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Improving the Low Temperature Resistance of Natural Rubber

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A series of vulcanised blends of natural rubber (NR) with high vinyl butadiene rubber (BR) have been prepared and these exhibit polymer miscibility, as demonstrated by using a number of techniques, over a broad range of blend compositions. The susceptibility to low temperature crystallisation of sulphur cured gum and black-filled blend vulcanisates containing up to 25% high vinyl BR has been determined. In the strained state this has been determined by measuring the loss of stress associated with crystallisation and in the unstrained state by measurement of the differential scanning calorimetry melting point endotherm. A number of factors have been shown to influence the resistance of the NR blends to low temperature crystallisation. These include high vinyl content of the blend, the nature of the cure system and the presence of carbon black filler. In blend compositions containing less than 20% high vinyl BR content, little significant loss of strain crystallisation in NR occurs, as indicated by the retention of both tensile and non-relaxing fatigue properties. The use of such blends where improved resistance to low temperature crystallisation is required is discussed.

Key words: low temperature, resistance, NR, blends, crystallisation, vinyl BR, PVE, DSC

The susceptibility of natural rubber (NR) to crystallisation is generally regarded as a useful attribute when induced by strain. It is responsible in a large part for the high strength properties of NR, especially in the absence of reinforcing fillers. However, crystallisation of NR may also be induced by exposure to temperatures in the range –50°C to 15°C for extended periods[1,2]. In the raw state, crystallisation in bales of NR is an inconvenience that requires placement of the affected rubber in a >hot room = for a short period prior to processing to melt any crystallites that have formed during shipping or warehousing. The possibility of crystallisation in vulcanised NR is seen as being a more serious problem and is sometimes cited as a reason to specify an alternative polymer where service conditions require a long-term low temperature capability.

Inhibition of low temperature crystallisation in NR is thus a desirable goal and may be achieved successfully by the use of either a >conventional = sulphur cure system[3,4] or main chain isomerisation[5]. The common feature of these methods lies in the ability of main chain modification, either as a result of vulcanisation or of isomerisation of the normal *cis*-orientation, to disrupt the stereo-regularity of the polymer chain so inhibiting the process of crystallite

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formation. However, the degree of disruption of crystallisation in NR must be sufficiently low as not to impinge significantly on the strength properties of NR imparted by strain crystallisation. Where neither of the above methods is viable, an alternative method to protect NR against crystallisation in environments where long term exposure to low temperatures occurs is required. Inhibition of low temperature crystallisation in NR vulcanisates as described in this paper is achieved through the use of miscibility with a second polymer to bring about partial disruption of the crystal structure of NR to delay onset of crystallisation at low temperatures.

Miscibility between polymer pairs is a very uncommon occurrence and despite the rapid increase in use and development of polymer blends by the rubber and plastics industry over the past four decades, the vast majority of polymer blends are either immiscible or display traits only of partial miscibility. For technical utility however, the components of a blend need only be 'compatible' to the extent that a satisfactory dispersion can be attained without subsequent de-mixing on a macroscopic scale[6].

For miscibility to exist in a polymer blend, the formula for the free energy of mixing (*Equation 1*) must be negative.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad \ldots 1$$

In the case of polar polymers this condition can be satisfied if there is an exothermic interaction between the blend components, this usually takes the form of hydrogen bonding between functional groups present on each component polymer chain. Such specific interactions are sufficiently large to offset the positive enthalpy change associated with the van der Waals interactions between blend components. The contribution from the entropy term is negligible, especially at higher molecular weights. Examples of miscible polar polymers are PVC/NBR, PS/Polyphenylene ether and ENR-25/PVC.

For non-polar polymers, where specific interactions between polymer components are absent, the mixing enthalpy arising from van der Waals interactions between dissimilar polymers is usually sufficient to bring about phase segregation, particularly at high molecular weights where the combinatory entropy change is very small. Miscible non-polar polymers do exist however, the most well known being *cis*-1,4-polyisoprene (PI) and atactic poly(vinylethylene) (PVE) as described by Roland *et al.*[7–12]. It was shown that this polymer pair act as a near ideal mixture, the polarisability and liquid structure of the components are very similar[10,11], inferring an extremely small Flory-Huggins interaction parameter[10].

The work described here involves blends of NR with a high vinyl BR, the vinyl content of which is significantly below that of PVE used by Roland *et al.*[7–12]. Investigation of the miscibility between NR and high vinyl BR is carried out using well established techniques. The effect upon crystallisation behaviour of NR/high vinyl BR blends is studied with a view to improving the low temperature crystallisation resistance of NR without compromising the strain crystallising ability of NR vulcanisates.

EXPERIMENTAL

The NR used was SMR L grade. The high vinyl BR was BR-90 as produced by Japan Synthetic Rubber Co., (vinyl content ~63%), or Vi 1979 as produced by Bayer AG (vinyl content ~69%).

