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# IMPROVING PHASE MORPHOLOGY AND PROPERTIES OF NR/NBR BLENDS WITH COMPATIBILIZERS

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## ABSTRACT

*Two compatibilizing agents have been identified for NR/NBR blends to improve the phase morphology and interfacial adhesion, thereby improving the physical & technological properties. Light and optical microscopy and Nuclear Magnetic Resonance have been used to study the phase contrast and crosslink distribution of the elastomer blends respectively, to support the observations made on the improvements in the physical properties of these blends.*

**Key words:** blends, compatibilizers, homogeneous, microscopy, phase morphology

## INTRODUCTION

It is known that truly miscible elastomer blends are rare, particularly in commercial use, due to a number of factors which arise in blends of elastomers. These factors may be summarized as:

- Polymer ratio
- Interfacial adhesion/crosslinking
- Phase morphology
- Distribution of fillers, plasticizers and crosslinks between the elastomers

Contacts between the two elastomers hence become unfavorable causing large phase sizes and difficulties in achieving a good balance of properties and adequate crosslinking between them.

When blending polymers it is necessary to achieve one of the following morphologies.

1. complete homogeneity; so that the two components cannot be identified as discrete phases.

2. partial compatibility; so that although two phases may be present, the boundary regions are diffuse and consist of compatible mixtures of the two components.

Deleterious effects are experienced when the two polymers are totally incompatible and two distinct phases with sharp interfacial boundaries are obtained. The mechanical properties for instance, are impaired because the interfacial surface energy is so low that a tear or crack can easily propagate between the boundaries. Other properties, such as solvent resistance and vapour diffusion, would also suffer as a result of the weak boundary regions between the two phases. The actual available spaces for the diffusion of a solvent into these regions are much greater than those offered by the free volumes of the individual polymer components.

Blending of highly incompatible elastomers may sometimes be improved by the addition of small amounts of another polymer. Setua & White (1991) applied this technique to improve the homogeneity of binary and ternary blends of CR, NBR and EPDM. When a small amount of chlorinated polyethylene is added to NBR/EPDM or CR/EPDM blends, they mix more rapidly. The chlorinated polyethylene act as a compatibilizing agent which appears to form a skin on the EPDM particles that helps the larger NBR chunks adhere to them. This increased adhesion and polarity at the EPDM surface increases the compatibility. The presence of block or graft copolymers can also alleviate blending of incompatible elastomers as they can alter interfacial properties (Gaylord, 1975; Locke & Paul, 1973; Barentsen *et al.*, 1973 and 1974). Ideally the block or graft component should contain a segment which is chemically identical to those in the respective phases, but the desired effect may still be achieved if one polymer of the graft were to be miscible with or adhered to one of the phases.

NR and NBR are two well known incompatible polymers (especially at high acrylonitrile content of NBR) and their elastomeric blends are not homogeneous, even in well mixed blends. Although the blends of NR/NBR were successfully produced and reported (Lewan, 1996) there was no attempt to reduce the phase sizes of the elastomers in the blend to optimize the properties of the vulcanizates.

It is possible to obtain considerable improvement in phase morphology and tensile properties of NR/NBR gum blend vulcanizates by incorporating typically 5-20% of methyl methacrylate grafted rubber (*e.g.* Heveaplus MG30) or chloroprene rubber (CR). MG30 is a mixture of grafted and ungrafted NR and poly (methyl methacrylate), PMMA, present as a homopolymer. It was considered that there would be sufficient interaction between the PMMA graft chains and the acrylonitrile repeat units of NBR for the graft copolymer to locate at the NR/NBR interface and thus reduce interfacial tension and hence phase size.

