J. Rubb. Res., **11(1)**, 13–28

Assessing Effects of Mixing Parameters on Interphases in Blends of Dissimilar Rubbers Using M-TDSC

S. OSTAD-MOVAHED*, A. ANSARIFAR*# AND M. SONG*

A modulated-temperature differential scanning calorimetry (M-TDSC) method was used to calculate the mass fraction of interphase and determine its composition in some SBR/BR and NR/BR blends. Effects of mixing time, mixing temperature, rotor speed, silica nanofiller, and mass fraction of pure rubbers on the mass fraction and composition of the interphase in the blends were investigated. It emerged that increases in mixing time and temperature, incorporation of the filler in the rubbers, and changes in the blend composition affected the properties of the interphase. Furthermore, M-TDSC was found to be a useful technique for studying interphases in blends of dissimilar as well as partially miscible rubbers and estimating their compositions. The measurements were also sensitive to the mixing conditions, rubber composition and silica filler in the rubbers.

Key words: styrene-butadiene rubber; polybutadiene rubber; natural rubber; physical mixture; rubber blend; mixing conditions; interphase; modulated temperature differential scanning calorimetry

The expansion and success of the rubber industry world-wide owes a great deal to the hard work and brilliance of rubber chemists who over the years produced a wide range of synthetic rubbers such as styrene-butadiene rubber, polybutadiene rubber and nitrile rubber. These rubbers and many more were subsequently mixed together with natural rubber to produce blends for use in tyre tread compounds, hoses, and conveyor belts[1–3]. To increase durability, performance and service life of rubber blended components, it is essential to optimise the interfacial adhesion strength between dissimilar rubbers such as the ones mentioned above. Moreover, this will help to minimise the risk of unexpected sudden joint failure in service, enhance materials selection and joint design as well as improve environment and safety in service.

The formation of any heterogeneous system, *e.g.* a polymeric one, is accompanied by the formation of an interphase, which determines important properties of that system[4]. Thermal diffusion between two miscible or partially miscible polymers results in an interfacial phase developing. With increasing diffusion time, in most cases, the thickness of the interphase increases and the concentration profile changes[5]. The interface is characterised

---

*Institute of Polymer Technology and Materials Engineering, Loughborough University, Leicestershire, LE11 3TU, UK.

Corresponding author (e-mail: m.a.ansarifar@lboro.ac.uk)

by a two dimensional array of atoms and molecules which are impossible to measure, while the interfacial layer or interphase has a large enough assembly of atoms or molecules to have its own properties for example modulus, strength, heat capacity and density[4]. According to Sharpe[6], interphase is a region intermediate for two phases in contact, the composition, structure and properties of which may vary across the region and differ from the composition, structure and properties of either of the two contacting phases.

It is therefore assumed that interphase is the result of molecular diffusion between pure phases. Rubber blends have a significant role in the tyre industry, which continuously tries to attain a better compromise between wear resistance, rolling resistance and ice- and wet-grip properties of tyre tread compounds. Rubbers used in the manufacture of tyre tread compounds for instance SBR, BR and NR, are partially miscible when blended and may form weak interfacial adhesion[7]. The development of a strong interphase between dissimilar rubbers is an important factor in the durability and performance of rubber blends in service.

Many techniques have been used to determine the fraction of polymers contained in the mixed regions between micro phases. They include Fourier transform-infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), dynamic mechanical spectroscopy (DMS), nuclear magnetic resonance (NMR), transmission and scanning electron microscopy (TEM and SEM), X-ray photoelectron spectroscopy (XPS) and gel permeation chromatography[8–15]. However, it is also possible to measure the volume fraction of interfacial material by means of thermal techniques[16]. One method applied to phase separated block copolymers uses the change in heat capacity due to the glass transition of each block relative to the corresponding values for the present homopolymers to estimate the quantity of polymer in the micro phase[17]. It is difficult to determine the heat capacity accurately and directly using conventional differential scanning calorimetry (DSC).

M-TDSC has several advantages in comparison with conventional DSC. For example, it is sufficiently sensitive and has a good enough resolution to separate overlapping thermal events, which include T_g and signals from interphases developing from partially miscible rubbers during blending[18]. Moreover, M-TDSC differs from the conventional DSC in that a low-frequency sinusoidal (*e.g.* sawtooth) perturbation, ranging from approximately 0.001 to 0.1 Hz (1000-10s), is overlaid on the baseline temperature profile. In this instrument, the calorimeter block is subjected to a temperature ramp that is linear when averaged over time, but which has a sinusoidal modulation. Heat capacity values can be determined readily and accurately by using this technique. A full review of the technique was carried out by Reading[18].

The aim of this study was to use the M-TDSC method to calculate the mass fraction of interphase and estimate its composition in SBR/BR and NR/BR blends for different mixing times and temperatures, rotor speeds and mass fractions of pure SBR and BR rubbers in the SBR/BR blend. Silica nanofiller was also added to the SBR/BR blend, and the mass fraction and composition of the interphase in the filled blend was determined.

THEORETICAL

Heat capacity can be defined as the amount of energy required to increase the temperature of a material by 1 degree Kelvin or Celsius. Thus:

COPYRIGHT © MALAYSIAN RUBBER BOARD

$$Cp = Q / \Delta T \qquad \dots 1$$

where Cp is the heat capacity, ΔT is the change in temperature, and Q is the amount of heat required to achieve ΔT. Often, this is the heat stored reversibly in the molecular motion in the material, that is the vibrational and translational motions. Thus, the heat given out by the sample when it is cooled by 1ºC is exactly the same as that required to heat it by the same amount. This type of heat capacity is often called vibrational heat capacity. When temperature changes, the rate of heat flow required to achieve this is given by:

$$dQ / dt = CpdT / dt \qquad \dots 2$$

where dQ/dt is the rate of heat flow, and dT/dt is the heating rate. Clearly, if one wishes to increase the temperature of the material twice as fast, twice the amount of energy per unit time must be supplied. If the sample has twice the heat capacity, this also doubles the amount of heat required per unit time for a given rate of temperature rise. Considering a linear temperature programme, such is usually employed in scanning calorimetry:

$$T = T_o + \beta t \qquad \dots 3$$

where T is the temperature, T_o is the starting temperature, and β is the heating rate, dT/dt. This leads to:

