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Polymer 47 (2006) 3298–3301

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Visualisation of carbon black networks in rubbery matrix by skeletonisation of 3D-TEM image

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Received 13 October 2005; received in revised form 1 March 2006; accepted 2 March 2006

Abstract

The first visualization of nanofiller networking due to association of carbon black in natural rubber is achieved by a transmission electron microscopy combined with computerised tomography (3D-TEM), and the resulted skeleton displays the characteristics of the filler network, which has long been assumed on the percolation behaviour in electron conductivity and on the mechanical behaviours of filled rubbers.

Keywords: 3D-TEM; Carbon black; Nanofiller networking

1. Introduction

Transmission electron microscopy (TEM) has been an indispensable instrument to elucidate nanometer scale structures in materials [1]. However, it has a serious drawback due to the fact that it projects three-dimensional (3D) body onto 2D plane. The information along the thickness direction of the sample is only an accumulated one, possibly resulting in tricky interpretations. This situation has been well known, and is specifically noted [2]. The satisfactory solution is to be provided with TEM combined with computerised tomography (3D-TEM) [3–5]. Recent advances of 3D-TEM or electron tomography have elucidated 3D structures in biopolymers [3] and recently in non-biopolymers, first on block copolymers [6–9] and then on rubbery composites [10–12] at nanometer scale. The 3D-TEM technique so far is based on the mass-thickness contrast [4–12], and many diffracting materials, which seem to be quite common in materials science field in general, pose a problem in reconstructing 3D images [4,5]. On such samples, some other methods have to be developed. For example, the high-angle annular dark field (HAADF) mode is now under active development [4,5,13,14].

Fortunately, not only in bioscience field but in polymeric materials we have a lot of amorphous objects [5,10–12]. Rubber products are soft composites from nanofiller (mainly carbon black [12,15,16] or silica [10,11,17]) and rubbers. The latters are of course basically amorphous, and good contrasts are enjoyed between inorganic nanofillers and the rubber without any electron staining [10–12]. Therefore, 3D-TEM is expected to be the most powerful tool for elucidation of 3D nanostructure of them, which is recently proved to be the case [5,10–12]. Fig. 1 schematically shows nanostructures of reinforcing filler in rubbery matrix. Due to the filler-to-filler interaction, which is usually higher than the filler-to-rubber one, aggregate formation is generally accepted [15], but the morphology formed by further association of the aggregates, i.e. agglomeration supposedly leading to filler networking is still controversial. Thus, the skeletonisation of 3D-TEM images of carbon black in natural rubber (NR) is conducted to elucidate the details of the networks based on the dependency of conductivity on the amount of carbon black loading and one of nanostructural parameters obtained from the 3D-TEM images [12]. The nanofiller networking of carbon black in rubber matrix has long been assumed on the observed percolation behaviour in electron conductivity [2,18,19] and on the mechanical behaviours of filled rubbers [16,20–22].

2. Experimental

Vulcanizates were prepared as follows [12,16]: NR (RSS No. 1) was masticated and mixed with carbon black (HAF

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doi:10.1016/j.polymer.2006.03.008

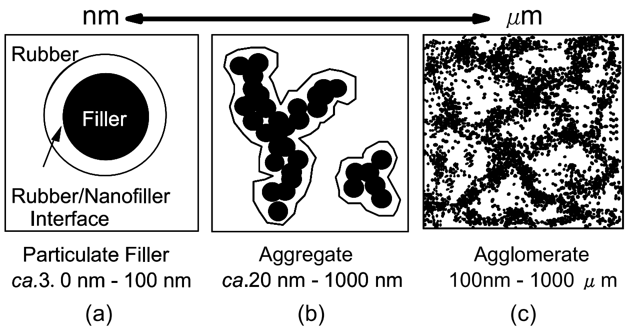

Fig. 1. Schematic representation of nanometer scale morphology of reinforcing filler in rubbery matrix.

grade, N330) and the other reagents for curing on a two-roll mill. The total mixing time was between 20 and 30 min depending on the loading amount of carbon black. The compounds (mixes ready for curing) are subject to press-curing in a mold at 150 °C for 20 min. The recipe for preparation of NR vulcanizates was as follows; in parts per one hundred rubber by weight (phr), 1 phr of stearic acid, 5 phr of ZnO, 2 phr of sulfur, 1 phr of cyclohexylbenzothiazyl sulfenamide and 10, 20, 30, 40, 50, 60 or 80 phr of carbon black. All ingredients were commercially available ones, and used after a drying procedure. In case of carbon black, it was at 120 °C for 2 h. In the sample code, NR represents a NR vulcanizate, and the following figures represent parts per one hundred rubber by weight of mixed carbon black, e.g. NR-80 is a NR vulcanizate with 80 phr HAF black.