Dynamic measurements were performed at 1 Hz with the sample in dual cantilever mode (at ~0.01% strain at a heating rate of 2°C/min) using a Polymer Laboratory Ltd DMTS instrument. Differential scanning calorimetry (DSC) analyses were carried out on Perkin Elmer DSC 2 and 7 instruments. Glass transition temperatures (*Tg*) were determined both by DMTA and DSC, either as the temperature of loss angle maximum or as the onset temperature of change in ΔG. DSC was calibrated with raw NR at the heating rate used (20°C/min) at a *Tg* of –72°C. Mixing of gum polymers was carried out in a Brabender Plasti-corder PLV 151 internal mixer whilst black filled compounds were prepared in a BR Banbury internal mixer. Masterbatches were finalised on a two-roll mill, typically at 70°C for 5 min. Rheometry was carried out using Monsanto ODR-100 or MDR2000E instruments. Vulcanised sheets were prepared by moulding and curing under pressure at 150°C.

DSC was used for unstrained low temperature crystallisation measurements. Pre-weighed vulcanisate samples (18 mg ∀2 mg) were sealed in DSC specimen holders prior to being stored in glass sample tubes in an aluminium block cooled to –26° ∀2°C in a freezer. The samples were cooled in a dry ice bath during transfer to the calorimeter, which was held at –50°C. After 4 min, each sample was heated at 20°C/min up to +20°C. The degree of crystallisation was determined after periods of time up to 150 days by integration of the melting point endotherms of typically 3 samples. Strained low temperature crystallisation measurements were made using a six station, constant strain (150%) test jig, each station was fitted with a strain gauge to monitor the reduction of stress in tension set test pieces.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of tan δ on temperature for both NR and high vinyl BR (BR-90) as determined by DMTA. It can be seen that the respective *Tg*s, as indicated by the peak tan δ value, are well separated and that unlike NR the *Tg* for BR-90 is quite broad. A range of NR/BR-90 blends at differing polymer ratios were prepared in a Brabender Plasti-corder PLV 151. DMTA data for these blends is also shown in *Figure 1*, the single *Tg*s indicating miscibility for blends containing 50% or less BR-90. At the higher blend ratio of 25:75 NR:BR-90, the presence of a very broad *Tg* suggests that phase separation may be occurring although evidence from both DSC and microscopy suggest the contrary. Literature reports[13] would tend to support this latter view.

The ease with which miscibility between NR and BR-90 is achieved in the internal mixer was also studied. *Figure 2* shows the effect on DMTA response of reducing the mixing time from 4 min to 2 min for 50:50 gum blends. In each case, as soon as possible after dumping, the mix was pressed at 100°C for 1 min then rapidly quenched in liquid nitrogen. Essentially no difference was observed in the DMTA or DSC traces of the blends after mixing for 1 min in a Plasticorder internal mixer. Indeed, it was observed that in a sample mixed for only 30 s, extending the pressing time at 100°C to 8 min was sufficient to bring about improved miscibility (*Figure 3*).

Having established miscibility in NR/BR-90 blends having a blend ratio of up to 50 p.h.r. BR-90, a series of semi-EV gum vulcanisate blends were prepared with the aim of investigating their physical properties. It is of interest also to note the cure characteristics of the NR/BR-90 blends as shown in *Table 1*. It can be seen that increased levels of high vinyl BR increase the time to maximum cure quite significantly. This may be rationalised by consideration of the reduced chemical reactivity towards sulphur based curatives of

