



Reinforcement of Bakelite Moulding Powder in Acrylonitrile Butadiene Rubber (NBR): In Comparison with Cashew Nut Oil Modified Phenolic Resin

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Abstract

The influences of two phenolic resins, that is, cashew nut oil modified phenol-formaldehyde resin (CN-m-PF) and Bakelite moulding powder (BMP), on properties of carbon black filled acrylonitrile butadiene rubber (NBR) were investigated and compared. Processability, cure characteristics, mechanical properties, thermal ageing resistance, and oil resistance of the NBR filled with various contents of phenolic resins (0-60 phr) were determined. The addition of both resins leads to a prolonged cure time with a greater value of torque difference. Regardless of the resin type, the improvement of compound processability and the enhancement of modulus and hardness of the NBR vulcanisates are observed with increasing resin content. However, many mechanical properties such as tensile strength, elongation at break and abrasion resistance are deteriorated. Thermal ageing resistance of the NBR vulcanisate is slightly improved in the presence of both resins, probably due to the dilution of NBR with the high heat-resistant phenol-formaldehyde resins. Results also disclose that all NBR vulcanisates demonstrate excellent oil resistance, regardless of the resin type and content. At any given resin content, CN-m-PF gives a better processability, higher stiffness and greater mechanical properties than BMP. However, due to its lower cost, BMP can be used to enhance stiffness of NBR vulcanisates without the risk of processing problem.

Keywords: Rubber; Phenolic resin; Reinforcement; Bakelite; Properties.

1. Introduction

Acrylonitrile butadiene rubber (NBR) is a synthetic rubber widely used in many applications in which high oil and abrasion resistances are required. By adjusting the filler content, a variety of hardness levels of NBR vulcanisates can be achieved. However, in certain applications where extremely high hardness level (>85 Shore A) is essential such as coupling generator for marine vessels, the sole addition of highly reinforcing fillers such as carbon black or silica might cause processing difficulty and, thus, the use of reinforcing phenolic resin is recommended. Generally, phenolic resin can be divided into two main groups, resol and novolac, depending on the catalyst used and the mole ratio of phenol (P) to formaldehyde (F). Resol resin (F>P, produced under basic catalyzed reaction) is highly reactive and can be used as a curing agent for unsaturated rubbers providing crosslinks via chroman ring reaction. It is widely used to cure butyl rubber in applications where high heat resistance is required such as tire curing bladders [1]. Use of resol resin as a curing agent for rubbers has extensively been reported [2-4]. Novolac resin (P>F, produced under acidic catalyzed reaction) can be used as tackifier, bonding agent and reinforcing agent. In contrast to the novolac tackifiers which have linear structure, the reinforcing novolac resins are more branched and offer good compatibility with the highly polar NBR. This type of resin is often modified with tall oil or cashew nut shell liquid for improved compatibility with various rubbers and increased scorch safety for the resins pre-blended with methylene donor such as hexamethylene tetramine (HEXA) or hexamethoxymethylmelamine

(HMMM) [5]. To function as a reinforcing agent, the novolac resin, when used in combination with methylene donor, can undergo self-condensation reaction and form crosslinked structure in the rubber network, the so-called interpenetrating network [6]. It is reported that the addition of reinforcing novolac resin improves stiffness, abrasion resistance, heat, oil and solvent resistance of the rubber products [5]. So far, the applications of phenolic resins in various rubbers have been extensively investigated such as NBR [7, 8], NBR blends [9, 10], ethylene propylene diene monomer (EPDM) [11, 12], natural rubber (NR) [13], butyl rubber [14, 15] and styrene butadiene rubber (SBR) [16, 17].

Bakelite is a trade name of phenol-formaldehyde thermoset resin blended with wood flour for cost reduction purpose. In most commercial Bakelite moulding powder (BMP), the phenol formaldehyde thermoset resin or its modified form acts as a binder. Due to its high mechanical strength, very low water absorption, great electrical insulation, high resistance to most chemicals and excellent temperature resistance, BMP is widely used to make kitchenware, buttons, toys, lamp holder, including electronic insulating components such as switches, plug and socket.

Although BMP has a wide range of applications in plastic industry, little attention is given to the application of BMP in rubber industry. Due to its relatively low cost, the use of BMP as a reinforcing filler for polar rubbers, particularly NBR, is of great interest. This work aims to investigate the effect of BMP on properties of CB-filled NBR. Various contents of BMP were added and properties of the BMP-filled NBRs were measured and compared with those of the NBRs filled with the more expensive counterpart, the cashew nut oil modified phenol-formaldehyde resin (CN-m-PF).