$$dQ / dt = \beta Cp \qquad \dots 4$$

or

$$Cp = (dQ / dt) / \beta \qquad \dots 5$$

This provides one way of measuring heat capacity in a linear rising temperature experiment where one simply divides the heat flow by the heating rate. If the temperature programme is replaced by one comprising of a linear temperature ramp modulated by a sine wave, this can be expressed as:

$$T = To + Bt + Bsin\ \omega t \qquad \dots 6$$

where B is the amplitude of the modulation, ω is the angular frequency of the modulation, and t is the time of modulation. The derivative with respect to time of *Equation 6* is:

$$dT / dt = \beta + \omega B\ cos\ \omega t \qquad \dots 7$$

Thus, it follows that:

$$dQ / dt = Cp(\beta + \omega B\ cos\ \omega t) \qquad \dots 8$$

For a special case where β is zero, this yields:

$$dQ / dT = Cp\omega B\ cos\ \omega t \qquad \dots 9$$

For the simplest possible case from *Equation 2*, the resultant heat flow rate must also be a cosine wave. Thus:

$$Ahf\ cos\ \omega t = Cp\omega Bcos\ \omega t \qquad \dots 10$$

where Ahf is the amplitude of the heat flow modulation. It follows that ωB is the amplitude of the modulation in the heating rate. Therefore:

$$CP = Ahf / \omega B \qquad \dots 11$$

However, ωB can be replaced with Ahr which is the amplitude of modulation in the heating rate. This provides a second method of measuring heat capacity by measuring the amplitude of modulation. The same relationship applies even if there is an underlying heating ramp. In essence, M-TDSC is based on simultaneously measuring the heat capacity of the sample using both methods which consists of responses to the linear ramp and to the modulation, and then comparing them. When there are no significant temperature gradients between the sample temperature sensor and the centre of the sample, both methods should give the same values. The interest lies in the fact that during transitions, these two methods give different values[18–19].

EXPERIMENTAL

Materials

The raw rubbers used were Standard Malaysian Natural Rubber Grade L (SMRL) (NR), styrene-butadiene rubber (23.5 wt % styrene) [SBR: Intol 1712, (Enichem)], and high-cis polybutadiene rubber (BR with 96% 1,4 cis) [Buna CB 24, Bayer; not oil-extended]. The reinforcing nanofiller was Coupsil 8113, which was supplied by Degussa Limited of Germany. Coupsil 8113 is a precipitated amorphous white silica-type Ultrasil VN3, the surfaces of which were pre-treated with bis-(3-triethoxysilylpropyl) tetrasulphane(TESPT). It has 11.3 wt % silane, 2.5 wt % sulphur (included in TESPT), a 175 m^2/g surface area (measured by N_2 adsorption), a 20 nm – 54 nm particle size.

Mixing

The rubbers were mixed in a HAAKE RHEOCORD 90 (Berlin, Germany), a small laboratory mixer with counter rotating rotors. In these experiments, the Banbury rotors and the mixing chamber were maintained at 25, 50 and 100ºC. The rotor speeds were 45 and 90 r.p.m. and the mixing times were 10 and 30 min for the raw rubber blends and 40 min for the silica filled blends. To prepare the silica filled SBR/BR blends, the two raw rubbers were mixed together for 30 min and then, the filler was added and mixed for an extra 10 min. The volume of the mixing chamber was 78 cm^3 and it was 55% full. HAAKE Software Version 1.9.1 was used for controlling the mixing conditions and storing data. It was noted that the mixing time of industrial rubber blends was much shorter, *i.e.* only a few minutes. The mixing times in this study were chosen arbitrary.

Sample preparation

The samples used were:

- pure SBR, BR and NR rubbers;
- pure SBR and NR placed in physical contact with pure BR (50:50 by mass) (SBR/BR and NR/BR physical mixtures);
- NR/BR (50:50 by mass) and SBR/BR (50:50, 60:40, 75:25 by mass) blends;
- SBR/BR blends filled with 60 parts per hundred rubber by weight (p.h.r.) silica nanofiller (60:40, 75:25 by mass).

The samples were prepared in the HAAKE mixer.

Measurement of viscosity, specific gravity, glass transition temperature, and mass fraction of the interphase in the blends

The viscosity of the rubbers was measured at 100ºC in a single-speed rotational Mooney viscometer according to the British Standard *1673*[20]. The results were expressed in Mooney units (MU) (*Table 1*). The specific gravity was determined using 2 g of each pure rubber and by measuring the liquid displacement in a calibrated cylindrical column of water (*Table 1*).

A modulated-temperature differential scanning calorimeter from TA Instruments was used. An oscillation amplitude of 1ºC and period of 60 s were used throughout the investigations which were conducted at a heating rate of 3ºC/min. The TA Instrument Graphware software was used to measure the heat flow, the heat capacity and the differential of heat capacity. The calorimeter was calibrated with indium standards. Both temperature and baseline were calibrated as for conventional DSC. Standard aluminium pan and lid were used, samples of rubber approximately 10-15 mg in weight were placed in the pan at ambient temperature and the lid was subsequently closed under some nominal pressure. The assembly was placed in the chamber of the calorimeter and the temperature was lowered to –140ºC with the flow of liquid nitrogen at a rate of 35 ml/min, which was used as the heat transfer gas. The temperature was allowed to modulate back to ambient as described above. The T_g of the pure rubbers (*Table 1*) and the mass fraction of the interphase and its composition for the SBR/BR physical mixture and SBR/BR and BR/NR blends were subsequently calculated for different conditions.

RESULTS AND DISCUSSION

The change of heat capacity, C_p, *vs*. temperature, and dC_p/dT *vs*. temperature for the NR/BR (50:50) blend and for a physical mixture of the two samples of NR and BR (50:50) are shown in *Figures 1* and *2*, respectively. The increase of increment in heat capacity, ΔCp, at the glass transition temperature of both rubbers can be seen in *Figure 1*. The value of ΔCp for a component is proportional to its mass fraction in the system under investigation. The heat capacity *vs*. temperature does not provide information about the interphase glass transition temperature and its composition distribution but the dCp/dT *vs*. temperature data (*Figure 2*) provides that information[19].

