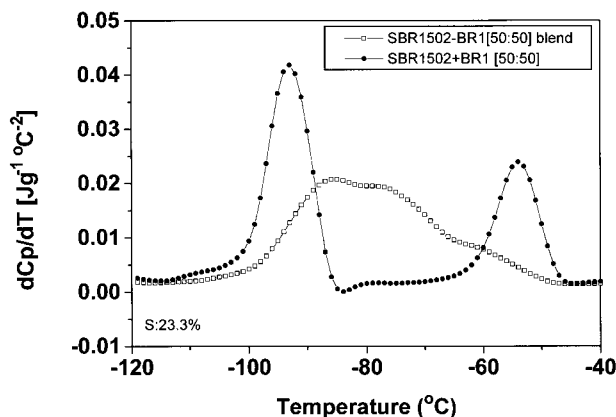


Figure 15 dCp/dT versus temperature plots for the SBR1502–BR1(50 : 50 by weight) blend.

$$B = B(1, 2)\phi^2[4 \tan^2\theta + B(2,3) \div B(1,2)(1 - \tan^2\theta)] \quad (13)$$

Thus, B is zero along the lines given by¹³

$$\tan \theta = \pm[-B(2,3)/(4B(1,2) - B(2,3))]^{1/2} \quad (14)$$

The value of B is negative inside the region defined by these lines and is positive outside it.

$B(i,j)$ is the interaction energy density. According to the above analysis, when the styrene content in SBR is fixed, changing the *cis* content in BR will affect the miscibility in the BR–SBR blends.

The 98% *cis*-content BR3 recrystallized at -50°C and melted at -26°C . The 36% *cis*-content BR1 is an entirely amorphous polymer. Figure 15 shows the dCp/dT versus temperature signals for BR1 blended with SBR1502. The miscibility of BR1 blended with SBR1502 is higher than that of BR3 blended with SBR1502. Thus, the *cis* content has an obvious effect on the weight fraction of the interface. This indicates that for the BR–SBR blends in which the content of styrene in SBR is fixed the weight fraction of the interface can be modified by changing the *cis* content of BR. To the best of our knowledge, little information is available in the literature as to how different microstructures of BR might affect its miscibility and the weight fraction of the interface with SBR. This may represent an important variable in the design of SBR–BR blends for the tire industry

because the interfacial structure is expected to exert a great influence on the mechanical properties of these materials.

CONCLUSIONS

It is reported for the first time for rubber–rubber blends that the dCp/dT versus the temperature signal from M-TDSC can be used to study interphases in rubber–rubber blends and allows the weight fraction of the interface to be calculated. SBR is partially miscible with BR. The *cis* content in BR has a clear effect on the amount of the interface in SBR–BR blends. With increasing SBR styrene content in SBR–BR blends, the amount of the interface decreases. NR is partially miscible with BR and SBR, respectively. NBR and NR are essentially immiscible. The maximum amount of the interface was found at the 50 : 50 composition in BR–NR and SBR–BR blends.

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