

T. 9 RAVINDRAN, T.—Studies on polyurethane elastomers based on liquid natural rubber—1989—Dr. D. Joseph Francis

Segmented polyurethanes are a class of thermoplastic elastomers of great commercial importance. These materials derive most of their useful properties from the incompatibility of the hard and soft segments and subsequent phase separation into separate domains. The soft segment is usually a polyether or polyester of molecular weight between 1000 and 5000 possessing a glass transition temperature (T_g) well below ambient temperature. Hard segments are typically formed by the extension of an aromatic diisocyanate with a low molecular weight diol or diamine and have a T_g or melting transition (T_m) above the used temperature. The hard segments provide physical crosslinking, act as reinforcing fillers and are responsible for the performance of these materials at high temperatures. The existence of phase separation into separate micro domains has been well documented for block copolymers and segmented polyurethanes. Hence the physical and mechanical properties are interpreted on the basis of a two phase model. Most polyurethane studies are complicated by one or more of the following effects. (1) Specific interactions between phases via hydrogen bonding (2) crystallinity in either phase and (3) the presence of chemical crosslinking. All the three effects may influence the nature and extent of phase segregation. These complications can be avoided by using a hydrocarbon backbone having nearly exact difunctionality. W.J. Macknight et.al studied a system of polyurethane elastomers where the backbone was hydroxyl terminated polybutadiene (HTPB) Taking these as a guideline we prepared polyurethanes with HTNR soft segments. Polyurethanes upto 70% hard segment content were synthesised.

Block copolymers based on HTPB and poly (ethylene oxide) (PEO) are reported in literature. The use of preformed poly(ethylene oxide) and carboxyl terminated polybutadiene for the preparation of block copolymers are also reported. Correlation between their structure and composition with tensile properties and water absorption capability have been conducted. These materials are excellent hydrogel forming substances. Hydrogels upto 82% water content were obtained. Based on the above references we studied the possibility of synthesising block copolymers from HTNR and preformed poly(ethylene oxide) with varying molecular weights. Block copolymers upto 64% PEO content were synthesised.

The thesis has been divided into five chapters.

In the first chapter an overview of the important research work in the area of Natural Rubber degradation and on the preparation of liquid Natural Rubber with reactive end groups is presented. The review highlights the important achievements in the field of NR degradation. This chapter also includes an introduction to the synthesis of polyurethanes based on hydroxyl terminated polybutadiene

(HTPB), which in turn forms the guideline for the synthesis of HTNR based polyurethanes and block copolymers.

The second chapter deals with experimental procedure for the depolymerization of natural rubber. The rubber used was Natural crumb rubber (ISNR-5, number average molecular weight (M_n): 8,20,000; Intrinsic viscosity in benzene at 30 C 4.45 dl/g; Wallace plasticity (P_o) 59.0) supplied by the Rubber Research Institute of India, Kottayam. 30 wt. % Hydrogen peroxide (supplied by E.Merck, India) was used. Toluene, methanol and tetrahydrofuran were of reagent grade, distilled before use.

Both masticated and raw natural rubber were used for the preparation of HTNR. The effect of ultraviolet light and sun light were studied on the photochemical depolymerization of NR. Detailed investigations conducted on the product obtained by analysing the IR, NMR,¹³ C-NMR spectra and the gel permeation chromatography results. Based on the above results a mechanism for the formation of HTNR and side products are also discussed.

Chapter three deals with the preparation and evaluation of mechanical and thermal properties of poly urethane elastomers based on HTNR. Materials used are HTNR (M_n -3000) prepared in our lab, butane 1,4 diol (Fluka, Switzerland), dibutyl tin dilaurate (Fluka, Switzerland) and toluene diisocyanate (Fluka, 80/20 mixture of 2,4 and 2,6 isomers).

The polyurethanes are synthesised by one stage, two stage (bulk) and two stage (solution) polymerizations. Their tensile properties are evaluated, using a Zwick-1445 universal testing machine, Thermogravimetry was conducted on a Dupont 1090 Thermo gravimetric Analyser at a heating rate of 20 C min⁻¹. Differential scanning calorimetry was performed on a Dupont 9000 thermal analyser system. A heating rate of 10°C min⁻¹ and a sensitivity 2 or 5 m.cal.5⁻¹ were used. Optical microscopy was done on a 'Leitz' Orthoplan microscope.

A series of HTNR containing polyurethanes have been synthesised by 3 different synthetic routes. The soft segment Tg value was found to be very close to that of free HTNR and independent of hard segment content indicating complete or very nearly complete phase segregation. Since the hard segments of TDI/BDO are amorphous, the driving force for phase segregation must arise from the large degree of incompatibility between the polar hard segment and non polar soft segment. Further in these samples there is also no opportunity for hydrogen bonding between hard and soft segments to enhance compatibility. With increasing hard segment content, the property vary from soft to rigid elastomers and rubber toughened plastics. This variation in properties is caused by changes in the sample morphology which depends on the relative fractions of hard and soft segments.

The contents of chapter four are the syntheses of block copolymers based on HTNR and preformed PEO with different molecular weights. Evaluation of mechanical and thermal properties are also included.

Block copolymerization was carried out by the coupling of equimolar amounts of these polymers, with toluene diisocyanate (TDI). Tensile properties and water absorption capability of these polymers were determined. Hydrogels upto 80% water content were obtained. Polymerizations were conducted using one stage, two stage (bulk) and two stage (solution) techniques. Two stage (solution) gave best results which can be attributed to homogeneous reaction conditions provided

by the solution polymerization technique, so that perfect $(AB)_m$ type poly. structure can be obtained where A refers to the soft rubbery segment and B to the hard PEO segment. Optical micrographs showed a two phase morphology which again arises from the reactant incompatibility. DSC studies show a single glass transition for the soft segment and the value of which is almost a constant for the series of block copolymers and is only 6°C above the glass transition temperature of free HTNR. It is already reported that an increase in T_g of 4°C of the soft segment in the block polymer above the corresponding homopolymer T_g , corresponds to complete phase segregation. Our results indicate that phase segregation in these samples is complete or very nearly so.

Fifth chapter gives an overall conclusion of the results and discussion of chapters 2, 3 and 4, a brief summery of all the chapters along with some suggested applications for the synthesised materials.