

Possible Use of Ultra-Fine Acrylonitrile Butadiene Rubber Powder as Filler in Natural Rubber Vulcanizates

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ABSTRACT: Possible use of ultra-fine acrylonitrile butadiene rubber powder (UFNBRP) as a filler for natural rubber (NR) was investigated. The UFNBRP was added into NR at various concentrations, and the compound properties were determined. It is found that, with increasing UFNBRP loading, the compound viscosity is increased, whereas both scorch time and optimum curing time are significantly reduced. The results also reveal that UFNBRP has negative effect not only on crosslink density but also on most mechanical properties of the vulcanizate, such as tensile strength, tear strength, compression set, and abrasion resistance. The deterioration of these mechanical properties is thought to arise mainly from the combined effect of large phase size of the dispersed UFNBRP and

low interfacial adhesion taking place from the polarity difference between UFNBRP and NR. Interestingly, it is found that, after aging, UFNBRP could promote postcuring phenomenon leading to increases of both relative 100% modulus and relative tensile strength. Oil resistance is also found to improve considerably with increasing UFNBRP loading. This improvement is mainly attributed to the dilution effect, i.e., the higher the UFNBRP loading, the lower the NR portion and, thus, the greater the oil resistance of the vulcanizate. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 353–358, 2010

Key words: rubber; aging; mechanical properties; fillers; blends

INTRODUCTION

Rubber blend technology is a novel technique widely used not only to develop and improve both processability and mechanical properties of rubber compounds but also to reduce the compound cost.^{1,2} With suitable selection of blend partners, the desired properties of rubber blend could be obtained because, principally, the blend should possess combined properties of both (or more) partners. However, great care must be taken into account in the application of blend technology because it is commonly found that the property levels of each rubber partner are not maintained in a blend. As truly miscible rubber blends are rare, most rubber blends therefore contain more than one polymer phase, and, thus, there are a number of factors affecting the blend properties. These include blend ratio, phase morphology, interfacial adhesion, and distribution of chemicals and crosslinks between the rubber phases.³ As a consequence, it is usually found that blends of highly immiscible rubbers such as natural

rubber (NR)/acrylonitrile butadiene rubber (NBR) blend have disappointed properties. Blending of NR with the polar NBR is intended to produce a vulcanizate with the best properties from each component, i.e., NBR's high oil resistance and NR's good mechanical properties. In practice, this NR/NBR blend faces many problems mainly because of the difference in polarity of the two rubbers causing maldistribution of crosslinks and also poor phase morphology. Maldistribution of crosslinks arises from the preferential solubility of the curatives. Proper selection of curing system could somehow alleviate the problem. The large phase size is another problem causing significant detrimental effect on the blend properties. Many attempts have been made to reduce the phase morphology and improve the properties of NR/NBR blends.^{4–7} Although control of phase size is highly complicated, the conditions of preparation of the blend have a major influence. The mixing conditions are always adjusted until sufficiently small phase size is obtained.

Recently, Qiao et al. have successfully developed a series of ultra-fine vulcanized rubber powder (UFRP).⁸ The UFRP is prepared by crosslinking the rubber latex using irradiation-curing method and then spray drying. Many types of UFRP, e.g., styrene butadiene rubber powder and acrylonitrile butadiene

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rubber powder (UFNBRP), are now commercially available. Possible applications of the UFRP include being a toughening or property modifier for plastics or being the major composition for thermoplastic elastomer preparation.^{9–14} Surprisingly, little attention is given to the application of UFRP as filler in rubber matrix. It is only reported that the use of UFNBRP as filler in EPDM could improve the mechanical properties of the vulcanizate.¹⁵ It is therefore the aim of this work to investigate the effect of UFNBRP content on properties of NR.

EXPERIMENTAL

Materials

All mixing ingredients were used as received. NR (STR 5L) was supplied by Union Rubber Product Corporation (Thailand). UFNBRP (NarpowTM VP401 with 26% of acrylonitrile (ACN) content and its reported median particle size is 100 nm) was manufactured by SINOPEC Beijing Research Institute of Chemical Industry, China. Ultrablend 6000 was obtained from Behn Meyer Chemical (Thailand). Stearic acid, zinc oxide (ZnO), and sulfur (S₈) were obtained from Chemmin Corporation (Thailand). The two accelerators used in this study, i.e., *N*-tert-butyl-2-benzothiazole sulfenamide (Santocure[®]TBBS) and tetrabenzylthiuram disulfide (Perkacit[®]TBzTD), were supplied by Reliance Technochem (Flexsys) (Thailand). The nonpolar hydraulic oil, TELLUS 100 (accordance with ASTM oil No. 5), was supplied by Shell (Thailand).