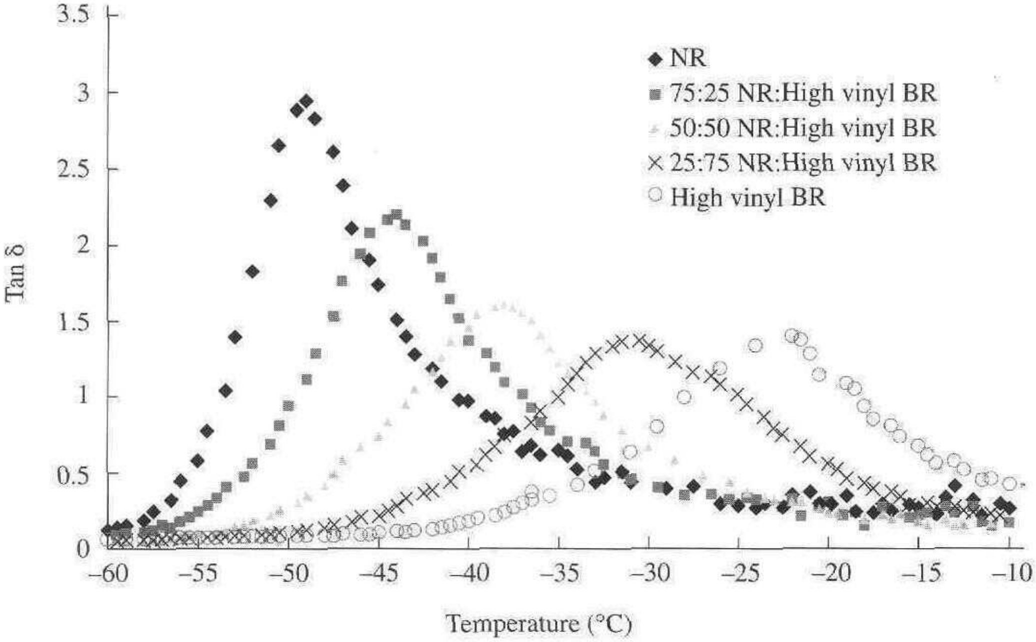

Figure 1. DMTA measurements of Tg *(1 Hz).*

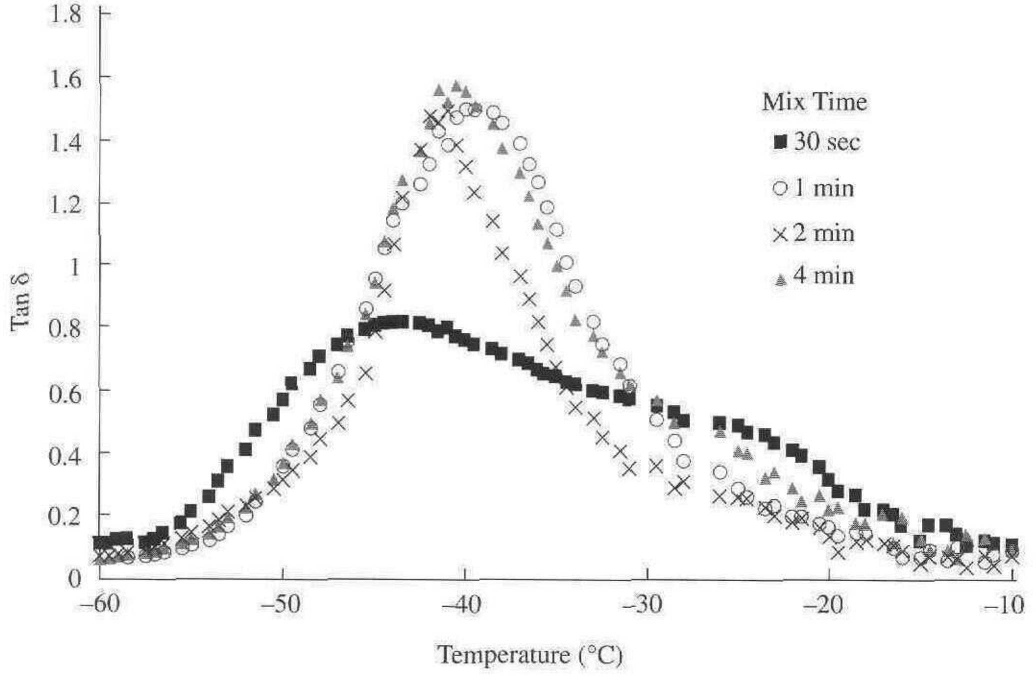

Figure 2. Effect of mixing time on miscibility of a 50:50 NR/High vinyl BR (BR-90) gum blend.

the less substituted double bond in high vinyl BR compared with that of NR. The tensile properties of the semi-EV gum vulcanisate blends that were prepared are also compared in *Table 1*. Tensile properties are largely maintained for blends containing 25 p.h.r. or less BR-90, suggesting retention of strain crystallisation behaviour in such blends. The total absence of strain crystallisation in BR-90 is illustrated by its very poor tensile strength.

In miscible blends, both increases or decreases in the rate of crystallisation can occur[14–18]. Modification of the crystallisation behaviour of NR is of interest both from the point of view of strain induced crystallisation and of low temperature crystallisation. The crystallisation behaviour of NR/PVE blends has been studied in some depth by Roland and his associates[19,20] and it has been shown that in gum blends both the degree of crystallisation and the rate of crystallisation were reduced by the presence of PVE. The rate of crystallisation decreases in proportion to the concentration of PVE in the blend whereas suppression of the extent of crystallisation was found to be independent of the PVE concentration.

Low temperature crystallisation measurements of NR/BR-90 blends were initially made with semi-EV gum vulcanisates strained to 150% by following the loss of tension with time at –26°C; the onset of low temperature crystallisation being considerably accelerated under the conditions of high strain. Inhibition periods, obtained as illustrated by *Figure 4*, are shown in *Figure 5*. These results show that significant retardation of low temperature crystallisation occurs in NR/BR-90 gum blends containing 10 p.h.r. or more BR-90. To get a more realistic measure of the effect that BR-90 has on delaying the onset of low temperature crystallisation in NR, the degree of crystallisation occurring in unstrained samples at –26°C was analysed by DSC. *Figure 6* shows the degree of crystallisation developed after 58 days at –26°C for a series of semi-EV gum vulcanisates. The maximum degree of crystallisation is in the order of 25% to 30%, which is in keeping with previous reported experience[4]. Again, the presence of 10 p.h.r. BR-90 has a considerable effect in delaying the onset of low temperature crystallisation whilst at a level of 25 p.h.r. BR-90, no crystallisation whatsoever is detected after 58 days.

