Polymer 113 (2017) 34–38

Contents lists available at ScienceDirect

Polymer

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

Short communication

Viscoelastic and electrical behavior of poly(methyl methacrylate)/carbon black composites prior to and after annealing

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ARTICLE INFO

Article history:
Received 24 October 2016
Received in revised form
21 December 2016
Accepted 13 February 2017
Available online 15 February 2017

Keywords:
Carbon black
Creep-recovery
Polymer nanocomposites
Viscoelastic properties

ABSTRACT

In this letter, both the viscoelastic and electrical properties of poly(methyl methacrylate)/carbon black (PMMA/CB) nanocomposites with different CB concentrations prior to and after annealing were investigated. The linear steady-state recoverable compliance of pure PMMA is independent of annealing as it reflects only polymer-polymer interactions. While the conductivity of PMMA/CB nanocomposites increases gradually with annealing, and the viscoelastic properties show different regions of response depending on the CB concentration. At CB contents below the percolation threshold the recoverable compliances increase after annealing, whereas the reverse trend is found at CB contents above the percolation threshold. This behavior is related to the interplay between network formation and particle-particle interactions.

1. Introduction

Adding fillers to a polymer is a way to tailor properties of the resulting composites. The properties of polymer nanocomposites depend on the type of fillers (e.g., size and shape), matrix and on the interface between fillers and the polymer [1–10]. Carbon black (CB) and carbon nanotube (CNT) are of special interest in case of electrically conducting composites. Therefore, the influence of filler particles on viscoelastic properties of polymer composites in the molten state (e.g. during processing or shear) is an increasing topic [6–13].

Rheology is a well-established science to get an insight into the deformation behavior of materials and reflects internal dynamics in complex fluids [4–10]. Typical experiments like oscillatory shear and creep-recovery tests are used in this context. Oscillatory shear experiments are frequently used to characterize particle filled polymers. In nearly all cases their aim is to get some insight into the formation of a network by the particles added, which is indicated by the storage modulus becoming more and more independent of frequency [4–6]. However, measurements at low frequencies require long experimental time. Contrary to dynamic mechanical test, creep-recovery experiments have been successfully applied to discriminate between viscous (steady-state viscosity) and elastic parts (recoverable compliance) of deformation especially in systems with long characteristic relaxation time [4–13]. Studies on the typical creep behavior of polymer nanocomposites systems in the solid state based on dynamic mechanical analysis or mechanical test are widely reported in the past three decades [14–18]. However, to our knowledge, there were few literature concerning specific creep-recovery behavior of polymer nanocomposites in the molten state.

Adding fillers to a polymer matrix can also lead to hydrodynamic reinforcement effects due to the substitution of matrix molecules by particles [10]. In addition, physical interactions of polymer molecules with the particle surface are introduced [19]. These results in an additional relaxation process with a long characteristic time which is separated from the entanglement relaxation [6–10]. At lower concentrations at which no particle network exists, the polymer-particle interactions become more

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http://dx.doi.org/10.1016/j.polymer.2017.02.050
0032-3861/

important and are the main reason for changes in rheological properties of nanocomposites. However, at higher CB concentration, the formation of CB conductive pathways should contribute most to the rheological properties. Münstedt et al. found that the recoverable compliance of poly(methyl methacrylate) (PMMA)/nanocaly nanocomposites became smaller with decreasing nanoclay content [9]. Nevertheless, most of investigations are only focused on nanocomposites with low filler concentration, i.e., below the percolation threshold, thus omitting the particle-particle interaction and particle network [4–8].

Recently, it has been proved that thermal annealing affects the conductive filler network and, thus, electrical performance of conductive polymer composites [20–23]. For example, the thermal annealing-induced enhancement of electrical conductivity for multi-walled carbon nanotube (MWCNT)-filled poly(ethylene-co-hexene) (PEH) composites was investigated by Li et al. [19]. They found that, during 120 min of annealing at 160 °C, the electrical conductivity of MWCNTs/PEH composites with a high MWCNT concentration increased about 3 orders of magnitude. The similar behavior was also reported in other conductive polymer composites, such as polystyrene (PS)/MWCNT composites [20], PMMA/PS/CB composites [21], polypropylene (PP)/MWCNT composites [22]. Therefore, it is conceivable that thermal annealing-induced CB aggregates and network formation may also influence the viscoelastic properties. However, to our knowledge, the influence of annealing treatment on the viscoelastic properties of CB filled polymer composites, monitored by creep-recovery experiments, has been scarcely reported in the open literature. Accordingly, in this work, the viscoelastic and electrical behavior of PMMA/CB composites prior to and after annealing were investigated based on a creep-recovery experiment.

