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

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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 system⁴. 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 changes⁵. The interface is characterised

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

THEORETICAL

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

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 interphasos developing and suscided (e.g. swelled) perturbation. Moreover, M-TDSC differs from the conventional DSC in that a low-frequency heating. Partially miscible rubbers during cooling from approximately 0.001 to 0.1 Hz (1000-1100), is overlaid on the baseline ranging from approximately 0.001 to 0.1 Hz (1000-1100). The full review of the technique was carried out and accuracy by using this technique. A capacity values can be determined readily but which has a sinusoidal modulation. Heat pump that is linear when averaged over time, calibration block is subjected to a temperature-comperature profile. In this instrument, the temperature profile, is overlaid on the baseline (1000-1100), is overlaid on the baseline (1000-1100).

The corresponding values for the present homopolymer to estimate the quantity of scanning electron microscopy (SEM).

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 scattering microscopy (TEM and SEM), X-ray powderselectron microscopy (TEM and SEM), and gel fractionation chromatography (GPC). One method applied to determine the fraction of each block relative to the change in heat capacity due to the separation of block copolymer uses fractionation of interfacial material by means of denatured redmusters¹. Our method applied is also possible to measure the volume per molecule of information capacity^{2,3}. However, it is also possible to measure the volume per molecule of information capacity^{2,3}.

H is a diene-ticeterate esterandomized triene interphase is the result of molecular diathermization between pure phases. Rubber blends have a significant role in the tire industry, which contimuously tries to obtain a better compromise between wear resistance, rolling resistance and ice- and wet-grip properties of tire tread compounds. Rubbers used in the manufacture of tire tread compounds for instance SBR, BR and NR, are partially miscible when blended and may form weak interfacial adhesion¹. The development of a strong interphase between rubber and polymerizes is an important factor in the durability and performance of rubber blends.

By a two-dimensional array of atoms and molecules which are impermeable to mesans, while the interfacial layer of mesans has a large enough accessibility of atoms or molecules to have its own properties for example modulus, strength, heat capacity and density according to Shultz, 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

$$C_p = Q / \Delta T \quad \dots 1$$

where C_p 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 1°C 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:

$$dQ/dt = C_p dT/dt \quad \dots 2$$

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:

$$T = T_0 + \beta t \quad \dots 3$$

where T is the temperature, T_0 is the starting temperature, and β is the heating rate, dT/dt . This leads to:

$$dQ/dt = \beta C_p \quad \dots 4$$

or

$$C_p = (dQ/dt) / \beta \quad \dots 5$$

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:

$$T = T_0 + Bt + B \sin \omega t \quad \dots 6$$

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:

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

Thus, it follows that:

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

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

$$dQ/dT = C_p \omega B \cos \omega t \quad \dots 9$$

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

$$A_{hf} \cos \omega t = C_p \omega B \cos \omega t \quad \dots 10$$

where A_{hf} is the amplitude of the heat flow modulation. It follows that ωB is the amplitude of the modulation in the heating rate. Therefore:

$$CP = A_{hf} / \omega B \quad \dots 11$$

However, ωB can be replaced with A_{hr} 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

(Table 7) The effect of temperature on the shear modulus

The viscosity of the rubbers was measured at 100°C in a single-speed water bath. Money viscometer according to the British Standard 1673a. The results were expressed in Mooney units (MU) (Table 1). The specific gravity was determined using a glass pyrometer rubber was calibrated cylindrical column of water and by measuring the liquid displacement in a calibrated cylindrical column of water.

Measurement of viscosity, specific gravity,
ultrafiltration of the interphase in the membranes

- 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.t.) silica smoother (60:40, 75:25 by mass).
- The samples were prepared in the HAAKE mixer.

unpublished address.

mixing conditions and storage date. 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.

The rubber was mixed in a HAAKE RHEOCORD 90 (Bielefeld, Germany), a small laboratory mixer with counter rotating rotors. In these experiments, the Lippbury rotors and the mixing chamber were maintained at 25° and 100°C. The rotor speeds were 45 and 30 rpm, 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 cm³, and it was 55% full. HAAKE Software Version 1.9.1 was used for controlling the

九四

The raw rubbers used were SIS (SISRL) Malaysian Natural Rubber Grade L (SMRL) (NBR), styrene-butadiene rubber (23.5 wt % styrene) [SBR] total 1712, (Enechem), and high-cis polybutadiene rubber (BR with 96% 1,4cis) [Buna CR 24, Bayer; not oil-extended]. The remaining nanohiller was Cognis S113, which was supplied by Degussa Limited of Germany. Coumaril S113 is a precipitated amorphous white silica-type ultrafine VN₃, the surfaces of which were pre-treated with bis-(3-triethoxyethylpropyl) tetrasulfophenylTESPT). It has 11.3 wt % silane, 2.5 wt % sulphur (measured by N₂ desorption), a 275 m²/g surface area (measured in TESPT), a 54 nm - 54 nm particle size.