Figure 2 shows dC_p/dT *vs*. temperature for a diffuse interphase in the NR/BR (50:50) blend prepared at 50ºC for 30 min, and for a physical mixture of the two pure NR and BR samples (50:50) prepared in the same way, respectively. The data in this figure shows that the value of the dC_p/dT *vs*. temperature for the NR/BR blend is larger than that for the pure NR and BR samples (physical mixture) between the glass transition temperatures of NR and BR. The NR/BR blend has a single interphase and this interphase does not exhibit a separate glass transition temperature, but occurs continually between the glass transition temperatures of the constituent rubbers.

BACKGROUND OF THE ANALYSIS

The dC_p/dT *vs.* temperature signal can be described by a Gaussian function for polymers and miscible polymer blends. However, the dC_p/dT *vs*. temperature signals for the rubber 1 + rubber 2 physical mixture cannot be

TABLE 1. RESULTS FROM THE MOONEY VISCOSITY, SPECIFIC GRAVITY AND GLASS TRANSITION TEMPERATURE MEASUREMENTS OF THE PURE RUBBERS

Raw rubber	Specific gravity	Mooney viscosity (MU)	T_g (ºC)
NR	0.92	97	–64
SBR	0.94	51	–50
BR	0.91	49	–107

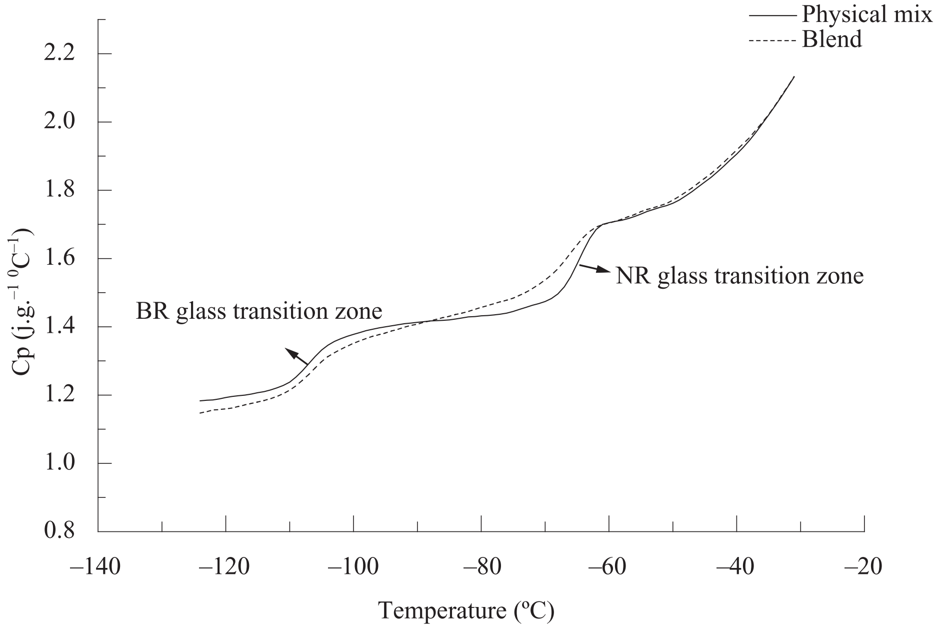

Figure 1. C_p versus temperature for NR/BR (50:50 by mass) blend (dotted line), and NR/BR (50:50 by mass) physical mixture (black line). Samples prepared at 50ºC for 30 min.

described well by the sum of two Gaussian functions because of the shift of the baseline between the glass transition temperatures. Thus, the dC_p/dT *vs.* temperature signal includes a non baseline for multi-phase systems, *e.g. Figure 3*. Because a Gaussian function was used for the quantitative analysis of interphase in these multi-phase systems, the non-constant baseline had to be corrected.

The values of the dC_p/dT *vs.* temperature signal for rubbers 1 and 2 physical mixtures above and below the two glass transition temperatures are considered as the baseline for the dC_p/dT signal of these multi-phase systems. For the glass transitions, baselines which were linear with temperature from the starting and end points of the glass transition temperature peaks were chosen. An example is given in *Figure 3* for the NR/BR (50:50) blend. When the dCp/dT *vs.* temperature signal is analysed using a multi-Gaussian function for multi-phase systems, this baseline must be subtracted from the raw dCp/dT *vs.* temperature signal. *Figure 4* shows the corrected differential of heat capacity, dCp/dT, *vs.* temperature signal for the NR/BR (50:50) blend and the NR/BR (50:50) physical mixture after 30 minutes at 50ºC.

For an interphase, the differential of heat capacity with temperature, dC_p/dT, may be considered as the sum of "i" sub systems with individual glass transition temperature for each sub-system, as follows:

$$[dC_p/dT]_{\text{interphase}} = \Sigma\, [dC_p/dT]_i = \Sigma\, \frac{\Delta Cp_i}{[\omega_{di}(\pi/2)^{0.5}]\exp\left[\frac{-2(T-T_{gi})^2}{(\omega_{di})^2}\right]} \quad \ldots 12$$

where ΔCp_i is the increment of heat capacity, T_{gi} is the glass transition temperature, and ω_{di} is the half width of the i^th^ sub-system at the interphase[19]. Using *Equation 12*, the interphase can be analysed quantitatively. *Figure 5* shows a typical interphase region after baseline correction and peak resolution. Finally, an interphase curve was obtained (*Figure 6*) by subtracting the blend curve from a Gaussian simulation of the same blend curve shown in *Figure 5*.

After determining the area under the curve of physical mixture for individual peaks as well as the simulated Gaussian one, the following equations may be used to determine the mass fraction of interphase and its composition[5].

$$\delta_1 = \omega_{10}\left(1 - \frac{\Delta Cp_1}{\Delta Cp_{10}}\right) \qquad \ldots 13$$

$$\delta_2 = \omega_{20}\left(1 - \frac{\Delta Cp_2}{\Delta Cp_{20}}\right) \qquad \ldots 14$$

where δ_1 and δ_2 are the mass fractions in the interphase of rubbers 1 and 2, respectively, ω_{10} is the mass fraction of the rubbers before mixing, ΔCp_1 and ΔCp_2 are increments of dC_p/dT at glass transition temperatures of pure rubbers in blend (area under curve of the Gaussian simulation curve), ΔCp_{10} and ΔCp_{20} are increments of dC_p/dT at glass transition temperatures of pure rubbers (area under curve of physical mixture). The amount of interphase in a blend is given as follows:

$$\text{Percent of interphase} = \frac{\text{Amount of interphase}}{\text{Total amount of blend}} \times 100 = (\delta_1 + \delta_2) \qquad \ldots 15$$

