

## ***Use of Reclaimed Nitrile Rubber Gloves as Partial Replacement of Virgin Nitrile Butadiene Rubber in Thermoplastic Vulcanisates***

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*Recycled gloves can be used as a cheapener to make conventional rubber products. In this study, the feasibility of reclaimed NBR gloves (r-NBRG) in thermoplastic vulcanisates (TPVs) based on nitrile butadiene rubber (NBR) and polypropylene (PP) blend using the injection moulding process was investigated. The NBR based TPV obtained from this process has many advantages compared to conventional rubber products. Among the outstanding advantages are the ability of TPV to be recycled easily and the higher value-added products obtained from TPV as compared to vulcanised rubber products. This paper will describe the effect of r-NBRG as a partial replacement for virgin NBR on the properties of the TPV system. The curing systems selected were based on the sulphur-accelerated curing system and peroxide curing system. The results indicate potential reduction in production costs with the possible replacement of up to 70 p.p.h.r. virgin NBR with r-NBRG in the TPV systems.*

**Keywords:** reclaimed; nitrile rubber gloves; thermoplastic vulcanisates; blends

Reclamation process and the study of reclaimed rubber from the process remains an interesting subject for many researchers and rubber industries. In a recent review, Adhikari *et al.*<sup>1</sup> discussed extensively various processes of reclaiming, with Rajan *et al.*<sup>2</sup> paying particular attention to natural rubber (NR)-based waste latex products. Some of the main advantages of using reclaims are easy mastication, reduction in mixing time and improvement in ageing properties. Large amounts of mechanical energy input is normally required during the reclaiming process. Thus, during the mixing process, compounds containing reclaims

mixes faster with less heat generation than pure virgin rubber<sup>3</sup>.

The development of quality reclaim is also important to ensure that the quality of reclaimed products is comparable to that of rubber products made from virgin rubber. Hence, production costs are expected to be reduced when reclaimed rubber is widely utilised in rubber products and thermoplastic vulcanisate (TPV) compounds. Since the properties of waste rubber vulcanisates are generally inferior to those of virgin vulcanisates, several investigations were carried out to study the

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cure characteristics and mechanical properties of waste rubber/virgin polymer blends. Tyres have become the largest scale rubber waste and a number of reports on the use of various forms and sizes of ground tyre rubber have been reported. Rattanasom *et al.*<sup>4</sup> reported that the addition of tyre tread reclaimed rubber in virgin NR caused a decrease in the mechanical properties of both conventional and efficient vulcanisation while Sreeja and Kutty<sup>5</sup> studied the cure characteristics and mechanical properties of nitrile butadiene rubber (NBR) compound by using NR reclaims. A review on thermoplastic elastomers based on waste rubber and plastics has been reported by Rajeev and De<sup>6</sup>. The report included waste from ground tyre rubber, latex, EPDM and nitrile rubber. The results showed that in many cases the material prepared from waste polymers exhibited comparable properties to those prepared from fresh polymers. However, little work has been published on TPV based on reclaimed NBR gloves (r-NBRG).

Thermoplastic elastomers (TPE) have been extensively studied<sup>7-9</sup> and received much attention because of their rubber-like properties and thermoplastic processability. In this context, the TPVs are basically produced by dynamic vulcanisation where the rubber phase is vulcanised in rubber/thermoplastic blend during mixing. This method gives improved elasticity and mechanical strength properties. Hence, the applications of TPV may be integrated into many major areas such as automobile parts, medical, engineering, appliances, tools, *etc.* Blending of good quality r-NBRG and suitable thermoplastics with adequate compatibilisation is expected to lead to the development of novel, low cost TPVs. In this work, NBR rejected gloves that have undergone extensive reclamation processes obtained from local manufacturers were used in the development of the TPVs. Investigation was carried out with various ratios of r-NBRG/virgin NBR blends using

sulphur and peroxide cure systems and their effects on the physical properties of the TPV were evaluated.