## NR/NBR blends

A number of mixing schemes have been investigated to evaluate how they affect the overall homogeneity and phase morphology of the different components of the elastomer blends. Work was also performed to identify cure systems which would give even crosslink distributions within the blends with compatibilizers, since successful curing systems would not necessarily be the same as those found for uncompatibilized NR/NBR blends. The type and percentage of the compatibilizer, viscosities of the elastomers, blending technique, the temperature of mixing and the type of accelerator appear to have a major influence on the phase morphology, and hence the homogeneity and the physical properties of the blends.

## EXPERIMENTAL

### Methods of blending

Three grades of NBR are considered here - Breon N41C80 and N41C45 (Zeon Chemicals), containing 41% acrylonitrile and with Mooney viscosities of 80 and 45 respectively, and Perbunan N28C45 (Bayer) containing 28% acrylonitrile and with a Mooney viscosity of 45. These will be referred to as NBR 41C80, NBR 41C45 and NBR28C45 respectively. NR used in this study was SMR L and the polychloroprene used was Neoprene WRL (Dupont).

Three mixing procedures has been used:

1. Separate masterbatches of NR,MG30 or CR and NBR containing 5 phr zinc oxide, 2 phr stearic acid and 1.5 phr TMQ were prepared in a BR Banbury internal mixer and the masterbatches were cross blended and finalized with curatives on a two roll mill.

2. NR and MG30 or CR were cross-blended and masterbatched with zinc oxide, stearic acid and TMQ in a BR Banbury internal mixer and cross-blended with NBR masterbatch and finalized with curatives on a two roll mill.

3. NR, MG30 or CR and NBR were crossblended in a Brabender PL2000 Plasticorder fitted with a 350S mixing head and Banbury rotors at a rotor speed of 100 rpm for 3 minutes. Zinc oxide, stearic acid, TMQ and curatives were added in a second stage mixing for 2.5 minutes at a circulating oil temperature of 40°C and a rotor speed of 80 rpm. The oil temperature in the first mixing stage was 50°C, 100°C or 110°C.

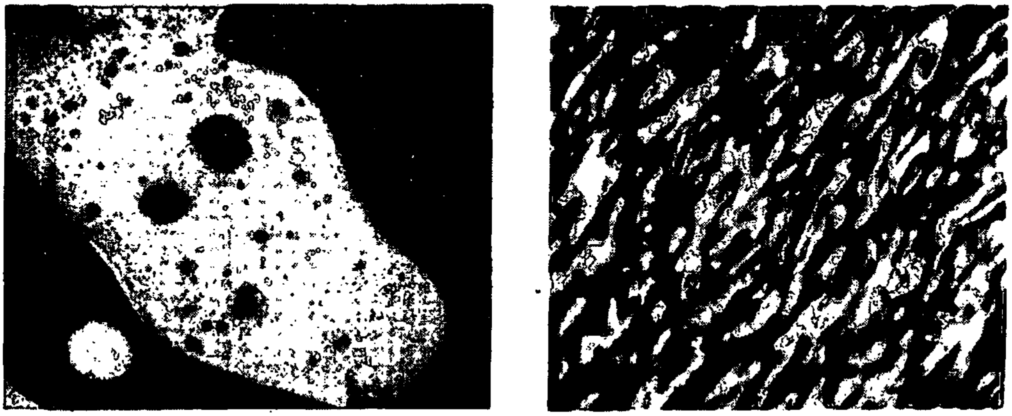
Test sheets (2 mm thick) were vulcanized in a press at 150°C for the time to maximum torque rise ($t_{max}$) as estimated from rheographs obtained using a Monsanto MDR 2000E rheometer operating at the same temperature. In addition to measurements of physical properties crosslink densities were determined by swollen-state $^1$H NMR spectroscopy, using a General Electric QE300 spectrometer and their H% values determined from the resultant spectra (Brown *et al.*, 1992). The phase morphology of NR/Breon N41 has been investigated previously by optical microscopy, but there are difficulties, due to low contrast between the phases and so S(T)EM, a modified SEM, was used instead (Loadman & Tinker, 1989).

