Polymer 55 (2014) 5140–5145

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Electrical and mechanical percolation in graphene-latex nanocomposites

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A R T I C L E I N F O

Article history:
Received 24 June 2014
Received in revised form
7 August 2014
Accepted 12 August 2014
Available online 19 August 2014

Keywords:
Nanocomposites
Electrical properties
Mechanical properties

A B S T R A C T

Conductive composites based on few layer graphene are of primary interests. In this work latex based composites were produced leading to a specific cellular morphology. Highly conductive graphene-based composite materials have been produced through a solvent-free procedure. Both the mechanical and conductivity behaviors were successfully described using a percolation approach that confirms the presence of a three dimensional filler network efficiently spread across the material. The influence of the aspect ratio between the conductive filler and the latex nanosphere drove the study. It was demonstrated experimentally that the tuning of the cell dimensions of the composite morphology influences the percolation threshold and the reachable maximum conductivity and reinforcement. These experimental results are consistent with phenomenological models based on the statistical percolation theory.

1. Introduction

Electrically conductive polymer-based nanocomposites have attracted considerable research interest in recent years, with the objective of obtaining functional flexible materials such as electromagnetic shielding [1], actuation [2], sensing [3] and electrostatic charge dissipation [4]. Many methods exist to incorporate nanofillers into the polymer matrix: solution mixing [5–6], melt blending, latex blending [7–8] or in-situ polymerization [9].

As more conductive fillers are added to the polymer matrix, a filler network begins to form that allows the composite to transition from insulator to conductor. The challenge is to reach the highest conductivity at lowest filler content so that desirable mechanical properties such as flexibility are not reduced. The latex blending route exhibits two major advantages compared to melt route or solution route. First, this synthetic route is sustainable as latex is made of polymer nanospheres in water suspension without using organic solvent. Second, the latex route favors the build-up of a tunable architecture of fillers. This specific architecture, in turn, favors the formation of a percolating network of fillers at lower filler content. As a result, the final nanocomposite microstructure counts two interpenetrated networks, one made of the polymer matrix and the other one made of percolating fillers [10]. This paper focuses on the influence of latex particle diameter on the electrical and mechanical behavior of the composite [11]. This behavior is related to the percolation behavior of the system.

The percolation theory is used to describe very different transition phenomena such as sol–gel transition or virus propagation [12]. In materials science, it is often used to describe transitional behavior of electrical and mechanical properties in composites [13]. The critical volume fraction (percolation threshold) is the filler fraction needed to obtain the first percolating path throughout the polymer matrix. In a percolation approach, the fillers embedded in the composite are described using two types of clusters: the finite clusters and the infinite or percolating clusters, comprising a backbone and dangling bonds (Fig. 1).

Around the percolation threshold, the conductivity and mechanical properties are closely related to the weight P of the infinite cluster defined as [14]:

$$P(\phi) = A(\phi - \phi_c)^{\beta} \quad (1)$$

where ϕ is the volume fraction of fillers relative to the total volume, ϕ_c is the critical volume fraction, A is a dimensionless constant and β is a critical exponent that only depends on the system dimension (for 3D-systems, $\beta = 0.4$).

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http://dx.doi.org/10.1016/j.polymer.2014.08.025

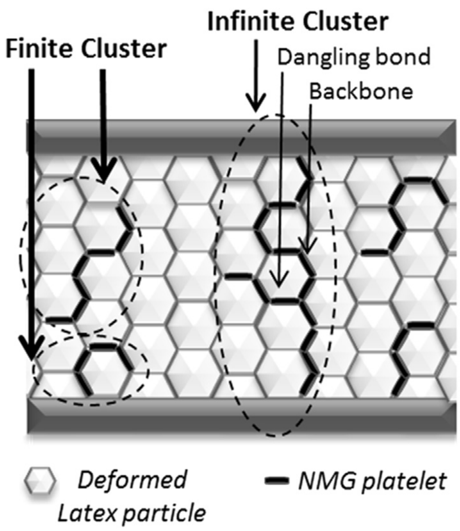

Fig. 1. Percolation behavior in a latex-based graphene nanocomposite.