## EXPERIMENTAL

### Material

Reclaimed rubber prepared from rejected NBR gloves was supplied by Fragrance Rubber Sdn. Bhd. The characteristics of the r-NBRG are summarised in *Table 1*. NBR grade Krynac 3345F with Mooney viscosity 41 [ML (1+4) at 100°C] and acrylonitrile content of 33%, was obtained from Luxchem Ltd. Homopolymer polypropylene (PP) grade EP 6431 with MFI of 7 g/10 min was from Titan Petchem (M) Sdn. Bhd. Peroxide systems were  $\alpha,\alpha'$ -Bis(t-butylperoxy) diisopropylbenzene (Luperox F40P) and trimethylolpropane trimethacrylate (Trim/s). The sulphur cure system consisted of the following ingredients: stearic acid, zinc oxide, 2-Mercaptobenzothiazole (MBT), TMTD and sulphur obtained from Luxchem Ltd., Metacop, Lim Teck Lee and Lin Ho (M) Sdn. Bhd. respectively. Other mixing ingredients such as titanium dioxide, plasticiser di-octyl phthalate (DOP), colour pigments (Hostasin Orange G and Hostasin Green GG) were of commercial grades.

### Preparation

#### Mixing

The r-NBRG was melt-mixed with virgin NBR and PP in a Banbury internal mixer (BR 1600). The internal mixer was used for easier transfer of technology or adoption by the local industry using their existing mixing facilities. The virgin rubber and r-NBRG was charged into the mixing chamber and allowed to mix for 2 min followed by other compounding ingredients. DOP was incorporated to the

mix in small increments at different stages of mixing. The TPV was then formed by dynamic vulcanisation using peroxide or sulphur curing systems. The duration of the whole mixing process was about 15 min.

In gum mix (TPE) *i.e.* pure blend of rubber and plastics, the r-NBRG was melt-mixed with virgin NBR and PP at rubber to PP ratio of 75:25. A laboratory scale batch mixer, Haake Rheomix 3000 OS with Banbury type rotors was used. Mixing was carried out at 180°C temperature and 100 r.p.m. rotor speed.

After mixing, the TPVs were sheeted off from the two-roll mill and granulated prior to injection moulding. Tensile specimens of 2 mm thick sheets, abrasion and compression set button were then injection moulded using a Toshiba (IS 80 EPN-2A) injection machine with a capacity of 80 tons clamping force.

TABLE 1. CHARACTERISTICS OF r-NBRG

Composition	(%)
Rubber	67.5
Total sulphur	1.2
Ash content	13.8
Calcium carbonate	6.4
Others	11.1

### Determination of Mechanical Properties

Three tensile test pieces were die-stamped from the 2 mm sheets of injection moulded TPV slabs using a dumbbell cutter. Tests were carried out using a Zwick universal testing machine according to *ISO 37* at room temperature with a crosshead speed of 500 mm/min. Properties measured were tensile strength, elongation at break and 100% modulus. Specimens were tested unaged and oven-aged for seven days at

100°C. Compression set test was determined according to *ISO 815* standards. Abrasion resistance was determined in accordance with *ISO 4649*. Hardness was measured using the *ASTM D-2240* test method using Shore A scale. Data are presented as a median in all cases.

### Oil Resistance

Determination of the volume swell was conducted according to *ISO 1817*. Samples of dimensions 30 mm × 20 mm × 2 mm were weighed ( $W_0$ ) and immersed in IRM 903 oil at 100°C for 70 h. The test specimens were then removed from the oil, quickly dipped in acetone and subsequently blotted lightly using tissue paper to eliminate excess oil on the surface before being weighed again ( $W_s$ ). The swelling percentage of the blends was calculated as:

$$\text{Swelling percentage} = \frac{W_s - W_0}{W_0} \times 100 \% \dots 1$$

### Melt Flow Index (MFI)

The MFI (g/10 min) was measured at a temperature of 190°C with a fixed load of 10 kg or 15 kg.

### Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical properties of peroxides cured TPVs were measured over a wide temperature range from -100°C to 140°C using a Dynamic Mechanical Thermal Analyser, DMTA MKIV Rheometric Scientific. The sample dimensions were 6 mm × 45 mm × 1.5 mm. The measurements were determined at a frequency of 10 Hz and heating rate of 20°C/min.

## Morphology

Scanning Electron Microscope (SEM) studies of cross-sections from selected etched TPE/TPV samples were performed with a JEOL (JSM-5300). The samples were gold-coated prior to analysis.