TABLE 1. CURE CHARACTERISTICS AND STRENGTH PROPERTIES OF SEMI-EV NR/BR-90 GUM BLENDS

BR-90 Content (p.h.r.)	Cure time (t_{max}) (min)	Tensile strength (MPa)
0	35	22.9
2	35	23.2
5	35	20.3
10	40	20.3
25	50	18.5
50	60	7.4
100	120	1.3

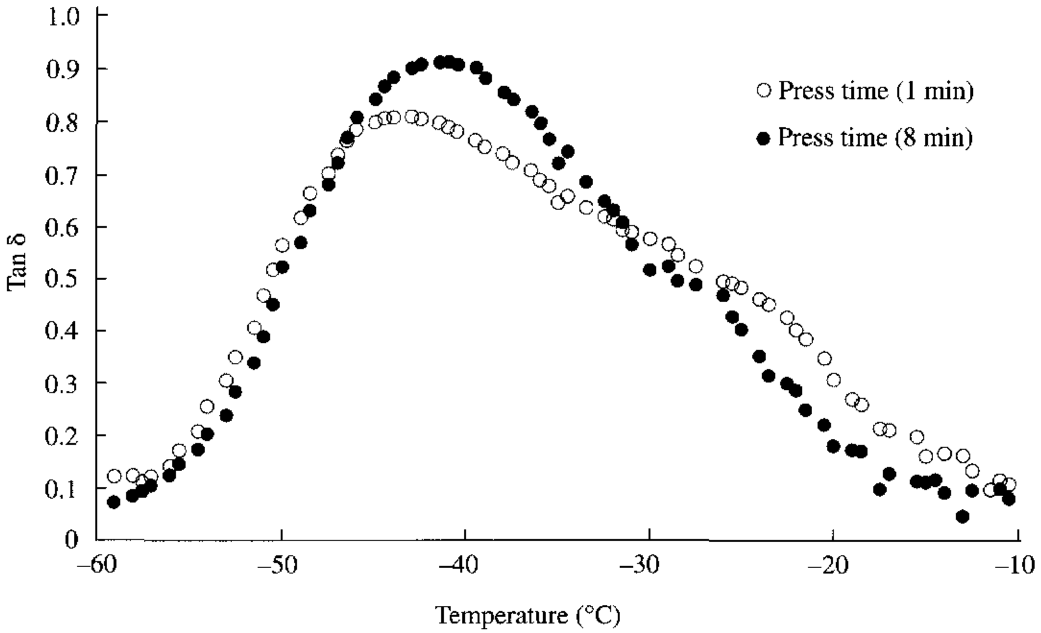

Figure 3. Effect of press time on miscibility of a 50:50 NR/High vinyl BR (BR-90) gum blend mixed for 30 sec.

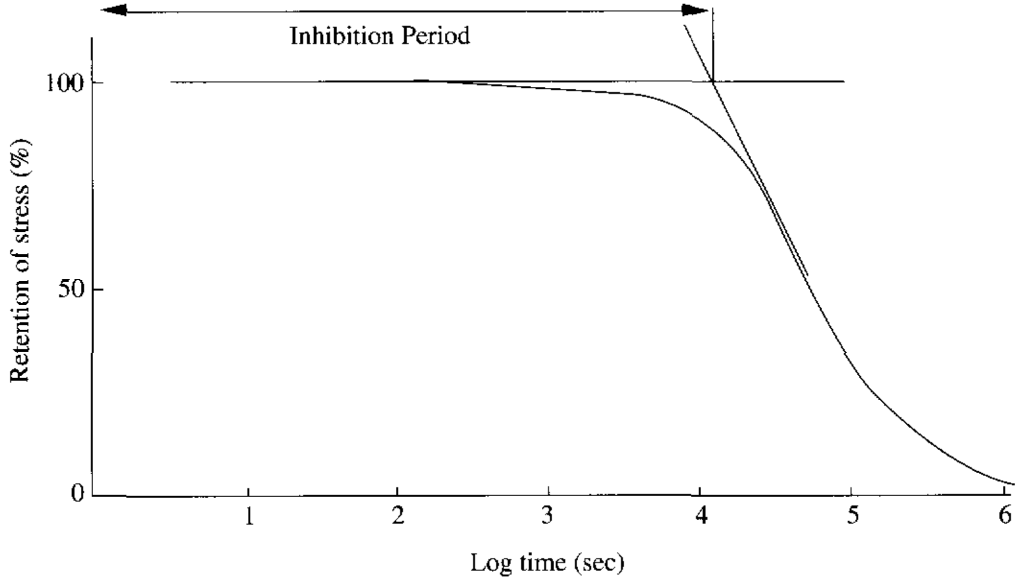

Figure 4. Determination of low temperature crystallisation inhibition periods in NR vulcanisates under conditions of high strain.

