

## Oil Resistance of Dynamically Vulcanized Poly(Vinyl Chloride)/Nitrile Butadiene Rubber Thermoplastic Elastomers

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### Summary

Dynamically cured poly(vinyl chloride)/nitrile butadiene rubber (PVC/NBR), thermoplastic elastomers (TPEs) were melt mixed at 150°C at 50 rev.min.<sup>-1</sup> with a Brabender Plasticorder. Curatives concentration was varied from 0 to 1 phr in order to study the effect of dynamic curing on the oil resistance of the plastified formulations. The compounds were characterized in respect to their mass swell, tensile properties, tear strength and hardness. The PVC/NBR formulations have been exposed to air and oil under otherwise identical conditions. The influence of oil and thermo-oxidative ageing on the mechanical properties were characterized at room temperature and 100°C. It was found that at ambient temperature the samples immersed in oil possessed similar properties to those that were exposed to air. Profound enhancement in mechanical properties were observed for both environments at 100°C. The observed scenario has been attributed to the increase in the degree of curing which was accompanied by a steady reduction in % mass swell with increased sulfur loading. The excellent mechanical behavior of the PVC/NBR TPEs even after immersing the samples in oil at 100°C evidenced for the good oil resistance of the materials.

### Keywords

Poly(vinyl chloride), Nitrile butadiene rubber, oil resistance, thermoplastic elastomers, dynamic curing.

### Introduction

Blends of NBR with PVC were originally introduced as a means of improving the ozone resistance of NBR [1-3]. The polar nature of NBR enhances the oil resistance of PVC, where NBR acts as permanent plasticizer for PVC over a wide range of applications, namely wire and cable insulation [4-5]. On the other hand the principal attributes of the PVC toward the NBR is improved chemical resistance of NBR,

thermal ageing and abrasion resistance. Recently the miscible nature of PVC/NBR blend has triggered the classification of such blend as a rubber based thermoplastic elastomer. Furthermore, dynamic curing plays a significant role in TPE technology where it produces thermoplastic vulcanizates that look, feel and perform like elastomers. NBR-polypropylene thermoplastic vulcanizates for instance exhibited excellent hot oil resistance as reported by Coran [6]. Furthermore, the dynamically cured epoxidized natural rubber/poly(vinyl chloride) thermoplastic elastomers has been reported and found to exhibit an improved oil resistance [7]. The investigation reported in this article was focused on the oil resistance of dynamically cured PVC/NBR TPEs after exposure to ASTM oil #3 at 100°C for 70h and for 22h at room temperature. An oil-resistance study is of interest to highlight the role of dynamic curing on the oil resistance of the TPE, the mass swell as well as the mechanical properties after immersion of the TPEs in ASTM oil #3 at ambient temperature and 100°C will be used as a measure of oil resistance. ASTM oil #3 was selected due to its high solvating power (lowest aniline point) as compared to ASTM oil #1 and 2.

## Experimental

### Materials

Suspension grade Poly (vinyl chloride) in powder form, with a K-value of 65 and degree of polymerization of 920-1060 was supplied by Malayan Electro Chemical Industry Sdn Bhd., Penang, Malaysia. Nitrile butadiene rubber (NBR) with 34 mole % acrylonitrile was obtained from Kumpulan Guthrie Bhd., Seremban, Malaysia. Lead stabilizer was obtained from Komita Sdn Bhd. Di-2-ethylhexyl phthalate (DOP), sulfur, tetramethylthiuramdisulfide (TMTD), 2,2-dithiobisbenzothiazole (MBTS), zinc oxide and stearic acid were supplied by the Bayer (M) Sdn. Bhd.

### Formulation

The formulations shown in Table 1 were used in this study. All NBR compounds were cured by semi efficient curing system (semi-EV). Such curing system has been proven to be effective in enhancing the heat stability and improving resistance to thermo-oxidative ageing [8].

Table 1: Recipe used to produce PVC/NBR TPEs, (phr).