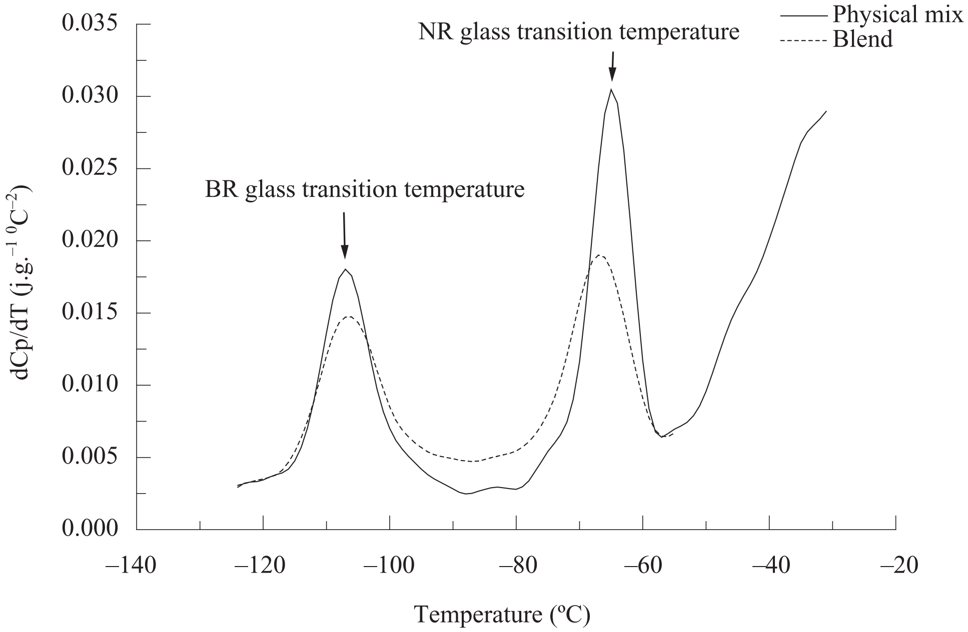

Figure 2. dCp/dT versus temperature for NR/BR (50:50 by mass) blend (dotted line), and NR/BR (50:50 by mass) physical mixture (black line). Samples prepared at 50ºC for 30 min.

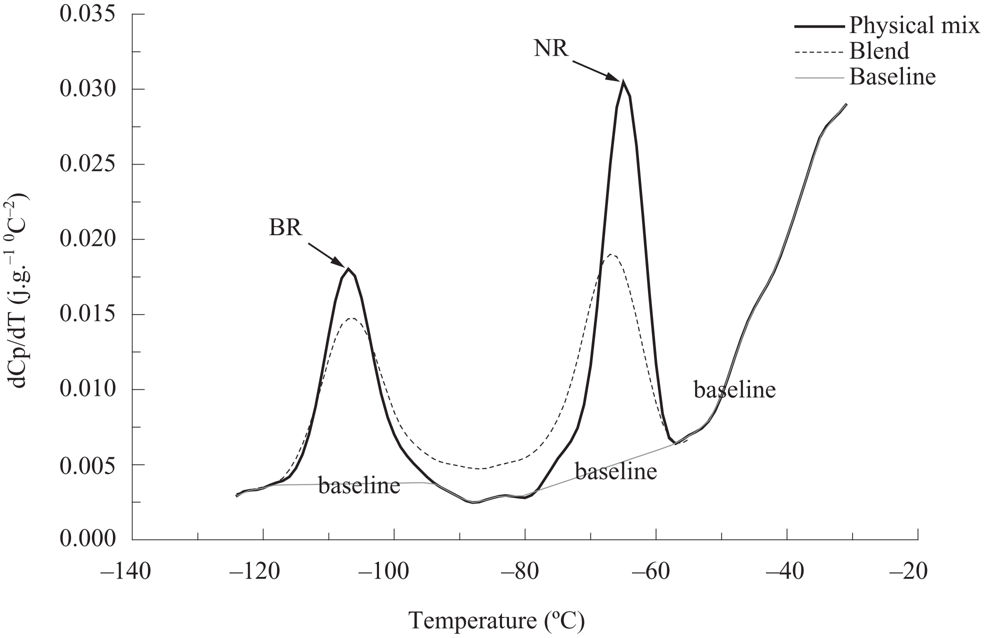

Figure 3. dC_p/dT versus temperature for NR/BR (50:50 by mass) blend (dotted line), and NR/BR (50:50 by mass) physical mixture (thick black line), showing a baseline. Samples prepared at 50ºC for 30 min.

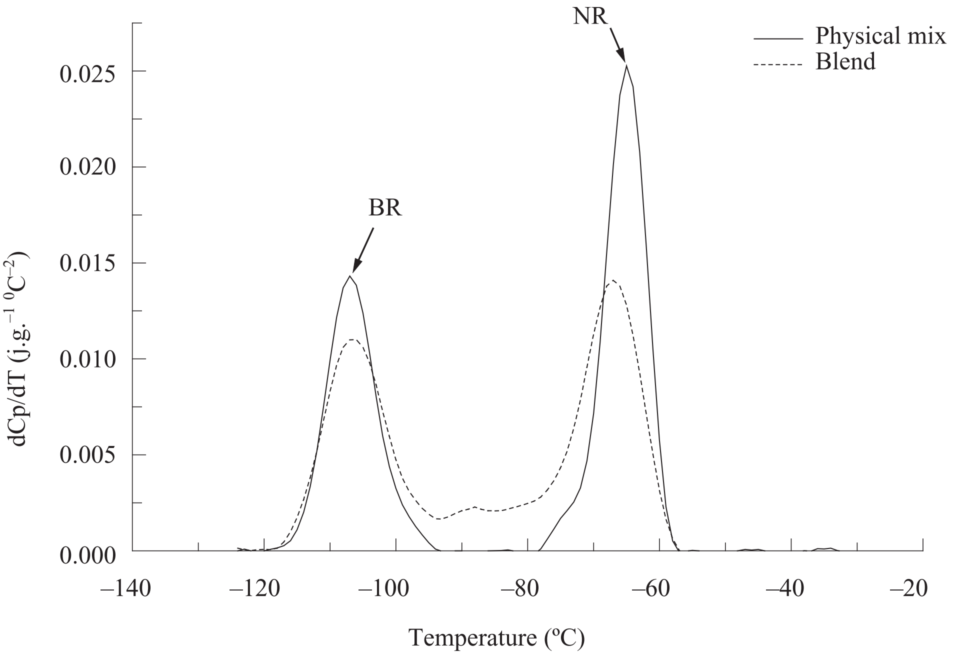

Figure 4. dC_p/dT versus temperature for NR/BR (50:50 by mass) blend and NR/BR (50:50 by mass) physical mixture after baseline correction in Figure 3. Samples prepared at 50ºC for 30 min.

