Radiation Physics and Chemistry 107 (2015) 89–94

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

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

The effect of gamma irradiation on the thermal behavior of dielectric properties of linear low-density/carbon black semiconductive composites

D. Dudić [a], A.S. Luyt [b], F. Marinković [c], I. Petronijević [c], J. Dojčilović [c], D. Kostoski [c,*]

[a] Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia
[b] Department of Chemistry, University of the Free State (Qwaqwa Campus), Private Bag X13, 9866 Phuthaditjhaba, South Africa
[c] Faculty of Physics, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

HIGHLIGHTS

- AC conductivity changes due to γ radiation in a composite depend on the CB contents.
- Stability of the AC conductivity at elevated temperature depends on the CB contents.
- Gamma radiation reduces NTC behavior of AC conductivity in the LDPE+CB composite.

ARTICLE INFO

Article history:
Received 12 March 2014
Accepted 8 October 2014
Available online 16 October 2014

Keywords:
AC conductivity
Gamma irradiation
LDPE–CB composites

ABSTRACT

Electrical AC conductivity of semiconducting low-density polyethylene (LDPE)–carbon black (CB) composites has been studied in the frequency range between 24 Hz and 75 kHz and the temperature range from 295 to 355 K. The composites were gamma irradiated at room temperature to different absorbed doses up to 300 kGy. The effects of gamma irradiation on the AC conductivity at room temperature and the conductive temperature coefficients (*CTC*) were observed. It was found that the effect of gamma irradiation on the stability of AC conductivity at elevated temperature (355 K) is dependent on the carbon black content and the gamma irradiation dose.

1. Introduction

Electrical DC conductivity of carbon black and metal polymer mixtures is the most widely investigated physical property of percolation systems [1–6]. Many review articles include sections on complex conductivity [1,7]. A comparison of the DC and AC conductivities of an LDPE/CB composite at the percolation concentration has been discussed in detail in our previous study [8]. Most conductive polymer composites show an increase in electrical resistivity at elevated temperatures close to the polymer melting point. This phenomenon is known as the positive temperature coefficient (PTC) effect [9–13]. The PTC effect is related to the difference in thermal expansion of the matrix and the filler that causes a gradual breakdown of the percolating network. However, at temperatures near the melting point, the composites show a negative temperature coefficient (NTC) effect of resistivity due to the redistribution of particles in the softened complexes, which has an adverse influence on the application of PTC composites due to conduction instability during thermal cycles. Crosslinking of the matrix is effective to reduce the mobility of CB particles and thus to reduce or even eliminate the NTC effect [9–14]. Furthermore, crosslinked composites have a satisfactory reproducibility of DC electrical conduction during thermal cycling [15–17]. This phenomenon has successful industrial applications, such as self-regulating heaters, current limiters, and over-current protectors [5,18]. In addition, due to the increasing application of polymeric composites in electronics and electromagnetic protection, thermal stability of their dielectric properties becomes important.

In our previous work [8] we have studied the effects of morphology on the DC and particularly on the complex AC conductivity of CB–LDPE composites, using DC conductivity measurements as a function of composition at room temperature, and measurement of complex AC conductivity as a function of frequency, composition and temperature. Contrary to the results of the DC measurements, the dielectric measurements do not show the sharp rises in AC conductivity (σ_{ac}), conductance (G) and

* Corresponding author.
E-mail address: kostovski@open.telekom.rs (D. Kostoski).

http://dx.doi.org/10.1016/j.radphyschem.2014.10.003
0969-806X/

susceptance (B) as the CB content increases. These measurements show a more pronounced increase in conductivity at about 15 and 23 wt% CB. Conductivity saturation occurred at about 30 wt% CB content. Because of this kind of AC conductivity behavior, we decided in this work to study the effects of gamma irradiation on the AC conductivity of the samples that contain 24 and 28 wt% of CB. In some of our previous studies we have studied the effect of charge trapping induced by gamma irradiation and their release in LDPE [19]. Among other mechanisms of electrical transport (hopping, tunneling and percolation), the charge trapping release can have some influence on the AC conductivity of LDPE–CB complexes. Because of that, one of the main goals was to study the effect of gamma irradiation on the thermally induced changes in the mechanism of electrical transport in these relatively cheap complexes.

2. Experimental

Low-density polyethylene (HIPTEN 22003, HIP Pancevo, Serbia, M_w=110,000 and ρ=0.922 g cm^{-3}) was used as the polymer matrix. Two mass concentrations (24% and 28% CB) of commercial type carbon-black fillers (3–5 μm) were mixed with the polyme in a Haake rheometer at 160 °C for 10 min. Isotropic sheets were obtained by compression molding at 180 °C and 1.75 MPa pressure for 5 min, followed by quenching in water at 25 °C. In order to provide samples with the same thermal history, all of them were annealed at 127 °C for 5 min and then cooled to room temperature at a rate of 1 K min^{-1}. The sheets were gamma irradiated in a ^{60}Co radiation facility, in air at room temperature, at a dose rate of 6 kGy h^{-1}. The radiation doses applied were up to 300 kGy. The samples in the form of discs (D=13 mm, d=1 mm) were cut from the center of the sheets. Electrodes were made on the major faces using fine copper powder. Prior to the measurements the samples were conditioned for two days at 23 ± 2 °C and 50 ± 2% humidity.