## RESULTS AND DISCUSSION

### Effect of Varying r-NBRG Content on TPV based on NBR (Sulphur Curing)

It is indeed a challenge to develop a low level of thermoplastic phase TPV composition, while maintaining its rubber performance and achieving the preferred rheological characteristics of good flow. Therefore, it is important to identify factors that contribute to the properties of the TPV such as selection and suitability of the thermoplastics phase, curing system and the proportion of rubber-plastics in the systems. In this paper, the ratio of the r-NBRG/virgin NBR was varied while the proportion of rubber-plastic and other factors were kept constant in all cases.

As the intention was to use an injection moulding machine to fabricate the end product, it is necessary to determine the MFI of the compound. In this work, the MFI of TPVs containing different ratios of r-NBRG used in the TPV formulation based on sulphur curing is shown in *Table 2*. The result indicates no reduction in the MFI value by partial replacement of virgin NBR with up to 60 p.p.h.r. r-NBRG. However, the MFI decreased slightly when the NBR was substituted with 70 p.p.h.r. r-NBRG.

The physical properties of 75 NBR/25 PP dynamically vulcanised thermoplastic elastomeric blends containing different ratios of r-NBRG are also given in *Table 2*. The incorporation of up to 70 p.p.h.r. of r-NBRG

as partial replacement of virgin NBR slightly increased the tensile strength of the TPV. There are new active crosslinking sites in the reclaimed rubber which continue to form crosslinks during revulcanisation<sup>10</sup>. Considering the fact that with higher partial replacement of r-NBRG, more vulcanisation would occur between reclaimed rubber and virgin rubber resulting in higher crosslink densities in the system. This explains a slight improvement in the tensile strength values. An opposite trend is observed for the elongation at break (EB) where an increase in r-NBRG ratio decreases the EB values. Higher crosslinking increases the tightness of the polymer network and reduces the molecular mobility of the polymer chains. As a result, the elongation at break of the resulting polymer is expected to decrease when higher ratio of r-NBRG was used. It can also be seen that higher r-NBRG ratios exhibited higher hardness compared to the control formulation.

Based on the volume swell data, TPVs with higher r-NBRG ratios gave better swelling resistance compared to the control. These results probably suggest that more inclusion of reclaimed rubber increased the crosslink density. Similar results were also observed in the compression set values. The increase of r-NBRG ratio resulted in the reduction of the compression set values. However, the compression set values (*Table 2*) for all TPV blends are generally poor due to the addition of the thermoplastics phase. In this regard, peroxide cure could give a better compression set.

### Effect of Varying r-NBRG Contents on TPV based on NBR (Peroxide Curing)

*Table 3* shows the physical properties and MFI values of peroxide cure TPV with various ratios of r-NBRG. It can be seen that partial replacement of virgin NBR with 40 p.p.h.r.

TABLE 2. PHYSICAL PROPERTIES OF TPV BLENDS CONTAINING r-NBRG WITH SULPHUR CURE SYSTEM

r-NBRG(p.h.r.)	0	40	60	70
MFI, 190°C/10 kg	8.0	9.1	8.0	6.2
Tensile Strength <sup>a</sup> , MPa	3.0	3.3	3.2	3.4
Elongation at Break <sup>a</sup> , %	250	160	105	75
Hardness, Shore A	70	77	79	81
Compression Set, 22 h /70°C	85	84	80	77
Volume Swell, % (IRM 903, 70 h at 100°C)	10	5	4	6

<sup>a</sup>Average of along and across grain values.

