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Influence of Radiation Structures on Positive-Temperature-Coefficient and Negative-Temperature-Coefficient Effects of Irradiated Low-Density Polyethylene/Carbon Black Composites

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ABSTRACT: The electrical-resistivity/temperature behaviors of low-density polyethylene (LDPE)/carbon black (CB) composites irradiated with ^{60}Co γ rays were studied. The experimental results showed that the irradiated composites could be separated into insoluble crosslinking networks with CB (gel) and soluble components (sol) by solvent-extraction techniques. When the sol of an irradiated LDPE/CB composite was extracted, the electrical conductivity of the system increased. The positive-temperature-coefficient (PTC) and negative-temperature-coefficient (NTC) intensities of the gels of the irradiated composites became extremely small and independent of the radiation dose. The sols and gels of the irradiated LDPE/CB composites, which had different thermal behaviors, played important roles in the appearances of the PTC and NTC effects. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 700–704, 2005

Key words: radiation; carbon black; composites; polyethylene (PE); irradiation

INTRODUCTION

Carbon black (CB), a common conductive filler, can be dispersed in a polymer [e.g., polyethylene (PE)] to impart antistatic and semiconducting properties to the material. Although the conductive mechanism is still in debate, PE/CB composites have found wide commercial applications as, for example, self-regulating heaters and resettable fuses, for over 20 years. The positive-temperature-coefficient (PTC) property is one of the most important practical uses of CB-filled polymer composites. The main feature of PTC materials is that heating causes the conductive system to show a sharp resistivity increase near the melting region of the semicrystalline polymer when the filler concentration is high enough.[1–3] However, continuous heating reduces the resistivity of the composites because of the negative-temperature-coefficient (NTC) effect. The NTC effect is believed to be related to the redistribution of CB in the molten polymer.[4] Crosslinking networks have been proven to effectively reduce the mobility of CB in the polymer matrix and to actually reduce the NTC effect.[5–7] PE/CB composites can be crosslinked via either chemical or radiation crosslinking, and the NTC effect can be nearly eliminated.[5,6] Furthermore, crosslinked composites have satisfactory electrical stability and reproducibility upon repeated heating–cooling cycles. The PTC effect of radiation-crosslinked PE/CB composites is dependent on the irradiation conditions. The high-temperature irradiation of PE/CB composites can significantly reduce the PTC intensity (I_p) because of their higher crosslinking densities in comparison with those treated at room temperature.[7] In our previous article,[8] the influence of the radiation dose on the electrical behaviors of low-density polyethylene (LDPE)/CB composites is discussed. In this article, the influence of the different radiation structures (sol and gel) on the PTC and NTC effects of the irradiated systems is discussed in detail.

EXPERIMENTAL

The LDPE used was a commercial resin (1I2A) from Yanshan Petrochemical Co. (Beijing, China) with melt index of 2 g/10 min and a density of 0.921 g/cm^3. The CB was acetylene black from Chun'an Chemical Co. (Zhejiang, China) with an average particle size of 40–50 nm, a surface area of 60–70 cm^3/g, a dibutyl phthalate (DBP) value of 300–320 mL/100 g, and a pH value of 5.0–7.0. The composite of LDPE and CB was