2. Experimental

2.1. Materials

All materials were used as received. Acrylonitrile butadiene rubber (NBR: KRYNAC 3345F with acrylonitrile content 33% and 45-ML1+4@100°C) was manufactured by Lanxess Deutschland GmbH, Germany. Carbon black (CB; N330 with specific surface area of 80 m²/g) was produced by Thai Carbon Black PCL, Thailand. Bakelite moulding powder (BMP; PF2A2-131 with approximately 70% wood flour content) was obtained from Zhejiang Jiamin Plastic Co., Ltd., China. The cashew nut oil modified phenol-formaldehyde resin (CN-m-PF; SP-6600 with HEXA content 7.5%) was purchased from Akrochem Corporation, USA. N-tert-butyl-benzothiazole sulfenamide (TBBS), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) were manufactured by Monflex Pte. Ltd., Singapore. Aromatic oil was supplied by PSP Co., Ltd., Thailand. Tetramethylthiuram disulfide (TMTD) was produced by Taminco, N.V., Belgium. Stearic acid was obtained from IOI Acidchem International Sdn. Bhd., Malaysia. Zinc oxide (ZnO) was produced by Thai-Lysaght Co., Ltd., Thailand. Sulfur was supplied by Siam Chemicals Public Co., Ltd., Thailand. The standard reference oil (IRM#903) was purchased from Chemical Innovation, Co., Ltd., Thailand.

2.2. Preparation and Testing of the Rubber Compounds

Rubber compounds were prepared in an internal mixer (Brabender-Plasticorder 350E, Germany) with fill factor and rotor speed of 0.75 and 40 rpm, respectively. A 2-step mixing technique was employed. In the first step, NBR was mixed with the following ingredients, i.e., 3 phr ZnO (activator); 2 phr stearic acid (activator); 2 phr 6PPD (antioxidant); 1.5 phr TMQ (antioxidant); 5 phr aromatic oil (processing aids); 80 phr CB (filler) and various contents (0-60 phr) of BMP or CN-m-PF (reinforcing agent), at the initial chamber temperature of 80°C for 10 minutes. The curatives (1.2 phr TBBS; 0.5 phr TMTD and 2 phr sulfur) were added into the compounds in the second step at lower mixing chamber temperature (60°C) for 2 minutes. After mixing, the compounds were immediately sheeted on a two-roll mill (Labtech LRM150, Thailand) and left overnight at room temperature before testing.

Mooney viscosity (MS1+4@100°C) of the rubber compounds was measured as per ISO 289-1 using a Mooney viscometer (TechPro viscTECH+, USA). A small rotor was selected for the test because of the high compound viscosity. Cure characteristics were evaluated by a moving die rheometer (MDR; TechPro MD+, USA) at 150°C using the procedures described in ISO 6502. Rubber vulcanisates were prepared in a compression mould at 150°C using the t_{c99} as determined from the MDR unless stated otherwise. Hardness was measured as per ISO 7619-1 using a Shore D durometer (Bareiss, Germany). Tensile properties were measured using a universal testing machine (Instron 3366, USA) according to ISO 37 (die type 1). Abrasion resistance was determined by DIN abrasion tester (Zwick, Germany) following ISO 4649. The cylindrical-shaped DIN specimens were prepared in a compression mould at 150°C using the curing time of $t_{c99} + 6$ minutes. Filler dispersion was characterized by scanning electron microscope (SEM, Hitachi 3400, Japan). The fracture surface of the tensile specimen was sputter coated with gold prior to the examination. Accelerated ageing test was carried out at 100°C for 24 hours using an ageing oven (Elastocon EB 10, Sweden) in accordance with ISO-188. After ageing, the tensile properties of the specimens were determined and compared with those of the unaged specimens. Oil resistance was also evaluated by immersing the dumbbell-shaped specimens in IRM#903 oil at room temperature for 72 hours. Weight change and tensile properties of the swollen specimens were investigated and compared with the unswollen ones.

3. Results and Discussion

Fig. 1 represents Mooney viscosity (MS1+4@100°C) of the rubber compounds. The addition of CN-m-PF noticeably reduced compound viscosity. The results are not beyond expectation because CN-m-PF is a phenol-

formaldehyde resin modified with a cashew nut oil which has excellent compatibility with NBR in all proportions, and thus, at high temperature ($>73^{\circ}\text{C}$), CN-m-PF melts and plasticizes the rubber compound. The addition of BMP, on the other hand, had very little effect on a compound viscosity even at a very high content (60 phr). This might be attributed to the combination of the high BMP softening point ($105\pm 3^{\circ}\text{C}$) and the presence of wood flour in BMP.

The MDR results shown in Fig. 2 and 3 reveal the prolonged cure time (t_{c99}) and the increased torque difference (M_H-M_L) with increasing both CN-m-PF and BMP contents. Since the resins do not crosslink with rubber molecules [5], it is thought that the increased cure time and the enhanced torque difference mainly arise from the curing nature of the added resins. More time is required to reach complete cure when a greater amount of CN-m-PF or BMP is added. In the meantime, this yields a greater level of crosslink density in the rubber products. Obviously, CN-m-PF gives a stronger effect on cure characteristics than BMP, i.e., at the same content, the compounds filled with CN-m-PF has longer cure time with higher torque difference than those filled with BMP. This is understandable because the BMP contains relatively large amount of wood flour ($\sim 70\%$) and, hence, a lower amount of curable phenol formaldehyde resin when compared with the unfilled CN-m-PF resin at the same content.