TABLE 3. PHYSICAL PROPERTIES OF TPV BLENDS CONTAINING r-NBRG WITH PEROXIDE CURE SYSTEM

r-NBRG (p.p.h.r.)	0	40	60	70	70 <sup>a</sup>
MFI, 190°C/15 kg	35	30	33	31	35
Tensile strength <sup>b</sup> , MPa	4.3	5.3	5.1	5.0	3.3
Elongation at break <sup>b</sup> , %	235	300	230	220	150
M100 <sup>b</sup> , MPa	3.0	3.3	3.5	3.7	3.2
Hardness, Shore A	69	73	75	77	75
Compression set, 22 h, 70°C	51.3	54.3	51.8	50.6	68.6
Volume swell, % (70 h, 100°C)	1.2	0.3	-1.0	-1.0	5.7
Abrasion resistance, ARI (%)	45.2	41.1	41.6	41.6	23.1

<sup>a</sup>No curing agent added<sup>b</sup>Average of along and across grain values.

of r-NBRG increases the tensile strength and the elongation at break properties. An increase of the EB values however, is not expected. At higher replacement of virgin NBR with up to 60 p.p.h.r. and 70 p.p.h.r. of r-NBRG, the tensile strength increases slightly but the EB decreases when compared to the control compound containing no r-NBRG. In comparison with the sulphur cure system discussed above, the peroxide cure resulted in higher tensile properties. It should be noted that the presence of sulphur in the reclaim probably resulted in a mixed cure system that produce a rubber network consisting of C-C, C-S and S-S linkages between the rubber chains. Therefore, the presence of both types of linkages resulted in higher strength

as compared to only C-S and S-S bonds in the sulphur curing system. However, this is also dependent on the type and amount of peroxides-co-agent.

A similar trend on the effect of partial replacement of r-NBRG at 40 p.p.h.r., 60 p.p.h.r. and 70 p.p.h.r. on modulus M100, hardness and compression set is observed in TPVs with sulphur cure system as well as the peroxide system. Higher contents of r-NBRG produced higher values of hardness and modulus M100 with lower compression set and volume swell in IRM 903. The advantage of using peroxide cure is clearly demonstrated by a better compression set property compared to sulphur cure. It is also seen from the results

that the volume swell shows a negative value for compounds containing 60 p.p.h.r. and 70 p.p.h.r. r-NBRG. This indicates the presence of dissolution of samples during the test. Proper adjustment of the TPV compounding ingredients is necessary in this case.

Overall, the TPVs with peroxide system showed a satisfactory melt flow index (MFI) although a marginal decrease is observed as the r-NBRG content increases. As for compounds containing 70 p.p.h.r. of r-NBRG with and without curing agent, dynamic vulcanisation resulted in substantial improvement in tensile strength, elongation at break, compression set and abrasion resistance properties.

### DMTA Analysis for TPVs Peroxide Cure

*Figure 1* shows the effect of r-NBRG content on the storage modulus of the compound. A slight improvement can be observed on the storage modulus property, especially with the inclusion of 70 p.p.h.r. of r-NBRG content. The trend in storage modulus generally follows the same trend as observed in tensile modulus (*Table 3*).

The increase in modulus is assumed to be due to the increase in formation of crosslinks between the reclaimed and virgin NBR. A reduction in the height of the  $\tan \delta$  peak with r-NBRG content is also evident in increased formation of crosslinks between them. This will result in restriction of their flexibility and decrease in mechanical damping as shown in *Figure 2*.

### Ageing Characteristics

Ageing characteristics of rubber vulcanisates containing reclaimed rubber should be given proper deliberation because reclaimed rubber itself is a degraded product<sup>1</sup>.

Thus, the effect of r-NBRG on heat ageing resistance was also investigated. As presented in *Figure 3*, the inclusion of compounds containing r-NBRG from 40 p.p.h.r. to 70 p.p.h.r. did not show any profound effect on tensile retention after air ageing at 100°C for 7 days for the peroxide cure system. The high retention in tensile properties could probably be due to the additional crosslinks formed during thermal ageing. A decrease in tensile retention is observed at 70 p.p.h.r. of r-NBRG for the sulphur cure system. These results indicate that additional antioxidants were not necessary for making rubber products based on reclaims in particular peroxide curing. Furthermore, the C-C bonds in peroxides cure have high thermal stability compared to the sulphur cure.

### Effect of Plasticiser on the Tensile Strength of TPE and TPV Blends

The effect of plasticiser on the tensile strength of gum mix (TPE) and TPV is shown in *Figure 4*. Based on observation of the unvulcanised TPE blend morphology (without plasticiser) in *Figures 5(a)* and *(b)*, the dispersion of r-NBRG in PP matrix reflects homogeneity, showing a large variation in the tensile strength values (*Figure 4*). At this preliminary stage, it is assumed that the r-NBRG is dispersed in the PP matrix. It can be seen that the irregular cavities left on the PP matrix is probably due to r-NBRG that has been etched out. At a higher concentration of r-NBRG (70 p.p.h.r.) (*Figure 5(b)*), similar patterns of micrograph was also observed.