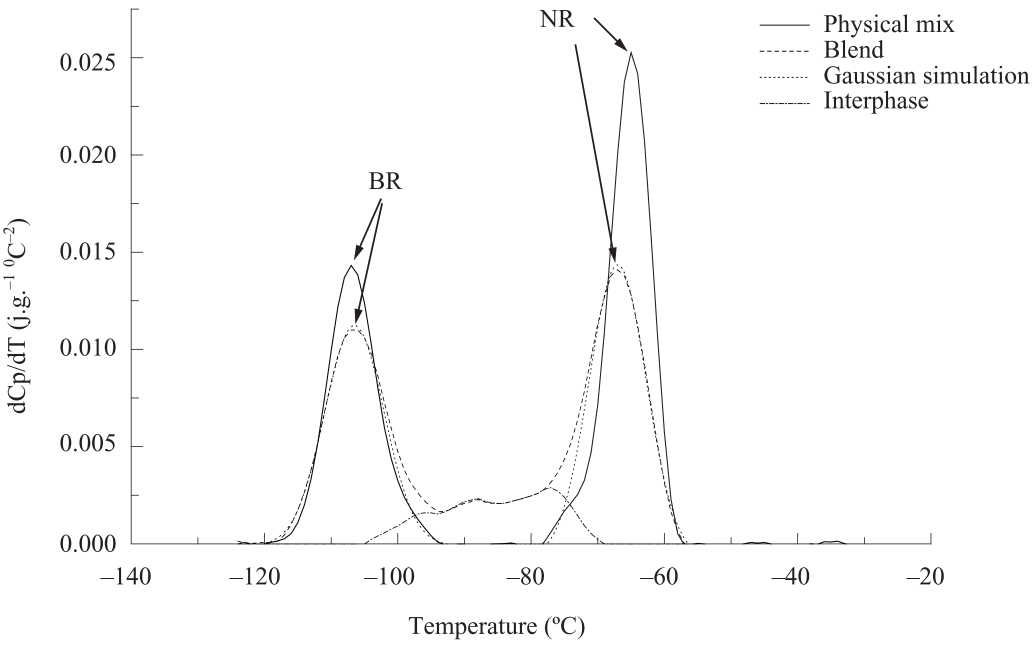

Figure 5. dC$_p$/dT versus temperature for NR/BR (50:50 by mass) blend after peak resolution in Figure 3 showing the interphase region.

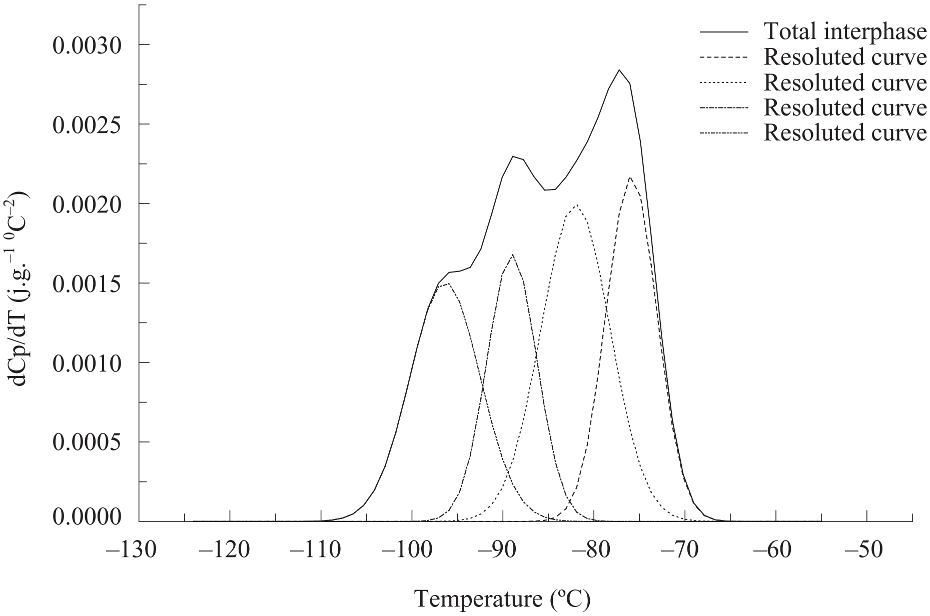

Figure 6. dC$_p$/dT versus temperature for NR/BR (50:50 by mass) blend showing typical interphase obtained by subtracting the blend curve from Gaussian simulation of the same blend curve shown in Figure 5. The area under the curve is a measure of the mass fraction of the interphase. Sample was prepared at 50ºC for 30 min.

It is important to get the ΔCp value accurately. The quantity ΔCp is defined as follows:

$$\Delta Cp = \int_{T_i}^{T_e} [dC_p/dT]\, dT \qquad \ldots 16$$

where T_i and T_e are the initial and final values of the temperature in the glass transition region (see *Figure 4*). Thus, according to *Equation 16*, it is possible to obtain accurate ΔCp values experimentally[21].