The influences of CN-m-PF and BMP on hardness (Shore D) of the vulcanisates are illustrated in Fig. 4. As expected, hardness is increased continuously with increasing CN-m-PF and BMP contents, which might be attributed to the reinforcement of interpenetrating crosslinked phenol formaldehyde resin. When mixed with rubber, the resins are molten and dispersed in a rubber matrix. During the vulcanisation of rubber, the resins react with methylene donor (HEXA) and form infusible thermoset networks dispersed in the vulcanized rubber leading to the significant increase of hardness [16, 18]. At the same content, CN-m-PF gives higher hardness than BMP which can be explained by the higher crosslink density of CN-m-PF as previously mentioned. It can be observed that hardness is increased almost linearly with increasing resin content. By performing a linear regression, the relationship between hardness (H) and resin content (C) can be given in Equations (1) and (2) for CN-m-PF and BMP, respectively.

$$H = 0.285C + 48.1 \quad \text{Equation (1)}$$

$$H = 0.167C + 47.8 \quad \text{Equation (2)}$$

From the equation, hardness of the rubber vulcanisate can be predicted from the resin content, i.e., an increase of 1 Shore D is obtained by the addition of 3.5 phr of CN-m-PF or 6.0 phr of BMP. Similar results are obtained for the moduli at 20% (M_{20}) and 50% (M_{50}) elongations as shown in Fig. 5 and 6, i.e., moduli tend to increase continuously with increasing resin content. A thorough look at the results reveals that, at any given resin content, CN-m-PF gives higher hardness and M_{20} than BMP and the difference seems to be larger at higher resin contents indicating the greater ability to enhance hardness and modulus at low strain of CN-m-PF when compared to BMP. The greater crosslink density offered by CN-m-PF might be the possible explanation. However, when considering modulus at higher strains (say, M_{50}), both CN-m-PF and BMP give similar values of M_{50} up to 30 phr. Even though further increase of resin content caused a difference in M_{50} between CN-m-PF-filled and BMP-filled vulcanisates, such discrepancy was not as large as that found in the low-strain modulus. This may be attributed to the presence of filler in BMP which could reinforce the vulcanisates at higher strains, the point where the rubber network in matrix is tightly stretched and stress is transferred to the tightly bound rubber located at the filler surfaces.

Table 1 discloses the effects of resin type and content on tensile strength and elongation at break of the rubber vulcanisates both before and after ageing test. Tensile strength and elongation at break do not change significantly with the addition of CN-m-PF up to 15 phr. The addition of CN-m-PF above this level results in a noticeable drop of both tensile strength and elongation at break. Similar observations have previously been reported by Al-Maamori, *et al.* [7]. They found the continuous decreases of tensile strength and elongation at break of the CB-filled NBR vulcanisates with the addition of novolac thermoset resin. However, different results have been reported by Nigam, *et al.* [8], showing the small enhancement of tensile strength of CB-filled NBR vulcanisate when 20 phr of reinforcing phenolic resin was added, explained by the improvement of CB dispersion in the presence of resin. Chuayjuljit, *et al.* [13], reported the improvement of tensile strength in unfilled NR with the addition of novolac thermoset resin up to 30 phr and further increase of the resin content also resulted in a significant drop of tensile strength. They proposed that the initial improvement of tensile strength was induced by the additional crosslinks from the thermoset resin and the co-crosslinks between unsaturated side-chain segments of the resins and the double bonds in NR. Unfortunately, the improvement of tensile strength in the presence of phenolic resins is not found herein, probably because the CB-filled NBR vulcanisate is highly crosslinked and possesses a good filler dispersion even without the addition of the resins (the aggregate size of CB is far below $1\ \mu\text{m}$ as shown in the SEM micrographs, Fig. 7(a)). The addition of resins does not improve filler dispersion in this case and the additional crosslinks from the thermoset resin might restrict molecular motion of the rubber chains making the rubber become stiffer but lower ability for energy dissipation. For the vulcanisates incorporated with BMP, tensile strength and elongation at break are continuously decreased with increasing BMP content. Similar explanation is applied.

At low resin contents (≤ 30 phr), CN-m-PF gives slightly higher tensile strength and elongation at break than BMP. The slightly poorer tensile strength and elongation at break found in the BMP-filled vulcanisate might be the consequence from the presence of large-sized particles such as wood flour acting as defects and, thus, causing the reductions of both tensile strength and elongation at break as clearly observed in the SEM micrographs, Fig. 7(c). However, at high resin contents (45 and 60 phr), the discrepancies of tensile strength and elongation at break between CN-m-PF filled and BMP-filled NBR vulcanisates are insignificant.