## RESULTS AND DISCUSSION

### Phase morphology

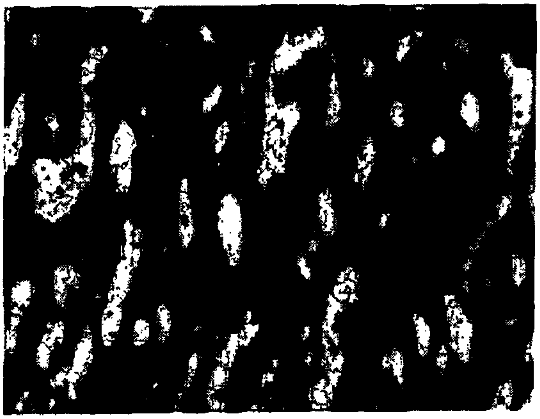
For a 65:35 NR:Breon N41C80 with 1.5phr S and 0.6phr TMTD blend (Fig.1a), the observations confirm the large phase sizes obtained in the absence of MG rubber and illustrate the weak interfacial adhesion (white areas) wherein a region of the two phases appears to have been pulled apart from each other during sectioning. This may be an significant factor in the low tensile strength observed for this blend. It has also been noted that there appears to be a reasonable amount of NR as a darker microphase structure within the lighter NBR phase. For a 50:50 MG:Breon NBR41C80 blend (Fig. 1b) and a 10:40:50 containing 10 parts of NR, 40 parts MG30 and 50 parts of Breon N41C80 (Fig. 1c) two co-continuous phases are seen, and both these exhibit fine structures. The lighter microphase in the NR phase is probably largely unstained PMMA in MG30; this will exhibit as microphases as in MG30 itself (Andrews & Turner, 1960). The darker phase in the NBR phase is probably an NR microphase, as seen in Fig. 1a.

Micrographs of blends of NR/Perbunan N28C45 with 1.3phr S and 1.17phr TBBS and with and without MG30 rubber, are depicted in Figure 2. As discussed earlier, it has been found that the morphology of immiscible rubber blends is dependent on the mixing procedure, the rheological properties of the blend components and their degree of compatibility. There is a greater incidence of co-continuity in the phases when the NBR has a low acrylonitrile content with similar viscosity to SMR L. Large variation in phase size (in cross-section) of the continuous NR phase within each sample is clearly seen, even with very low levels of MG30. As might be expected, the mean phase sizes appear to decrease with increasing MG content, such that the largest phase size is obtained with the blend which has no added compatibilizer (Fig. 2a). The NBR phase is discrete in each case except in Figure 2d where the morphology appears to be co-continuous: this takes no account of the morphology outside the plane of the section in which continuity of the NBR phase may be preserved. In the last three samples the NR phase contains a microstructure which is presumably PMMA.