PVC	70
NBR	30
DOP	50 phr PVC
Zinc oxide	3 phr NBR
Stearic acid	1.5 phr NBR
Sulfur	X
MBTS	X
TMTD	1/3 X

X is the amount of sulfur which was varied from 0-1 phr NBR.

### Melt Mixing

PVC was initially premixed with 3 phr lead stabilizer in a Janke and Kunkel IKA Labortechnik Model RE 162/P at 300 rpm for 10 min at 30°C. Melt mixing was

performed using a Brabender Plasticorder Model PLE 331 attached to a mixer/measuring head (W 50 H) at 150°C and 50 rpm rotor speed. The NBR was charged into the mixing chamber to equilibrate, followed by PVC and other additives. Mixing was allowed to proceed for 8 min after which curatives were added to the compound [7,9]. Mixing was then continued at a reduced speed of 30 rpm until a constant torque was obtained [8-9]. The compound was then removed from the mixer and sheeted on a cold two roll mill. It was passed once through the nip to produce approximately a 1 mm thick sheet. The sheets were cut into strips and again subjected to Brabender mixing at 150°C and 50 rpm for 2 min after which it was again sheeted out prior to compression moulding [8-9]. The cure characteristics were determined at T=150°C using a Monsanto oscillating disc rheometer (MDR 2000) at 1.667 Hz frequency and 0.5° arc. The curing time of the sheets agreed with the optimum cure time ( $t_{90}$ ) read from the curing curves of the MDR2000. The  $t_{90}$  was ranged from 8 min in the case of the control sample to 10 min in the case of the cured formulations. Sheets of 2 mm thickness were molded with a KAO Tieh compression molding machine with a force of 10 MPa at 150°C.

### Characterisation and testing

#### *Oil resistance*

The test was conducted according to ASTM D 471-98. The test specimens were immersed in ASTM # 3 oil (which is similar to IRM 903) at 100°C and ambient temperature for 70h. The test specimens were then removed from the oil, wiped with tissue paper to remove excess oil from the surface, and weighed. Percentage mass swell was then calculated as follows:

$$\text{Change in Mass} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

Where  $W_1$  and  $W_2$  are the weight of the samples before and after immersion respectively.

#### *Swelling index*

Circular discs specimens with a thickness of 2mm and a diameter 20 mm were immersed in toluene for a 36 h. The swelling index was determined as :

$$\text{Swelling Index} = \frac{\text{Final Mass}}{\text{Initial Mass}} \quad (2)$$

#### *Tensile tests*

The test specimens were immersed in ASTM #3 oil at room temperature and 100°C for 70h. For the purpose of comparison samples were also placed in an air oven and aged at 100°C for 70 hours. The samples were removed from oil and air oven. The tensile tests were performed on 2mm thick dumb-bells at (25 ± 2°C) on a Monsanto Tensometer T10 at a deformation rate of 500 mm min<sup>-1</sup> according to ASTM D412. Five specimens were used and the median value was taken in each case.

### *Tear tests*

Tear tests were carried out according to the ISO 34 Type III using the crescent shape specimens. A Monsanto Tensometer T10 was used at a cross head speed of 50 cm/min. Five specimens were used and the average value was calculated.

### *Hardness test*

ASTM Shore A was used to measure hardness in International Rubber Hardness Degrees (IRHD) according to ISO 48 (1979).

## **Results and Discussions**

### *Swelling index*

Figure 1 compares the effect of sulfur loading to the swelling index of the unaged and aged PVC/NBR TPEs. Note that swelling index decreases continuously with increasing sulfur concentration.

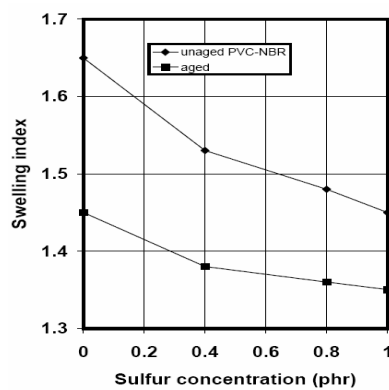


Figure 1: Effect of sulfur loading on swelling index of PVC/NBR TPEs.

