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Composites Science and Technology 65 (2005) 1769–1779
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

Effect of processing parameters on electrical resistivity and thermo-sensitive properties of carbon-black/styrene–butadiene–rubber composite membranes

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Received 3 March 2005; accepted 10 March 2005
Available online 27 April 2005

Abstract

Carbon-black-filled conducting composite membranes were prepared by using styrene–butadiene–rubber as matrices and incorporating with some organic crystals (2,6-di-*tert*-butyl-4-methyl phenol). A number of composite membranes exhibited a thermo-sensitive property which corresponded to a positive temperature coefficient (PTC) effect. It was found that processing parameters strongly affected the microstructure of composite membranes and in turn, the resistivity of membranes as well as their PTC characteristics. The effect of several main processing parameters, such as mixing parameters (temperature, time and nip gap) and vulcanization parameters (temperature, time and pressure), on the resistivity and PTC characteristic of composite membranes was investigated. The results obtained from resistivity measurements, DSC thermograms, SEM micrographs and X-ray diffraction patterns revealed that, by using optimized mixing and vulcanization parameters, the obtained composite membranes showed a microcrystal-embedded structure and their resistivity against carbon black content exhibited a tangible percolation behavior. It was also found that the PTC characteristics of some composite membranes prepared by optimized processing parameters appeared to be stable for an acceptable long term.

Keywords: Carbon-black/styrene–butadiene–rubber composite; Processing parameter; Microcrystal-embedded structure; Percolation behavior; PTC effect

1. Introduction

One of practical methods to obtain conducting polymer composites (CPCs) is adding conductive fillers like carbon blacks, carbon fibers, metallic powders, flakes and fibers as well as metallic hydrides into polymer matrices [1–3]. Most of the time, carbon blacks are chosen as fillers for conducting rubbers and conducting plastics because of their low cost, low density, high electrical conductivity and in particular, specific structures that enable a formation of conductive network inside a polymer matrix at relatively low filler concentration [4–7]. CPCs have been developed for numerous applications, such as electromagnetic interference shielding, self-regulating low-temperature heater, self-resetting over-current protection elements, electrostatic charge dissipation and many different sensors for vapors, chemicals, mechanical stress and temperature [8–11].

An important thermal-sensitive feature of some CPCs, that is, the resistivity increases with increasing temperature over a certain temperature range, which is

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doi:10.1016/j.compscitech.2005.03.006

also known as positive temperature coefficient (PTC) effect, is quite attractive for sensor applications. It is generally accepted that the PTC effect of CPC materials greatly depends on their own structures and properties which are mainly affected by the polymer matrices, conducting fillers as well as the processing methods and conditions. A few reports regarding the PTC effect of CPCs have mentioned that a greater PTC intensity (the ratio of maximum resistivity at a certain temperature to the resistivity at room temperature) can be obtained when several kinds of crystalline polymers are employed as matrices, and the further examinations have suggested that the degree of crystallinity and melting point of polymer matrices are quite closely related to the PTC intensity of CPCs [12–14]. Therefore, up to now, most attentions for CPCs showing a notable PTC effect have been focused on crystalline polymer/conducting filler composites. The PTC effect for the CPC materials having amorphous polymer or elastomer matrices has been extremely less explored because most CPCs with amorphous polymer matrices nearly do not show any PTC effect or only give a very poor PTC characteristic although these kinds of CPCs are obviously of interest and importance in view of their possible applications. To date, very few studies have involved in this issue. Zhang et al. has stated that a PTC phenomenon is observed for carbon black-filled silicone rubber [15]. Another example for a CPC material using elastomer as a matrix and showing a measurable PTC effect can be found in Ghosh's report [16]. However, both CPCs do not exhibit any satisfactory switching characteristics and their PTC intensity is recorded as a magnitude of around nine-fold. We have prepared a series of CPC membranes by adding some organic crystals (2,6-di-*tert*-butyl-4-methyl phenol, BMP) into a carbon-black-loaded styrene–butadiene–rubber (SBR) system. Some of them, loading with an appropriate amount of carbon black and organic crystal, show a well-defined switching characteristic and a relatively high PTC intensity [17]. BMP has been selected for these composite membranes by considering the properties of both SBR matrix and the BMP crystal themselves. It is quite well known that SBR is not able to keep its original properties for a long term in a thermal environment in which the temperature is higher than 100 °C because SBR could be rapidly aged and degraded at such a high temperature. Moreover, as a potential thermal sensor material, normally, working temperature of the composite membranes should be pronouncedly higher than room temperature since PTC intensity would be too low to be valuable for practical applications if corresponding thermo-sensitive temperature of composite membranes is near or even lower than room temperature according to the suggested PTC mechanism [18]. The expectant thermo-sensitive temperature of the composite membranes, therefore, should be altered in a certain temperature range markedly higher than room temperature and certainly lower than 100 °C. In addition, several another specific factors, compatibility of selected crystal with SBR matrix, mechanical properties and thermal stability of resultant composite membrane should be also taken into account for selecting a proper crystal. The BMP has a desired compatibility with SBR and has been used as a plasticizing agent [19]. Its crystalline structure can be stabilized under or near its melting point (ca. 70 °C) which is well located inside the working temperature range of expectant thermo-sensitive composite membrane. Furthermore, we have also found that if an appropriate processing condition is employed the BMP can reform crystal domains inside the SBR matrix after the composite membrane is vulcanized, and provide the composite membrane with a microcrystal-embedded structure. Thus, BMP is selected as a qualified crystalline filler.

It has been found that one of crucial aspects in the preparation of these composite membranes is the processing condition. Hence, it becomes obviously important to find out how the processing parameters affect the structures and properties of composite membranes. Our main concerns for these composite membranes are their structures, conductive properties and PTC characteristics. Therefore, in the present study, the effect of some processing parameters, such as mixing time, mixing temperature, nip gap, vulcanization time, vulcanization temperature, and vulcanization pressure, on the microstructures, resistivity and PTC characteristics of these composite membranes were systematically investigated.

2. Experimental

2.1. Materials

Styrene–butadiene–rubber (SBR, ASRC1500, 23.5% styrene content; Mooney viscosity (ML_{1+4}): 50 (at 100 °C); density: 0.91 g/cm^3) was provided by Synthetic Rubber Company (USA). Carbon black, Sterling SO-N550 (pore volume DBP: 1.21 cm^3/g; CTAB: 42 m^2/g; particle size: 40–48 nm; iodine absorption: 43 mg/g; volatile: 1.0%; pH: 6.5; density: 1.85 g/cm^3), was received from Cabot Corp. (USA). 2,6-di-*tert*-butyl-4-methyl phenol (BMP, powder separated by passing through a 100-mesh sieve, relative density: 1.048, melting point: 70–71 °C) and all other chemical reagents were obtained from Shanghai Chemical Reagents Inc. (China) and used as received. For simplification, carbon black Sterling SO-N550 was designated as N550 in following sections.

The composite membrane had such a basic composition (in portions per hundred portions of rubber, phr, by weight): SBR, 100; stearic acid, 1; carbon black (varying with samples); processing oil, 4; BMP 9; CZ