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The effect of the structural order of isotactic polypropylene containing magnetically aligned nickel particles on its electrical resistivity

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ABSTRACT

The effect of the high order structure of an isotactic polypropylene (PP) composite on the resistivity of composites containing magnetically aligned Ni particles was studied. Only a small amount of particles needed to be added for the composite material to become conducting after heating while in a magnetic field. The Ni columns formed on applying the field were distorted by the formation of large PP spherulites. Changes to the crystallization process due to the addition of a nucleating agent gave rise to changes in the columnar structure, resulting in large changes in the resistivity of the composite material. Controlling the high order structure of the polymer matrix including its morphology is very important in order to be able to control the magnetically aligned Ni structure.

1. Introduction

In recent years there has been a growing interest in conducting particle-filled composites, since, with the development of new electrical devices, the requirements for composite materials have diversified. These applications include electromagnetic interference shielding, transparent electrodes, solder replacement in surface mount technology and electrical interconnections [1–5]. Connections between the conducting particles are necessary in order that polymer composites become conducting. Generally, a particle volume fraction of more than 10% needs to be added in order to form percolating structures within a matrix [4,6,7], leading to an increase in the opacity, increase in weight, and deterioration in the mechanical properties.

In order to reduce the percolation threshold, some methods, such as the use of phase separated structures [8,9], the addition of multiple particles [10], and so on, have been considered. Another method is magnetic field processing [2,3,5,11,12]. When a magnetic material such as Ni in particle form is introduced into the composite, the particles form columnar structures parallel to an applied magnetic field [13], resulting in the composite becoming conductive. In this case, only a small amount of particles need to be added, and it has been reported that the increase in weight and deterioration in the mechanical properties of such composites are suppressed, providing properties that enable them to be applied as more flexible transparent electrodes [2].

Many composite materials are based on crystalline polymers that have special electrical properties such as the positive-temperature-coefficient (PTC) effect on electrical resistivity [7,11,14,15]. With the PTC effect the resistivity increases drastically with rising temperature. The effect takes place near the melting point of the base polymer and depends strongly on the chemical structure of the polymer matrix [7]. Therefore, it was believed that the PTC effect resulted from melting of the polymer matrix. However, the electrical conductivity of a composite with a crystalline polymer matrix depends on the crystallinity [16] and the PTC effect has also been observed below the melting point of the base polymer [16–18].

The details of the mechanism for the PTC effect have not yet been clarified from the perspective of the correlation between the high order structure of the polymer matrix and the electrical conduction phenomenon. One of the reasons it is difficult to understand the electrical conduction phenomenon is that the addition of many particles to make the composite material conducting prevents the structure from being examined. With a smaller amount of particles, examination of the structure is possible, even with an optical microscope [2,5,6].

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In this paper, we report on the relationship between the high order structure of a polymer matrix composite containing magnetically aligned Ni particles and its electrical properties. The conductivity of this composite can be significantly increased with the addition of just a small amount of particles and we claim that controlling the high order structure of the polymer matrix is important in order to obtain a composite material with excellent electrical properties.

2. Experimental

2.1. Materials

NOVATEC-PP MA03, provided by Japan Polypropylene Co. (Tokyo, Japan), was used as the composite matrix. This is an isotactic polypropylene (PP) and is a commonly used crystalline polymer. Its melt flow rate listed in the catalog is 25 g/10 min. The melting point of the as-received sample was 156 °C measured by DSC. Ni particles, with an average particle size of 2.5 μm in diameter, density of 8.91 g cm^{-3}, and resistivity of 7×10^{-5} Ω cm, manufactured by Inco Ltd. (Toronto, Canada), were used as the conducting material. ADEKASTAB NA11 (NA11) provided by ADEKA Co. (Tokyo, Japan) was used as a nucleating agent for the PP.

The PP pellets, Ni particles, and NA11 were melt-blended at 200 °C and mixed at 60 rpm for 15 min, using a 4M150, manufactured by Toyo Seiki Seisaku-sho Ltd. (Tokyo, Japan), as a two-roller mixer. The composite was molded into a film by hot-pressing. The hot-pressing was performed at 180 °C for 3 min under a pressure of 10 MPa, then the sample was cooled in air, resulting in a film of about 175 μm in thickness.