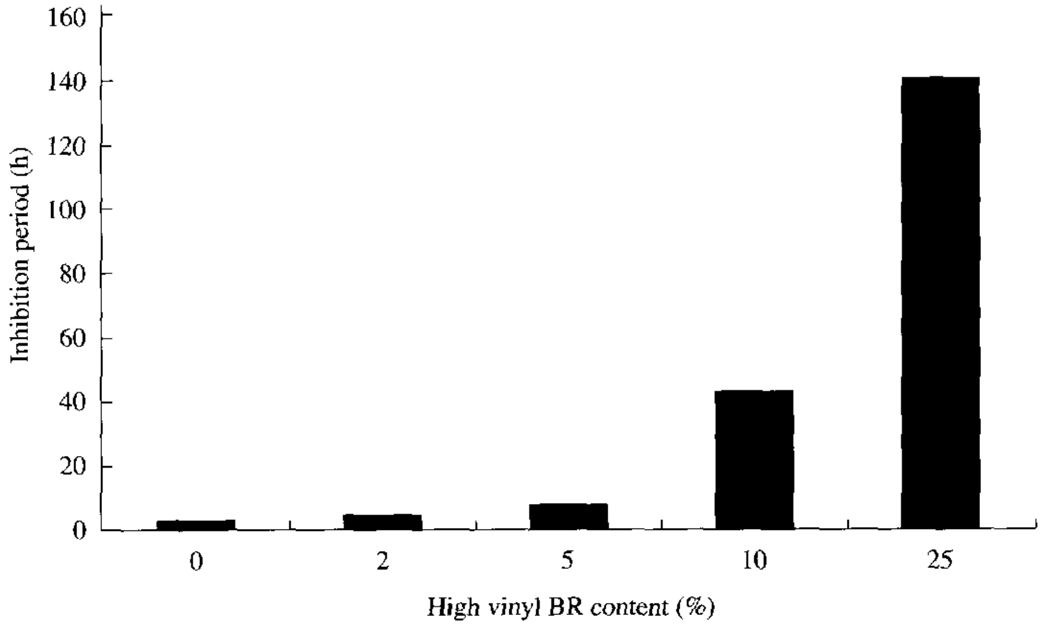

Figure 5. Low temperature crystallisation inhibition periods of strained semi-EV NR/High vinyl BR (BR-90) gum blends.

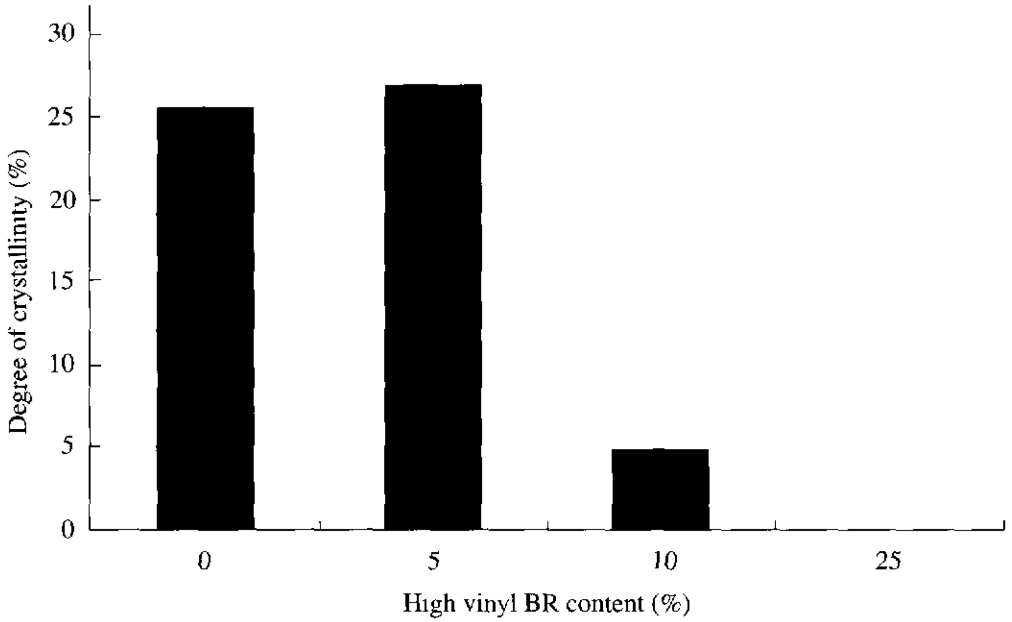

Figure 6. Degree of crystallisation in unstrained semi-EV gum NR/High vinyl BR (BR-90) blends (–26°C/58 days)

Mindful of the problem of improving the resistance of NR in technologically important applications, black filled NR/BR-90 blend vulcanisates having typical engineering application formulations (conventional — 2.5 S/0.6 CBS, semi-EV — 1.2 S/1.2 CBS and EV —0.5 S/6.0 CBS cure systems containing 45 p.h.r. N762 black and 4.5 p.h.r. process oil) were prepared. Tensile properties of these vulcanisates are shown in *Figure 7*. Whilst tensile properties show a gradual reduction with an increased high vinyl BR blend ratio they remain acceptable even up to 20 p.h.r. high vinyl BR indicating, as with unfilled vulcanisate blends, the maintenance of a degree of strain crystallisation. Relaxing and non-relaxing ring fatigue test results also support the view that strain crystallisation is largely retained at modest levels of BR-90 as no loss of fatigue performance has been observed in blends containing up to 15 p.h.r. high vinyl BR. Whilst tear strengths for these compounds show reductions of between 20% - 40% with increased high vinyl BR content, comparisons are highly dependent upon compound formulation as indicated in *Figure 8*. Here the tensile and tear strengths of a NR compound with a semi-EV type cure designed for high damping applications are compared with a similar compound where NR has been substituted to the extent of 15 p.h.r. with high vinyl BR. For the compound containing the high vinyl BR, tensile strength is essentially maintained and rather unexpectedly, there is also a significant improvement in tear strength. Low temperature modulus measurements at low strain (2.5%) of a high damping compound containing 10 p.h.r. high vinyl BR (Bayer Vi 1979) have shown significantly improved low temperature crystallisation behaviour at –10°C and –25°C compared with a similar all NR control compound[21], as seen in *Figure 9*.