Effect of different mass fractions of SBR and BR rubbers on the mass fraction and composition of the interphase in the SBR/BR blend

Understanding how increases in mixing time and temperature affect the mass fraction of interphase and its composition in blends of dissimilar and partially miscible rubbers is of significant importance in optimising adhesion development at rubber-rubber interfaces and ultimately the final properties of rubber blends[22–23]. *Table 2* shows the effect of temperature changes on the mass fraction of the interphase in the NR/BR (50:50) and SBR/BR (50:50) blends after 10 minutes mixing. For these blends, the mass fraction of the interphase was 0% at 25ºC and then increased to approximately 23% and 39%, respectively at 100ºC. The mass fraction of NR to BR and SBR to BR in the interphase were 0.96 and 7.33, respectively at this temperature. Clearly an increase in mixing temperature was beneficial to the formation of an interphase in each blend. A similar trend was also seen when the temperature was increased from 50 to 100ºC at 30 min mixing time. For the NR/BR (50:50) blend, the mass fraction of the interphase was 16.5% at 50ºC and approximately 24% at 100ºC, respectively. The mass fraction of NR to BR in the interphase also increased from 3.76 to 6.69, respectively. Evidently, a longer mixing time and a higher mixing temperature increased the mass fraction of the interphase and altered its composition in these blends (*Table 3*).

When mixing time was increased from 10 to 30 min at 100ºC, the mass fraction of the interphase for the SBR/BR (50:50) blend rose from 39% to 44%. However, the increase for the NR/BR (50:50) blend was only 0.5% (*Table 4*). Interestingly, the effect of temperature rise on the composition of the interphase was even more significant. For the NR/BR blend, the mass fraction of NR to BR in the interphase rose from 0.96 to 6.69 as the temperature was raised, whereas for the SBR/BR blend, the mass fraction of SBR to BR in the interphase decreased from 7.33 to 3.76 indicating a substantial change in the make up of the interphase layers.

Effect of rotor speed on the mass fraction and composition of the interphase in the SBR/BR and NR/BR blends

One important factor in optimising filler dispersion and improving rubber blend properties is rotor speed, which helps to control the level of shear stresses in rubber compounds during mixing. Two rotor speeds were used in these experiments, *i.e.* 45 and 90 r.p.m. The mixing temperature and mixing time were 100ºC and 30 min, respectively. For the SBR/BR (50:50) blend, the mass fraction of the interphase was 44% at 45 r.p.m. and subsequently decreased to approximately 39% at 90 r.p.m. The mass fraction of SBR to BR in the interphase also reduced from 3.76 to 0.96 as the rotor speed was increased. Similarly, for the NR/BR (50:50) blend, the mass fraction of the interphase decreased from 23% to 20% as a function of rotor speed, and there was no change at all in the mass fraction of NR to BR in the interphase, which remained essentially unchanged at 6.69, irrespective of the rotor speed (*Table 5*). An increase in the rotor speed

TABLE 2. COMPOSITION AND MASS FRACTION OF INTERPHASES IN NR/BR AND SBR/BR BLENDS PREPARED AT DIFFERENT TEMPERATURES FOR 10 MIN

Blend	NR/BR (50:50)	NR/BR (50:50)	SBR/BR (50:50)	SBR/BR (50:50)
Temperature (ºC)	25	100	25	100
I* (%)	0	22.9	0	39
I**		(NR=49%, BR=51%)	0	(SBR=88%, BR=12%)
I***		0.96		7.33

I*   Mass fraction of the interphase
I** Composition of the interphase
I*** Mass fraction of NR to BR and SBR to BR in the blends.
The mass fraction of the rubbers in the interphase was calculated as follows:
For NR/BR, 49/51=0.96, and for SBR/BR, 88/12=7.33.

TABLE 3. COMPOSITION AND MASS FRACTION OF INTERPHASES IN NR/BR AND SBR/BR BLENDS PREPARED AT DIFFERENT TEMPERATURES FOR 30 MIN

Blend	Temperature (ºC)	I* (%)	I**	I***
NR/BR(50:50)	50	16.5	(NR=79%, BR=21%)	3.76
NR/BR(50:50)	100	23.4	(NR=87%, BR=13%)	6.69
SBR/BR(50:50)	50	49	(SBR=83.5%, BR=16.5%)	5.06
SBR-BR(50:50)	100	44	(SBR=79%, BR=21%)	3.76

I*   Mass fraction of the interphase
I** Composition of the interphase
I*** The mass fraction of NR to BR, and SBR to BR in the interphase was calculated as described in Table 2.

TABLE 4. COMPOSITION AND MASS FRACTION OF INTERPHASES IN NR/BR AND SBR/BR BLENDS PREPARED AT DIFFERENT MIXING TIMES AND AT 100ºC

Blend	Mixing time (min)	I* (%)	I**	I***
NR/BR(50:50)	10	22.9	(NR=49%, BR=51%)	0.96
NR-BR(50:50)	30	23.4	(NR=87%, BR=13%)	6.69
SBR-BR(50:50)	10	39	(SBR=88%, BR=12%)	7.33
SBR-BR(50:50)	30	44	(SBR=79%, BR=21%)	3.76

I*   Mass fraction of the interphase
I** Composition of the interphase
I*** The mass fraction of NR to BR, and SBR to BR in the interphase was calculated as described in Table 2.

was detrimental to the mass fraction of the interphase and altered its composition, at least for the SBR/BR blend.

Effect of different mass fractions of pure SBR and BR rubbers on the mass fraction and composition of the interphase in the SBR/BR blend

Altering the mass fraction of pure rubbers in blending may affect the mass fraction and composition of the interphase in the blend. Three SBR/BR (50:50, 60:40, 75:25) blends were prepared at 50 and 100ºC mixing temperatures and 30 minutes mixing time. For the SBR/BR (50:50) blend at 100ºC (*Table 6*), the mass fraction of the interphase was 44%. However, when the mass fraction of pure SBR and BR in the blend was increased to 60:40 and 75:25, the mass fraction of the interphase decreased to 41% and 31.2%, respectively. Evidently, an increase in the mass fraction of pure SBR was not beneficial to the mass fraction of the interphase in the blend. Moreover, the mass fraction of SBR to BR in the interphase also decreased from 3.76 to 1.56, in spite of using a significantly larger mass of SBR in the blending process.

TABLE 5. COMPOSITION AND MASS FRACTION OF THE INTERPHASE IN THE SBR/BR AND NR/BR BLENDS AS A FUNCTION OF THE ROTOR SPEED. BLENDS WERE PREPARED AT 100ºC FOR 30 MIN

Blend	Rotor speed (r.p.m.)	I* (%)	I**	I***
SBR/BR(50:50)	45	44.0	(SBR=79%, BR=21%)	3.76
SBR/BR(50:50)	90	38.7	(SBR=49%, BR=51%)	0.96
NR/BR(50:50)	45	23.4	(NR=87%, BR=13%)	6.69
NR/BR(50:50)	90	20.0	(NR=87%, BR=13%)	6.69

I* Mass fraction of the interphase
I** Composition of the interphase
I*** The mass fraction of NR to BR, and SBR to BR in the interphase was calculated as described in Table 2.