2.2. Heating in a magnetic field

A home built heating system was used for heating the samples while in the magnetic field. A schematic drawing of this system is shown in Fig. 1. The temperature was controlled using a DSMP21 manufactured by Shimaden Co., Ltd. (Tokyo, Japan). A RESIOPAK R33 platinum resistance thermometer,manufactured by Okazaki Manufacturing Co. (Kobe, Japan), was used as a temperature sensor in order to avoid effects due to the magnetic field. The housing of the heating unit was made of aluminum. The heater was a SAMICONE SUPER 340 rubber heater manufactured by Sakaguchi E.H VOC Co. (Tokyo, Japan). The heating unit was set in the center of the magnetic field generated by a superconducting magnet manufactured by Sumitomo Heavy Ind. (Tokyo, Japan). Since the magnet could be rotated, it was possible to apply the magnetic field either parallel or perpendicular to the plane of the film.

In order to measure the resistance, the sample was placed between Sn foil which formed electrodes on both sides of the sample. At the same time, another sample was placed between two cover glasses in order to make observations with an optical microscope. Magnetic ordering of the Ni particles was done by annealing the composite in a magnetic field at 180 °C for 30 min. After annealing, the samples were cooled to room temperature for 20 min in the magnetic field.

2.3. Characterization

A KEITHLEY 2000 multimeter was used to measure the resistance using a four-terminal method. The resistivity ρ was calculated using the equation $\rho = RS/d$ for given values of resistance R, sample area S, and sample thickness d. The sample area was 1.00 cm^2 and the sample thickness was 175 μm.

The structure of the Ni particles and the high order structure of the crystalline PP were examined using an Olympus BX51 optical microscope with crossed polarizers and a 530 nm retardation plate.

3. Results and discussion

3.1. Effect of the growth of PP spherulites on the conducting path

Fig. 2 shows polarized optical microscope images for the original PP and the PP composite containing Ni particles (PP/Ni). Clear shaped spherulites can be seen in the original PP. With increasing

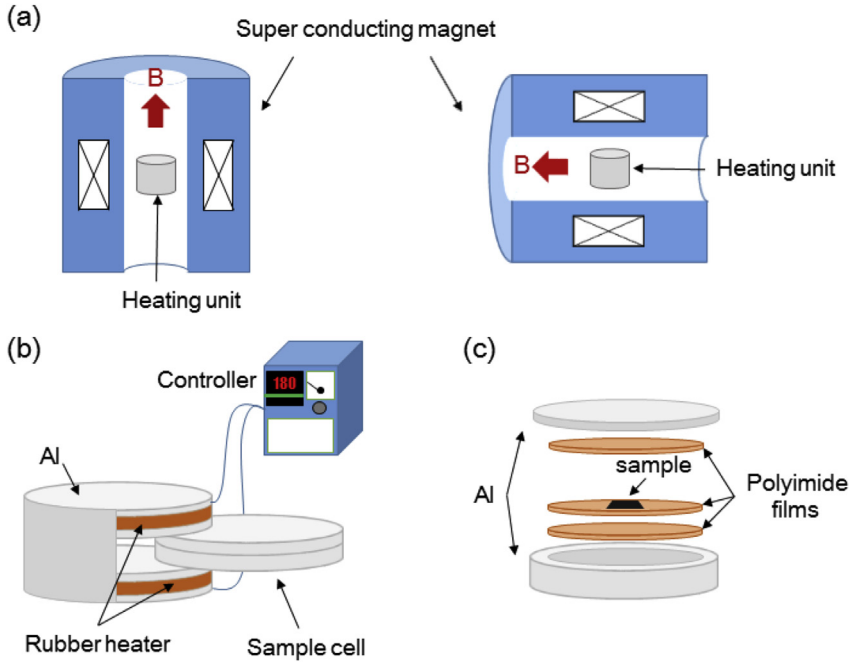

Fig. 1. Schematic illustration of the heating system in a magnetic field. (a) Setup of the heating unit in the magnetic field. The direction of the applied field with respect to the heating unit can be changed by rotating the superconducting magnet. (b) The heating unit comprises aluminum parts and rubber heaters. The sample cell is inserted into the heating unit. (c) The sample cell is also made of aluminum and contains a square sample within a polyimide spacer between two polyimide films.