PHYSICAL CHARACTERIZATION OF PIVALOLACTONE GRAFTED ELASTOMERS

II. ORIENTATION BEHAVIOR

W. H. Buck

E. I. du Pont de Nemours and Company, Incorporated

Elastomer Chemicals Department, Wilmington, De 19898

INTRODUCTION

Thermoplastic elastomers formed by grafting short, highly crystallizable chains of polypivalolactone (polyPVL) onto various elastomeric backbone polymers have been the subject of several recent publications (1-7). These polymers are synthesized by an anionic solution polymerization of pivalolactone initiated by the tetraalkylammonium salts of carboxyl groups pendent from pre­formed elastomeric backbone polymers. Details of the synthesis and physical properties of the graft copolymers have been des­cribed elsewhere (1-7). The previous paper in this series (6) proposed a morphological model for these polymers based upon the results of characterization by transmission electron microscopy, wide and small angle x-ray diffraction, thermal analysis, and solvent swelling. This paper describes the morphological changes which occur during the uniaxial deformation of the copolymers, citing the specific examples of polyPVL grafts on an ethylene propylene diene elastomer (EPDM) and an alternating ethylene ethyl acrylate (E/EA) copolymer.

Previous work (6) showed that over a fairly wide composition range (10-40% by wt. polyPVL), the general morphology of the polyPVL graft copolymers remained the same; discrete domains of polyPVL in a continuous elastomeric phase. As the molecular weight of the grafted polyPVL side chains and the average spacing between the graft sites exceeded about two thousand molecular weight units, spherulitic structures tended to form. The spheru­lites were composed, however, of discrete polyPVL domains.
Various experimental techniques indicated that considerable order exists at the polyPVL crystallite-elastomer interface. Each polyPVL domain is thought to consist of a highly crystalline core of α-form polyPVL surrounded by a layer of ordered elastomer chains. Consideration of polyPVL chain dimensions and domain size has led to the hypothesis that the grafted chains crystallize in a head-to-head fashion, perhaps stabilized by association of the free acid end groups of the polyPVL (6).

The polyPVL domains act as both thermally labile crosslinks and reinforcing filler. The size of these domains depends upon the length of the grafted chain, the average separation of the grafted chains along the elastomer backbone, and, to some extent, upon the structure of the graft site. In general, domain size increases as the length of the grafted chains increases and the average separation between grafted chains decreases.

Annealing of the graft copolymers causes improvement in several important physical properties such as tensile strength and resistance to creep under tensile and compressive stress (3-5). Analysis of annealed samples by transmission electron microscopy and x-ray diffraction has shown that the average domain size decreases and the size distribution is markedly narrowed relative to unannealed samples.

With the aid of wide and small angle x-ray diffraction and infrared dichroism the morphological changes accompanying deformation have been followed. A morphological model of the deformed state has been developed from this data.

**EXPERIMENTAL**

The graft copolymers of polyPVL of EPDM were supplied by R. C. Thamm of this laboratory. The EPDM base polymer was a commercial grade of "Nordel" hydrocarbon rubber, Du Pont's hydrocarbon elastomer, to which carboxyl functionality had been introduced by thermal reaction with maleic anhydride. Full details of synthesis and physical properties have been given elsewhere (1,3,5).

The polyPVL grafts on a backbone of alternating ethylene-ethyl acrylate copolymer were prepared by J. M. Meyer of this laboratory. The backbone elastomer was synthesized by the free radical catalyzed polymerization of ethylene with the boron trifluoride complex of ethyl acrylate (8). Carboxylate graft sites were generated by partial saponification with tetrabutylammonium hydroxide. The grafting reaction was similar to that described for polyPVL grafts on poly(ethyl acrylate) (1,4,5).

Wide angle x-ray diffraction data were obtained with Ni filtered Cu Kα radiation using a flat plate camera. Small angle data were obtained using a Rigaku-Denki camera with Cu Kα radiation.