Effects of the Filler Loading and Aging Time on the Mechanical and Electrical Conductivity Properties of Carbon Black Filled Natural Rubber

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ABSTRACT: The effects of the filler loading and aging time on the mechanical and electrical conductivity properties of natural rubber were investigated. In this work, carbon black (type N220) was used as a filler, and its loading was varied from 0 to 50 phr. The mechanical properties (e.g., the tensile strength and catastrophic tearing energy) increased with a filler loading up to a certain loading, and a decrease in the mechanical properties was observed with higher filler loadings. The tensile strength and catastrophic tearing energy of the aged samples decreased after 3 and 6 days of aging at 100°C. The results for the electrical conductivity properties of unaged samples showed a percolation threshold at 20 phr, and the values were consistent with further filler loadings. After aging, the percolation threshold was still maintained at 20 phr. The morphologies of unaged and aged samples were significantly different: holes were observed to occur in the aged samples. This might have been due to the movement of fillers when the materials were subjected to heat, and this subsequently influenced the mechanical properties of the natural rubber composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 747–752, 2008

Key words: ageing; conducting polymers; fillers; mechanical properties; rubber

INTRODUCTION

Conductive polymers and plastics are increasingly desired for a growing number of sophisticated end users. An active interest has been shown in electroconductive polymer composites as cheap and efficient materials sensitive to pressure variations, deformation, and temperature. This can be achieved with a matrix of insulating polymers filled with conductive particles such as carbon black or metals.[1] Carbon black is most often used because its conduction results from a strong electric field effect between the conductive particles or just direct physical contact.[2] For example, higher concentrations of special grades of carbon black are typically necessary, especially for electrical purposes.[3–5] The upper limit of conductivity that can be achieved is about 100 Ω^{-1} m^{-1}.[6] Besides commonly used carbon black and metal powders in various shapes, intrinsically conducting polymers are another class of important fillers for the preparation of composite conducting polymers.[7]

Current investigations on conducting polymer composites have led to some important revelations related to the attainable electrical conductivity range and trends of changes in the conductivity parameters with variations in (1) the size and type of the filler, (2) the loading level, (3) the geometrical structure of the filler, (4) the nature of the matrix polymer, (5) the degree of the filler dispersion, and (6) the temperature.[8,9] At a certain concentration of the filler in the insulating matrix, an electroconductive channel forms, so the insulator materials turn into conductor materials. This process is thought to be related to a critical phenomenon and can be described within the framework of percolation theory. A percolation type is a second-order phase transition from a nonconductive state to a conductive state that is supposed to occur.[9,10] Recent developments in conductive elastomers have provided the possibility of controlling the heating of these materials, which can be used as liners, surface coatings, food packages, and portable heating pads.

Aging is the deterioration of desirable properties during storage or service. This is a phenomenon common to a wide variety of natural and synthetic elastomers, including natural rubber.[11] Various changes can occur in an elastomer component as a result of the conditions under which it is used or stored.[12,13] The industrially important aspects of aging are changes in physical properties such as the tensile strength, hardness, or modulus of elasticity. If the conditions are too severe, the rubber may rapidly become unserviceable.

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The aging process of natural rubber is complex, but it is known that oxidation is a significant degradation process. The rate of degradation is significantly accelerated at higher temperatures.

In this work, the effects of the carbon black loading on the mechanical properties (tensile and catastrophic tearing energy) and conductivity properties of carbon black filled natural rubber composites were investigated before and after aging for 3 and 6 days at 100°C. The compounds were prepared with different carbon black loadings, and testing was done according to the standard test methods. The main objective of this work was to determine how the addition of a filler loading influences the mechanical and electrical conductivity properties of carbon black filled natural rubber composites and their behavior after aging.

EXPERIMENTAL

Materials

Natural rubber (SMR CV60) was purchased from RRIM (Malaysia), whereas carbon black (type N220) was supplied by Cabot Co. (M) Sdn. Bhd. (Selangor, Malaysia). Other mixing ingredients such as stearic acid, zinc oxide, *N*-cyclohexyl 1,2-benzothiazole-2-sulfemide (CBS), *N*-(1,3-dimethylbutyl)-*N*′-phenyl (6PPD), and sulfur were all purchased from Bayer (M), Ltd. (Selangor, Malaysia). All ingredients were used as received.