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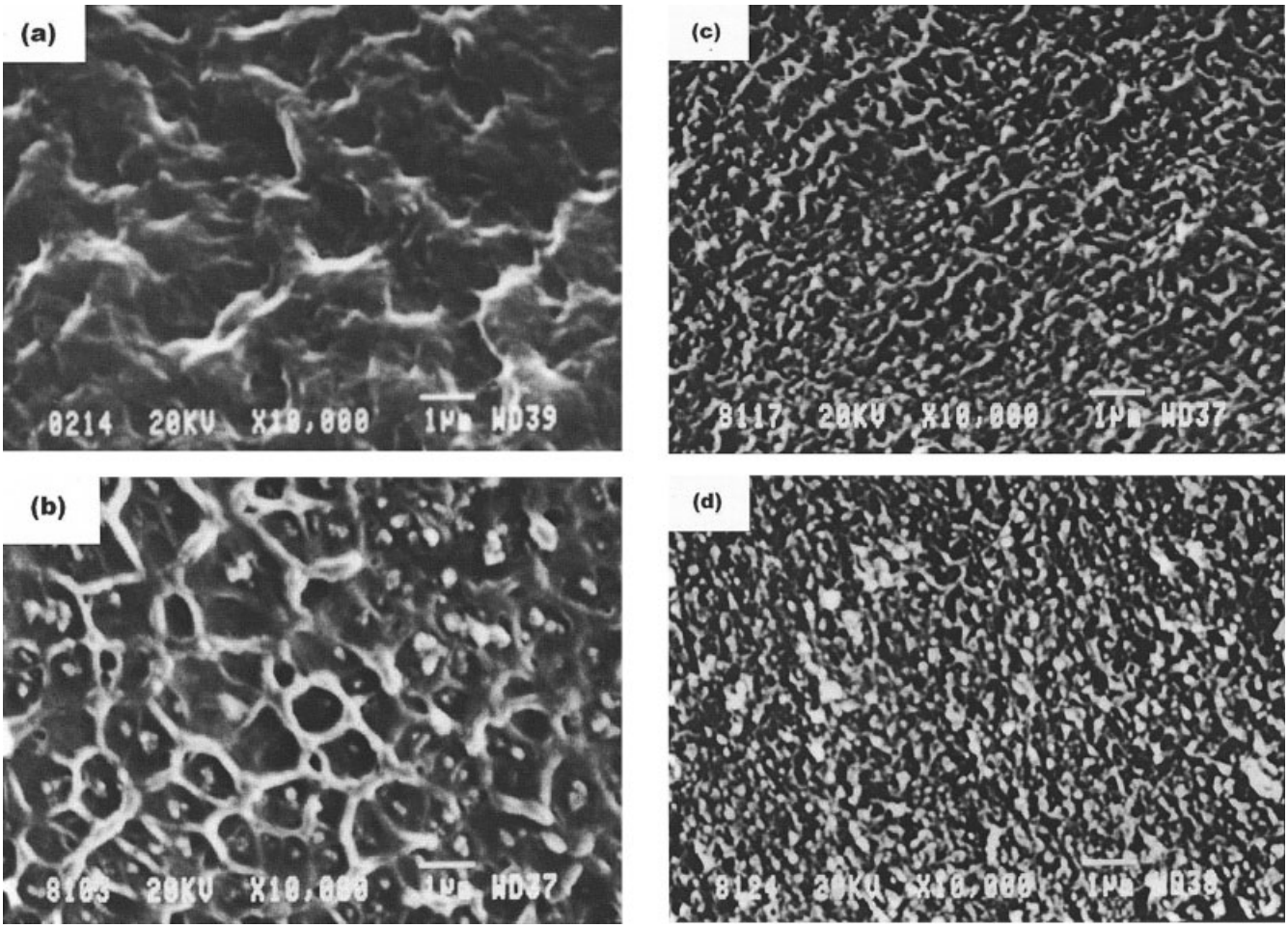

Figure 1 SEM photographs of gels irradiated LDPE/CB composites with different CB contents: (a) 0, (b) 5, (c) 20, and (d) 30 wt %.