2. Experimental section

2.1. Materials

Commercially available PMMA Plexiglas 7 N with a density of 1.19 g/cm^3 and carbon black (CB) Printex XE2 with a of density 2.13 g/cm^3 were provided by EvonikRöhm GmbH, Germany. The mean diameter of the primary CB particles is around 35 nm according to the manufacturer, and the specific surface area of the CB is about 886 m^2/g as measured by the BET-method and DBP-absorption is 380 ml/(100 g).

2.2. Sample preparation

All materials were dried at 80 °C in a vacuum oven for at least 12 h prior to processing. The nanocomposites with different CB volume filler concentrations were prepared by melt mixing (Haake PolyDrive 557–8310, Thermo Scientific, Germany). Both polymers and CB particles were introduced directly into the mixer at a rotation speed of 20 rpm for 2 min, and then the rotation speed was increased to 60 rpm for another 8 min. After the melt mixing, the composites materials were cooled down to room temperature and then granulated using a blade granulator (Wanner Technik). The granulate obtained was compression molded in a hot press (Voigt) into 2 mm thick disks with a diameter of 25 mm. For the un-annealed samples, they were first preheated at 200 °C for 5 min under vacuum; and then pressed at 100 bar for 2 min before being cooled to room temperature for 10 min. For the an-samples, thermal annealing treatment was conducted at a given temperature, such as 180 °C, 200 °C or 220 °C in the hot press at 100 bar for a given time (30 min, 60 min or 90 min).

2.3. Characterization

Creep-recovery tests (Fig. S1) were carried out at 200 °C in a nitrogen atmosphere using a stress-controlled shear rheometer Gemini from Malvern Instruments. Before starting any experiment, the sample was allowed to equilibrate for 10 min in the measuring chamber at 200 °C. It should be pointed out that the 10 min equilibrating also has influence on the evolution of the CB network formation. A constant shear stress $\tau = 200$ Pa was applied to the sample for a creep time $t_c = 600$ s followed by the recovery test for at least 1200 s. The electrical resistance R of the PMMA/CB nanocomposites was measured at room temperature by a Keithley 6487 picoammeter. The conductivity σ was estimated from the resistance R using the equation:

$$\sigma = d \Big/ R\pi r^2 \quad (1)$$

where R, d and r are the resistance, thickness and radius of the sample, respectively.

3. Results and discussion

Fig. 1 shows the conductivity as a function of CB loading prior to and after annealing for PMMA/CB nanocomposites. For the un-samples, it was seen that, on addition of 2 vol.% CB, the conductivity exhibited a tremendous jump of about six orders of magnitude, indicating that the formation of conductive pathways, which can be confirmed by the transmission electron micrographs (TEM) results in Fig. S2, and the percolation threshold ϕ_c of this system was between 1.5 and 2 vol.% CB. Moreover, it was interesting to find that the conductivity increased dramatically due to annealing. For example, the conductivity increased by about two orders of magnitude for samples with 2 vol.% CB after annealing. For nanocomposites with 1.5 vol.% CB, the nanocomposites changed from an electric insulator (~10^{-12} S/cm) to a conductor (~10^{-5} S/cm), which gave a first hint to a decrease of ϕ_c after annealing and the formation of new conductive pathways (Fig. S3). This behavior has been well-proved in the literature and the reason of the formation of new CB conductive pathways is attributed to the Brownian diffusion of CB aggregates during the annealing treatment [12,19–21].

To describe the conductivity of the polymer composites as a function of the filler concentration, different models were used in

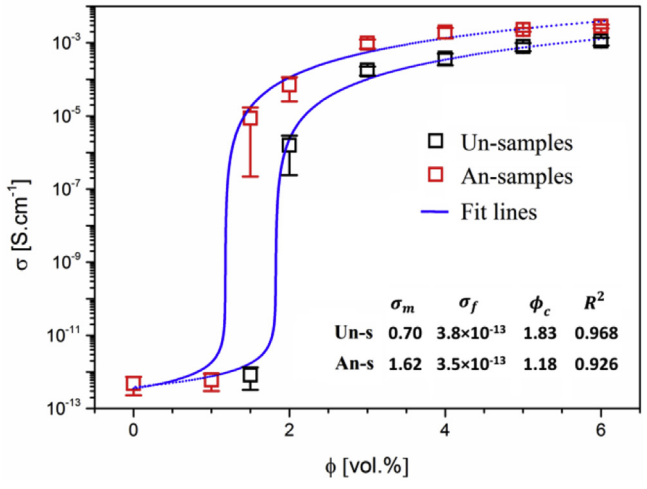

Fig. 1. Conductivity σ vs. CB loading ϕ for PMMA/CB nanocomposites prior to and after annealing (60 min, 200 °C).The data averaged from at least five individual samples.