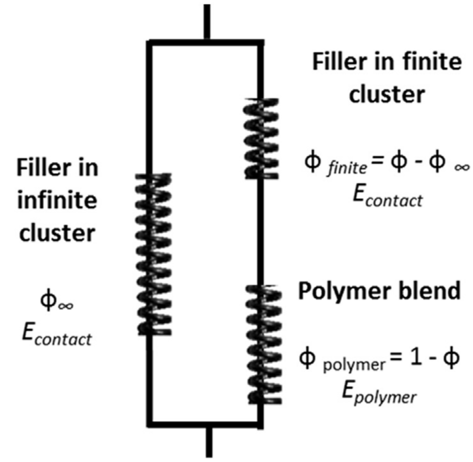

Fig. 2. Series/parallel model extended with a percolation concept.

Because of the close relationship between conductivity σ and weight P of infinite network, it was demonstrated that in percolating systems, σ follows a similar power law [15]:

$$\sigma = \sigma_0 \left(\frac{\phi - \phi_c}{1 - \phi_c}\right)^t \tag{2}$$

where σ_0 is the macroscopic conductivity of the fillers. Except for rare symmetric situations, all the backbone bonds will carry some current when a voltage is set between the upper and lower edges of the cluster. Most of the mass of the infinite cluster at the threshold belongs to dangling bonds, not to the backbone. Thus most of the mass contained in P makes no contribution to the conductivity σ, and therefore, the critical exponent t differs from the critical exponent β [15]. In literature, the critical exponent t is found between 1.6 and 2.0 for 3D-systems [16]. As expected, the critical exponent t is higher than β as β takes into account the non-conductive dangling bonds of the infinite clusters.

$$\phi_\infty = \left(\frac{\phi - \phi_c}{1 - \phi_c}\right)^b \tag{3}$$

The value of the critical exponent b lies between 0.4 and 1.6. If $b = 0.4$, the reinforcing effect of the dangling bonds is considered as similar to the one of the backbone and if $b = 1.6$, the dangling bonds are considered as non-reinforcing, similarly to the conductivity behavior. The stronger the interaction between fillers and polymer matrix, the lower the value of critical exponent b will be. In nanocomposites where interfacial surface is developed, a low value for b is expected. In literature, Bauhofer et al. used $b = 0.7$ in composites of single walled nanotubes in polymethylmethacrylate [19] and Nawaz used $b = 0.8$ for graphene oxide/elastomer composites [20], Faucheu et al. used $b = 0.4$ in clay-polymer nanocomposites [21]. In this paper, b will be set to the intermediate value 0.6 close to 0.4 as we consider that the contacts between fillers of good quality are developed.

Based on this series-parallel phenomenological model, the elastic modulus, $E_{composite}$, of the composite is then given by:

$$E_{composite} = \frac{(1 - 2\phi_\infty + \phi_\infty\phi)E_{filler-filler}E_{polymer} + \phi_\infty(1-\phi)E^2_{filler-filler}}{E_{polymer}(\phi - \phi_\infty) + E_{filler-filler}(1-\phi)} \tag{4}$$

The percolation approach for mechanical properties is more complex. Indeed, while the question of conductivity has a binary response, either the cluster conducts, either it does not, in the case of mechanical properties, both finite and infinite (backbone and dangling bonds) clusters can influence the final mechanical response, to various extents. The infinite cluster will have the most reinforcing effect, the finite cluster the lowest one, and the effect of the dangling bonds will lie in between. A phenomenological model associating springs in series and parallel (Fig. 2) has been proposed to describe the effects of filler percolation on the mechanical response of composites [17–18]. In that model, the reinforcement due to fillers in finite clusters are considered as low (associated in series with the polymer matrix) while fillers in infinite clusters are associated in parallel. In this description, for $\phi < \phi_c$, the volume fraction of the infinite cluster ϕ_∞ is zero. For $\phi \geq \phi_c$, ϕ_∞ defined using eq (3).

where $E_{filler-filler}$ and $E_{polymer}$ are respectively the elastic moduli of the reinforcing and the soft components (the polymer matrix). $E_{filler-filler}$ represents the stiffness of the filler–filler clusters and so takes into account both the intrinsic stiffness of the filler and the stiffness of the filler–filler contacts. In literature, the filler–filler stiffness for cellulose nanofibrils was set at 1.9 GPa [22], and for polymer blends this value was set at 2.0 GPa [17] and 1.8 GPa [18], depending of the composition. As a consequence, in this paper, $E_{filler-filler}$ for NMG was set at 1.8 GPa.

In this work, Nanosize Multilayered Graphene (NMG) is blended with acrylate copolymer latex of two different diameters (300 nm and 650 nm) to fabricate conductive free standing composite films after drying around room temperature. The filler arrangement throughout the composite will be characterized to verify the build-up of cellular architecture known to be favored by the latex route. These materials are studied to illustrate the usability of percolation