Results also reveal the improvement of thermal ageing resistance of the rubber vulcanisates with the addition of both CN-m-PF and BMP. Without the resins, tensile strength of the vulcanisate is reduced approximately 10% after ageing at 100°C for 24 hours. However, in the presence of the resins, tensile strength of the vulcanisate is slightly

enhanced (2-10%) after thermal ageing. Similar results are observed for elongation at break, i.e., the elongation at break of the vulcanisate without resin is reduced approximately 30% after the thermal ageing, attributed to the post-curing effect leading to excessive crosslinks between NBR molecular chains. The change of elongation at break is reduced in the presence of both resins. Results show that the addition of phenol-formaldehyde resins can improve thermal ageing resistance of the vulcanisate, probably due to the dilution of NBR with the high heat-resistant phenol-formaldehyde resin. The enhanced thermal ageing resistance of the CB-filled NBR from the addition of phenolic thermoset resin has also been previously reported [8].

Fig. 8 illustrates the effect of resin content on abrasion resistance which is represented in terms of volume loss. Unexpectedly, despite the increases of hardness and modulus, abrasion resistance of the vulcanisate is deteriorated with increasing resin content, regardless of the resin type, as can be seen from the continuous increase of volume loss. The impaired abrasion resistance is thought to arise from the reduced strength of the vulcanisate in the presence of the thermoset resins. However, contradictory results have earlier been reported in NR vulcanisate in which the addition of phenolic thermoset resin increased abrasion resistance [13]. Consequently, the role of reinforcing phenolic resins on abrasion resistance of rubbers is still inconclusive because it might depend on many factors, particularly the rubber formulation. At any given resin content, BMP shows slightly inferior abrasion resistance compared with CN-m-PF, probably due to the existence of large-sized filler in BMP which has poor interfacial interaction with the matrix.

Oil resistance of the rubber vulcanisates was also characterized by immersing the specimens in oils for 72 hours at room temperature before measuring their swelling degree and changes of mechanical properties. Table 2 displays the effects of resin type and content on oil resistance of the rubber vulcanisates, represented in terms of property changes after oil immersion. It is widely known that NBR is highly polar and, thus, has high resistance to non-polar oil. The oil resistance of NBR is further augmented by the addition of reinforcing fillers such as carbon black or silica. In this work, NBR was heavily filled with carbon black (80 phr) and densely crosslinked (high sulfur content), the NBR samples (both with and without resins) therefore possessed excellent oil resistance, i.e., the swelling degree of all samples is negligible (less than 0.2%). It can be observed that the change of tensile strength after oil immersion is also insignificant (<10%), confirming an excellent oil resistance of the rubber vulcanisates. Despite the extremely low swelling degree, modulus of the rubber vulcanisates tends to increase slightly (~10-20%) whereas the elongation at break is slightly decreased (<18%) after oil immersion which could be attributed to the more tightened rubber network in the swollen specimens. Similar findings have previously been reported [19, 20]. Taking as a whole, the densely crosslinked and heavily filled NBR vulcanisates possess an excellent oil resistance and, thus, the effects of resin type and content on oil resistance of the NBR vulcanisates are not obvious (the variations found herein are within the experimental error limits), even though the addition of crosslinked phenolic resin into the rubber network should theoretically increase oil resistance of the rubber vulcanisates due to the existence of additional resin network which can resist the oil swelling. In addition, with increasing resin content, the volume fraction of CB in the test specimen is reduced whereas the crosslink density of the specimen is increased. The counterbalance of these effects might be another reason for the insignificant change of oil resistance in this work.

4. Conclusions

Both CN-m-PF and BMP can be used to enhance modulus and hardness of the CB-filled NBR vulcanisates in the applications where extremely high hardness is essential. Due to its low melting point, CN-m-PF noticeably improves processability of the rubber compounds whereas such processability improvement is not obvious with the addition of BMP. The addition of CN-m-PF up to 15 phr has no significant effect on tensile strength and elongation at break of the rubber vulcanisates. Further increase of CN-m-PF content, however, leads to the deteriorations of tensile strength and elongation at break. However, for the BMP-filled system, tensile strength and elongation at break are decreased continuously with increasing BMP content. Results also reveal the improvement of ageing resistance of the NBR vulcanisates with the addition of both CN-m-PF and BMP. Excellent oil resistance is found in all NBR vulcanisates, regardless of the resin type and content. When compared at any given resin content, CN-m-PF gives better processability and mechanical properties than BMP. However, for cost reduction purpose, BMP might be used to replace the more expensive phenolic resins in the applications where extremely high hardness is preferred.