MATERIALS

EXPERIMENTAL

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.

period of 60 s were used throughout the investigations which were conducted at a heating rate of 3°C/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 –140°C 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, ΔC_p , at the glass transition temperature of both

rubbers can be seen in Figure 1. The value of ΔC_p 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 dC_p/dT vs. temperature data (Figure 2) provides that information¹⁹.

Figure 2 shows dC_p/dT vs. temperature for a diffuse interphase in the NR/BR (50:50) blend prepared at 50°C 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 I. RESULTS FROM THE MOONEY VISCOSITY, SPECIFIC GRAVITY AND GLASS TRANSITION TEMPERATURE MEASUREMENTS ON THE PURE RUBBERS

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

$$\frac{dC/dT}{\Delta C_0} = \left[\frac{\exp[-(T-T_c)/T_g]}{(T-T_c)^2} \right]^{1/2} \quad 12$$

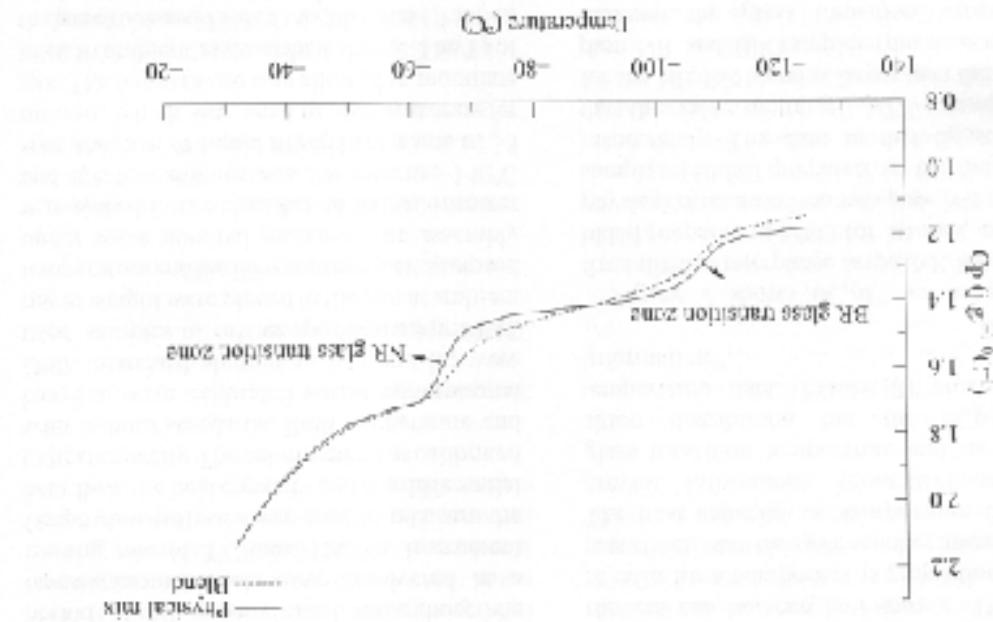
For an imerphase, the differential of heat capacity with temperature, dC/dT , may be considered as the sum of "i" sub systems with individual glass transition temperature for each sub-system, as follows:

For an imerphase, the differential of heat capacity with temperature, dC/dT , may be considered as the sum of "i" sub systems with individual glass transition temperature for above and below the two glass transition signals for rubbers 1 and 2 physical mixtures (50:50) prepared at 50°C.

An example is given in Figure 3 for the NR/BR (50:50) blend when the dC/dT vs. temperature peaks were chosen. The starting and end points of the glass transition were linear with temperature from which were considered as the baseline for the dC/dT signal of these multi-phase systems. For the glass transition temperatures are considered as the baseline temperatures above and below the two glass transition signals for rubber 1 and 2 physical mixtures (50:50) prepared at 50°C.

