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Investigation of dynamic characteristics of nano-size calcium carbonate added in natural rubber vulcanizate

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ABSTRACT

The nano-calcium carbonates (NCC) with spherical and chain polymorphs and 30 nm, 50 nm, and 80 nm sizes of cube shape particle have been used to prepare nano-calcium carbonate (nano-$CaCO_3$)/natural rubber (NR) nano-composite. The influence of NCC on the properties of rubber vulcanizates such as Mullins effect, Payne-effect, loss factor and the dynamic compressed heat generation on the structure of nano-composite were investigated. The results showed that the Mullins effect of rubber composite filled chain shape NCC was high and it was comparable to the large particle size (80 nm) of cubic NCC. For the analysis of Payne effect, the value of $\Delta G'$ of rubber composite filled with spherical shape has the lowest value due to weaker filler network resulted largest inter-aggregate distance occurred in the rubber matrix. Meanwhile, the chain and large particle size cubic NCC have more significant $\Delta G'$ with the increasing of strain. The value of damping factor corresponds to energy loss showed that large particle size NCC has more pronounced values. Both chain and 80 nm cubic NCC have highest rising of temperature compared to spherical NCC added rubber composites.

1. Introduction

Calcium carbonate ($CaCO_3$) has been widely used as filler in plastics and rubber industry. It is produced from chalk, limestone, or marble found in upper layers of the earth's crust. $CaCO_3$ source from natural ground is the most common and cheapest used in the plastics and rubber industry. There is also exist of chemically produced form of $CaCO_3$ known as precipitated $CaCO_3$ which is finer and high purity, yet also more costly than the natural type. The most widely reason of blending $CaCO_3$ with polymer is to reduce cost without scarifying the tensile strength significantly. In addition, $CaCO_3$ can act as processing aids, toughener, improved productivity from a combination of high thermal conductivity and lower specific heat in comparison to the polymer materials relatively. According to Khanna and Xanthos [1] that all these benefits can further be optimized with the selection of appropriate particle size distribution and surface treatments with hydrophobic agent such as stearic acid, silane.

While nano-size $CaCO_3$ (NCC) has been produced for 25 years ago [2], the applications of NCC have gained great attention of the researchers in recent decade because of NCC particles can produce higher modulus as well as increasing the impact strength in the acrylonitrile–butadiene–styrene (ABS) system as compared to micro-scale $CaCO_3$ [3]. Manroshan and Baharin [4] observed that acrylic dispersed NCC added in vulcanized latex showed modulus at 100% elongation and modulus at 300% elongation increased with NCC loading. At the mean time, tensile strength and elongation at break increased up to 10 phr of filler loading and then decreased again. Recently study conducted by He et al. [5] on the compression properties of NCC/epoxy and its fiber composites revealed a remarkable improvement of 13.5%, 6.1%, 42.5% and 106.3% in compressive strength, elastic modulus, displacement and the total fracture work of epoxy resin cast filled with 4 wt.% NCC contrasted to neat epoxy casts. It showed that the modified nano-$CaCO_3$ particles had a strengthening and toughening effect. Also, Kumar et al. [6] conducted morphological analysis on nanocomposites fractured surfaces found that that the NCC stearic acid modification induced homogeneous and fine dispersion of nanoparticles into polymer as well as strong interfacial adhesion between the two phases. An increment in the T_g and storage modulus of the

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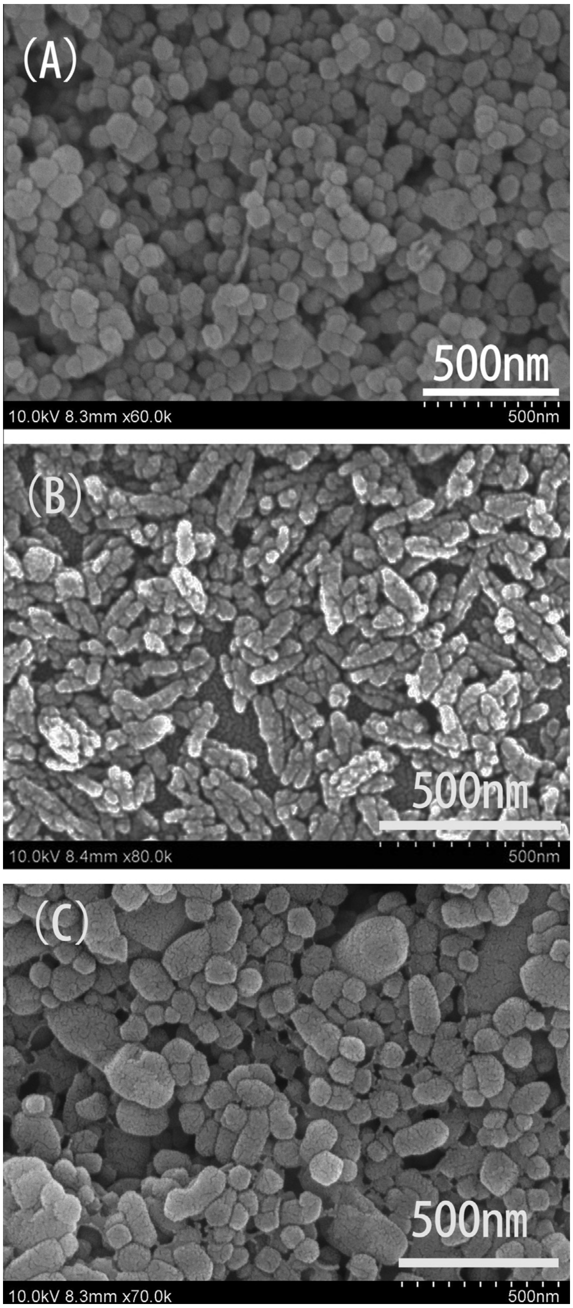