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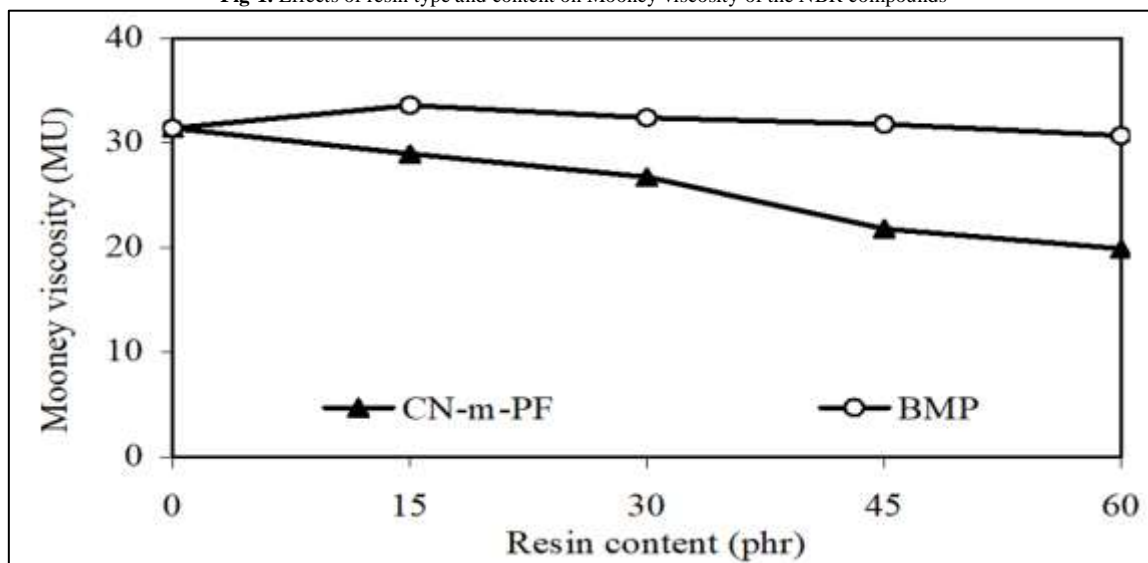
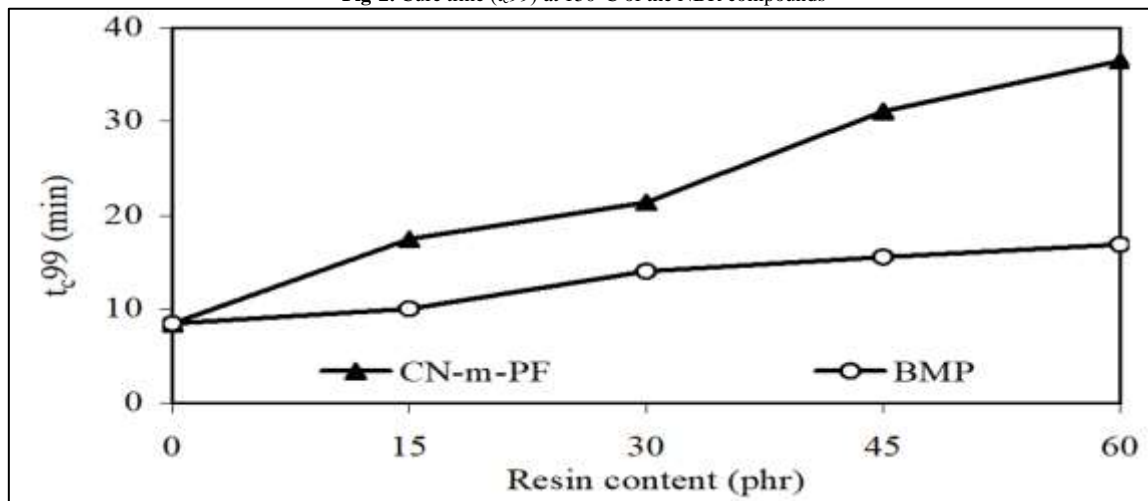
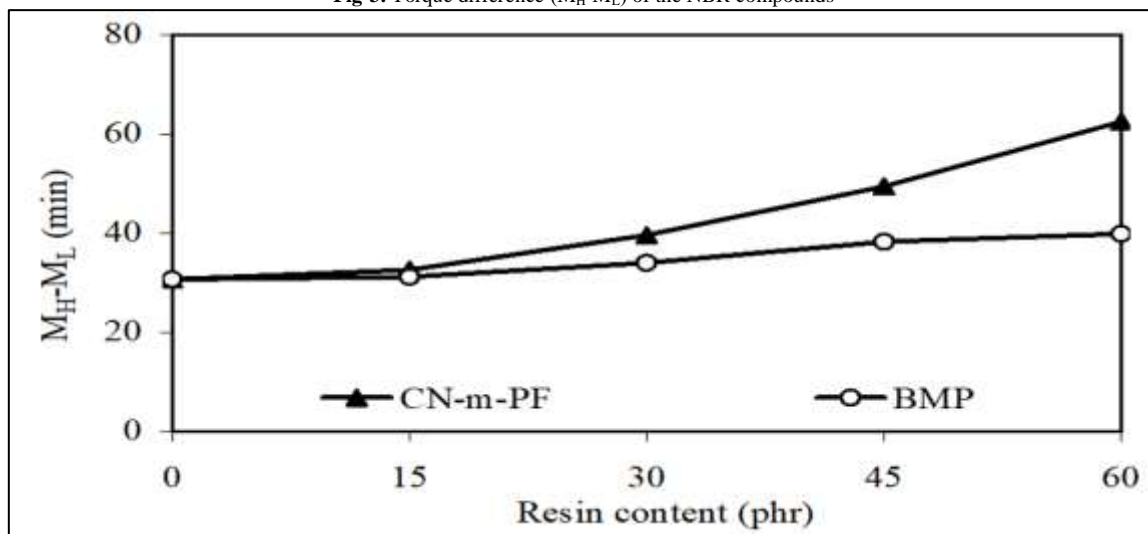
Table-1. Tensile strength and elongation at break of the NBR vulcanisates before and after thermal ageing

