Electrical Conductivity of a Polyurethane Elastomer Containing Segregated Particles of Nickel

It has been shown previously that composite materials with a high electrical conductivity may be made from various insulating polymers by inclusion of a relatively low volume fraction of a metal such as nickel or copper. Suitable segregated composites were made from mixtures of polymeric and metallic powders.¹ Segregation is realized initially through the tendency of small particles of metal to adhere to the surface of much larger particles of polymer. This segregation is preserved by compaction under conditions which cause coalescence of the polymeric particles and yet do not result in sufficient flow to disturb seriously the runs of metal-to-metal contacts which serve as conducting paths.

The composites reported previously were all made from polymers which provided a rigid matrix such as poly(vinyl chloride) and polyethylene. The purpose of the present letter is to describe how the method was extended to provide an elastomeric material. One obvious problem is how to obtain a free-flowing elastomeric powder, since such materials are usually tacky at room temperature and tend to agglomerate. A general solution would be to pulverize and mix an elastomer in the glassy state, at low temperature. A convenient, though limited, modification of this solution is to use an elastomer that has a molecular structure which allows the formation of crystallites which can act as intermolecular crosslinks. Such crosslinks serve to prevent the polymer from being tacky at room temperature but can be softened at higher temperatures to provide a plastic material which can be processed by conventional methods such as compression molding.

A sample of a polyurethane elastomer (TPU-123, Goodyear Tire and Rubber Company) was scanned by differential calorimetry and found to display first- and secondorder transitions, respectively, in the range of 120° to 150°C and near -35°C. The crystalline fraction, as judged from the area under the scan associated with the firstorder transition, was only 0.1 to 0.2.

The elastomer was ground in a Waring blender with liquid nitrogen cooling for 5 min. The powder obtained in this way did not agglomerate but, instead, remained free flowing even after warming to room temperature. Individual particles were observed to be irregularly shaped, with a length-to-width ratio, generally, of less than 3 to 1. The powder was sieved to provide fractions varying in particle size. A fraction in the nominal size range from 250 to 417 μ was selected for further investigation. This fraction was mixed with spiky, equiaxed 3- to 7μ particles of nickel (Nickel 123; International Nickel Corporation), 10% by volume, in a twin-shell conical blender for 15 min. Five cm³ of the mixture was placed in a cylindrical stainless steel die (diameter 1 in.) at room temperature and compacted under a pressure of 4200 psi in a Buehler mounting press. The temperature was raised to 120°C and held for 30 min before the sample was cooled under pressure to room temperature before removal from the die.

The electrical conductivity of the elastomer without metal was measured with a Keithley micro-microammeter as 10^{-9} (ohm cm)⁻¹. The conductivity of the composite sample was found to be in the range $10^{0}-10^{-1}$ (ohm cm)⁻¹ (using a Leeds and Northrup-K3 potentiometer). This high conductivity was reproduced at intervals throughout the period of one year since the sample was first made. Use of guard rings showed that the conductivity was a bulk property and not a surface effect. On the contrary, the surface had a skin which conducted less readily than the interior of the sample. This skin was sufficiently thin that electrical contact with the bulk could be made by applying the electrode with a pressure ≥ 10 psi. Alternatively, electrical contact could be made at somewhat lower pressures when the layer had been removed by buffing with a fine polishing wheel.

A matter of practical importance is the question of what minimum volume fraction of metal would suffice to give a large increase in electrical conductivity. Attempts have not been made to answer this question because the principles involved are best approached by studies of rigid rather than elastomeric systems. Accounts of such work

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have been reported for the cases of poly(vinyl chloride)² and polyethylene.³ In the case of poly(vinyl chloride), the distribution of the metallic particles could be studied quantitatively by the examination of polished sections in a metallograph. The polishing technique failed with the present polyurethane samples because of their rubbery nature. As an alternative, sections were exposed by cutting with a razor and then examined in a Bausch and Lomb metallograph. The technique is crude, but it nevertheless does show that the metallic particles (white) are, indeed, segregated around much larger elastomeric particles (black) which correspond in size and shape to the polymeric particles in the original powder (Fig. 1).

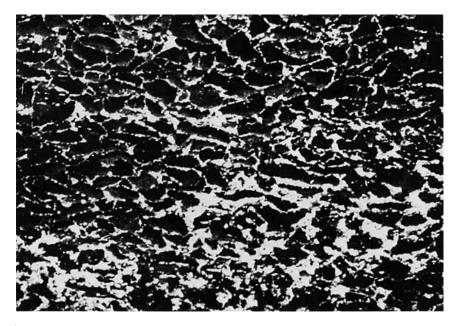


Fig. 1. Section of sample containing 10% by volume of nickel viewed by reflected light $(26 \times)$.

In order to attain a high electrical conductivity by the technique described above, it seems to be necessary to accept a decrease in mechanical strength. For example, inclusion of 10% nickel was found to reduce the tensile strength of the polyurethane from 2450 psi to only 675 psi and to reduce the elongation at break from 550% to 150%. It has been found that this loss of strength may be largely offset, yet with attainment of a high conductivity, by γ -ray-induced crosslinking of samples containing a polyfunctional monomer such as allyl methacrylate. As the details of this radiation processing are involved, they will be presented elsewhere.⁴

In conclusion, it has been found that, using polyurethane and nickel powders, an elastomeric composite material can be made which has a high electrical conductivity, 10° to 10^{-1} (ohm cm)⁻¹, for a relatively low volume loading of metal, 10%. The composite has a low tensile strength, but this can be improved by radiation processing.

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NOTES

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