PREPARATION AND PROPERTIES OF STYRENE - SILOXANE BLOCK COPOLYMER ELASTOMERS

by

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submitted

in fulfilment of the requirements of the degree of

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To my

Beloved Parents

CERTIFICATE

This is to certify that the thesis entitled "Preparation and Properties of Styrene-Siloxane Block Copolymer Elastomers" being submitted by Mr. Sunil K. Varshney to the Indian Institute of Technology, Delhi for the award of the Degree of Philosophy in Textile Technology, is a record of bonafide research work carried out by him. Mr. Sunil K. Varshney has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

A series of triblock copolymers, poly(siloxane-b-styrene-b-siloxane) were synthesized by the sequential anionic polymerization of styrene and cyclic siloxane monomers, like hexamethylcyclotrisiloxane (D_3), Octamethylcyclotetrasiloxane (D_4) and hexaphenylcyclotrisiloxane (P_3) with lithium or sodium biphenyl as initiator. The effect of initiator concentration, gegenion and the polymerization temperature for styrene on molecular weight distribution (MWD) has been investigated by gel permeation chromatography (GPC). GPC data show broader MWD of polystyrene and block copolymers prepared by sodium biphenyl in comparison to that produced by lithium biphenyl.

The intrinsic viscosity of block copolymers was determined in solvents of varying solubility parameter. In toluene, higher $[\eta]$ values are observed in all the styrene-dimethylsiloxane copolymers irrespective of the composition. These results suggest expansion of the polymer coils by polymer-solvent interactions. In cyclohexane, however, agglomeration of polystyrene is responsible for the least $[\eta]$ value in cyclohexane. Conversely, poly(diphenylsiloxane-b-styrene-b-diphenylsiloxane) copolymers showed highest $[\eta]$ value in O-dichlorobenzene and lowest in toluene.

The films of poly(dimethylsiloxane-b-styrene-b-dimethylsiloxane) copolymers cast from different solvents showed significant changes in both the phase morphology and tensile behavior. The use of THF and cyclohexane which selectively solvate either the polystyrene segment or polydimethyl siloxane block respectively gave films which show better separation of microphases. On the other hand, in toluene, a mutual solvent for both the segments produced lamellar type structure.

It is interesting to note that methylethyl ketone and tetrahydrofuran which are selective solvents for polystyrene segment produced films with high initial modulus characteristic of plastic rather than of a rubber. The influence of solvents on dynamic elastic modulus of block polymer films (cast from different solvents) has also been observed.

As block copolymers have unique ability to show partial compatibility with their corresponding homopolymers, an attempt has been made to blend polydimethylsiloxane diol with hydroxyl terminated (siloxane-b-styrene-b-siloxane) copolymers. The crosslinking of blends was accomplished at room temperature by reacting hydroxyl chain ends with tetrafunctional silane using dibutyltin dilaurate as catalyst. The crosslink density was evaluated by swelling studies.

Various fillers like Cab-O-sil, Dicalite and titanium dioxide were also incorporated. The tensile strength of crosslinked polydimethylsiloxane was found to increase by blending with block polymers or fillers. The tensile failure of these blended samples has been explained from the fractured surfaces studied by scanning electron microscopy.

Effect of thermal aging on tensile properties of block polymers has also been reported. Thermal stability of block polymers as studied by thermogravimetry is influenced by the nature and size of the block segment.

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