| Resin type | Resin content (phr) | Tensile strength | | | Elongation at break | | |
|------------|---------------------|---------------------|--------------------|------------|---------------------|------------------|------------|
| | | Before ageing (MPa) | After ageing (MPa) | Change (%) | Before ageing (%) | After ageing (%) | Change (%) |
| CN-m-PF | 0 | 21.8±1.2 | 19.5±0.5 | -10.7 | 183±5 | 127±8 | -30.5 |
| | 15 | 21.8±0.8 | 22.4±1.4 | 2.8 | 191±11 | 160±15 | -16.6 |
| | 30 | 19.1±0.7 | 19.4±1.6 | 1.9 | 166±8 | 133±8 | -20.2 |
| | 45 | 17.2±0.2 | 17.6±0.8 | 1.9 | 121±7 | 93±8 | -23.3 |
| | 60 | 16.5±0.3 | 18.1±0.5 | 9.4 | 92±9 | 71±3 | -23.2 |
| BMP | 0 | 21.8±1.2 | 19.5±0.5 | -10.7 | 183±5 | 127±8 | -30.5 |
| | 15 | 19.0±1.1 | 19.7±0.5 | 3.8 | 156±11 | 131±6 | -15.6 |
| | 30 | 18.0±0.2 | 18.8±0.3 | 4.2 | 136±9 | 113±4 | -17.1 |
| | 45 | 17.0±0.4 | 17.2±1.0 | 1.3 | 122±4 | 97±4 | -20.7 |
| | 60 | 15.3±0.5 | 16.9±0.4 | 10.8 | 99±8 | 83±6 | -16.6 |

Table-2. Property changes of the NBR vulcanisates after oil immersion

| Resin type | Resin content (phr) | Weight change (%) | Changes of mechanical properties (%) | | |
|------------|---------------------|-------------------|--------------------------------------|-------------|---------------------|
| | | | Tensile strength | 20% modulus | Elongation at break |
| CN-m-PF | 0 | 0.1 | 1.0 | 15.8 | -5.6 |
| | 15 | 0.0 | 4.2 | 19.5 | -8.8 |
| | 30 | 0.1 | 4.3 | 16.7 | -9.5 |
| | 45 | 0.2 | 9.2 | 10.8 | -3.3 |
| | 60 | 0.2 | 2.3 | 11.2 | -7.9 |
| BMP | 0 | 0.1 | 1.0 | 15.8 | -2.8 |
| | 15 | 0.1 | 0.6 | 20.2 | -10.4 |

| | | | | | |
|--|----|-----|-----|------|-------|
| | 30 | 0.1 | 3.7 | 15.1 | -3.8 |
| | 45 | 0.0 | 0.7 | 12.9 | -14.1 |
| | 60 | 0.2 | 7.8 | 15.5 | -1.5 |

Fig-1. Effects of resin type and content on Mooney viscosity of the NBR compounds**Fig-2.** Cure time (t_{c99}) at 150°C of the NBR compounds**Fig-3.** Torque difference ($M_H - M_L$) of the NBR compounds**Fig-4.** Effects of resin type and content on hardness of the NBR vulcanisates