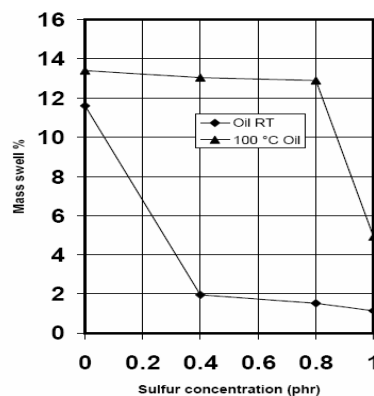


Figure 2: Effect of sulfur loading on mass swell of PVC/NBR TPEs.

This indicates an increase in the crosslink density with sulfur dosage. Thus, it can be inferred that the vulcanisates have been converted to a stiffer and less penetrable materials by the solvent. The further reduction in swelling index of the aged counterpart at all sulfur concentrations is an evidence of additional crosslink formation within the NBR phase during ageing, which might be attributed to postcuring. Recall that torque can be used to assess crosslink formation.

Table 2: The variation of stable torque with sulfur loading of PVC/NBR TPEs.

Sulfur concentration (phr)	Stable torque (N.m)
0.0	12
0.4	14
0.8	17
1.0	19

Thus, the torque values derived from Brabender plastograms at the stable end as a function of sulfur loading were presented in table 2. One can recognize that the stable values of the torque at the end of mixing increase continuously with curative concentration. This also provides evidence of an increase in the crosslink formation. Remember that the value of torque is a direct function of the extent of crosslinking that has occurred. Thus, it can be inferred from the above observation that, increase in torque with sulfur content can be related to the formation of a network structure. Such structure becomes rigid and strong as the extent of crosslinking increases which is expected to enhance the oil resistance of the PVC/NBR formulations.

#### *Mass swell*

Figure 2 displays the effect of sulfur loading on the mass swell of PVC/NBR TPEs at room temperature and 100°C. A sharp decrease in the mass swell with the addition of sulfur is initially shown, however the rate of decrease lessens at higher concentrations of sulfur. Some ideas on the swelling behavior of the TPEs can perhaps be obtained from Flory - Hugins equation which correlates osmotic pressure and the degree of curing [10]:

$$\frac{\pi}{C} = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2} \left[ \frac{1}{2} - \mu \right] C \quad (3)$$

where  $\pi$  is the osmotic pressure;  $C$ , the concentration;  $R$ , the gas constant;  $T$ , the absolute temperature;  $M_1$ , the molecular weight of the solvent;  $M_2$ , the molecular weights of the polymer;  $d_1$ , the density of solvent;  $d_2$ , the density of polymer;  $\mu$ , the reciprocal constant. Based on the above equation, it can be anticipated that swelling will not take place until the osmotic pressure of the solvent (i.e. ASTM # 3 oil used in the present study) is stronger than the intermolecular bonding of the molecules in the PVC/NBR blend. As the number of crosslinks increases the molecular weight between two adjacent crosslinks decreases due to the increased degree of curing, this will decrease the osmotic pressure. Thus, the diffusion of the solvent into the blend which is expected to be in its minimum will result in less swelling. Additional aspect that should be considered is the cohesive energy density (C.E.D) which is defined as the energy required to separate all the molecules in a given material from each other [11]. The C.E.D becomes stronger as the intermolecular forces increased due to crosslinking while the penetrating power of the solvent remains constant. Thus, the

cured PVC/NBR blend will become more resistant to the solvent attack, (in this case, ASTM #3 oil), thus leading to a reduction in mass swell as shown in Figure 2. At 100°C, the rate of reduction of the mass swell with increasing sulfur concentration is initially low but decreases sharply at higher concentration (i.e. 1 phr sulfur). The reduction in mass swell with increasing sulfur loading is in agreement with a previous work reported by Coran and Patel [12] on PP/EPDM dynamic vulcanizates. The PVC/NBR behavior toward ASTM oil #3 agrees quite well with our recent work on the oil resistance of the dynamically cured epoxidised natural rubber based poly (vinyl chloride) TPEs [7].