In contrast, the variation in the tensile strength values is much smaller for vulcanised TPE blends (TPV-with plasticiser) and unvulcanised TPE (with plasticiser) compared to unvulcanised blends (without plasticiser). This clearly shows that the addition of plasticiser produced better dispersion as

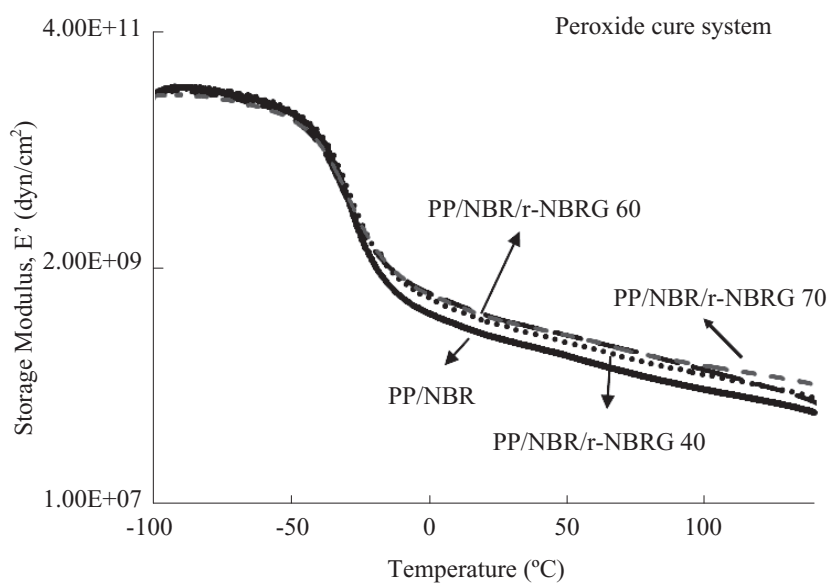


Figure 1. Effect of reclaimed rubber content on storage modulus ( $E'$ ) as a function of temperature.

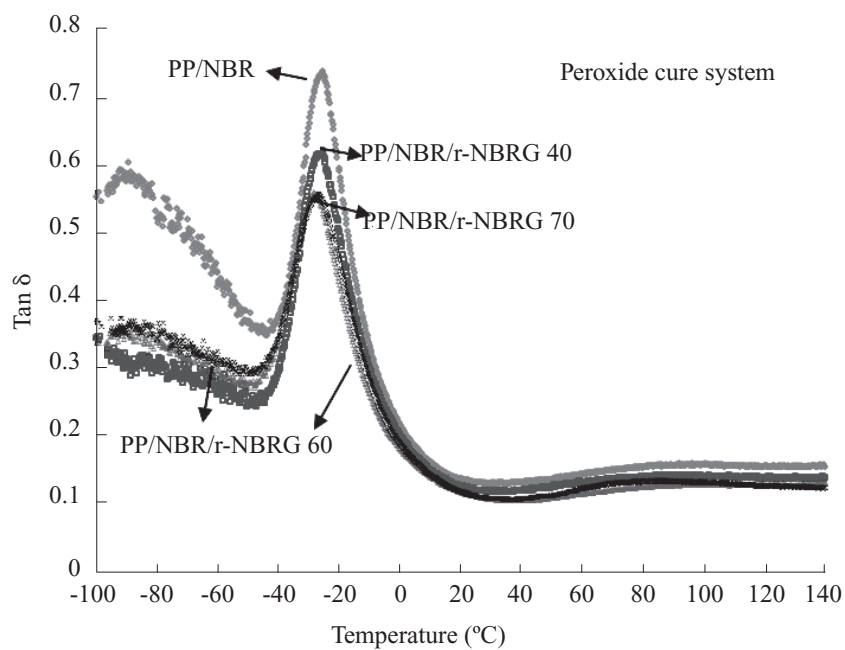


Figure 2. Effect of reclaimed rubber content on tangent  $\delta$  as a function of temperature.