Preparation of the rubber compounds and vulcanizates

The compound formulations for the carbon black filled natural rubber composites are given in Table I. In part 1, the amount of carbon black loading in the natural rubber composite was varied from 0 to 50 phr. All mixing was carried out on a laboratory 160 × 320 mm two-roll mill (model XK-160) (Dalian, China) at room temperature. The samples were compression-molded at 160°C. The experimentation proceeded to part 2, in which the samples were aged for 3 and 6 days at 100°C in an air oven to investigate the effect of the aging time on the mechanical and conductivity properties of carbon black filled natural rubber composites.

Tensile properties

Dumbbell-shaped samples were cut from molded sheets according to ASTM D 412. Tensile tests were performed at room temperature with an Instron model 3366 machine with a speed of extension of 500 mm/min.

Tearing energy properties

The tests were carried out per ISO method 34-2:1999 with razor-nicked trouser test pieces cut from the vulcanized sheets. The tests were carried out at room temperature with an Instron model 3366 machine with a speed of extension of 100 mm/min.

TABLE I
Compound Formulations of the Carbon Black Filled Natural Rubber Composites

Material	phr
SMR CV60	100.00
Carbon black (N220)	0, 10, 20, 30, 40, or 50
Zinc oxide	5.0
Stearic acid	2.0
Sulfur	1.5
Accelerator (CBS)	1.5
Antioxidant (6PPD)	3.0

Conductivity properties

The conductivity tests were carried out with an Advantest R 8340 (Glendale, CA). The value of conductivity for each sample was determined according to Ohm's Law [eq. (1)] and eq. (2):

$$V = IR \tag{1}$$

$$\rho = \frac{RA}{t} \tag{2}$$

where V is the voltage, I is the current, ρ is the resistivity, R is the resistance, A is the area of the conductor, and t is the thickness of the sample test pieces measured with a thickness gauge.

Scanning electron microscopy (SEM)

The fracture surfaces of carbon black filled natural rubber composites were investigated with a Zeiss Supra 35VP scanning electron microscope (Oberkochen, Germany). The fracture ends of specimens were mounted on aluminum stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

Tensile strength

An increased in the filler loading caused an enhancement of the mechanical properties up to a certain loading and a reduction at very high filler loadings. From Figure 1, it can be seen that as the filler loading increased, the tensile strength increased up to 20 phr and decreased with further filler loading. The decrease observed in the tensile strength might be due to the weak interaction and bonding between the carbon black particles and natural rubber matrix. According to the theoretical aspect of the concept of reinforcement by fillers, as the reinforcing

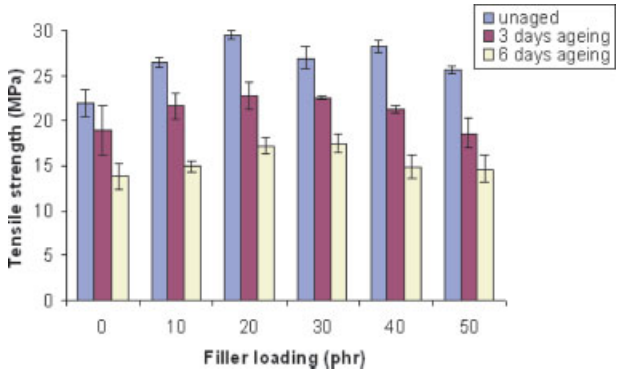

Figure 1 Tensile strength at different filler loadings before and after aging at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