Study of UFNBRP morphology

The morphology of UFNBRP was studied using a scanning electron microscopy (SEM) technique (JEOL JSM-6301F). The SEM micrographs were taken after the powder was sputtered with gold to prevent charging on the surface.

Compound preparation

The compound formulation used in this study is given in Table I. The mixing process was carried out using a laboratory-sized internal mixer (Brabender Plasticorder). The mixing conditions were set as follows: fill factor = 0.8, initial chamber temperature = 60°C, rotor speed = 40 rpm, and mixing time = 10 min. After mixing, the compounds were sheeted on a two-roll mill (Labtech LRM150). Measurement of Mooney viscosity (ML1+4@100°C) was carried out according to ISO R289 using a Mooney viscometer (TechPro viscTECH+). The cure characteristics, e.g., scorch time (*t*_{s2}) and optimum cure time (*t*_{c90}) including minimum torque (ML) and maximum tor-

TABLE I
Compounding Formulation

Ingredients	Loading (parts per hundred of rubber, phr)
NR	100.0
UFNBRP	Variables (0.0–40.0)
Zinc oxide	5.0
Stearic acid	2.0
Ultrablend 6000	1.0
Santocure [®] TBBS	1.0
Perkacit [®] TBzTD	0.3
Sulfur	2.0

que (MH), were investigated using a moving die rheometer (TechPro MD+) at 150°C following ISO 6502. It was reported earlier that the torque difference (MH – ML) is directly proportional to the degree of crosslinking; therefore, it is used here to indirectly represent the crosslink density of the blend vulcanizates.^{15,16}

Testing of rubber vulcanizates

After vulcanization, determination of hardness was measured using a Wallace Shore A durometer according to ISO 7619 Part 1. The tensile properties and tear strength were determined using a universal testing machine (Instron 5566 series) following ISO 37 (die Type 1) and ISO 34 (die B), respectively. The abrasion resistance of the vulcanizate was investigated using an abrasion tester (Zwick 6102) according to DIN 53516. The rebound resilience was determined according to ISO 4662 using a Dunlop tripsometer (Toyoseiki 221). The compression set at elevated temperature was investigated according to ISO 815 (method B) at 70°C for 22 h. The degree of UFNBRP dispersion was examined using an atomic force microscope (AFM, Multimode Nanoscope IIIA). The AFM micrographs were taken on the newly exposed surface of the rubber specimens cut by microtome after embrittling in liquid nitrogen.

The aging resistance of the vulcanizate was also studied. The specimens were aged in an aging oven at 70°C for 72 h before the determination of tensile properties. The aging resistance is represented in terms of the relative properties, i.e., the ratio of the properties after aging to those before aging. Oil resistance was measured according to ISO 1817 by immersing the specimens in hydraulic oil (Shell-Tellus 100) for 7 days at room temperature (23°C). After the immersion, the specimens were blotted off with filter paper and rinsed with acetone before the determination of both mass change and tensile strength. The oil resistance of the vulcanizate is represented in terms of both swelling ratio and the relative tensile strength.

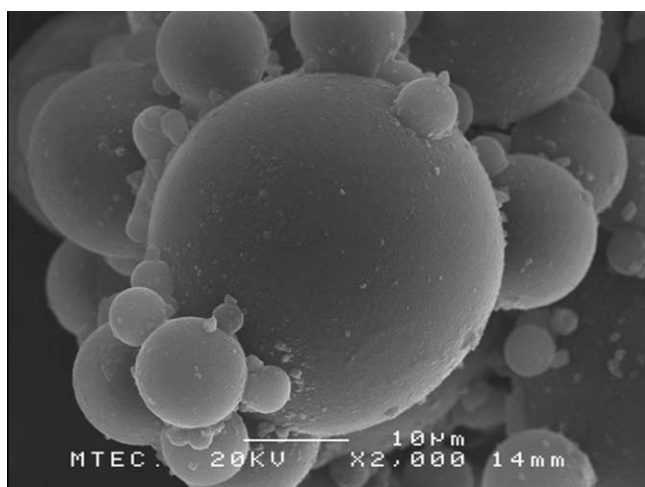


Figure 1 SEM micrograph of UFNBRP.

