STUDIES ON
COPOLYMERIZATION OF STYRENE
AND
ACRYLONITRILE WITH FUNCTIONAL SILANES

by

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DEPARTMENT OF TEXTILE TECHNOLOGY

submitted
in fulfilment of the requirements of the degree of
DOCTOR OF PHILOSOPHY
to the
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Dedicated

TO MY

Beloved Parents

CERTIFICATE

This is to certify that the thesis entitled "Studies on Copolymerization of Styrene and Acrylonitrile with Functional Silanes", being submitted by Mr. Dinesh Chandra Gupta, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in the Department of Textile Technology, is a record of bonafide research work carried out by him. Mr. Dinesh Chandra Gupta has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

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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(D.C. Gupta)

ABSTRACT

Radical copolymerization of styrene and acrylonitrile with functional silanes is reported in the present thesis. Two types of functional silanes were selected for copolymerization. In the first category, vinyl double bond is in the vicinity of silicon atom e.g. vinylmethyldiacetoxysilane (VMDAS) and vinylmethyldiethoxysilane (VMDES). Second type of silanes are those in which silicon is not directly attached to the vinyl double bond e.g. [(2-methacryloyloxy)ethoxy] - trimethylsilane (2-MAETMS), [(2-methacryloyloxy)propoxy] - trimethylsilane (2-MAPTMS), [(2-methacryloyloxy)propoxy] - dimethylphenylsilane (2-MAPDMPS), [(2-methacryloyloxy)propoxy] diphenylmethylsilane (2-MAPDPMS).

Styrene and acrylonitrile were copolymerized with vinylmethyldiacetoxysilane and vinylmethyldiethoxysilane in bulk and toluene at temperatures 60-100°C using benzoyl-peroxide and azobisisobutyronitrile (AIBN) as radical initiators. The reactivity ratios were calculated by intersection, Fineman-Ross and Kelen-Tüdős methods. The reactivity ratio, r_1(styrene) is higher in styrene-VMDAS system as compared to styrene-VMDES, thereby indicating higher reactivity of VMDAS towards polystyryl radical. Reactivity ratio, r_2 (VMDAS or VMDES) is zero confirming the poor polymerizability of vinylsilanes due to electronic and steric effects.

In the second series, styrene and acrylonitrile were copolymerized with silylated methacrylates in bulk and solution at different temperatures. The influence of solvents on reactivity ratios in both the systems has been interpreted in terms of association or solvation of the monomers in these solvents depending upon the polarity of the medium.

The intrinsic viscosity data, molecular weight distribution, infrared and proton magnetic resonance spectra for all the copolymers has been reported. A drop in intrinsic viscosity with increase in silane comonomer in styrene copolymers has been observed. Molecular dispersity also broadens in copolymers in comparison to homopolystyrene.

The second order transition temperatures as indicated from differential scanning calorimetry, dielectric and thermo-mechanical analysis are lower for the copolymers as compared to homopolystyrene or polyacrylonitrile. Thermal degradation of all the copolymers as assessed by thermogravimetry clearly shows that the threshold degradation temperature is lowered by the introduction of functional silanes. Higher rate of decomposition in the initial stage may be related with the polarity and the chemical nature of the side substituents of silane comonomers. However, the relative thermal stability of some of the styrene copolymers (St-VMDAS/VMDES) as evaluated from integral procedural decomposition temperature

(IPDT) and the activation energies for decomposition indicates the higher thermal stability of copolymers.

Crystallinity of polyacrylonitrile copolymers was assessed from X-ray, density and dielectric measurements. Though the degree of crystallinity is influenced by the introduction of silylated methacrylate comonomers, the crystalline lattice remains similar to that of homopolyacrylonitrile.

Elastomers based on polydimethylsiloxane are considered to be good toughening additives because of their well known resistance to degradation and their very low glass transition. Hence, an attempt has been made to prepare toughened polystyrene by blending polystyrene with styrene-siloxane block and graft copolymers. The mechanical properties have been related with the morphology and the amount of siloxane content in the blended polystyrene.

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