The values of the dC/dT vs. temperature non-equilibrium baseline had to be corrected of interphase in these multi-phase systems. Thus, the dC/dT vs. temperature single 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 dC/dT vs. temperature signal between the glass transition temperatures described well by the sum of the baselines because of the shift of the glass transition described well by the sum of the glass transition

Figure 1. (a) dC/dT vs. temperature for NR/BR (50:50 by mass) blend (dotted line), and



where ΔCp is the increment of heat capacity, T_g is the glass transition temperature, and ω_{10} is the half width of the 1st sub-system at the interphase⁹. 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 composition¹.

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

$$\delta_1 = \omega_{10} \left(1 - \frac{\Delta Cp_{10}}{\Delta Cp_{11}} \right) \quad \dots 13$$

$$\delta_2 = \omega_{10} \left(1 - \frac{\Delta Cp_{21}}{\Delta Cp_{20}} \right) \quad \dots 14$$

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_{10} and ΔCp_{20} are increments of dC/dT at glass transition temperatures of pure rubbers in blend (area under curve of the Gaussian simulation curve), ΔCp_{11} and ΔCp_{21} are increments of dC/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:

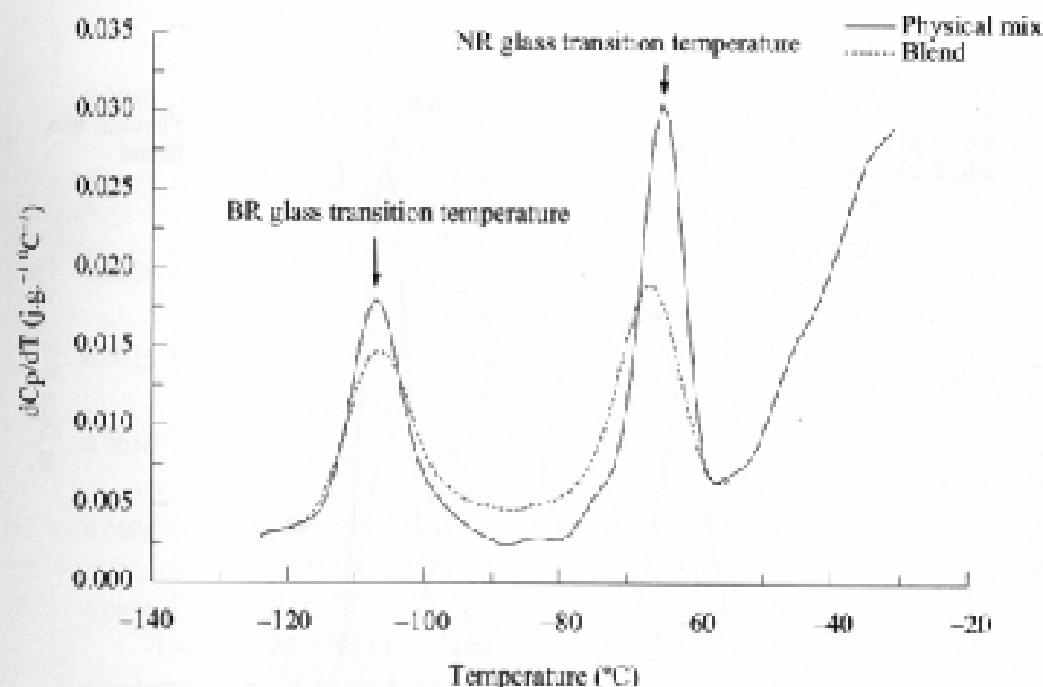


Figure 2. dCp/dT versus temperature for NR/BR (50:50 by mass) blend (dotted line), and NR/BR (50:50 by mass) physical mixture (black line). Samples prepared at 50°C for 30 min.

Figure 4. dC_v/dT versus temperature curve for NR/BR (50/50 by mass) blend and NH/HB (50/50 by mass) prepared at 50°C for 30 min.