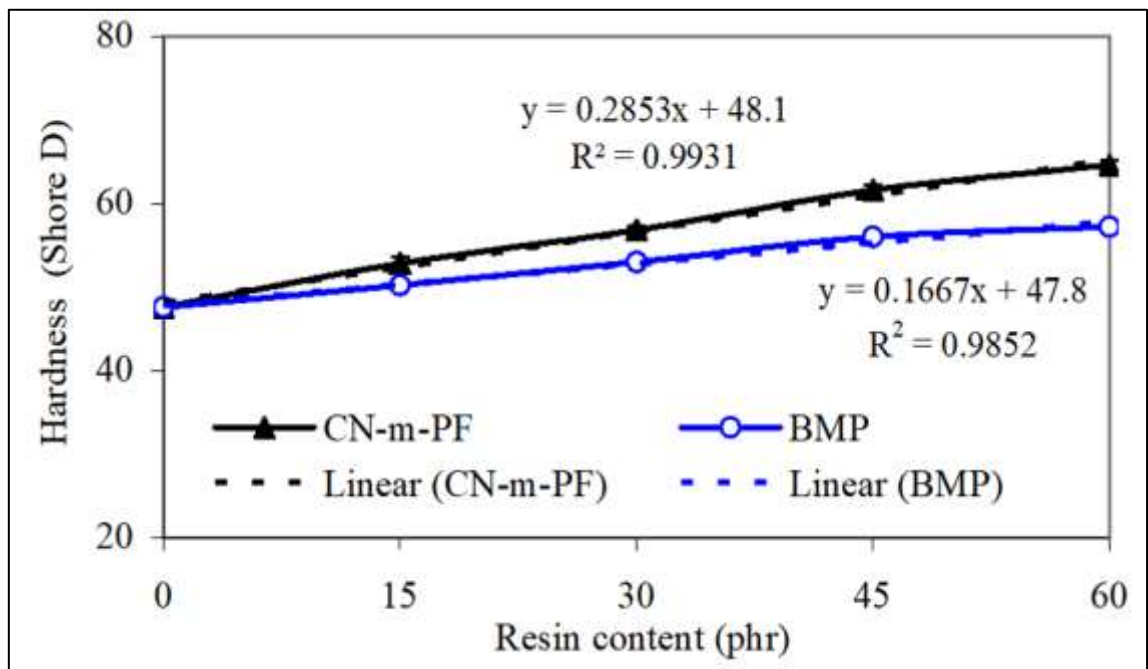


Fig-5. Dependence of 20% modulus of the NBR vulcanisates on resin type and content

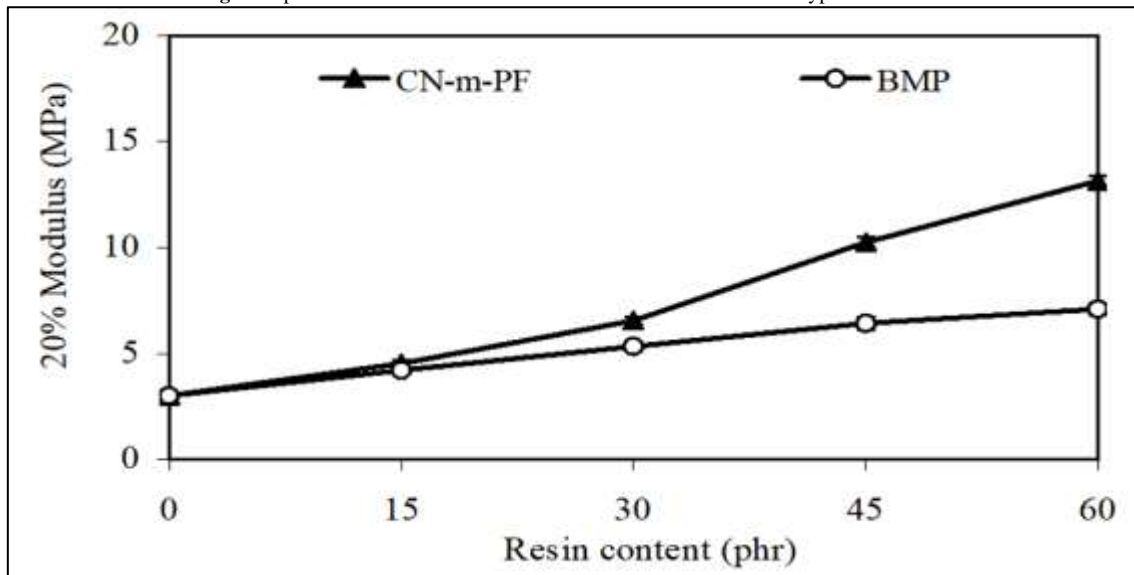


Fig-6. Dependence of 50% modulus of the NBR vulcanisates on resin type and content