(a) 65:35 NR:Breon N41C80

(b) 50:50 MG30:Breon N41C80

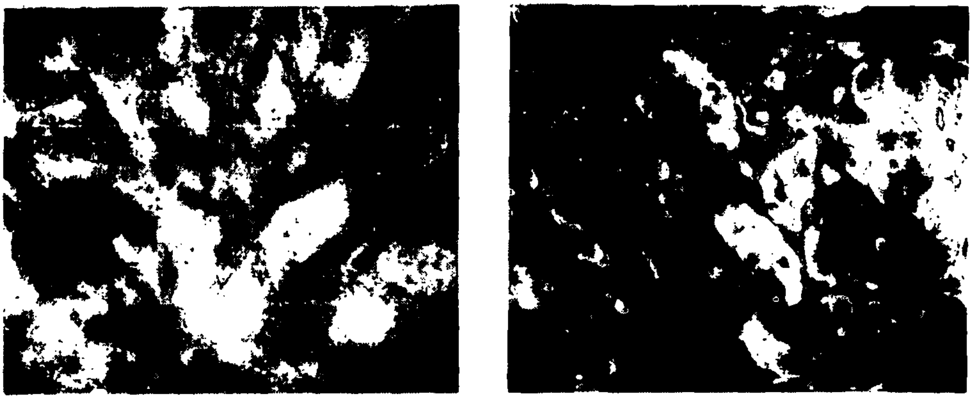


(c) 10:40:50 NR:MG30:Breon N41C80

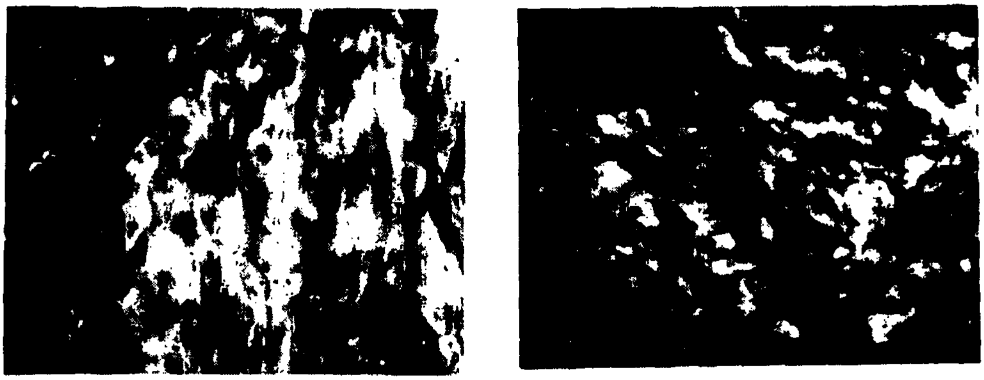
Fig. 1. S(T)EM micrographs of gum vulcanizates containing 1.5phr S and 0.6 phr TMTD at 5000 times magnification.

(a) 65:35 NR:Breon N41C80 with no compatibilizer
(b) 50:50 MG30:Breon N41C80 with no NR
(c) 10:40:50 NR:MG30:Breon N41C80

The probable reason for phase sizes in the blends containing MG30 being larger than seen in Figure 1a and 1c may be the lower shear prevailing during mixing in a Plasticorder compared to mixing on a two roll mill. The blends shown in Figure 1 were mixed according to Method 1, whereas those shown in Figure 2 were mixed



(a) 50:50 NR:NBR N28C45 (b) 40:15:45 NR:MG30:NBR N28C45

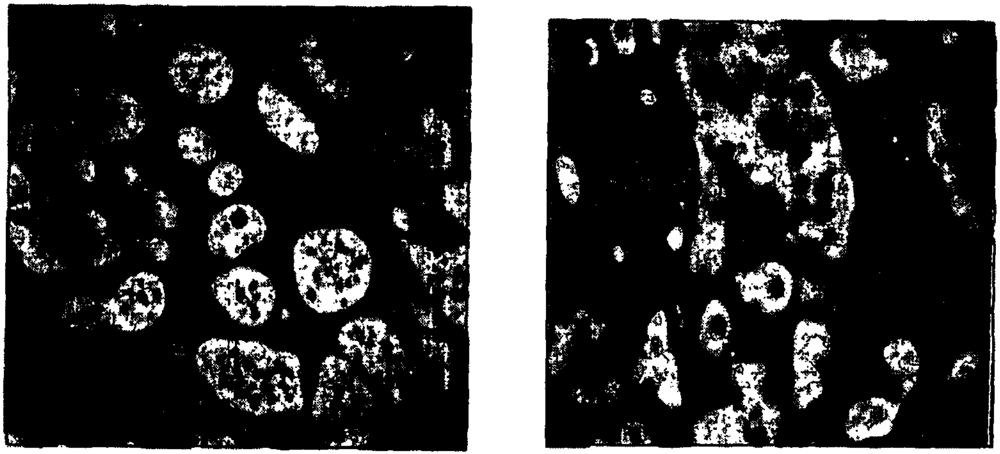


(c) 25:25:50 NR:MG30:NBR N28C45 (d) 50:50 MG30:NBR N28C45

Fig. 2. S(T)EM micrographs of NR/MG30/perbunan N28C45 gum vulcanizates with 1.3 phr S and 1.17phr TBBS at 1500 times magnification; the NR phase is dark

according to Method 3. Cross-blending on a mill shown to give superior properties over mixing procedure 3 in the Plasticorder. However, the introduction of compatibilizers produced the most significant improvements.