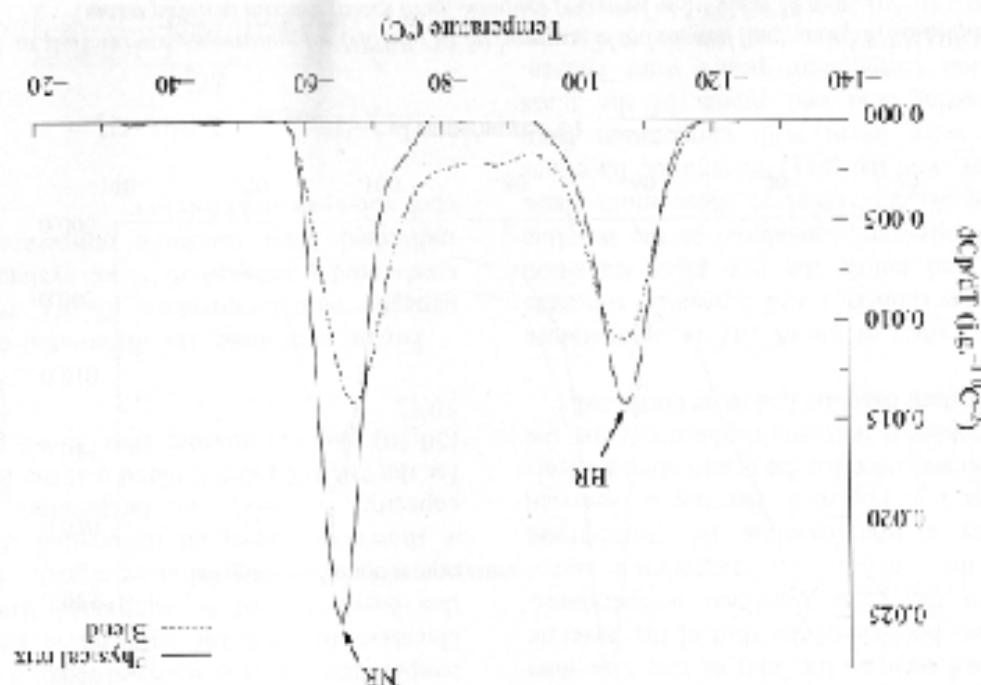
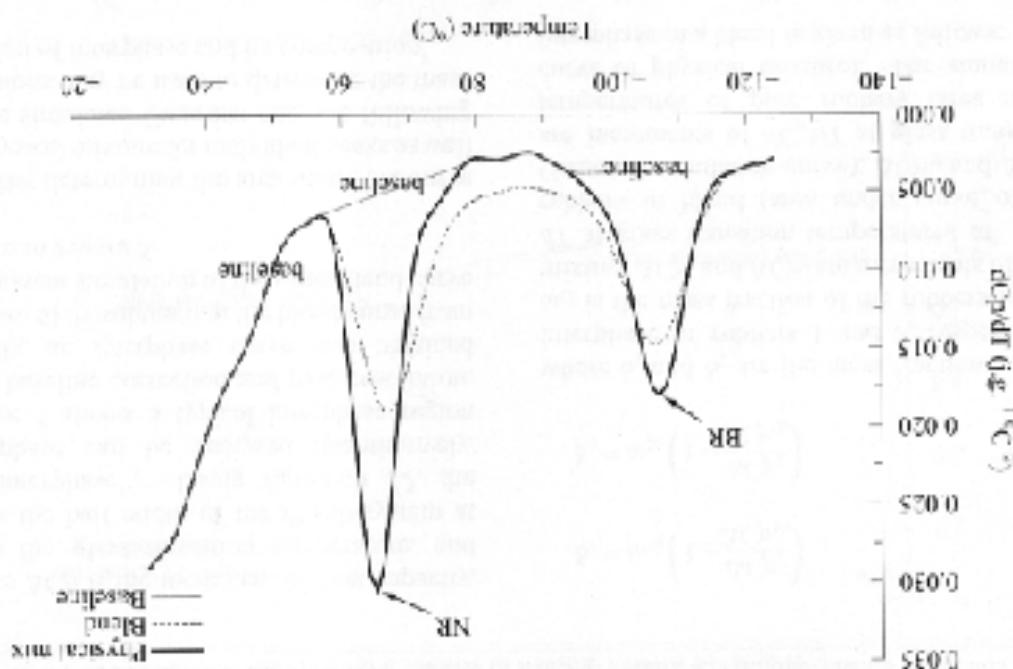


Figure 3. dC_v/dT versus temperature for NR/BR (50/50 by mass) blend (dotted line), and NR/BR (50/50 by mass) physical mixture (solid line).



