STUDIES ON STYRENE-ISOPRENE-STYRENE TRIBLOCK COPOLYMER BASED BLENDS AND COMPOSITIONS AS HOT-MELT PRESSURE-SENSITIVE ADHESIVES

by

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Adhesives

CERTIFICATE

This is to certify that the thesis entitled "**STUDIES ON STYRENE-ISOPRENE-STYRENE TRIBLOCK COPOLYMER BASED BLENDS AND COMPOSITIONS AS HOT-MELT PRESSURE-SENSITIVE ADHESIVES**" being submitted by **B.S.Goud** to the Indian Institute of Technology, Delhi, for the award of the degree of DOCTOR OF PHILOSOPHY, is a record of bonafide research work carried out by him. B.S.Goud has worked under our supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in the 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

Pressure sensitive adhesive (PSA) is a visco-elastic material which in solvent free form remains permanently tacky. Such materials will adhere instantaneously to most solid surfaces with the application of very slight pressure. There are various types of pressure-sensitive adhesives of which Hot-melt pressure sensitive adhesives (HMPSAs) have gained wide commercial significance due to their maximum coating speeds, required performance at low coat weights, environmental friendly technology, less energy costs and offer excellent adhesion to low energy substrates like polyolefins. Applications of HMPSAs include packaging tapes, double face tapes, paper labels, film labels, removable labels and assembly applications like diaper construction, footwear etc.

The first chapter of the thesis deals with the general introduction and the literature relating to styrenic block copolymer based hot-melt pressure sensitive adhesives and an objective of the proposed study. The study was worked out with an intention to understand the chemical modifications that occur in SIS copolymer when one or more modifiers are present. The structural variations observed in the blends are intended to correlate with surface and bulk adhesive properties for a clear understanding of the internal structure of a PSA.

In the second chapter, the experimental procedures for various studies are reported. Four types of blends with the SIS copolymer (15% styrene and MFI 9)

and its modifiers [aliphatic resin, pentaester, poly(apha methyl styrene) and oil] were prepared by the melt blending technique using a high shear equipment sigma Z blade mixer.. The first type of the blend is a final blend (the SIS copolymer and four modifiers) as per the model PSA developed for the study. The second type of the blends are blends of the SIS copolymer with each of its modifier in similar composition as used in the final PSA referred here as binary blends. Third type of the blends are blends of the SIS copolymer with two of its modifiers called ternary blends and blends of the SIS copolymer with three modifiers are referred to as quarternary blends. Various studies of the blends such as spectroscopic, thermal, melt rheology and surface and bulk properties have been performed.

Third chapter deals with the spectroscopic characterization of original materials and blends using IR, ^{1}H and ^{13}C NMR spectroscopic techniques. Original materials were characterized and compared with few known model compounds for confirmation. It was observed from the spectroscopic studies of the binary blends that, when the aliphatic hydrocarbon resin is blended with the SIS copolymer, change in both 1,4 cis- and 1,4 trans- isoprene positions take place without interfering with the polystyrene. In case of the blend of the SIS copolymer and the pentaester, change in the aliphatic region of the SIS copolymer phase is observed and the pentaester has interconverted its structure to new structured position of rosin derivative with shift in -OH peak and change in vinyl or methyne positions. Poly(alpha methyl styrene) associated with the polystyrene phase of the SIS copolymer without affecting polyisoprene phase. The oil was observed to interact only at the aliphatic region of SIS copolymer. In case of the ternary blends, due to the presence of the two modifiers, interactions with the two phases of the SIS copolymer were observed. Modifiers showed different reactivity when present in combinations than was present alone with the SIS copolymer. This was observed due to the domination of one modifier over the other.

In the quarternary blends, where three modifiers are present, due to the close compatibility of the modifiers, the SIS copolymer has undergone wide chemical modifications in the blends. With all the modifiers present with the SIS copolymer in the final PSA, from IR, it appears to be a different product with a modified structural composition of the SIS copolymer thus responsible to behave as a PSA.

The fourth chapter describes the degradation and thermal behaviour of the blends. It was observed from the DSC study that the transitions present in the original materials have completely disappeared in the blends. Blends containing oil showed lesser thermal resistance followed by pentaester. Aliphatic resin and poly(alpha methyl styrene) because of their close association with polyisoprene and polystyrene respectively of the SIS copolymer showed better thermal resistance in blends.

From the molecular weight and the TGA studies, it was apparent that oil at processing temperature degrades the SIS copolymer irrespective of oxygen or inert atmosphere, whereas the reverse trend was observed for the other modifiers. This confirms that the SIS copolymer behave quite differently with each modifier when processing conditions are changed. The change in polymer molecular weight or in degradation behaviour with modifiers are different in air or in an inert atmosphere.

Fifth chapter describes the melt rheological study of the Final PSA and the blends. It was observed that, in case of the final PSA, with increase in shear rate, melt viscosity decreased linearly indicating non-newtonian flow. Also, it was observed that the final PSA is shear thinning and followed power law equation. Activation energy of viscous flow of final PSA was estimated and found that it is a free flowing material.

Blends of the SIS copolymer when present with its modifiers showed non-newtonian behaviour. But, presence of modifiers reduce or increase the viscosity of pressure sensitive blends. Poly(alpha methyl styrene) increased the viscosities of blends as observed with pentaester to certain extent. Aliphatic hydrocarbon resin and hydrocarbon oil having solubility parameter close to the continuous phase (polyisoprene) of the SIS copolymer when present in blends reduced the melt viscosities of blends.

In the sixth chapter, dynamic mechanical analysis carried out for the final PSA to understand the visco-elastic response was explained. The dynamic moduli vs temperature revealed that the drop in storage modulus broadened significantly because of the presence of tackifier resins, with the center of drop in G' at approximately 20 ^{0}C. Similarly tan delta peak is observed at 20 ^{0}C indicating higher adhesive strength that is required for permanent label applications. The storage modulus (G') at room temperature of 25 ^{0}C is 4 X 10^5 Pa with tan delta value 2.1. These values are well within the "application window for PSA" suggested by Chu.

Also, the blends and the final PSA were studied for the surface and the bulk adhesive properties like roll ball tack, loop tack, peel strength and shear strength. Surface energies of the blends were also determined using contact angle method. Morphological studies of these blends were also made using small angle x-ray scattering and scanning electron microscopy. The aliphatic resin and the oil led to intimate intermolecular contacts at the surface or at the interface with the polyisoprene components of the rubber to exhibit good adhesive properties required for a high tack permanent pressure sensitive adhesive. The presence of the pentaester in the system aided to achieve enhanced peel strength as it induces certain amount of strain in the matrix and ascribed to increasing the surface free energy of the blend. Poly(alpha methyl styrene) increased the cohesiveness and heat resistance of the adhesive.

Chapter seven presents the summary of the preceding chapters and a conclusion was drawn on the basis of the results. A generalized mechanism has been outlined on the internal structure of a pressure sensitive adhesive to explain the role of each modifier in achieving a set of performance properties. Future scope of the Thesis is included at end of the chapter.

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