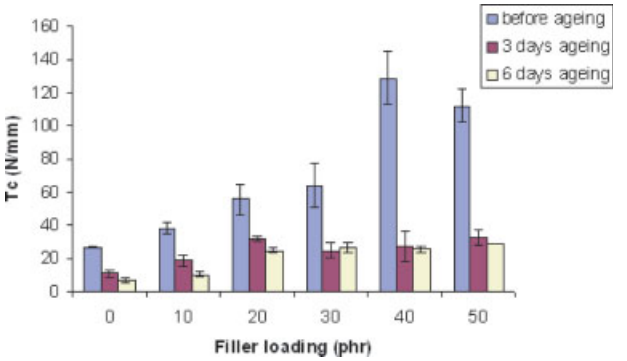

Figure 2 Catastrophic tearing energy (T_c) at different filler loadings before and after aging at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

filler loading increases, additional carbon black surface becomes available for polymer attachments. When the loading reaches a limiting value, the carbon black will not act as a reinforcing filler anymore.[14–16]

According to Figure 1, unaged and aged samples showed maximum values at 20 phr before a reduction with further loadings. However, the value of the tensile strength clearly showed a decrease with the aging time. This was due to the effect of heat, which caused a movement of the filler within the polymer matrix and degradation of the polymer matrix itself, which led to the breaking of the filler–filler, filler–rubber, and rubber–rubber bonding. The breaking of this bonding then led to less energy being required to break the samples, and this subsequently influenced the mechanical properties.[17,18] According to Barker,[19] aging of natural rubber compounds for up to 7 days at 100°C with similar curing systems reduced the tensile strength up to 50% and with more aging further degraded the strength properties of natural rubber vulcanizates.

Catastrophic tearing energy properties

The tearing energy can be considered the driving force for crack propagation. Experimental measurements have shown that when crack propagation is expressed in terms of the tearing energy, the relation is independent of the specimen type and geometry.[20] Similar to the tensile strength, the catastrophic tearing energy also showed an increase up to a certain loading (40 phr) before decreasing with the filler loading, as shown in Figure 2. The addition of more filler beyond the optimum limit leads to an increase of the filler–filler interaction in comparison with the filler–rubber interaction. An increase of this filler–filler interaction will lead to the formation of an aggregate of carbon black, which tends to detach from the rubber matrix more easily and thus make the crack easier to propagate. An aggregate of carbon black also can act as a stress concentration and result in a reduction of the tearing energy.[15]

The results for the catastrophic tearing energy also showed a decrease with the aging time. Samples aged for 6 days at 100°C showed a slightly lower tearing energy than samples aged for 3 days at 100°C. As mentioned previously, the degradation of the properties were due to the morphology of the aging samples, which showed the formation of holes from the movement of the filler within the matrix and the degradation of the polymer matrix, which also caused breakage of crosslinks and made it easier for cracks to propagate when the samples were subjected to stress.[21,22]

Conductivity properties

Figure 3 shows the values of the log resistivity for carbon black filled natural rubber composites at different filler loadings. The addition of carbon black resulted in a reduction of the log resistivity up to 20 phr before it became constant with further filler

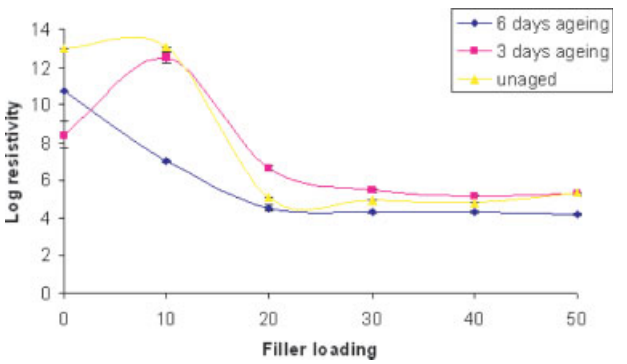

Figure 3 Log resistivity at different filler loadings before and after aging at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