### Effect of dynamic curing

#### *Mechanical properties at ambient temperature*

Figures 3-5 demonstrate the influence of sulfur content on the tensile properties of the PVC/NBR formulation. Note that a moderate increase in tensile strength with increasing sulfur concentration is shown in Figure 3. This could be attributed to the progressive increase in the degree of curing. As indicated by the swelling index values presented in Figure 1 and the Brabender torque data in table 2, the degree of curing increases with sulfur loading. Thus the number of macromolecular chains increases albeit they become shorter being stiffer and more numerous require a higher applied stress to cause rupture. The observed trend agrees quite well with our earlier investigation on PVC/ENR TPEs [7]. Coran and Patel [6] have reported similar results on EPDM/PP thermoplastic dynamic vulcanizates. The same explanation could also be used to account for the effect of sulfur loading on the modulus at 100% elongation as shown in Figure 4. Since M100 is directly proportional to the number of crosslinks formed [13], the data presented provides a suitable means for assessing the degree of curing. This notion is strongly supported by the decrease in swelling index presented in Figure 1. The percent elongation at break (%EB), initially increases with 0.4 phr loading of sulfur followed by a gradual increase with subsequent addition (Figure 5). This trend is expected since ductility is known to increase with increase in the degree of curing for lightly cured rubber [14].

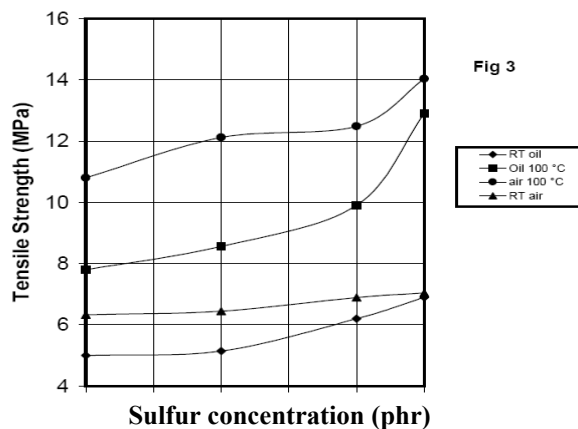


Figure 3: Effect of sulfur loading on tensile strength of PVC/NBR TPEs.

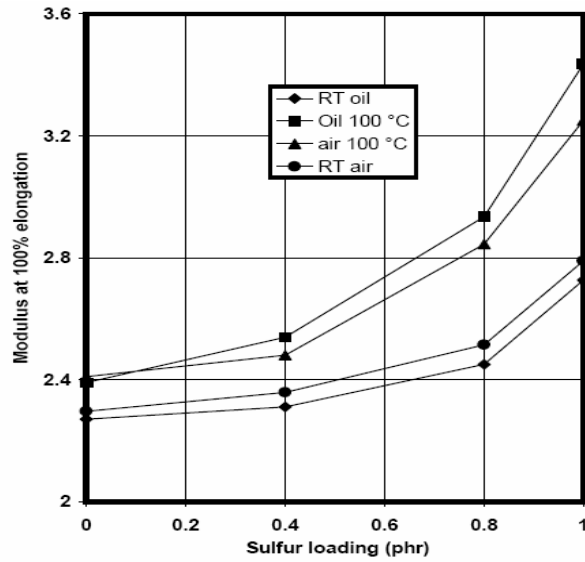


Figure 4: The effect of sulfur loading on modulus at 100% elongation of PVC/NBR TPEs.