Unstrained low temperature crystallisation testing of black-filled blends show that none of the vulcanisates having a conventional cure system exhibit any signs of crystallisation after more than 90 days at –26°C. This result is not unexpected considering the known[4] resistance to low temperature crystallisation of vulcanisates cured using a 'conventional' cure system. Good resistance to low temperature crystallisation is also shown by the semi-EV and EV blend vulcanisates (*Figures 10* and *11*) at levels above 10 p.h.r. BR-90 with the EV vulcanisates showing slightly better resistance than comparable semi-EV samples. This observed difference is believed to be because of the increased level of cure achieved in the EV blends compared with the semi-EV blends which serves to decrease NR and high vinyl BR chain mobility, thus reducing the rate at which NR is able to form crystal laminae at low temperature.

Differences in low temperature crystallisation behaviour between gum and black-filled blends have also been shown to exist. Whilst inhibition periods for black filled blends are shorter than for gum blends, the overall rate of crystallisation is higher for unfilled blends (*Figure 12*). It is suggested that the carbon black acts to nucleate crystallites[22] but that it also restricts mobility of the NR and high vinyl BR polymer chains, so reducing the rate of crystallisation at low temperature.

CONCLUSIONS

Miscibility has been demonstrated in gum blends of NR and high vinyl BR containing up to 75 p.h.r. high vinyl BR. In both gum and black-filled blends containing less than 25 p.h.r. high vinyl BR, it has been shown that strain crystallisation together with most other physical properties are retained. Tear strength properties may however be reduced

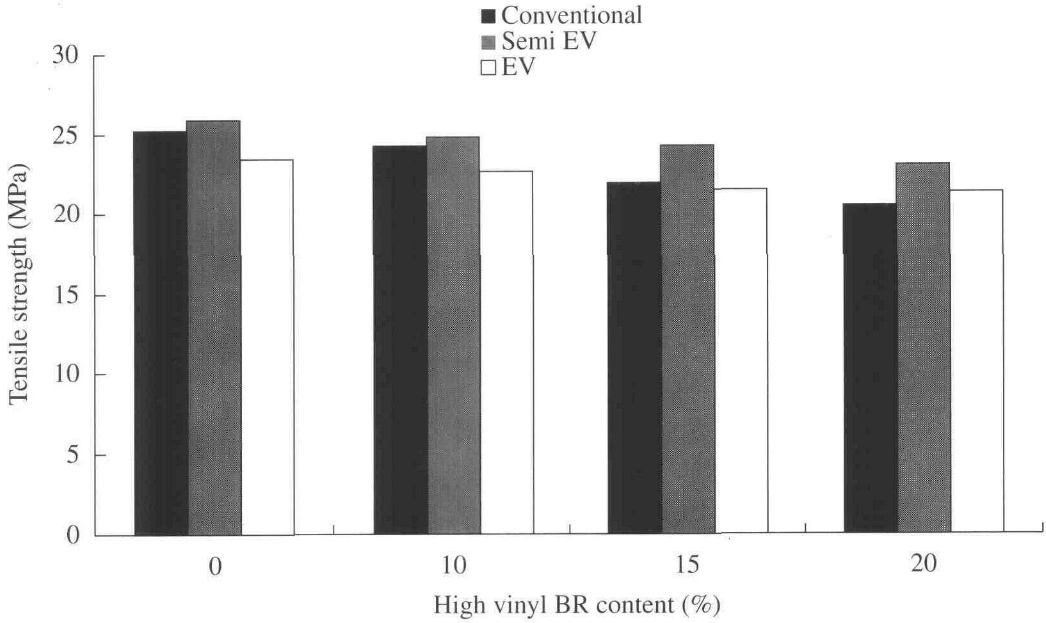

Figure 7. Tensile properties of black-filled NR/High vinyl BR (BR-90) blends.