Comparison of samples containing 40:50 NR:Breon N41C45 incorporating 10 parts MG30 or polychloroprene are shown in Figures 3a and 3b respectively. In both cases the lighter NBR phase contains inclusions of darker NR phase. In Figure 3a a number of light regions are also evident in the NR phase, which are the regions of microphase separated PMMA. In figure 3b, dark regions are present around all the phase interphases, and these are believed to be the polychloroprene rubber. Thus the polychloroprene rubber preferentially locates at the interfaces in its role as a compatibilizer.



(a) 40:10:50 NR:MG30:NBR N41C45 (b) 40:10:50 NR:CR:NBR N41C45

Fig.3. S(T)EM micrographs of compatibilized NR/Breon N41 C45 gum vulcanizates (S/TBBS) at a magnification of 5000 times; the NR phase is dark and the CR is the black region around the boundary between the NR and NBR in (b)

## Physical properties

The benefit of having a compatibilizer, such as MG30 rubber or chloroprene rubber, in the system is evident when the properties are compared to those of NR/NBR vulcanizates without compatibilizers. Examples of blends vulcanized with 1.5 phr sulphur and 0.6 phr TMTD or 1.5 phr sulphur and 1.93 phr ODIP cure systems are presented in table 1 and 2 respectively.

Table 1. *Physical properties of NR/NBR41C80 blends cures with 1.5phr S and 0.6phr TMTDS/TMTD*

| NR:MG30:NBR | M100 (MPa) | Tensile Strength (MPa) | Elongation at break (%) | Trouser tear strength (N/mm) | Oil swell ASTM #1 (%)[a] |
|---|---|---|---|---|---|
| 25:0:75 | 0.89 | 5.6 | 485 | 2.72 | 29 |
| 4.5:20.5:75 | 1.74 | 11.5 | 475 | 4.32 | 19 |
| 50:0:50 | 0.68 | 4.3 | 600 | 1.80 | 201 |
| 9:41:50 | 2.07 | 20.5 | 465 | 2.84 | 61 |
| 75:0:25 | 0.77 | 14.3 | 770 | 1.83 | 214 |
| 13.5:61.5:25 | 2.20 | 21.0 | 470 | 4.46 | 109 |

[a] Volume swelling after 70 h at 100$^0$C

Table 2. *Physical properties of NR/NBR41C80 blends cured with 1.5 phr S and 1.93 phr ODIP system*

| NR:MG30 NBR | M 100 (MPa) | Tensile strength (MPa) | Elongation at break (%) | Trouser tear strength (N/mm) | Oil swell ASTM #1 (%)[a] |
|---|---|---|---|---|---|
| 25:0:75 | 0.86 | 4.6 | 1000 | 7.88 | 28 |
| 4.5:20.5:75 | 1.50 | 14.8 | 780 | 7.31 | 12 |
| 50:0:50 | 0.78 | 12.7 | 960 | 7.68 | 89 |
| 9:41:50 | 2.17 | 13.7 | 565 | 5.50 | 37 |
| 75:0:25 | 0.70 | 15.8 | 870 | 5.01 | 205 |
| 13.5:61.5:25 | 2.37 | 18.6 | 570 | 4.04 | 78 |

[a] Volume swelling after 70 h at 100°C

Higher tensile strengths are observed in the presence of MG30 rubber than for comparable binary blends.. Whilst part of the improvement may be attributed to a reinforcing effect of the substantial amounts of MG30, a reduction in phase size will also play a role. The higher strengths observed for some vulcanizates cured with S/ODIP may be attributed to the differing cross-link distributions. TMTD is known to produce crosslink distributions which are strongly biased in favour of the NBR phase, whilst the use of ODIP, which has longer chain aliphatic substituents, favours crosslinking in the NR phase in this blend system (Lewan, 1996).