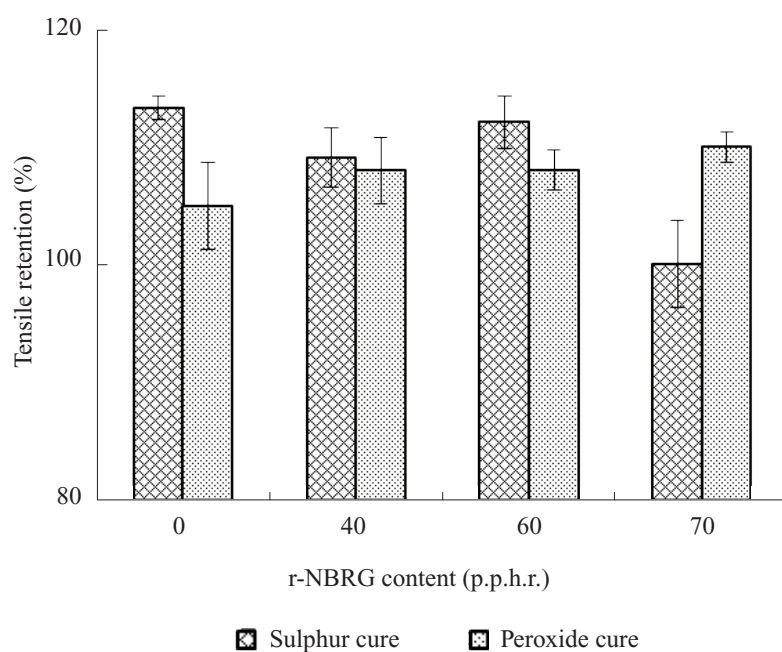


Figure 3. Tensile retention of NBR vulcanisates as a function of r-NBRG content.

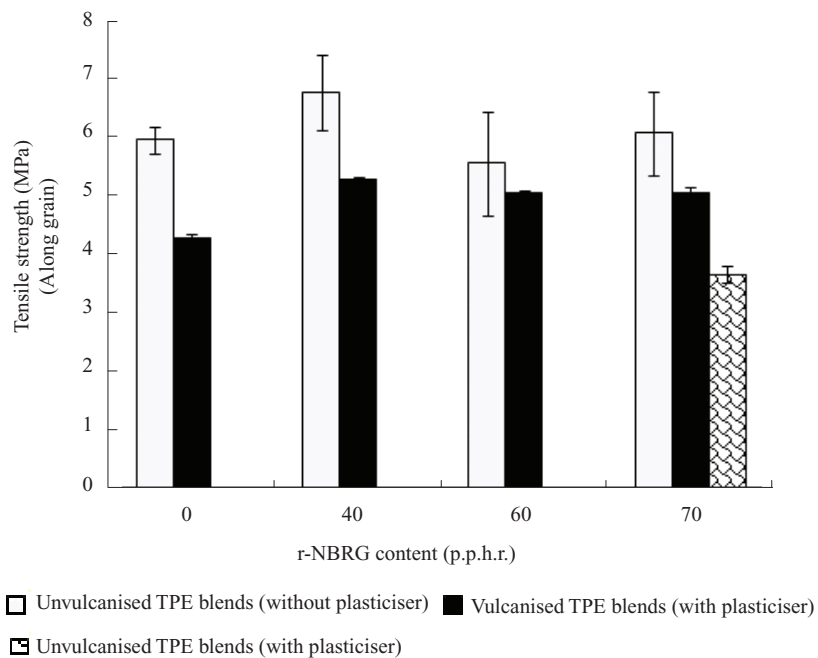


Figure 4. Effect of plasticiser on variation in tensile strength.