RESULTS AND DISCUSSION

Morphology of UFNBRP

SEM micrograph of the received UFNBRP is given in Figure 1. Obviously, the particles of UFNBRP are not isolated but tend to form agglomerates. It could be observed that the shape of UFNBRP particle is relatively spherical and its surface is relatively smooth. It could also be seen from the SEM micrograph that the particle size distribution is apparently broad, and the sizes of most particles lie within a microscale, which is considerably larger than that reported by the manufacturer.

Compound properties

The effect of UFNBRP loading on Mooney viscosity of the rubber compound is illustrated in Figure 2. The compound viscosity is found to increase contin-

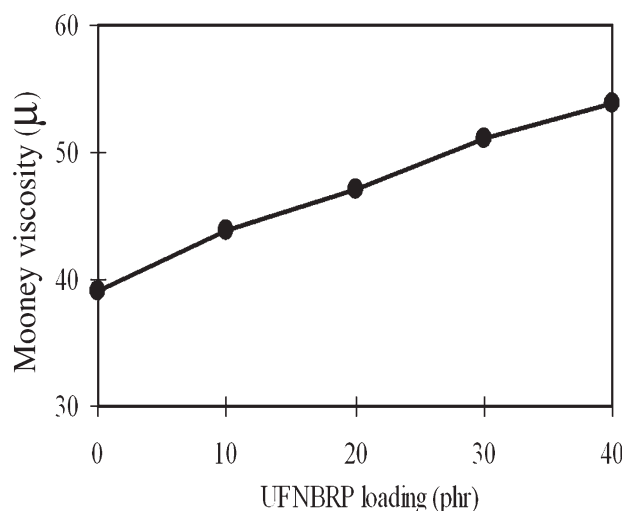


Figure 2 Effect of UFNBRP loading on Mooney viscosity of the rubber compounds.

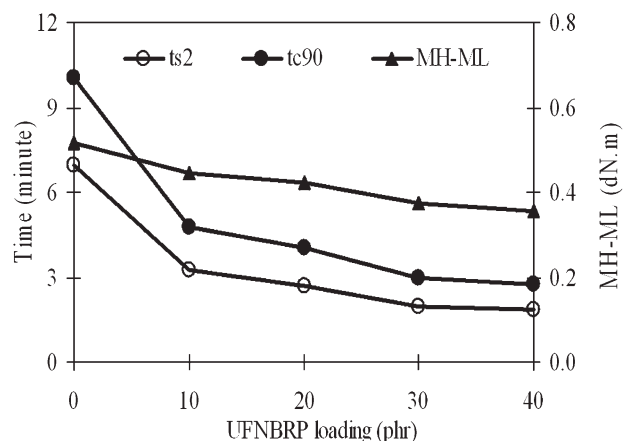


Figure 3 Dependence of cure characteristics on UFNBRP loading.

uously with increasing UFNBRP loading. This is simply due to the flow restriction effect caused by UFNBRP particles. Because of its vulcanized structure, UFNBRP possesses very high viscosity compared with uncured NR and hence it can hardly flow. When added into NR, UFNBRP therefore behaves more or less like a kind of special filler. Thus, the higher the amount of UFNBRP, the greater the Mooney viscosity. Figure 3 represents the dependence of cure characteristics on UFNBRP loading. Clearly, the results reveal that both scorch time (t_{s2}) and optimum cure time (t_{c90}) of the compound are reduced consecutively with increasing UFNBRP loading. A sharp reduction in cure time is observed even if small amount of UFNBRP is added. The results imply that UFNBRP could somehow accelerate the onset of sulfur vulcanization for NR. However, the torque difference (MH – ML) is found to decrease slightly with increasing UFNBRP loading. It is accepted that the torque difference can be used to reflect the degree of crosslinking. The results then indicate that the presence of UFNBRP could lead to significant drop of crosslink density. Similar observation is also reported in other work.¹⁵ As UFNBRP particles are already vulcanized, the mixing ingredients such as accelerators and sulfur could not be dispersed within them during the mixing step. However, these chemicals could be absorbed or diffused into the UFNBRP particles leading to further vulcanization of the UFNBRP particles. Because of the chemical diffusion, the concentration of curatives in NR matrix is decreased giving rise to the reduction of crosslink density.

Mechanical properties

The mechanical properties, i.e., hardness, tensile properties, abrasion resistance, and tear strength of the UFNBRP-filled vulcanizates, are given in Table II.