A common sulphenamide accelerator TBBS gives an even distribution of crosslinks in blends of NR and NBR containing 41% acrylonitrile and vulcanized at 150$^0$C (Lewan, 1993). The effect of NR:NBR polymer ratio and MG30 content on the physical properties of blends with N41C80 are demonstrated in Table 3. The decline in tensile strength with increasing NBR content noted for comparable binary NR/NBR blends in Table 1 is not evident when MG30 is present. Tear strength also does not show the expected decrease with increasing NBR content of the blend. The tensile strength and the resistance to swelling by oils depends upon the composition of the blends.

Table 3. *Physical properties of NR/MG30/NBR41C80 blends cured with S/TBBS (1.3/1.17phr)*

| NR:MG30:NBR | M100 (MPa) | M300 (MPa) | Tensile strength (Mpa) | Elongation at break (%) | Trouser tear strength (N/mm) | Oil swell ASTM #1 (%)[a] |
|---|---|---|---|---|---|---|
| 60:15:2 | 0.94 | 2.14 | 24.6 | 715 | 2.75 | 114 |
| 50:15:35 | 1.00 | 2.12 | 24.9 | 705 | 3.35 | 80 |
| 40:15:45 | 1.04 | 2.16 | 24.0 | 720 | 4.40 | 66 |
| 45:05:50 | 0.83 | 1.43 | 19.9 | 805 | 11.3 | - |
| 40:10:50 | 0.90 | 1.68 | 21.5 | 780 | 10.9 | - |
| 35:15:50 | 1.11 | 2.27 | 23.6 | 710 | 3.86 | 58 |
| 30:20:50 | 1.20 | 2.65 | 24.6 | 672 | 4.07 | 49 |
| 30:15:55 | 1.16 | 2.28 | 22.4 | 690 | 4.14 | 50 |
| 20:15:65 | 1.25 | 2.31 | 23.4 | 750 | 5.45 | 38 |

[a] Volume swelling after 70 h at 100$^0$C

The very high tensile strengths which may be obtained in unfilled NR/MG 30 NBR blends is demonstrated by the entries in table 4. The tensile strengths of blends containing N 41C45 are higher than those of comparable blends containing the higher viscosity N41C80 (Table 3). Although NR has a high initial viscosity, comparable to, or higher than, that of N41C80, it breaks down rapidly during mixing, producing a mismatch in viscosities which is not conducive to the development of a fine phase morphology. Smaller phase sizes have been seen in blends of NR with N41C45, and this finer phase morphology may be responsible for the higher tensile strengths.

Table 4. *NR/MG30/NBR blends with high tensile strength*[a]

| NR:MG30:NBR | NBR Grade | M100 (MPa) | M300 (MPa) | Tensile strength (MPa) | Elongation at break (%) | Trouser tear strength (N/mm) |
|---|---|---|---|---|---|---|
| 55:05:40 | NBR41C45 | 0.89 | 1.63 | 27.1 | 760 | 4.94 |
| 50:10:40 | NBR41C45 | 0.93 | 1.93 | 27.7 | 715 | 4.01 |
| 45:05:50 | NBR41C45 | 0.90 | 1.59 | 24.2 | 740 | 4.15 |
| 40:10:50 | NBR41C45 | 0.94 | 1.75 | 25.0 | 745 | 4.30 |
| 60:15:25 | NBR28C45 | 0.87 | 2.00 | 26.6 | 700 | - |
| 30:30:40 | NBR28C45 | 1.31 | 3.99 | 27.3 | 610 | - |

[a] Mixed by method 3 and cured with S/TBBS (1.3/1.17phr)

Given the higher cost of MG 30 relatively to NR and to a lesser extent NBR, it is note worthy that most of the entries contain only modest levels of MG 30. These results show that higher physical properties are obtainable even with 5% or 10% of the compatibilizers incorporated in NR/NBR blends.