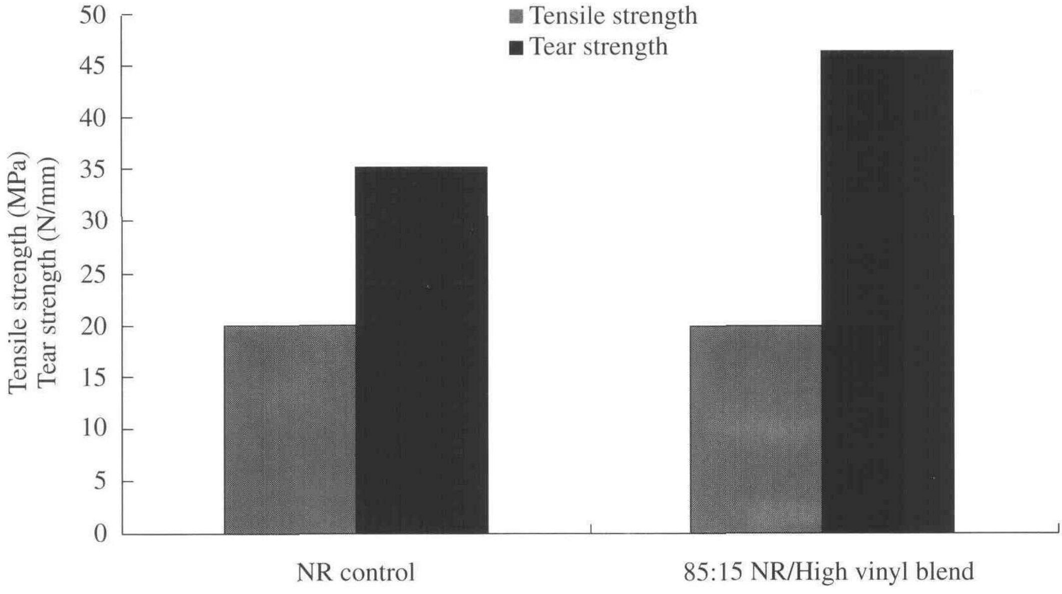

Figure 8. Strength properties of NR and NR/High vinyl BR high damping compounds.

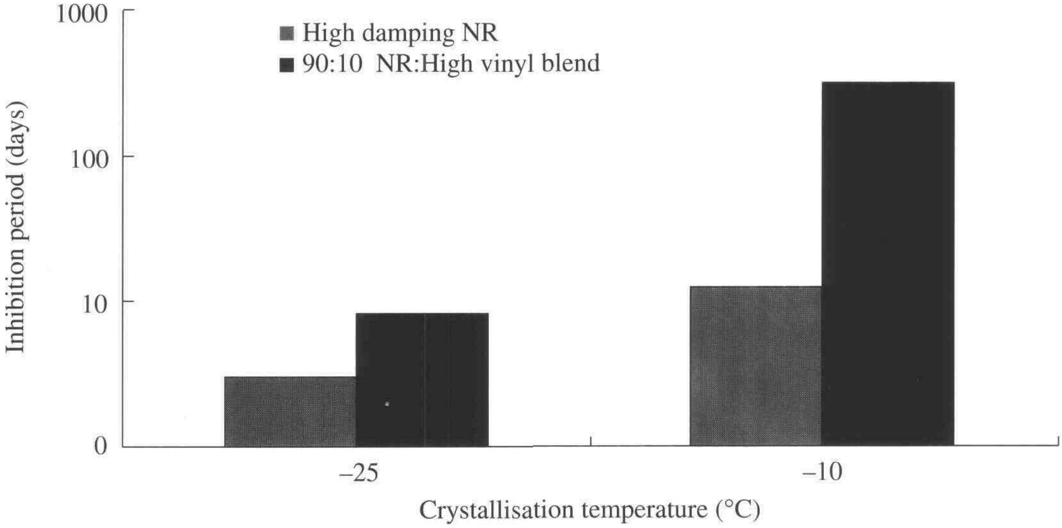

Figure 9. Inhibition of low temperature crystallisation in NR and NR/High vinyl BR high damping compounds.

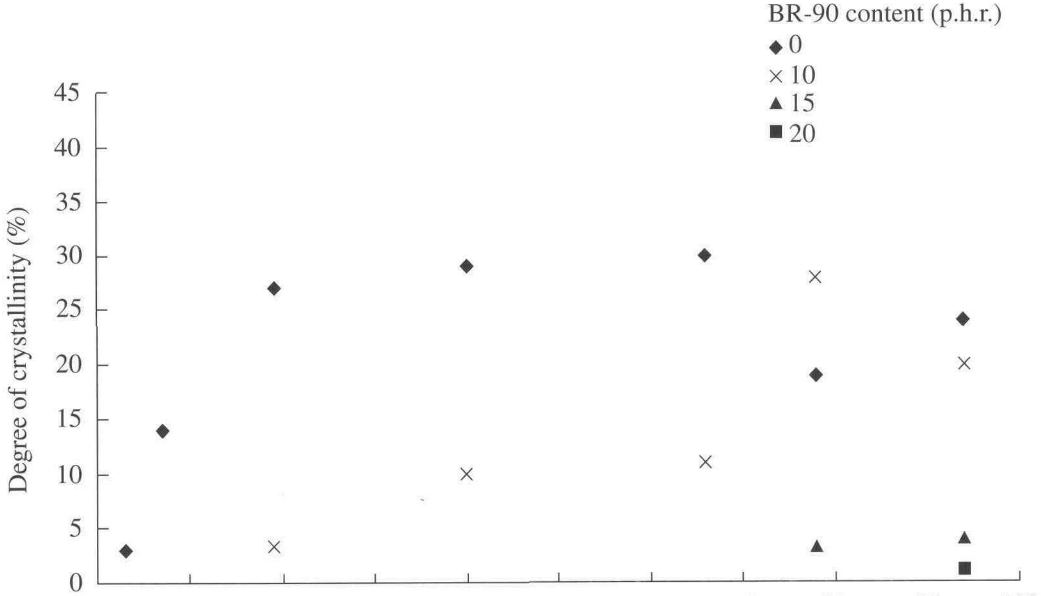

Figure 10. Degree of crystallisation in unstrained semi-EV black-filled NR/High vinyl BR (BR-90) blends.