TABLE II
Mechanical Properties of the UFNBRP-Filled Vulcanizates

UFNBRP loading (phr)	Hardness (Shore A)	100% Modulus (MPa)	Tensile strength (MPa)	Abrasion loss (mm ³)	Tear strength (N/mm)
0	46.3 ± 0.3	0.94 ± 0.01	25.7 ± 1.1	195 ± 5	72.5 ± 1.7
10	45.8 ± 0.3	0.89 ± 0.02	22.7 ± 1.1	224 ± 6	70.1 ± 2.0
20	45.5 ± 0.0	0.88 ± 0.01	20.2 ± 0.8	246 ± 5	63.7 ± 4.7
30	45.4 ± 0.2	0.88 ± 0.02	16.4 ± 0.2	296 ± 7	57.3 ± 1.3
40	44.7 ± 0.4	0.87 ± 0.02	12.7 ± 1.0	365 ± 6	50.3 ± 1.9

As can be seen, the rubber hardness is found to decrease slightly with increasing UFNBRP loading. Even though UFNBRP behaves like a filler in NR matrix, unlike other hard solid fillers such as silica or carbon black, it does not enhance hardness of NR because its hardness is not very high. On the contrary, when greater amount of UFNBRP is added, the degree of crosslinking is decreased resulting in a slight reduction of the rubber hardness. As hardness is closely related to modulus, similar trend is also observed for 100% modulus results. The same explanation applies.

For tensile strength, it is evident that the tensile strength noticeably decreases with increasing UFNBRP loading. With 40 phr of UFNBRP, the tensile strength of the filled vulcanizate is reduced by half. This is understandable because the particle size of UFNBRP is relatively large. Moreover, UFNBRP has great tendency to form aggregate during mixing. This is supported by the AFM micrographs shown in Figure 4 in which the dark dispersed phase is UFNBRP and the continuous phase is NR. The micrographs elucidate that the phase size of UFNBRP is relatively large ranging from 5 to 25 μm. It is also found that the phase size of UFNBRP tends to increase with increasing UFNBRP loading. The results imply that the degree of aggregation is strongly dependent on UFNBRP loading, i.e., the higher the UFNBRP loading, the greater the degree of aggregation. Because of its large particle size, the received UFNBRP should therefore be classified as a nonreinforcing filler. In addition, because of great discrepancy in polarity between UFNBRP and NR, poor interfacial adhesion exists leading to the detrimental effect on tensile strength. Similar to tensile strength, other mechanical properties of the vulcanizate such as tear strength and abrasion resistance are also impaired in the presence of UFNBRP. The higher the loading of UFNBRP, the greater the extent of property deterioration. Possible explanation is given by the combined effect of large dispersed phase size of UFNBRP, reduced crosslink density, and poor interfacial adhesion as mentioned earlier.

Figure 5 represents the effects of UFNBRP loading on rebound resilience and compression set at elevated temperature. As expected, the rebound resili-

ence tends to decrease with increasing UFNBRP loading. It is the fact that rebound resilience directly reflects the degree of elasticity of the vulcanizate. The reduction of rebound resilience is therefore attributed to the impaired elasticity caused by UFNBRP. As mentioned earlier, the addition of UFNBRP results in the reduction of crosslink density, as measured indirectly from the torque difference value, and thus the reduction of elasticity degree. The reduction of rebound resilience with