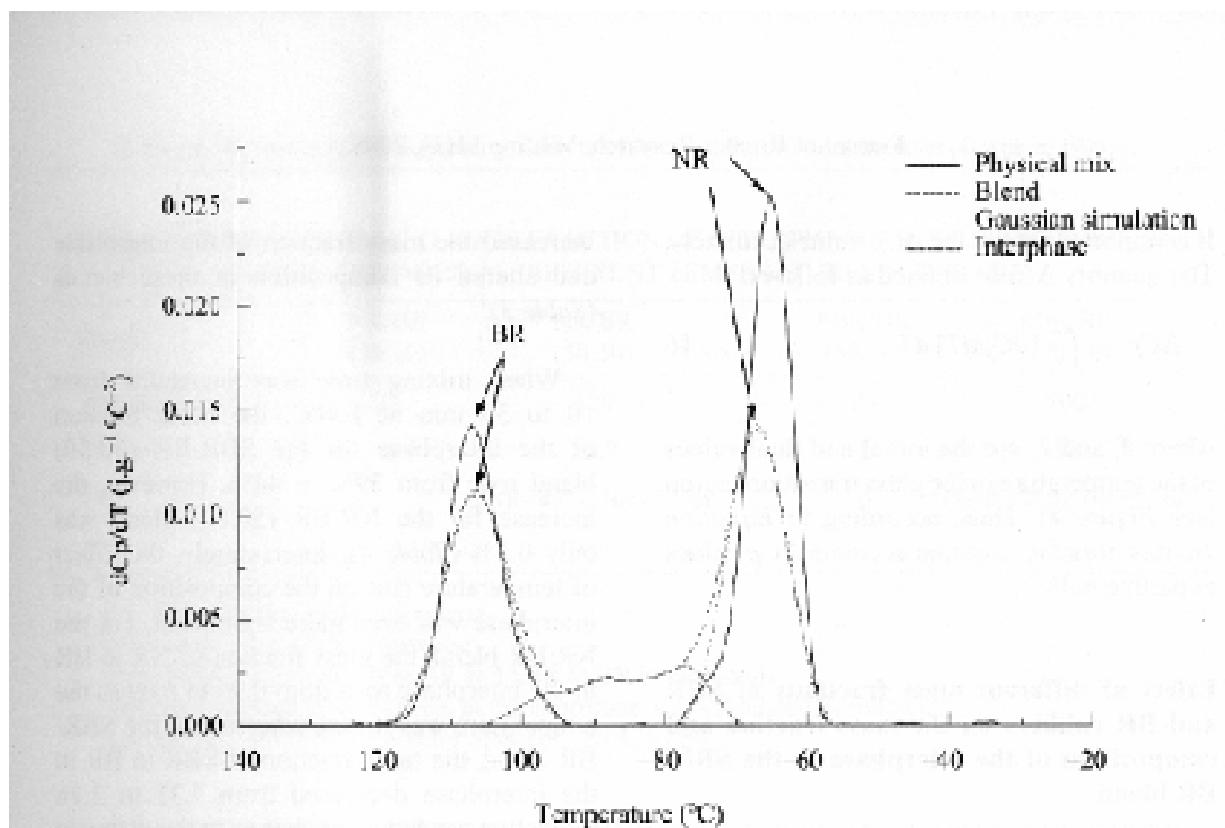


Figure 5. dC_p/dT versus temperature for NR/BR (50:50 by mass) blend after peak resolution in Figure 3 showing the interphase region.