The samples were subjected to 3D-TEM measurement using TECNAI G2 F20 (FEI Co.), where 2D-projection images with tilt angles ranging from −65 to +65° with 2° increment (totally 66 TEM images) were automatically acquired at 200 kV by a CCD camera using the attached software in the TECNAI G2 F20 [11]. The specimen for 3D-TEM was prepared to ca. 200 nm thickness using an ultra-microtome FC-S (REICHERT Co). Three-dimensional images were reconstructed and presented using IMOD [23] and amira [24] together with a few other hand-made soft wares as previously reported [10–12]. AC conductivity measurements were carried out in accord with JIS (Japan Industrial Standards) K6911 [12], which is equal to ASTM D257.

3. Results and discussions

Fig. 2 shows 3D-TEM images of NR vulcanisates, CB-10, CB-40 and CB-80 containing 10, 40 and 80 phr carbon black, respectively. In the black and white images the contrast was reversed, and the white is identified as the carbon black. Associations are observed even in CB-10 (volume fraction is 0.0498). This is reasonable, because HAF carbon is produced by the oil furnace method in which process it has already aggregated [25]. For easy recognition of the association, each aggregate is painted by a different colour from the neighbouring ones to result in the multi-coloured images in Fig. 2. It is recognized that all particles are in aggregation practically leaving no isolated particles. The aggregate is the fundamental entity of carbon black existence in NR matrix.

Fig. 3 shows dependencies on carbon black loading of two variants; one is volume resistivity of the NR vulcanisates at room temperature (ρ_v) and the second is the distance between the most neighbouring aggregates (d_p) measured by that between the two perimeters of the aggregates, which is one of the structural parameters calculated from volume-rendering images shown in Fig. 2. The resistivity decreased, or the conductivity increased, with carbon black loading, and the change clearly shows a percolation-like behaviour between 20 and 40 phr. The percolation threshold seems to be around 40 phr (in volume fraction, 0.173) in accord with the reported ones [18]. The behaviour of d_p is similar to that of resistivity, i.e. decreased with carbon black loading together with percolation-like behaviour at the same region. The distance tends to converge to a constant value, which is approximately

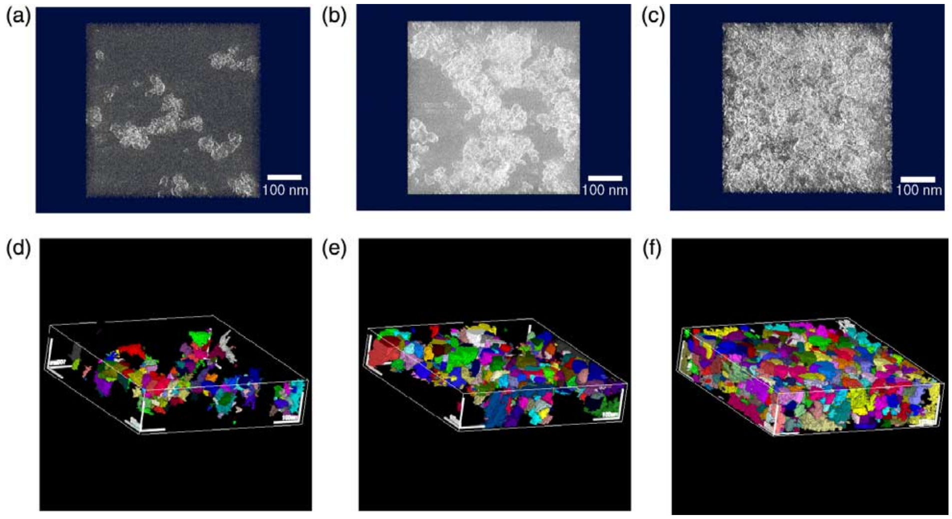

Fig. 2. Reconstructed 3D-TEM images of carbon black loaded natural rubber in black and white (upper) and in multicoloured (lower) displays. (a) and (d) CB-10; (b) and (e) CB-40; (c) and (f) CB-80. In the black and white, the contrast was reversed, and the white parts represent carbon black. Coloured ones are for easy recognition of an aggregate, which is painted differently from the neighbouring ones. The white bar for each direction shows the distance of 100 nm.

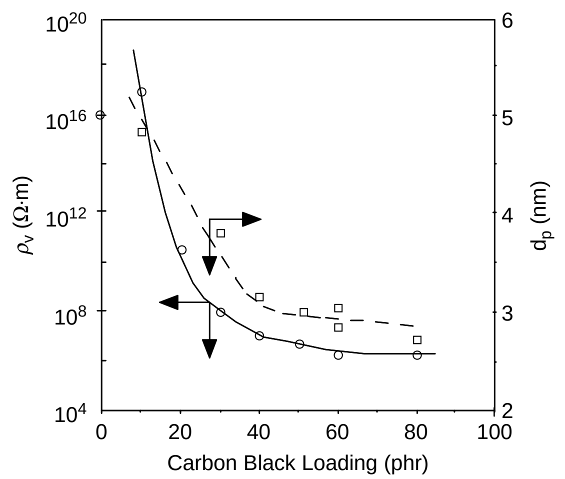

Fig. 3. Dependency on carbon black loading of volume resistivity at room temperature and perimeter distance between the nearest aggregates obtained from the 3D-TEM images.