TABLE 6. COMPOSITION AND MASS FRACTION OF INTERPHASE IN THE SBR/BR BLEND AS A FUNCTION OF MASS FRACTION OF PURE SBR AND BR RUBBERS IN THE BLENDS. BLENDS WERE PREPARED AT 100ºC FOR 30 MIN

Blend	I* (%)	I**	I***
SBR/BR(50:50)	44	(SBR=79%, BR=21%)	3.76
SBR/BR(60:40)	41	(SBR=77%, BR=23%)	3.45
SBR/BR(75:25)	31.2	(SBR=61%, BR=39%)	1.56

I* Mass fraction of the interphase
I** Composition of the interphase
I*** The mass fraction of SBR to BR in the interphase was calculated as described in Table 2

When the SBR/BR (50:50) and (75:25) blends were prepared at 50ºC for 30 min, the mass fraction of the interphase and its composition were substantially affected. For the SBR/BR (50:50) blend, the mass fraction of the interphase was 49%, and for the SBR/BR (75:25) blend, it was 22.2%. The mass fraction of SBR to BR in the interphase also reduced from 5.06 to 1.40 (*Table 7*).

Effect of silanised silica nanofiller on the mass fraction and composition of the interphase in the SBR/BR blend

Silanised silica nanofiller is used extensively in green tyres where SBR and BR rubbers are blended[1]. To investigate the effect of this filler on the mass fraction of the interphase and its composition in the SBR/BR blend, raw SBR and BR rubbers were mixed for 30 min and then, 60 p.h.r. silica was added and mixed for an extra 10 min at 100ºC to produce SBR/BR (60:40) and SBR/BR (75:25) blends (*Table 8*). In addition to these blends, SBR/BR (60:40) and SBR/BR (75:25) blends with no silica filler were also made. For the SBR/BR (60:40) blend, the mass fraction of the interphase increased from 41 to 60% when silica was added. However, the mass fraction of SBR to BR in the interphase decreased from 3.35 to 2.57, which indicated a change in the composition of the interphase. Similarly, for the SBR/BR (75:25) blend, the mass fraction

TABLE 7. COMPOSITION AND MASS FRACTION OF INTERPHASE IN THE SBR/BR BLENDS WITH DIFFERENT SBR TO BR MASS FRACTIONS. BLENDS WERE PREPARED AT 50ºC FOR 30 MIN

Blend	I* (%)	I**	I***
SBR/BR(50:50)	49.0	(SBR=83.5%, BR=16.5%)	5.06
SBR/BR(75:25)	22.2	(SBR=58.3%, BR=41.7%)	1.40

I* Mass fraction of the interphase
I** Composition of the interphase
I*** The mass fraction of SBR to BR in the interphase was calculated as described in Table 2.

TABLE 8. COMPOSITION AND MASS FRACTION OF INTERPHASES IN THE SBR/BR BLENDS FILLED WITH 60 P.H.R. SILICA NANOFILLER. BLENDS WERE PREPARED AT 100ºC FOR 40 MIN

Blend	I* (%)	I**	I***
SBR/BR(75:25)	31.2	(SBR=61%, BR=39%)	1.56
SBR/BR(75:25)/ 60 p.h.r. silica	50.0	(SBR=76%, BR=24%)	3.17
SBR/BR(60-40)	41.0	(SBR=77%, BR=23%)	3.35
SBR/BR(60:40)/ 60 p.h.r. silica	60.0	(SBR=72%, BR=28%)	2.57

I* Mass fraction of the interphase
I** Composition of the interphase
I*** The mass fraction of SBR to BR in the interphase was calculated as described in Table 2.

of the interphase also increased from 31.2 to 50%, and the mass fraction of SBR to BR in the interphase increased from 1.56 to 3.17 as a result of incorporating silica in the rubbers. It appeared that for both blends the mass fraction of the interphase benefited from the filler and at the same time its composition changed.

Empirical equations for the prediction of mass fraction of interphases in the rubber blends

From the results, it may be assumed that the dependence of the mass fraction of interphase upon mixing time and temperature for the NR/BR (50:50) and SBR/BR (50:50) blends could be expressed as following:

$$I_f = At^aT^b + C \qquad \dots 17$$

where I_f is the mass fraction of the interphase in the blend, t is the mixing time, and T is the mixing temperature. A, a, b, and C are constant coefficients for a given blend. After substituting the experimental results in *Equation 17* and finding the best possible graphical fit to the data, an empirical *Equation 18* for the NR/BR and SBR/BR blends is found:

$$I_f = 0.0215t^{0.02}T^{0.504} \qquad \dots 18$$

This equation is valid for the NR/BR (50:50) and SBR/BR (50:50) blends, for mixing times 10-30 min and mixing temperatures 50-100ºC and, therefore, may be used to calculate the mass fraction of the interphases in these blends. Finally, it is worth mentioning that the SBR and BR rubbers had similar viscosities, *i.e.* 51 and 49 MU, respectively, whereas NR, had a much higher viscosity of 97 MU (*Table 1*). Since the rubber viscosities were different, this might have affected the dispersion of the NR/BR blend components and formation of the interphase between the two rubbers[24].

CONCLUSIONS

It was concluded that for the NR/BR (50:50) and SBR/BR (50:50) blends:

- At 10 min mixing time, a rise in temperature from 25 to 100ºC increased the mass fraction of the interphase in the NR/BR (50:50) and SBR/BR (50:50) blends.

- At 30 min mixing time, a rise in temperature from 50 to 100ºC increased the mass fraction of the interphase in the NR/BR (50:50) blend, and reduced it in the SBR/BR (50:50) blend.

- At 100ºC mixing temperature, an increase in mixing time from 10 to 30 min, increased the mass fraction of the interphase in the NR/BR (50:50) and SBR/BR (50:50) blends. The increase for the latter was more significant.

The rotor speed also influenced the mass fraction and composition of the interphase in the blends. For the SBR/BR (50:50) and NR/BR (50:50) blends:

- At 100ºC mixing temperature and 30 min mixing time, the mass fraction of the interphase decreased for both blends as the rotor speed was increased from 45 to 90 r.p.m.