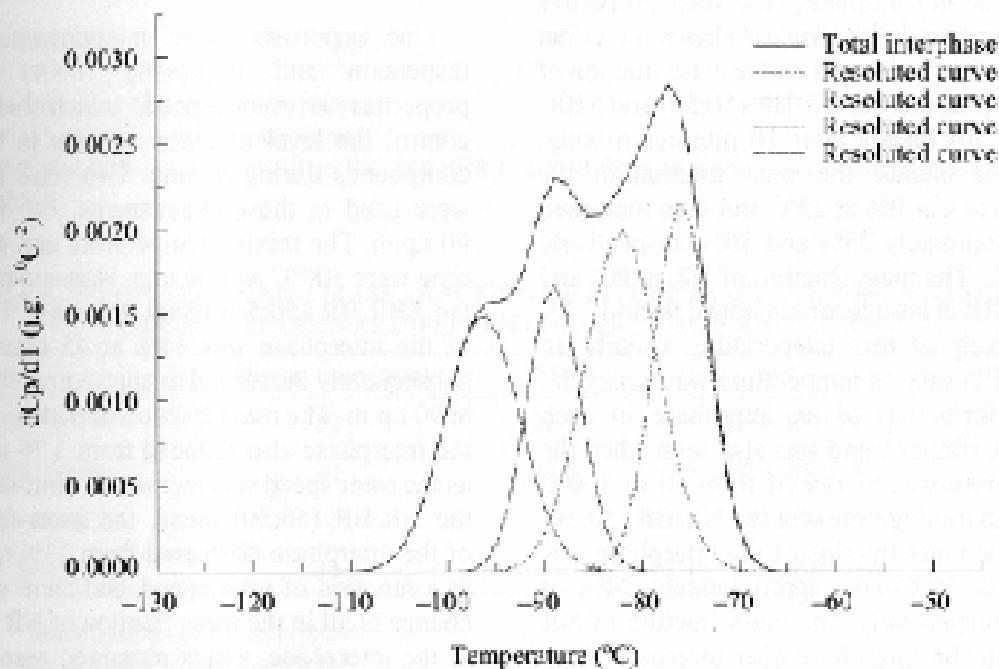


Figure 6. dC_p/dT versus temperature for NR/BR (50:50 by mass) blend showing typical interphase obtained by subtracting the blend curve from Gaussian simulation of the same blend curve shown in Figure 5. The area under the curve is a measure of the mass fraction of the interphase. Sample was prepared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

EFFECT OF ROTOR SPEED ON THE MASS TRANSFER AND COMPOSITION OF THE INTERPHASE IN THE SBR/BR AND NBR/BR BLENDS

increased the mass fraction of the intermediate and altered its composition in these blends (Table 3).

$$91 \cdots \quad \quad \quad L^p [d^2C/dT] = C_p \nabla$$

It is important to get the Δp value accurate.

[View Details](#)

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 (°C)	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 (°C)	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 100°C

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.

Blend	ϵ (%)	ϵ_{**}	ϵ_{***}	ϵ_{****}
SBR/BIR(50:50)	44	(SBR=79%, IIR=21%)	3.76	
SBR/BIR(60:40)	41	(SBR=77%, IIR=23%)	3.45	
SBR/BIR(75:25)	31.2	(SBR=61%, IIR=39%)	1.56	
Mass fraction of the interphase **** Composition of the interphase **** The mass fraction of SBR in the interphase was calculated as described in Table 2				

Blend	Blender speed (imp. min.)	η_s (%)	η_{ss}	η_{sss}	Blends were prepared at 100C for 30 MIN.
SBR/BR(50:50)	45	44.0	(SBR-75%, BR-25%)	3.76	SBR AND NBR BLENDS AS A FUNCTION OF THE ROTOR SPEED.
SBR/BR(50:50)	90	38.7	(SBR-49%, BR-51%)	3.76	TABLE 3. COMPOSITION AND MASS FRACTION OF THE INTERPHASES IN THE
NR/BR(50:50)	45	23.4	(NR-87%, BR-13%)	0.96	SBR/NBR BLENDS AS A FUNCTION OF THE ROTOR SPEED.
NR/BR(50:50)	90	20.0	(NR-87%, BR-13%)	0.69	TABLE 2.
*** Mass fraction of the interphases **** Composition of the interphases **** The mass fraction of NR to BR, and SBR to BR in the interphase was calculated as described in					

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. For the SBR/BR (50:50) blend at 100°C temperature and 30 minutes mixing time, the mass fraction of the interphase was determined to be 0.44% (Table 6). 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 pure SBR/BR increased to 0.41% and 0.312%, respectively. Obviously, an increase in the interphase decreased the mass fraction of pure SBR in the blend. Moreover, the mass fraction of pure SBR in the blend was 0.44% at 100°C and 30 minutes mixing time, while it was 0.41% at 100°C and 10 minutes mixing time. This indicates that the mass fraction of pure SBR in the blend decreased with increasing mixing time.

When the SBR/BR (50:50) and (75:25) blends were prepared at 50°C 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

blended¹. 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 20 min and then, 60 p.h.r. silica was added and mixed for an extra 10 min at 100°C 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 50°C 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=58.2%, 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 PH.R. SILICA NANOFILLER. BLENDS WERE PREPARED AT 100°C FOR 40 MIN

Blend	I* (%)	I**	I***
SBR/BR(75:25)	31.2	(SBR=51%, BR=49%)	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.

At 50 and 100°C mixing temperatures and 30 min mixing time, the mass fraction of de interparticle deoxygenated progressively as the mass fraction of SBR to BR in the SBR/BR blend increased from 50:50 to 75:25.