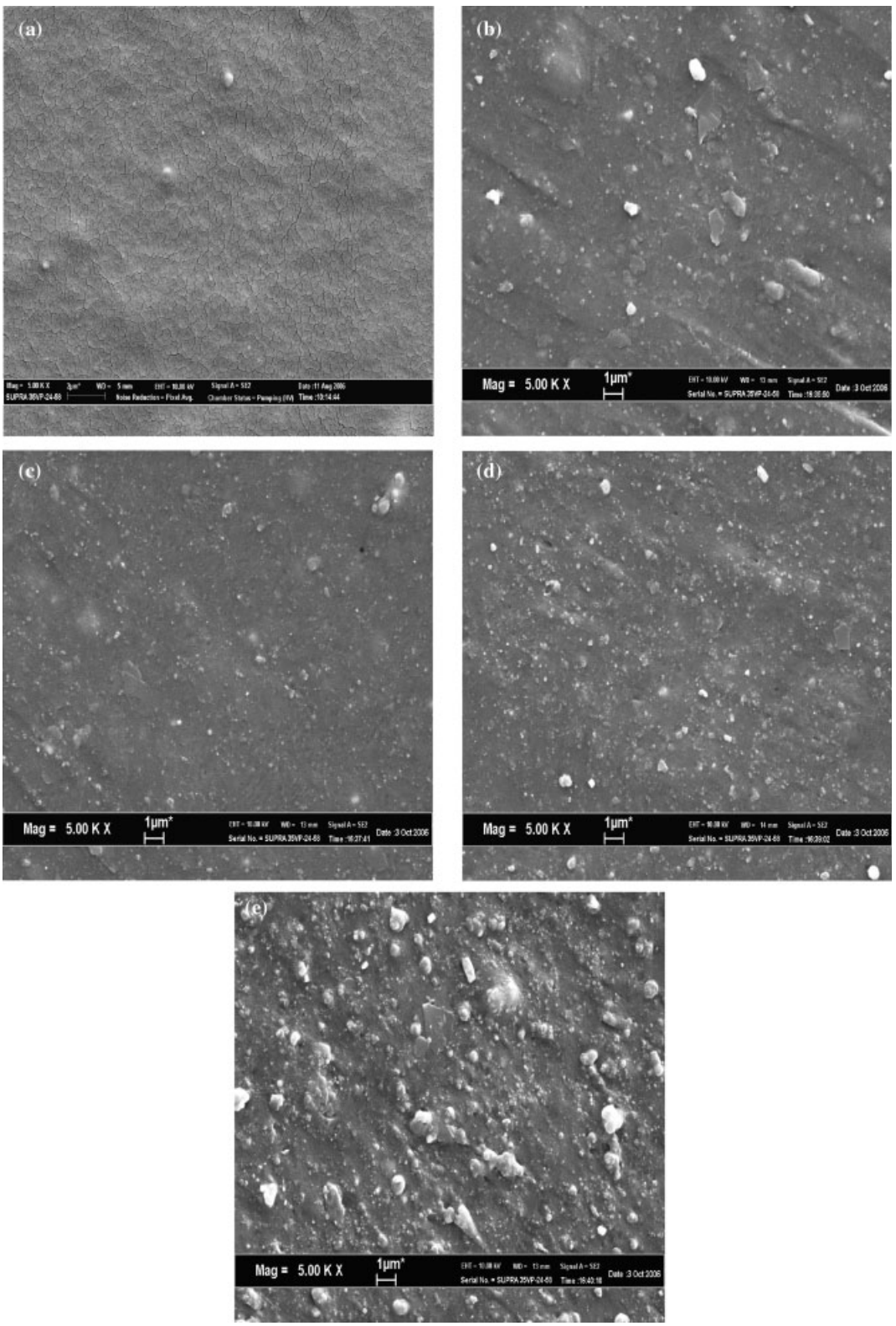

Figure 4 (a) 10 phr, (b) 20 phr, (c) 30 phr, (d) 40 phr, and (e) 50 phr.

loading. At this point (20 phr), the percolation threshold phenomenon was observed. This percolation threshold phenomenon, according to Markov et al.,[9] may depend on the type of filler and its content, the form of the filler particles, their ability to restructure, and the physical–chemical condition of their surface, the type of polymer matrix and its physical properties, and the processing condition

of the composite. Kozlowski and Frackowiak[1] also suggested that the percolation threshold should be related to a specific shape of a carbon black grade and the morphology of the polymer matrix.