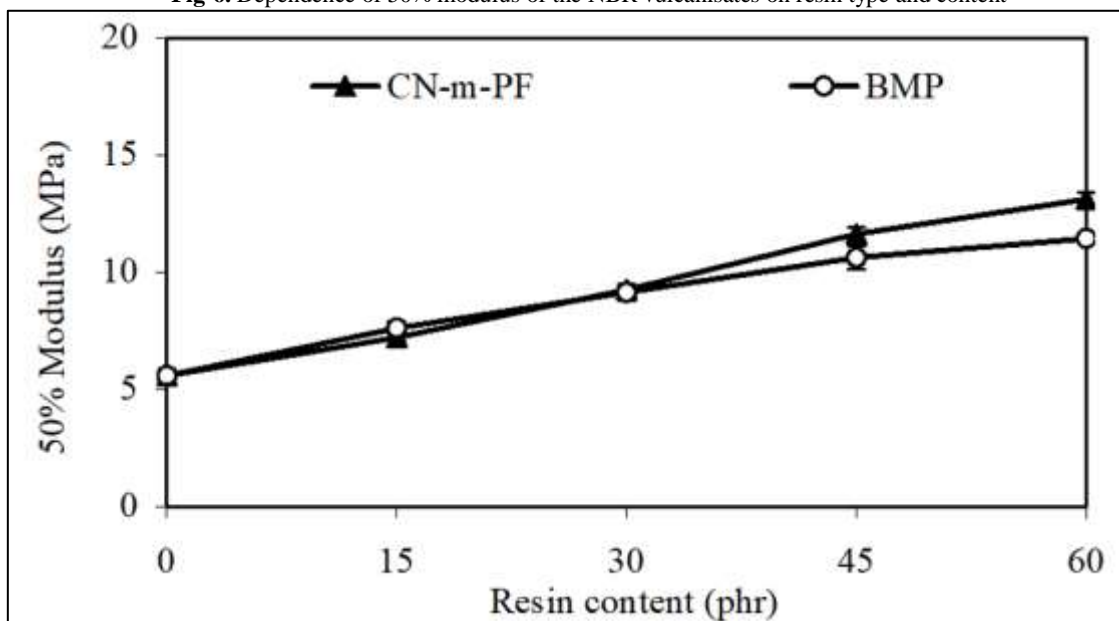


Fig-7. SEM micrographs (x20,000) of (a) CB-filled NBR, (b) CB-filled NBR with 60 phr of CN-m-PF and (c) CB-filled NBR with 60 phr of BMP

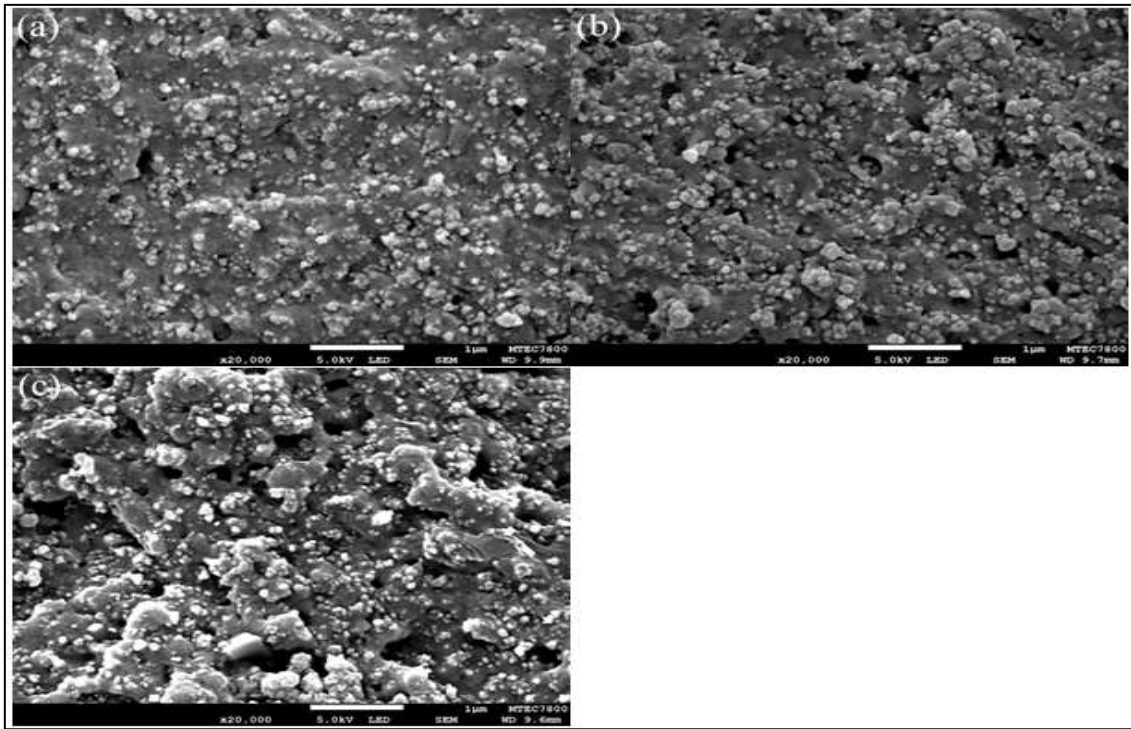


Fig-8. DIN abrasive volume loss of the NBR vulcanisates