When the mass fraction of pure SBR is 0.5, the rubber changed in the SBR/BR blend, the interparticle were significantly affected. It

At 100°C mixing temperature and 30 min mixing time, the mass fraction of the interphase decreased for both blends as the role speed was increased from 45 to 90 rpm.

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

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

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

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

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

CONCLUSIONS

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 50-100°C 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, as 51 and 49 MU, respectively, whereas NR, had a much higher viscosity of 97 MU (Table 7). 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 rubber.

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where r is the mass fraction of the interphase in the blend, t is the mixing time, and T is the mixing temperature. A, ϵ , b , and C are constants for a given blend. After substitution of the experimental results in Equation 17 and finding the empirical relation in Figure 17 and fitting the best possible graphical fit to the data, an empirical equation for the NR/BR and SBR/BR blends is found:

$$\mathcal{D} + \text{ad}_P J^P = \int_{\Gamma}$$

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:

Empirical equations for the prediction of interphases in the rubber blends

out 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 rubber. It is supposed that low shear blends the mass fraction of the interphase because the rubber and oil at the same time the composition changed.

When 60 phr silanised silica nanofiller was incorporated in the raw SBR/BR blend at 100°C 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.

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REFERENCES

1. DKEI, 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., HAMMICHÉ, 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. ANSARIAR, M.A., FULLER, K.N.G. AND LAKE, G.J. (1993) Adhesion of Unvulcanised 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 Boundary 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 Modelled on the Concept of Interphase. *J. Appl. Polym. Sci.*, **27**, 3019–3025.
10. KOBBERSTEIN, I.I., MORRA, S. AND STEIN, R.S. (1980) Determination of Diffuse-Boundary Thickness of Polymers by Small-Angle X-Ray Scattering. *J. Appl. Crystallogr.*, **13**, 34–45.
11. ROD, R.J. (1982) Estimation of Errors in the Determination of Phase Boundary Thickness by X-Ray. *J. Appl. Crystallogr.*, **25**, 182–189.
12. RULAND, W. (1987) Small-Angle Scattering of the Statistical Structure of Domain Boundaries. *Macromolecules*, **20**, 87–95.
13. ANNIGHOFER, E. 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. ANNIGHOFER, E. AND GRONSKI, W. (1984) Block Copolymers with Board

15. KREISSLER, J., HIGASHIDA, N., INOUE, T., HECKMAN, W. AND SEITZ, E. (1993) Study on Polymer-Polymer Interactions: A Comparison of Ellipsometry and TEM of Testig Raw Rubber and Immiscible Compounded Rubber Methods of Polymer Testing. *BSI 1623-Part 3*
16. BECKMAN, E.L., KARASZ, F.E., PORTER, R.S., MACKINIGHT, W.L., HUNSEL, D.V. AND KONINGSVELD, R. (1988) Estimation of the Interfacial Friction in Partly Miscible Polymer Blends from DSC Measurements. *Macromolecules*, **21**, 1193-1194.
17. READING, M., HAHN, B. AND CROWS, B. (1993) *CSPATENT 5224775*.
18. READING, M. (1993) Modelled Differential Scanning Calorimetry - A New Way Forward in Materials Characterisation Trends. *Joyce Seifert Ltd., UK*, 248-255.
19. SONG, M., HOUSTON, D.L. READING, M., WILDCRICK, H.M. AND HAMMICH, J. (1993) *Rubber Chem. Technol.*, **75**, 365-427.
20. BRITISH STANDARDS (1969) Methods of Testing Raw Rubber and Immiscible Compounded Rubber Methods of Polymer Testing. *BSI 1623-Part 3*
21. SONG, M., HOUSTON, D.L. AND SCHAFER, H.L. (1999) Modelled Differential Scanning Calorimetry. *12. International Conference on Polymers and Composites, London, UK*, 2094.
22. VOVITSKII, S.S. AND VAKUL'IA, V.L. (1963) The Role of Diffusion in Polymer-*Polymer Adhesion at High Temperature*. *Vysokomol. Soi.*, **7**, 475-491.
23. JABBARI, ESMAIL, AND PEPPAS, N.A. (1995) A Model for Interdiffusion in Interfaces of Polymers with Dissimilar Properties. *Polymers Preprints*, **36**(3), 575-586.
24. MANOORAL, D. (2002) Heteromer blends. *Rubber Chem. Technol.*, **75**, 365-427.