For a low carbon black loading (<20 phr), the conducting carbon black particles in the rubber are relatively separated. Large gap widths between the conducting filler particles stand as physical barriers to electrons flowing through the rubber matrix, thereby resulting in a relatively low level of electrical conductivity. Over the percolation concentration (20–50 phr), as the carbon black particle concentration increases (leading to effective and progressive lowering of the gap width between the conducting filler particles), the barrier or hindrance to electron mobility will drop, and current will flow easily within the rubber matrix.[8] Figure 3 also shows the log resistivity of the samples before and after aging. From the graph, it can be seen that the percolation threshold did not change after the composites were subjected to aging at 100°C. Schwartz et al.[23] in their study suggested that a correlation between the increments of electrical conductivity and thermal aging is caused by polymer chains and polymer–filler interactions instead of filler–aggregate movement.

SEM

Figure 4(a–e) presents SEM images of the samples with the addition of 10–50 phr carbon black. From the SEM images, it can be seen clearly that the addition of carbon black fillers into the rubber matrix affected the dispersion of the filler and the interaction between the filler and matrix. As the filler loading increases, the interaction between the filler and matrix will become poorer.[15] The addition of fillers also will increase the formation of filler–filler interactions rather than filler–rubber interactions. Higher filler–filler bonding in comparison with filler–rubber bonding will cause agglomeration, and this will lead to decreased toughness of the composite and lead to lower resistance to break.[5] At a very high SEM magnification, composites with different filler loadings showed increased filler agglomeration with increased filler loading, and this agreed with the results for the mechanical and conductivity properties

The morphologies of unaged and aged samples were significantly different: holes were observed to occur in the aged samples. This might have been due to the movement of the filler when the material was subjected to heat and the degradation of the matrix itself, which subsequently influenced the mechanical properties of the natural rubber. As shown in Figures 5(a–c) and 6(a–e), the samples aged for 6 days showed many more holes than those with 3 days of aging because of the longer aging time, which allowed more filler movement within the polymer matrix and degradation of the polymer matrix itself.[23] The existence of these holes and the degradation of the polymer matrix led to a decrease in the mechanical properties of these composites. These

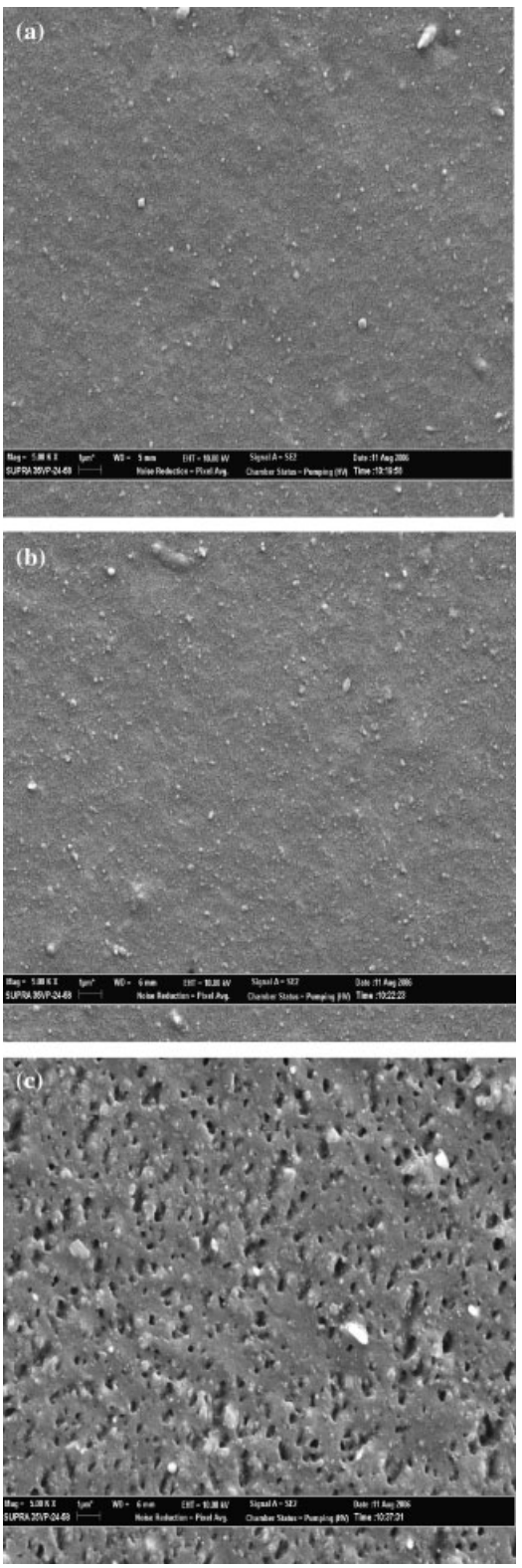

Figure 5 (a) 10 phr, (b) 20 phr, and (c) 30 phr with 3 days of aging at 100°C.