blended in a Brabender instrument (Chang Chun, China) at 160°C for 5 min; this was followed by further mixing on a two-roll mill at 160°C for 5 min. After being removed and granulated, samples of the composites with pre-embedded electrodes were compression-molded at 150°C and then cooled down in air to room temperature; this made sheets with dimensions of approximately $100 \times 10 \times 3$ mm^3. The sheet samples were rested overnight for the release of residual thermal stress. The samples were irradiated with ^{60}Co γ rays at a dose rate of 13.8 kGy/h at room temperature. All the samples were held for 1 day after radiation crosslinking to eliminate the postradiation effect. The gels of the irradiated LDPE/CB composites were obtained by the exposure of 4-cm-long sheet samples with electrodes to refluxing xylene in a Soxhlet apparatus for 72 h, with a change of the solvent every 24 h. After being washed with acetone, the samples were dried in a vacuum oven at 100°C overnight. The electrical resistivity was measured with a digital multimeter when it was lower than 2×10^7 Ω, and a high-resistance meter was used when the resistivity exceeded 2×10^7 Ω. All values of the resistivity reported in this work were values of the direct-current resistivity. The thermal analysis was performed with a PerkinElmer DSC-7 (Boston, MA) differential scanning calorimeter at 2.5°C/min in nitrogen. Morphology observations were made with a JOEL JXA-840 (Tokyo, Japan) scanning electron microscope; before this, the irradiated composites were etched with refluxing xylene for the removal of the sol, the samples were fractured under liquid nitrogen, and the etched surfaces were vacuum-coated with a thin gold layer.

RESULTS AND DISCUSSION

Structures of the irradiated LDPE/CB composites

Scanning electron microscopy (SEM) photographs of gels of irradiated LDPE/CB composites with different CB contents are shown in Figure 1. There were many cavities in the liquid-nitrogen-fractured surfaces of the irradiated composites after xylene refluxing. It is well known that when CB is dispersed in semicrystalline

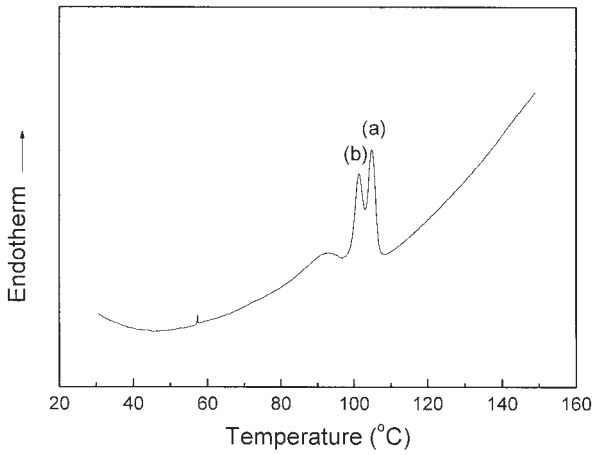

Figure 2 Melting behavior of irradiated LDPE/CB composites at 400 kGy and a heating rate of 2.5°C/min: (a) high-temperature and (b) low-temperature peaks.

polymers, the CB particles are excluded from the crystalline region and aggregate in the amorphous region of the polymer.[9] For irradiated LDPE/CB composites, insoluble three-dimensional networks (gels) are produced in the amorphous region during radiation crosslinking. In this case, the irradiated composites could be separated into two fractions: insoluble crosslinking networks with CBs (gel) and soluble components (sol). After xylene refluxing, the sol was dissolved in the solvent, and this led to cavities left around the gel. Because of the good interaction between LDPE and CB during the radiation crosslinking of the matrix, the cavities of the irradiated composites with CB were more regular than those of irradiated pure LDPE. In addition, the size of the cavities of the irradiated LDPE/CB composites decreased with the CB content.

For irradiated PE crystallizing at low supercooling, the low-molecular-weight fraction of the material, known as the sol, may remain uncrystallized. The uncrystallized material will crystallize subsequently upon cooling to room temperature when it can be separated from the rest by extraction with a hot solvent.[10,11] It can be shown by analogy to this segregation by molecular weight that there can also be segregation between crosslinked and uncrosslinked chains for irradiated LDPE/CB composites upon a subsequent heat treatment. The composite sample irradiated at 400 kGy was heated to 150°C, quenched in ice water, annealed at 110°C for 4 h, and finally cooled to room temperature. The differential scanning calorimetry (DSC) curve of the treated sample at a heating rate of 2.5°C/min is shown in Figure 2. Two distinct DSC melting peaks appear after the subjection of the sample to the radiation and heat treatment; the high-temperature and low-temperature peaks correspond essentially to uncrosslinked material (sol) and crosslinked (gel), respectively, arising through better and poorer crystallizability, respectively. Hikmet and Keller[10] proved that this double endotherm peak arises through the segregation of the gel and sol into different crystals during the heat treatment. For the irradiated LDPE/CB composites, the difference in the thermal behaviors between the sol and gel had a significant effect on the PTC and NTC effects of the systems.