Dielectric spectroscopy measurements were performed in a shielded vacuumed cell using a Hameg 8118 instrument in the frequency range between 24 Hz and 75 kHz (1.5 V applied voltage) during temperature treatment, which consisted of heating from 295 to 355 K (1.5 K min^{-1}), and keeping at the softening temperature of 355 ± 0.2 K for 30 min (total softening time). Measurements of AC conductivity were performed in the dynamic regime every 2 min using Lake Shore temperature controller. Conductance (G) and susceptance (B) were measured in the C_p measurement model of the instrument. In this case AC conductivity (σ_{ac}) can be calculated as $\sigma_{ac} = \sqrt{B^2 + G^2}$, tan $\delta = G/B$ and $B = 2\pi fC$, where f is frequency and C is capacity. The conductive temperature coefficients (CTC) were determined from the relation CTC_σ $(T) = 100(\sigma(T+\Delta T) - \sigma(T))/(\Delta T)/\sigma(T)$. All the measurements were repeated on at least two samples.

3. Results

3.1. AC conductivities at room temperature

Fig. 1 presents the frequency dependencies of the real (G) and imaginary (B) part of AC conductivity of the samples with 24 wt% (Fig. 1a) and 28 wt% (Fig. 1b) of CB at room temperature. The sample with 24 wt% CB shows an increase in conductance and a decrease in susceptance with increasing radiation dose. In the sample with 24% CB a dose of 200 kGy caused a significant increase in the conductance. On the other hand, the samples irradiated with 200 and 300 kGy show a practically frequency-independence of conductance in the observed frequency range. The increase in conductance with increasing absorbed dose can be related to the processes of crosslinking and grafting of CB particles onto LDPE [1,10,14,18]. Based on the results obtained by Chen et al. for gamma irradiated PE/carbon composites [18], the expected content of grafted LDPE in our samples is less than 2% of the total amount of polymer. We therefore believe that the decrease in the mobility of the CB particles is primarily the result of a networked polymer matrix. Lower mobility increases the direct contact between CB particles and decreases the capacitive contacts which can be seen as a decrease in the susceptance in Fig. 1a. The existence of polar

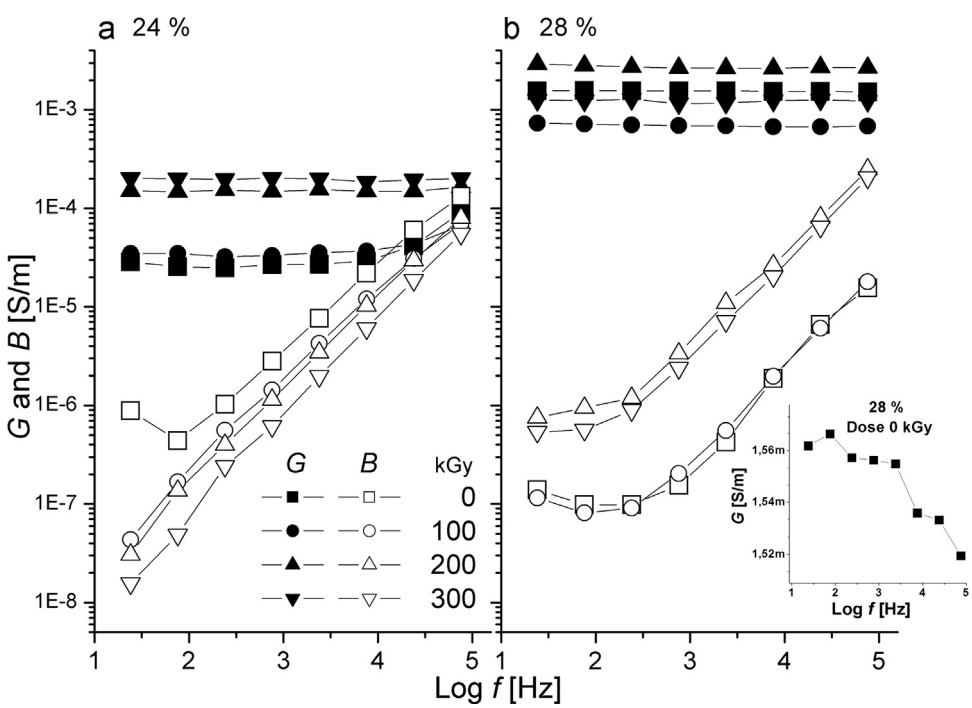

Fig. 1. AC conductivities at room temperature of samples (a) 24 wt% CB and (b) 28 wt% CB.