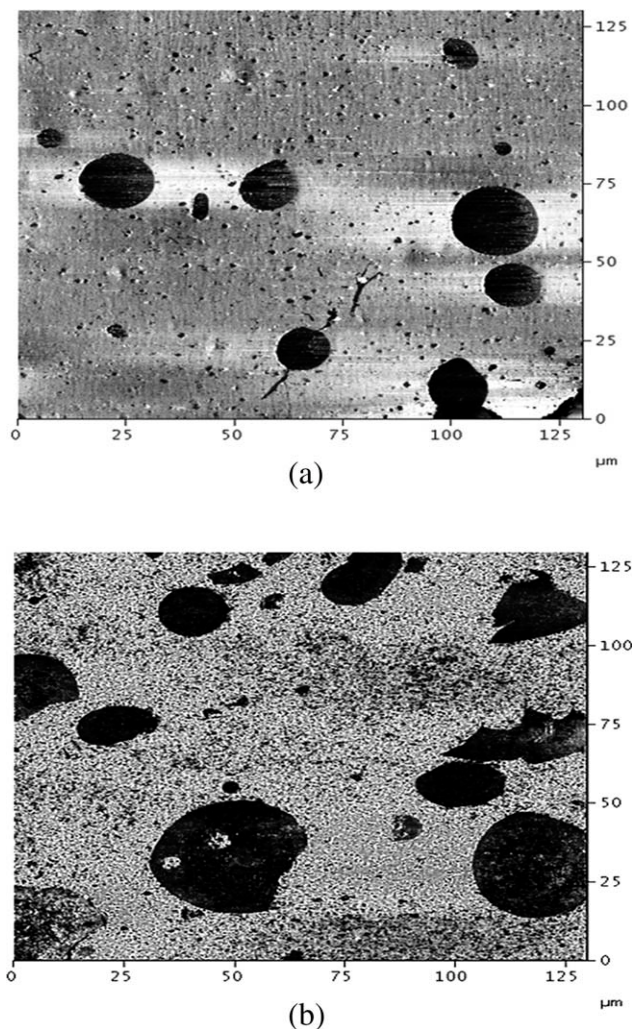


Figure 4 AFM micrographs of the UFNBRP-filled vulcanizates (a) 20 phr of UFNBRP and (b) 40 phr of UFNBRP.

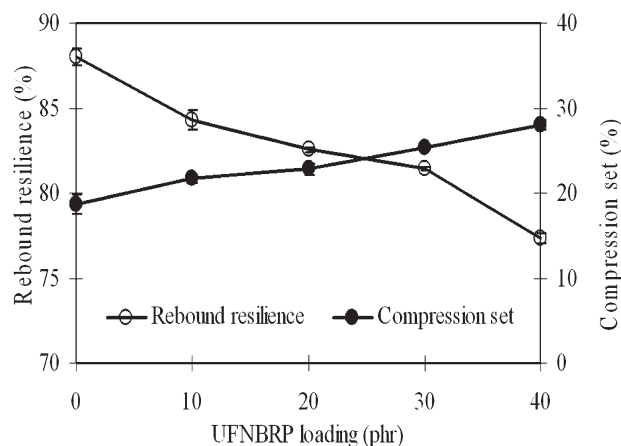


Figure 5 Effects of UFNBRP loading on rebound resilience and compression set at elevated temperature.

increasing UFNBRP loading might also arise from the dilution effect because it is widely known that vulcanized NBR has lower degree of elasticity than vulcanized NR. This is simply because of the existence of bulky polar ACN group in NBR.

Similar to other mechanical properties, the compression set at elevated temperature is also impaired in the presence of UFNBRP, i.e., the compression set value continuously rising with increasing UFNBRP loading. This is easily understandable because the compression set is directly related to the degree of elasticity. Increasing UFNBRP loading gives negative effect on the degree of elasticity and hence the compression set of the vulcanizate.

Thermal aging and oil resistance

Figure 6 depicts the effect of UFNBRP loading on thermal aging resistance of the vulcanizate represented in terms of the relative 100% modulus and the relative tensile strength. Obviously, it is found that the relative 100% modulus is greater than 1 in all cases. The results indicate that the modulus of the vulcanizate is increased after being subjected to

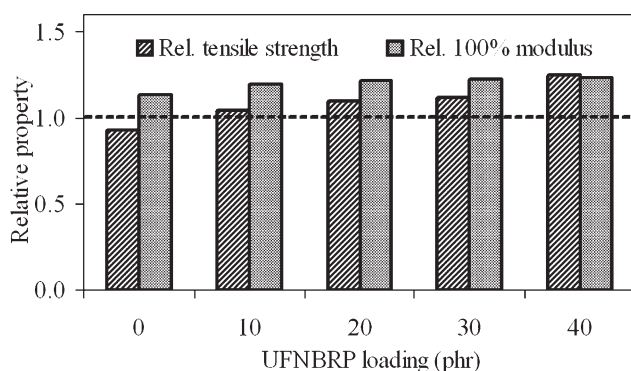


Figure 6 Effect of UFNBRP loading on thermal aging resistance of the vulcanizate.