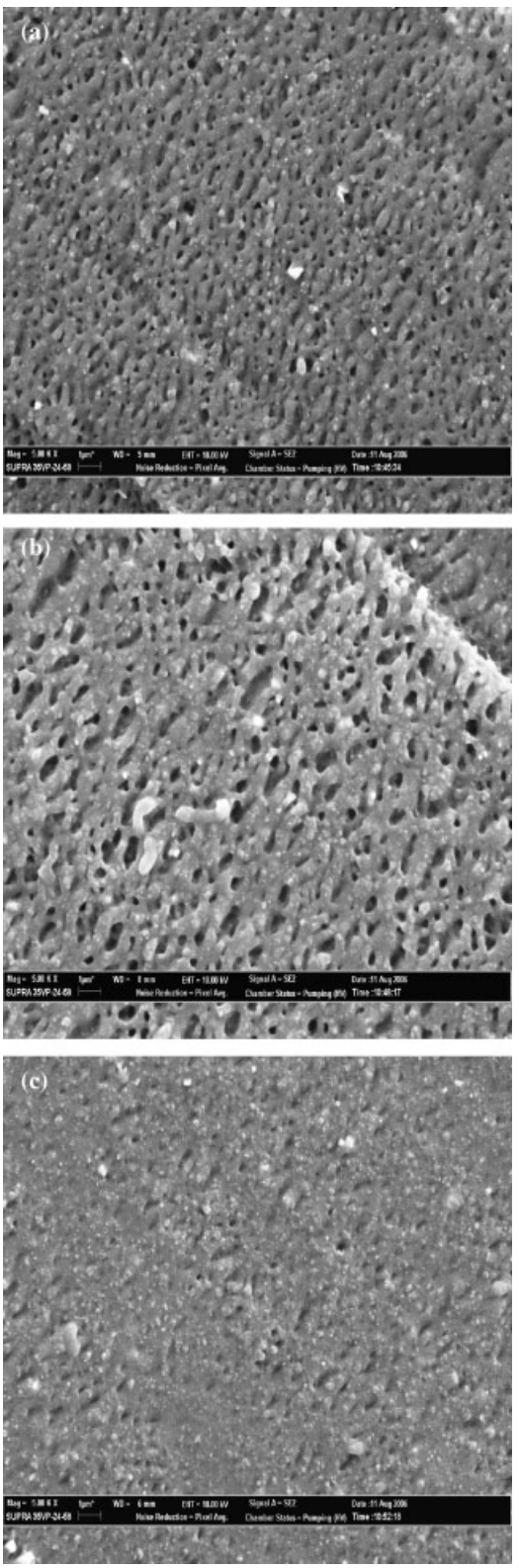

Figure 6 (a) 10 phr, (b) 20 phr, and (c) 30 phr with 6 days of aging at 100°C.

observations agreed with the results for the mechanical properties (tensile strength and catastrophic tearing energy), which showed decrements in the mechanical properties with increased aging time.

CONCLUSIONS

Mechanical property measurements showed that the optimum properties were achieved at a certain filler loading and that the further addition of carbon black fillers only reduced the properties. After aging for 3 and 6 days at 100°C, all properties decreased because of the degradation behavior of natural rubber. Electrical conductivity measurements showed that the percolation threshold occurred at 20 phr before it became constant with further loading. Aging for 3 and 6 days at 100°C did not change the percolation threshold. SEM at a very high magnification showed that composites with different filler loadings had increased filler agglomeration with an increase in the filler loading. Holes caused by aging were observed in the aged samples. This might have happened because of the movement of the filler when the materials were subjected to heat and degradation, which influenced the mechanical properties.

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