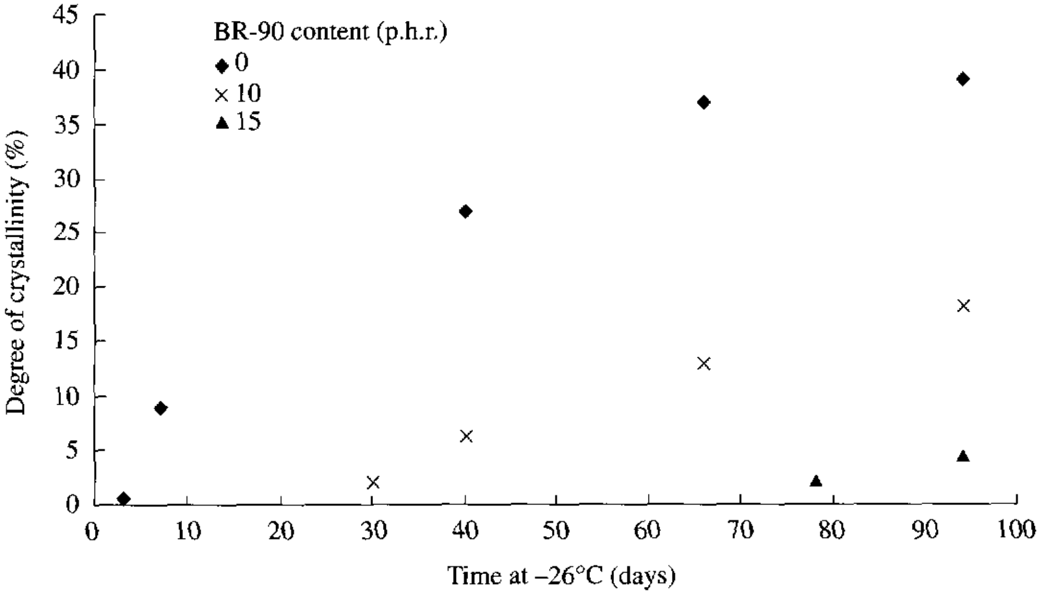

Figure 11. Degree of crystallisation in unstrained EV black-filled NR/High vinyl BR (BR-90) blends.

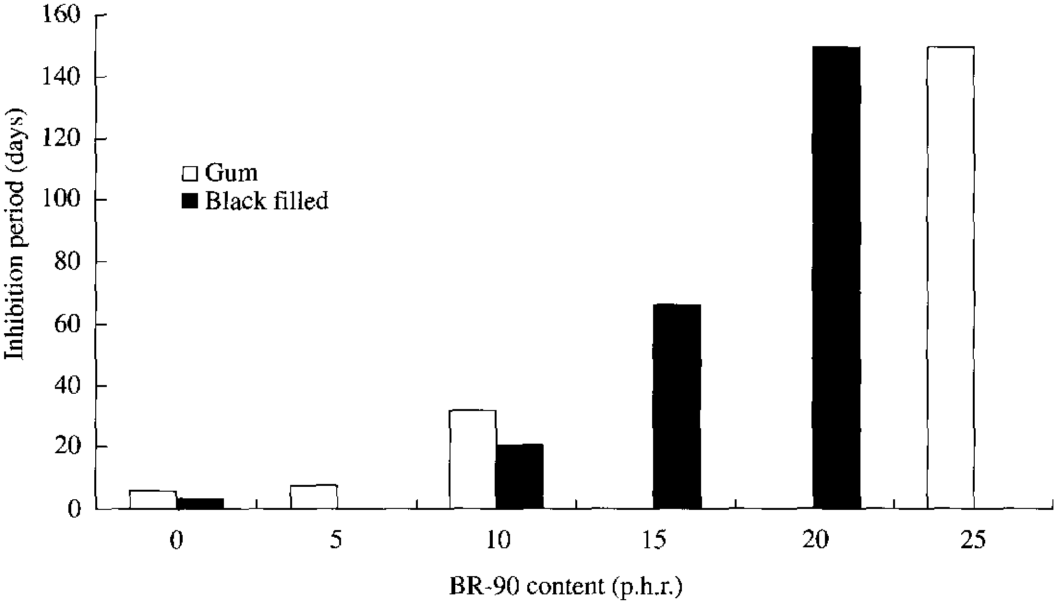

Figure 12. Low temperature crystallisation inhibition periods for gum and black-filled semi-EV NR/High vinyl BR blends (–26°C/150% strain).

in blends containing high vinyl BR. Low temperature crystallisation investigated in both the strained (150%) and unstrained states is considerably inhibited in both filled and unfilled blends where the blend ratio of high vinyl BR exceeds 10%. Thus, NR/high vinyl BR blends containing between 10 p.h.r. and 20 p.h.r. would be expected to show promise in applications requiring resistance to low temperature. One such application which has been under evaluation at Tun Abdul Razak Research Centre is in the area of seismic bearing compounding where a NR/high vinyl BR blend has been shown to have superior resistance to low temperature crystallisation compared with a NR based seismic bearing formulation currently in use.

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