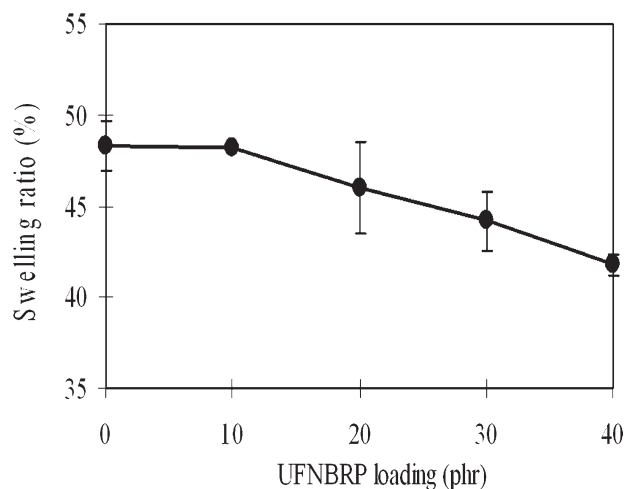


Figure 7 Relationship between swelling ratio and UFNBRP loading.

high temperature. The increase in 100% modulus is thought to arise from the postcuring effect. It could also be observed that the relative 100% modulus tends to increase gradually with increasing UFNBRP loading. This is possibly due to the consequence of the dilution effect because it is widely known that postcuring is more prone to occur in NBR compared with NR. Thus, increasing UFNBRP loading results in an increase in the relative 100% modulus. Similar trend is also found for the relative tensile strength in which the relative tensile strength has the tendency to increase with increasing UFNBRP loading. For unfilled vulcanizate, the relative tensile strength is slightly less than 1, meaning that the tensile strength is impaired after thermal aging. This is the case in which the effect of oxidative degradation is greater than that of postcuring. However, for UFNBRP-filled vulcanizate, the relative tensile strength is greater than 1. The results indicate that, in the presence of UFNBRP, the effect of postcuring is more pronounced than that of oxidative degradation.

The plot of swelling ratio against UFNBRP loading is given in Figure 7. As can be seen, the swelling ratio is hardly changed when 10 phr of UFNBRP is added. Nevertheless, further increase of UFNBRP loading leads to significant drop of swelling ratio. As swelling ratio is inversely proportional to oil resistance, it could be said that the presence of UFNBRP could enhance oil resistance of NR vulcanizate, particularly at high loadings. Again, the dilution effect could be used to explain the results, i.e., the dilution effect is more pronounced than the effect of crosslink reduction. With increasing the polar UFNBRP loading, the oil-swellaible NR portion is reduced giving rise to the enhancement of oil resistance. The improvement of oil resistance in the presence of UFNBRP is further confirmed by the results shown in Figure 8 in which the relative tensile

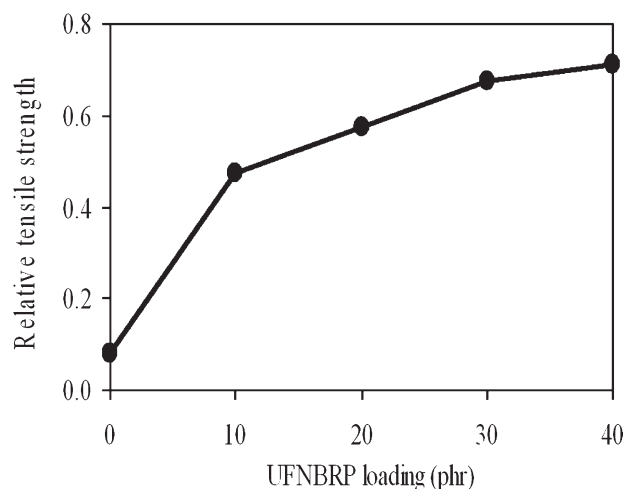


Figure 8 Effects of UFNB RP loading on relative tensile strength after oil immersion.

strength after being subjected to oil immersion is plotted against UFNB RP loading. Interestingly, the results reveal that, with small addition of UFNB RP (~10 phr), the relative tensile strength and, hence, the oil resistance of the vulcanizate are greatly enhanced. The improvement of oil resistance is even more obvious when the loading of UFNB RP is increased.

CONCLUSIONS

Because of its high viscosity, when added into NR, UFNB RP would behave as a kind of filler dispersed throughout NR matrix. Although the presence of UFNB RP gives detrimental effect not only on compound processability but also on the mechanical properties of the NR vulcanizate, both aging and oil resistance are found to improve with increasing UFNB RP loading. The negative effect on mechanical

properties of the vulcanizate is thought to arise from the combination of large dispersed phase size, reduced crosslink density, and poor interfacial adhesion, whereas the positive effect on aging and oil resistance is brought about mainly by the dilution effect.

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