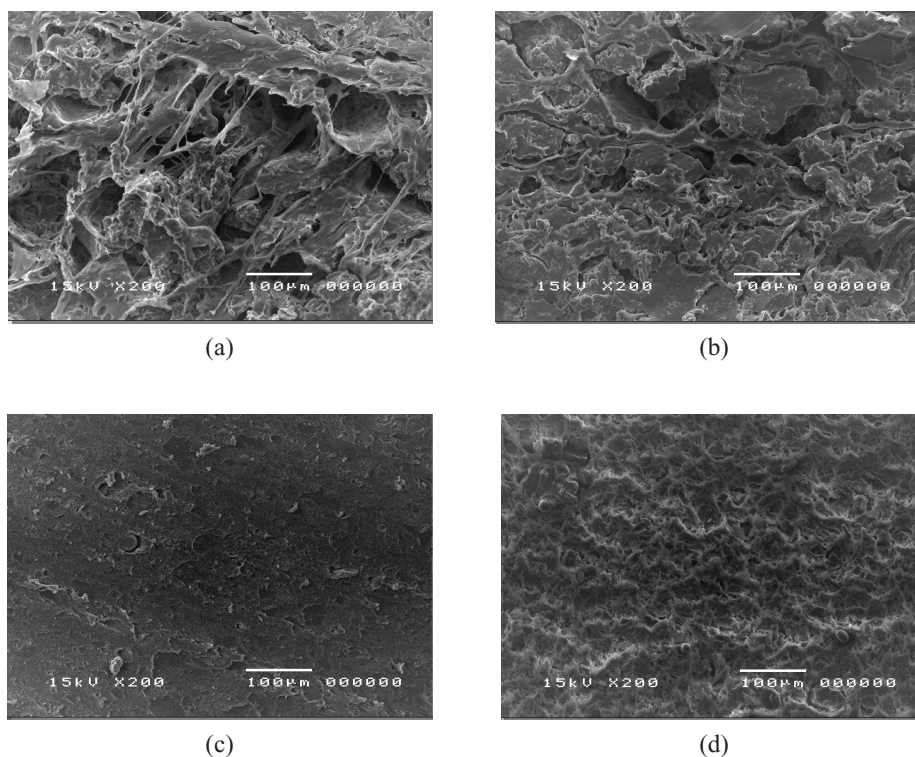


Figure 5. SEM micrograph of (a) TPE with 40 p.p.h.r. r-NBRG (without plasticiser) (b) TPE with 70 p.p.h.r. r-NBRG (without plasticiser) (c) Vulcanised TPE with 70 p.p.h.r. r-NBRG (with plasticiser, peroxide cured) and (d) Unvulcanised TPE 70 p.p.h.r. r-NBRG (with plasticiser).

observed in Figure 5(c) and (d). Figure 5(d) displays finer morphology and the structure formed a regular pattern. Therefore, incorporation of plasticiser in the blends is desirable to improve the morphology structure which also influenced the properties of the TPE and TPV blends.

As in the case of crosslinked samples (Figure 5(c)), the SEM micrograph did not show any significant changes in the morphology after etching. Pan *et. al*<sup>12</sup> have studied the morphology of vulcanised PP/NBR (30/70) with a transmission electron microscope (TEM). After staining with osmium tetroxide ( $\text{OsO}_4$ ) and observing *via* TEM, they reported

that the NBR particles were enclosed by the PP continuous phase. This clearly indicates that the extraction of the rubber phase by solvent etching in this work is not sufficient; therefore SEM analysis of the morphology of the TPV blends is quite difficult. Further work needs to be carried out to find a suitable solvent or alternative treatment such as chemical etching.

## CONCLUSION

The present work has shown that with the incorporation of r-NBRG from 40 p.p.h.r. to 70 p.p.h.r., TPVs still retained its properties

especially tensile strength compared to the control compound. Dynamic vulcanisation had significantly improved TPV's properties. It was also found that the elongation at break decreases slightly with increasing content of r-NBRG, which however showed an opposite trend in hardness properties. Nevertheless, the volume swell, compression set and ageing characteristics were further improved with higher percentage of r-NBRG. In addition, the results also showed that the peroxide cured system exhibited much better compression set compared to the sulphur cured system. Therefore, there is a potential use of r-NBRG as replacement for the NBR virgin material in thermoplastic vulcanisates that is expected to result in substantial reduction in the production cost. By addition of special ingredients such as compatibilisers and control of the crosslinking system, it is possible to modify and optimise its properties to suit specific technical applications.

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