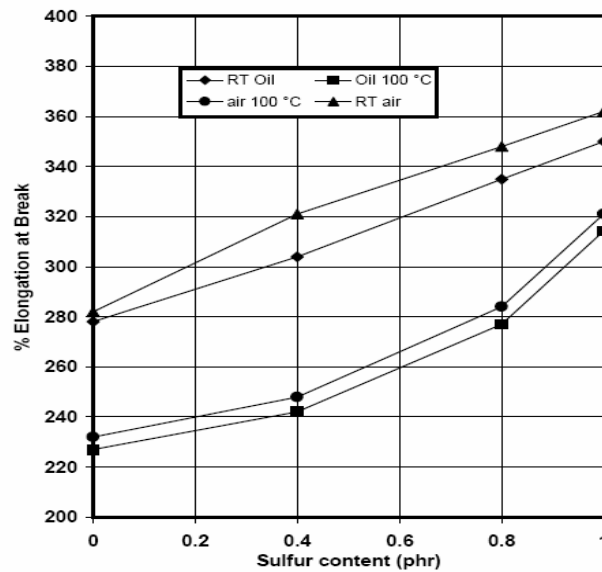


Figure 5: The effect of sulfur loading on elongation at break of PVC/NBR TPEs.

The continuous rise in EB with increase in degree of curing indicates that crosslink formation in the blend has not yet peaked off. This again suggests that the NBR in the blend is lightly cured. The influence of sulfur loading on tear strength of the cured formulations at various sulfur loadings is presented in Figure 6. Tear strength is a toughness related property which is known to increase with the degree of curing for lightly cured elastomers [14].

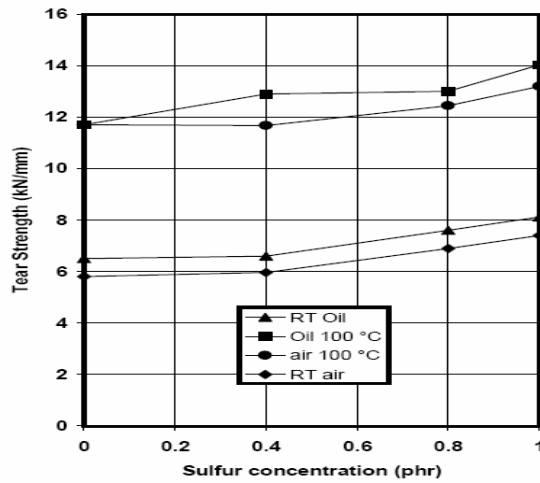


Figure 6: The effect of sulfur concentration on tear strength of PVC/NBR TPEs at various exposure conditions.

### Hardness

Figure 7 demonstrates the influence of sulfur loading on the hardness of cured formulations. The continuous increase in hardness with increasing sulfur concentration is rather expected since hardness is known to be strongly related to the degree of curing. This can be attributed to the shorter and therefore more rigid network chains as the level of curing increases.

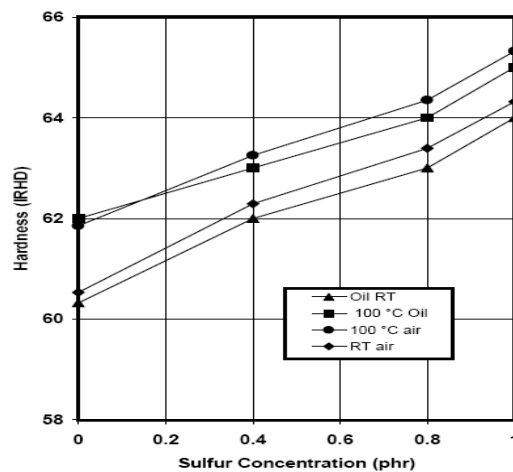


Figure 7: The effect of sulfur concentration on hardness of PVC/NBR TPEs.

### Oil resistance and mechanical properties

The introduction of crosslinks in the plastified blend as discussed above has also conferred tremendous changes in the oil resistance of the TPEs as elaborated below.



### *Tensile properties*

Figure 3, also illustrates the effect of various exposure conditions on the tensile strength of PVC/NBR TPEs. One can observe that at room temperature the tensile strength of the blend samples immersed in oil is more or less the same as those exposed to air. This indicates that there is no significant changes in the microstructure of the materials. The similarity in the behaviour of both uncured and cured formulation in air and in oil provides an indication of good oil resistance for the two environments.