When the mass fraction of pure SBR to BR rubbers changed in the SBR/BR blend, the mass fraction and composition of the interphase were significantly affected. It emerged that:

- At 50 and 100ºC mixing temperatures and 30 min mixing time, the mass fraction of the interphase decreased progressively as the mass fraction of SBR to BR in the SBR/BR blend increased from 50:50 to 75:25.

When 60 p.h.r. silanised silica nanofiller was incorporated in the raw SBR/BR blend at 100ºC for 40 min, the mass fraction of the interphase changed. It was concluded that:

- For the SBR/BR (60:40) and SBR/BR (75:25) blends, the mass fraction of the interphase increased.

In all cases, the composition of the interphase in the blends also changed. In summary, M-TDSC was found to be a useful technique for measuring the mass fraction of the interphase and estimating its composition in the SBR/BR and NR/BR blends.

ACKNOWLEDGEMENT

The authors thank Degussa Limited of Germany for supplying the silica filler and providing technical information on their product.

Date of receipt: September 2007
Date of acceptance: December 2007

REFERENCES

1. OKEL, T.A. AND WADDELL, W.H. (1994) Silica Properties/Rubber Performance Correlation. Carbon Black-Filled Rubber Compounds. *Rubb. Chem. Technol.*, **67**, 217–236.
2. WADDELL, W.H. (1996) Use of Non-black Fillers in Tire Compounds. *Rubb. Chem. Technol.*, **69**, 377–423.
3. BYERS, J.T. (2002) Fillers for Balancing Passenger Tire Tread Properties. *Rubb. Chem. Technol.*, **75**, 527–547.
4. VASILE, C. AND KULSHREWSHTHA, A. K. (2003) Interphases in Mixed Polymer Systems. 3A, 103–134. Handbook of Polymer Blends and Composites Publishers: Rapra Technology, United Kingdom.
5. HOURSTON, D.J., SONG, M., HAMMICHE, A. POLLOCK, H.M. AND READING, M. (1997) Modulated Differential Scanning Calorimetry: 6. Thermal Characterisation of Multicomponent Polymers and Interfaces. *Polymer*, **38**, 1–7.
6. SHARPE, L. (1993) The Interfacial Interactions in Polymer Composites. Dordrecht, Kluwer Academic Publishers. Netherlands.
7. ANSARIFAR, M.A., FULLER, K.N.G. AND LAKE, G.J. (1993) Adhesion of Unvulvanised Elastomers. *Int. J. Adhesion and Adhesive*, **13(2)**, 105–110.
8. SPATHIS, G.D., SIDERIDIS, E.P. AND THEOCARIS, P.S. (1981) Adhesion Efficiency and Volume Fraction of the Boundry Interphase in Metal Filled Epoxies. *Int. J. Adhes. Adhes*., **1**, 195–201.
9. THEOCARIS, P.S. AND SPATHIS, G.D. (1982) Glass-Transition Behaviour of Particle Composites Modulated on the Concept of Interphase. *J. Appl. Poly. Sci*., **27**, 3019–3025.
10. KOBERSTEIN, J.T., MORRA, S. AND STEIN, R.S. (1980) Determination of Diffuse-Boundry Thickness of Polymers by Small-Angle X-Ray Scattering. *J. Appl. Crystallogr*., **13**, 34–45.
11. ROE, R.J. (1982) Estimation of Errors in the Determination of Phase Boundry Thickness by X-Ray. *J. Appl. Crystallogr*., **25**, 182–189.
12. RULAND, W. (1987) Small-Angle Scattering of the Statistical Structure of Domain Boundries. *Macromolecules*, **20**, 87–93.
13. ANNIGHOFFER, F. AND GRONSKI, W. (1983) Block Polymers of Styrene and Isoprene with Variable Interphase: Morphology and Dynamic Viscoelastic Behaviour. *Colloid Polym. Sci*., **261**, 15–25.
14. ANNIGHOFFER, F. AND GRONSKI, W. (1984) Block Copolymers with Board

Interphase. *Makromol. Chem.*, **185**, 2213–2231.

15. KRESSLER, J., HIGHSHIDA, N., INOUE, T., HECKMANN, W. AND SEITZ, F. (1993) Study on Polymer-Polymer Interfaces: A Comparison of Ellipspometric and TEM Data of PMMA/Polystyrene and PMMA/SAN Systems. *Macromolecules*, **26**, 2090–2094.

16. BECKMAN, E.J., KARASZ, F.E., PORTER, R.S., MACKNIGHT, W.J., HUNSEL, J.V. AND KONINGSVELD, R. (1988) Estimation of the Interfacial Fraction in Partially Miscible Polymer Blends from DSC Measurements. *Macromolecules*, **21**, 1193–1194.

17. READING, M., HAHN, B. AND CROWS, B. *US PATENT 5224775*.

18. READING, M. (1993) Modulated Differential Scanning Calorimetry - A New Way Forward in Materials Characterisation. *Trends Polym. Sci.*, **1(8)**, 248–253.

19. SONG, M., HOURSTON, D.J., READING, M., POLLOCK, H.M. AND HAMMICHE, A. (1999) Modulated Differential Scanning Calorimetry. J. *Thermal Analysis and Calorimetry*, **56**, 991–1004.

20. BRITISH STANDARDS (1969) Methods of Testing Raw Rubber and Unvulcanised Compounded Rubber: Methods of Physical Testing. *BSI 1673*: Part 3.

21. SONG, M., HOURSTON, D.J. AND SCHAFER, F.U. (1999) Modulated Differential Scanning Calorimetry: 12. Interphase Boundries and Fractal Scattering in Interpenetrating Polymer Networks *Polymer*, **40**, 5773–5779.

22. VOYUTSKII, S.S. AND VAKULA, V.L. (1963) The Role of Diffusion in Polymer-to-Polymer Adhesion. *J. appl. Polym. Sci.*, **7**, 475–491.

23. JABBARI, ESMAIEL. AND PEPPAS, N. A. (1995) A Model for Interdiffusion at Interfaces of Polymers with Dissimilar Physical Properties. *Polymer*, **36(3)**, 575–586.

24. MANGARAJ, D. (2002) Elastomer blends. *Rubb. Chem. Technol.*, **75**, 365–427.