## Crosslinking density distribution in the blends

It has been reported previously (Lewan,1996) that 50:50 blends of NR and NBR with 41% acrylonitrile content have uneven NR/NBR crosslink distributions, when cured at 150$^0$C with 1.5 phr sulphur and 0.6.phr TMTD or 1.93 phr ODIP respectively. Similar or more extreme maldistributions have also been observed in blend containing NR:MG30:NBR in the proportion 9:41.50. The reduction in phase size due to the presence of the compatibilizer does not appear to have a profound effect on the crosslink distributions given by these two cure systems.

On the other hand, the sulphur/TBBS cure system which gives the desired even distribution of crosslinks on blends of NR with NBR containing 41% acrylonitrile no longer does so when MG 30 is used as the compatibilizing agent (Table 5). Blends with part substitution of either NR or NBR with MG30 consistently show a significant bias of crosslinks in favour of the NR phase This may be due to the reduction in phase size in the presence of MG30 The crosslink distribution in blends with such large phase sizes as are encountered in blends with NBR containing 41% acrylonitrile is largely determined by the distribution of curatives prior to vulcanization. Migration of curatives or vulcanization intermediates by diffusion during vulcanization can only influence the relatively small proportion of the blends within a few microns of the interface: When the phase size is reduced migration can play a more significant role in determining the crosslink distribution.

Table 5. *Crosslink densities in NR/MG30/NBR blends cured with 1.3 phr S and1.17 phr TBBS*

| NR:MG30:NBR | NBR grade | Crosslink density (mol/m$^3$) | |
|---|---|---|---|
| | | NR | NBR |
| 45:05:50 | NBR41C80 | 46.1 | 26.2 |
| 40:10:50 | NBR41C80 | 52.8 | 22.0 |
| 55:05:40 | NBR41C45 | 50.2 | 29.3 |
| 50:10:40 | NBR41C45 | 47.8 | 32.7 |
| 45:05:50 | NBR41C45 | 46.2 | 32.7 |
| 40:10:50 | NBR41C45 | 50.4 | 31.8 |
| 50:00:50 | NBR28C45 | 44.9 | 48.7 |
| 50:15:35 | NBR28C45 | 58.6 | 55.2 |
| 30:20:50 | NBR28C45 | 58.1 | 41.9 |
| 00:50:50 | NBR28C45 | 66.0 | 41.4 |

The crosslink distribution observed for blends containing NBR with 28% acrylonitrile content including the 50:50 binary blends are not expected from the marked biased towards the NBR phase observed for comparable blends containing NBR with 34% acrylonitrile content (Lewan, 1996). This further demonstrates the sensitivity of crosslink distribution to even rather small changes in relative polarity of the rubbers in a blend. The addition of MG30 appears to reduce the maldistribution in crosslink density presumably as a result of reduced phase sizes and the greater role of migration of the intermediates during vulcanization.

## CONCLUSION

It has been shown that an addition of a compatabilizer of NR/NBR blends can reduce phase sizes attained in the blends over a wide range of acrylonitrile content of the NBR. The addition of MG30 is beneficial to tensile strength. Whilst this may simply be a consequence of the small phase sizes, it also suggests an improved integrity of the vulcanized blends and hence improved interfacial addition

The addition of MG30 alters the distribution of crosslinks between the faces of the blends This may be due to the reduction in phase size permitting migration of vulcanization intermediates by diffusion during vulcanization to play a more important role in determining the final crosslink distribution. It suggests that optimization of the cure system should be made in the compatibilized blend if it is intended to use compatibilizing agents. A cure system shown to be appropriate or even ideal in the binary blend may no longer be suitable.

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