PTC and NTC effects of the irradiated LDPE/CB composites

The electrical-resistivity/temperature behaviors of different LDPE/CB composites and gels of LDPE/CB composites irradiated at 200, 600, 900, and 1200 kGy are shown in Figure 1. The existence of the sol had a significant effect on the electrical properties of the irradiated composites. The difference in the room-temperature resistivity between the irradiated LDPE composites and the gels of the irradiated LDPE composites decreased with the radiation dose. As shown in Figure 3(a), the room-temperature resistivity of the LDPE/CB composites was much greater than that of the gels of the irradiated composites at 200 kGy, whereas at 1200 kGy, the results were just the opposite, and the room-temperature resistivity of the gel was a little greater than that of the irradiated composites with the sol [Fig. 3(d)]. In addition, after the sol was extracted from the irradiated LDPE/CB composites, the resistivity of the gels became very small in comparison with that of the irradiated composites with the sol inside throughout the whole heating temperature range, except that the resistivity was less than 60°C at 1200 kGy. As discussed in our previous work,[8] the degree of crosslinking (DOC) of the irradiated LDPE/CB composites increased with the irradiation dose. This meant that the concentration of the sol decreased with increasing irradiation dose. The existence of the sol in the irradiated system hampered the electrical conductivity of the CB aggregates, and the room-temperature resistivity depended on the content of the sol in the irradiated composites.

To compare the influence of the existence of the sol on the PTC and NTC effects of irradiated LDPE/CB composites, we can define I_p as follows:

$$I_p = \log\left(\frac{\rho_m}{\rho_{RT}}\right) \tag{1}$$

where ρ_m is the maximal resistivity of the composites near the melting temperature of the polymer matrix. ρ_{RT} is the room-temperature resistivity of the composites. For the NTC intensity (I_n) of irradiated composites, to average out any random fluctuations, it is more common to use the slope as a means of comparison. Therefore, I_n can be expressed as follows:

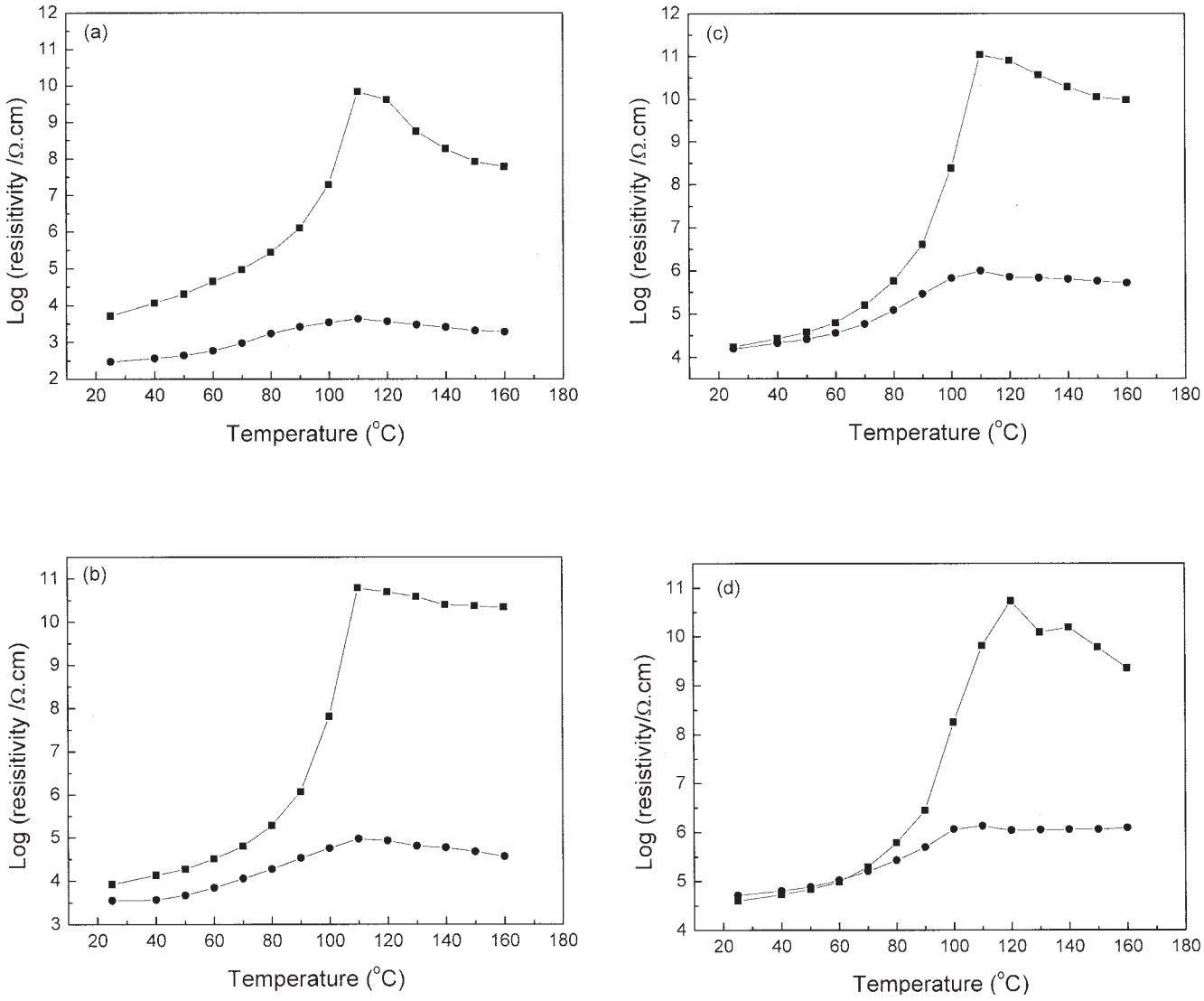

Figure 3 Resistivity/temperature behavior of (■) irradiated LDPE/CB composites and (●) gels of irradiated LDPE/CB composites at different radiation doses: (a) 200, (b) 600, (c) 900, and (d) 1200 kGy.

$$\log \rho = -I_n T \tag{2}$$

where ρ is the resistivity at a certain heating temperature. T is the heating temperature from the beginning of the NTC effect to the end of it, that is, from the temperature of maximal resistivity to the final temperature of the experiment. A plot of the heating temperature versus the logarithm of resistivity of both the irradiated LDPE/CB composites and the gels of the irradiated composites at 200 kGy is shown in Figure 4. I_n of the irradiated composites was much greater than that of the gels of the irradiated composites.

The values of I_p and I_n for the irradiated LDPE/CB composites with both sol and gel and for the gels of the irradiated composites at different radiation doses are listed in Table I. Without sol, the PTC intensity of the gels of the LDPE/CB composites ($I_{p,\text{gel}}$) was

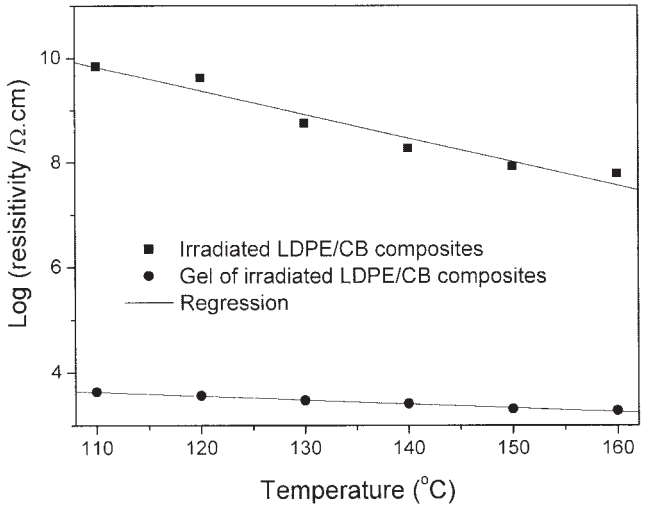

Figure 4 Plot of the heating temperature versus the logarithm of the resistivity.