Fig. 1. SEM images of NCC with (A) spherical shape, (B) chain shape and (C) cube shape.

resulting nanocomposites was observed with the increasing of $CaCO_3$ ratio. Moreover, thermogravimetric results showed a lower degradation temperature with the increase of $CaCO_3$ ratio in the polymer matrix.

In the rubber industry, NCC is also commonly used as the filler for acrylonitrile–butadiene rubber [8], styrene–butadiene rubber (SBR) [9], chloroprene rubber [10] and etc. Addition of NCC can produce outstanding stiffness, toughness, and dimensional stability rubber compound. Nevertheless, the outstanding performance of rubber compound by addition of NCC is still greatly depending on the dispersion of its nano-particles in rubber matrix [7]. Hence, the depth understanding on the relationship between microstructure and mechanical properties of NCC are essential to improve the end-use properties of rubber composite. Most of the elastomeric components in practical applications are deformed statically and dynamically where specific dynamic properties characterizations are crucially required. Commonly, the durability of elastomeric compounds was analyzed in accordance to the effect of strain amplitude on the dynamic modulus. The modulus of filled rubbers decreases with increasing of applied dynamic strain up to intermediate amplitudes. After adding the filler, the low strain modulus G_o rises more than the high strain modulus G_∞, resulting in a non-linear viscoelastic behavior, which is known as Payne-effect G_o–G_∞ [11,12]. The Payne effect happens in rubber vulcanizates due to the diminishing of filler–filler interactions or separation of polymer chains from filler surface when subjected to strain. Ramier et al. [13] reported the Payne effect of the styrene–butadiene-rubber vulcanizates can be reduced by silane treatment of the nano-size silica. On the other hand, the improvement of mechanical properties, however, is always limited because NCC with high surface energy tends to agglomerate. Such condition was observed by Qu et al. [14] who compared the mechanical properties of bulk NCC and co-precipitated NCC in SBR vulcanizates. They found that when the amount of co-precipitated NCC and bulk NCC is identical, the mechanical properties of the former can achieve tensile strength of 13.38 MPa which was superior over the later. This was due to the NCC in the former had better dispersion and interface bonding force than that in the later, which led to the better mechanical properties. Zhang et al. [15] showed that the surface modified NCC also exhibited better processing capability than that of carbon black. Subsequently, they suggested that the processability of carbon black filled rubber could be improved by the combination of NCC.

This study is aiming to analyze the mechanical properties of rubber nano-composites filled with the NCC in the context of Mullins effect, Payne effect, the loss factor tan δ and dynamic heat generation. In particular, the influence of specific surface area, polymorph, structure and different of particles size of NCC on the Mullins effect and Payne-effect of natural rubber (NR) composite were investigated. The strength of the filler network and the filler–polymer interaction in the green compound and vulcanizate were studied using a wide range of shear amplitudes performance to correlate with the fracture mechanism [16].

2. Experimental

2.1. Materials

Natural rubber (NR) grade SCR 20 was supplied by Xi Shuang Ban Na Tian Zheng Trade Co., Ltd., China. Nano-size calcium carbonate (NCC) with cube shape with particle size 30 nm, 50 nm, 80 nm, spherical shape, and chain shape were purchased from Henankeli New Material Co., Ltd., China. Zinc oxide, stearic acid, sulfur, N-isopropyl-n′-phenyl-p-phenylenediamine (IPPD 4010), N-oxyoliechylene benzothiazole-2-sulfenamid (NOBS) were obtained from Rhein Chemie Rheinau GmbH, Germany. IPPD 4010 is used as antioxidant and NOBS is used as curing accelerator. All were used as received.

2.2. Preparation of rubber nano-composites

The blends of rubber were prepared in accordance with the basic combination of natural rubber (100 phr), zinc oxide (5 phr), stearic acid (2 phr), IPPD 4010 (2 phr), NOBS (0.75 phr) and sulfur (2.5 phr). Meanwhile, the amount of NCC was varied accordingly. All these ingredients were compounded using a two rolls mill machine with the cooling water heat removal function. The prepared compounds were moulded into sheets using a hydraulic press at 150 °C and 10 MPa. All specimens were then cut into form of testing sheets.