3 nm, even with the further increase of carbon black loading. This observation may be related with so called 'bound rubber' or 'filler gel', which are often assumed to explain the reinforcement effect of particulate fillers on rubber [15,16]. However, our observation suggests that the particle was in direct contact with each other in an aggregate, and the rubber layer was on the surface of carbon black aggregates, not on the surface of each particle. This point is not clearly described in the technological textbooks on rubbers [15,26]. However, these observations are consistent with the statement that the aggregate is the basic entity of carbon black. Thus, it is questionable at least for a moment to assume that each carbon black particle is wetted by rubber molecules as shown in Fig. 1(a). This picture will be evaluated, only when the isolated particles are recognized to be present in rubbery matrix.

The similar dependencies of the two independent quantities, i.e. the resistivity and the distance between two neighbouring aggregates, strongly suggest that electron can hop or jump over the 3 nm layer of insulating rubber between the aggregates to conduct electricity. In other words, the agglomeration of carbon black aggregates within 3 nm distance form electron-conductive path to give rise to a conductive path of network structure. For visualization of the path, we carried out a kind of skeletonisation; connecting the centres of gravity of aggregates, which are within 3 nm distance using home-made softwares. The procedure used here is a very simple one compared with the conventional methods [27,28], and the skelton obtained connecting the centres of gravity of aggregates is only approximated one. However, the essential feature of conducting networks is retained.

This procedure resulted in the images shown in Fig. 4. This figure visualises the conductive networks formed by agglomeration of carbon black aggregates in NR matrix. It is noted that even in CB-10 (before the percolation threshold) the network formation (as pregels) is observed, which suggests a strong tendency of association of carbon black aggregates in rubbery matrix. Increasing the amount of carbon black has brought about the extension of the conductive network to the whole, which is the percolation (and/or gellation). This is against the common understanding that the agglomeration networks of carbon black are formed only when conductivity threshold is reached [19]. The expanded image of the skeleton in CB-40 (Fig. 4(d)) suggests much complicated network structure, but branching points and terminating chains (dangling chains) are recognized from the image. Quantitative treatments of the networks are currently under investigation.

The morphology of the agglomerates has long been assumed to be one of the determining factors of many practically important macroscopic properties of soft nanocomposites, for examples, tear, abrasion and wear properties of the tread rubber in pneumatic tyres. The design of them in term of reinforcing fillers has been so far dependent upon the trial-and-error method because of the difficulty in controlling the morphology of agglomeration. Therefore, the structural information derived from the visualized network structure will be of utmost importance for improving the material design of nanocomposites, which should be based on scientifically elucidated structures in 3D space.

We have observed very similar 3D-TEM images on silica/NR composites [10,11]. Hence, it may be assumed that the agglomeration of silica aggregates also gives rise to a network formation, and the skeletonisation may be possible for visualization even though the conductivity results are not available (silica particles are not electron-conductive). It is very probable that nanofillers are associating under many circumstances, and in rubbery matrix they tend to further agglomerate to form network structures. This tendency may be based on the nature of nanometer size particles, and it is vital to take this into account for the design of nanocomposites for various novel applications as well as conventional ones including pneumatic tyres for automobiles and aeroplanes.

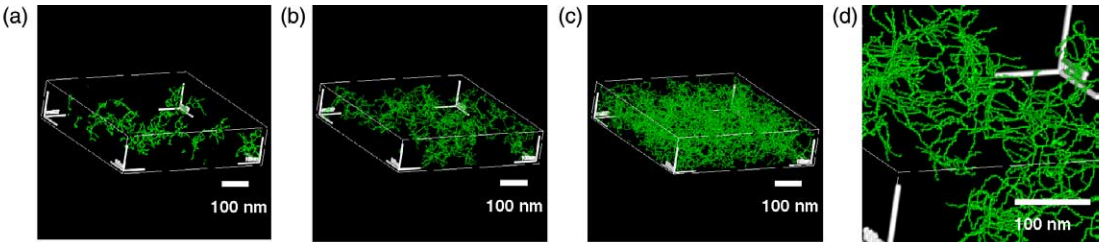

Fig. 4. Visualisation of the network structures of carbon black in natural rubber matrix by skeletonising the 3D-TEM images. (a) CB-10; (b) and (d) CB-40; (c) CB-80. The image in (d) shows the expanded image of the network skeleton for CB-40. The white bar for each direction shows the distance of 100 nm.

Further quantitative analyses to extract characteristic structural parameters from these skeletonised networks are now in progress, and will be reported in a near future.

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