These findings is in line with our previous investigation on PVC/ENR TPEs [7]. The oil resistance of specialty rubbers originates mainly from their polarity whereby the oil resistance is expected to increase with increase in polarity. Since NBR is a polar elastomer, the presence of polar groups is believed to be responsible for the observed good oil resistance. As the immersion temperature is increased to 100°C, a noticeable increase in tensile strength was observed. In comparison samples exposed to oil display a relatively lower tensile strength than those exposed to air for the same duration. The good correlation between the two tests implies that the exposure of the samples at higher temperature results in the formation of more crosslink network, which eventually leads to higher tensile strength. The ability to sustain the tensile strength upon exposure at 100°C for 70 hours is an indication of good oil resistance of PVC/NBR TPEs. This performance is comparable to the mid-performance specialty rubbers [15]. The tremendous increase in tensile strength can be attributed to postcuring. For example the tensile strength increased from about 5 MPa for the unvulcanized blend at room temperature to almost 13 MPa for the 1 phr sulfur blend after exposure to oil at 100 °C for 70 hours. This observation also reveals that dynamic curing has conferred excellent oil resistance to the PVC/NBR TPE. In other word, this observation demonstrated that the dynamically cured PVC/NBR TPE is capable of withstanding exposure to oil at 100°C for reasonable period of time. Also, this exposure is synonymous to an accelerated ageing test and the observed synergism in tensile strength signals good service life at ambient conditions. Further tests will still be required for prolonged exposure at high temperatures. The increased tensile strength correlates well with the increased crosslink density predicted by the swelling index and the modulus at 100% elongation as a consequence of post curing.

### *Elongation at Break*

Figure 5 shows the effect of sulfur concentration on elongation at break (EB) of PVC/NBR TPEs under different exposure conditions. Again, the samples exposed to air at room temperature displayed more approximate EB values to that for the sample immersed in oil at room temperature. On the contrary, at 100°C the EB reduced for all sulfur concentrations. This can be attributed to the formation of new crosslinks which will then shorten the network chains. Thus, the sample cannot be stretched to higher ranges. It is obvious, however, that EB increases with increase in sulfur concentration to the extent that with 1 phr of sulfur, EB is still well above 200% which is within acceptable range for a TPE of this nature.

### *Tear strength*

Figure 6 depicts the variation of tear strength of PVC/NBR TPEs with different concentrations of sulfur at different exposure conditions. A gradual increase in tear strength with sulfur loading was demonstrated for all the formulations. As in the case of tensile strength (Fig. 3), there is a very close resemblance between the tear strength

of the samples exposed to air and those immersed in oil at room temperature. This indicates the good oil resistance of the cured PVC/NBR TPEs. It can also be seen that the tear strength of the samples increased significantly after being exposed at 100°C to oil and air. Thus a higher applied force is needed to fail the samples. The superior performance of tear strength in oil at 100°C compared to air at 100°C again highlights a good oil resistance of PVC/NBR TPEs. This scenario can be attributed to the formation of extra crosslinks which impart better resistance against tearing forces.

### *Hardness*

Figure 7 illustrates the effect of sulphur loading on the hardness of PVC/NBR TPEs under various exposure conditions. The hardness values for the samples in both media at room temperature and 100°C are more or less the same. This may again be related to a good oil resistance of the TPEs. It is obvious that the hardness of the formulations at 100°C is higher than that at room temperature. This again may be attributed to the formation of new crosslinks with increasing in the degree of curing. In addition, the increase in hardness is closely related to the increase in (M100) shown in Figure 4.

### **Conclusions**

The following conclusions can be made:

1. Oil resistance of the PVC/NBR TPEs has been improved dramatically with the addition of curatives, which leads to the formation of crosslinks.
2. The excellent retention of the tensile properties upon exposure to oil at higher temperature i.e. 100°C provide a clear indication on the good oil resistance of the dynamically cured PVC/NBR TPEs. The enhancement in tensile and tear strength of the samples upon immersion in oil and exposure to air at 100°C, could be attributed to the post curing effect which resulted in the formation of more crosslinks. These crosslinks, however, is believed to be responsible for the hardening and embrittlement of the samples, which, consequently, leads to a reduction of EB.

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