TABLE I
I_p and I_n of Irradiated LDPE/CB Composites and Gels of Irradiated LDPE/CB Composites

	LDPE/CB composites with different radiation doses (kGy)					
Intensity	0	200	400	600	900	1200
I_p	4.35	6.13	6.85	6.78	6.75	6.13
$I_{p,gel}$	—	1.17	1.23	1.42	1.80	1.41
I_n ($\times 10^4$)	761	453	54	98	231	144
$I_{n,gel}$ ($\times 10^4$)	—	73	9.1	81	48	3.6

smaller than that of unirradiated CB-filled composites (it can be assumed that the content of the sol in the composites was 100%) and was too small to be used in practice. Furthermore, in comparison with the irradiated composites, the radiation dose had less effect on $I_{p,gel}$. These results showed that the content of the sol (or gel) was very important for high I_p values to be obtained for the irradiated CB-filled composites. The I_n values of the irradiated LDPE/CB composites depended on the radiation dose. At 400 kGy, I_n became very small, and this meant that the NTC effect was effectively eliminated. However, the NTC intensity of the gels of the irradiated LDPE/CB composites ($I_{n,gel}$) was very small and was independent of the radiation dose. The results showed that for the irradiated LDPE/CB composites, both the sol and the gel played important roles in the occurrence of the PTC and NTC effects.

As shown in Table I, the NTC effect reappeared when the radiation dose was greater than 400 kGy because of the radiation-induced oxidative degradation of the crosslinked chains in the presence of air.[12] Figure 5 shows the PTC curves of the irradiated composites at different radiation doses *in vacuo*. After radiation *in vacuo*, the NTC effect decreased with an increasing radiation dose. At 1200 kGy, the irradiated sample displayed an excellent PTC performance with no appearance of an NTC effect.

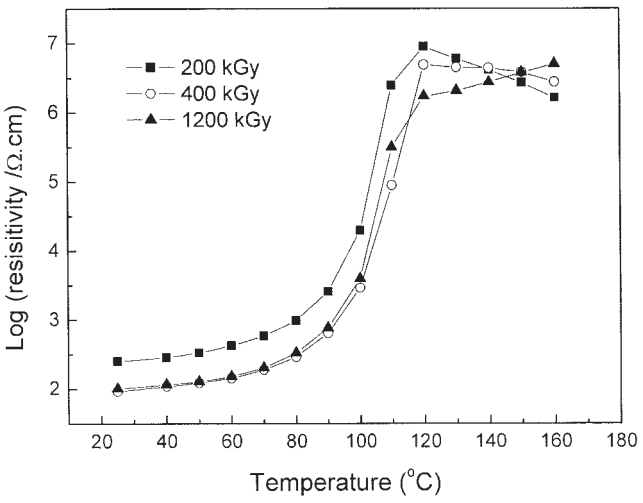

Figure 5 Resistivity/temperature behaviors of LDPE/CB composites irradiated at different radiation doses *in vacuo*.

CONCLUSIONS

The influence of the radiation structure (sol and gel) on the electrical-resistivity/temperature behaviors of irradiated CB-filled LDPE composites was investigated. The experimental results showed that the irradiated LDPE composites could be separated into two fractions, insoluble crosslinking networks with CB (gel) and soluble components (sol), with different thermal behaviors. The sol and gel had a significant influence on the occurrence of PTC and NTC effects of the irradiated composites. Without sol, the electrical conductivity of the irradiated LDPE/CB composites increased and depended on the irradiation doses. Furthermore, the intensities of the PTC and NTC effects became very small and were independent of the radiation dose. In particular, the PTC effect was too small to use in applications. According to the experimental results, we can conclude that, for irradiated LDPE/CB composites, both the sol and the gel play very important roles in the occurrence of PTC and NTC effects.

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