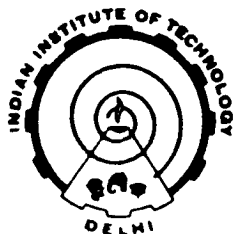


**STUDIES ON POLY (VINYL CHLORIDE)/
STYRENE-(ETHYLENE-BUTYLENE)-STYRENE BLOCK
COPOLYMER BLENDS AND SYNTHESIS OF SEBS**

By
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*Thesis submitted
in fulfilment of the requirements for the degree of*
DOCTOR OF PHILOSOPHY



**Centre for Materials Science & Technology
INDIAN INSTITUTE OF TECHNOLOGY, DELHI**

JANUARY, 1992

Dedicated

To

My Parents

C E R T I F I C A T E

This is to certify that the thesis entitled "STUDIES ON POLY(VINYL CHLORIDE)/STYRENE-(ETHYLENE-BUTYLENE)-STYRENE BLOCK COPOLYMER BLENDS AND SYNTHESIS OF SEBS" being submitted by Mr. Rakesh Chandra Sood to the Indian Institute of Technology, Delhi, for the award of degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Mr. Rakesh C. Sood has worked under our guidance and 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 this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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A C K N O W L E D G E M E N T S

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A B S T R A C T

The development of new plastic materials through alloying or blending is experiencing a period of tremendous growth. The ability to tailor the properties through a combination of materials to meet the unique set of specifications is a key force driving this growth. Other factors influencing the rapid growth of these products include the high cost of developing new polymer systems, shorter life cycles for end use products and broader application base.

In terms of tonnage consumption poly(vinyl chloride) is one of the most important plastic material available today. In spite of its many inherent excellent properties, it suffers from some major drawbacks such as poor impact strength, low thermal stability and difficult processability. These shortcomings of PVC have been overcome by addition of impact modifiers, processing aids and stabilizers.

The main objective of the present studies was to study the effect of styrene-(ethylene-butylene)-styrene triblock copolymer on processability and properties of rigid PVC. Synthesis of SEBS was also carried out by anionic polymerisation of styrene and butadiene followed by hydrogenation of styrene-butadiene-styrene block copolymer.

The thesis has been divided into five Chapters. General introduction and literature on the blends of PVC with various rubbery polymers and synthesis of SBS block copolymer and its modification by hydrogenation has been described in Chapter I.

Preparation of PVC/SEBS blends and studies on physico-mechanical properties of these blends forms the basis of Chapter II of the thesis. PVC was blended with SEBS in ratios ranging from 5-20% (w/w) by melt blending technique. These blends have been designated as P/S₅, P/S₁₀, P/S₁₅ and P/S₂₀. During melt blending at elevated temperature no degradation of PVC was noticed. The density of blends decreased with increasing SEBS content.

The impact strength of blends was much higher in comparison to rigid PVC. An optimum value was observed in P/S₅ blend. Further increase in SEBS resulted in a decrease in impact strength. Tensile strength and modulus decreased with increasing SEBS content in PVC. Incorporation of SEBS introduces ductility in the rigid glassy material, which was supported by yielding behaviour and decrease in Shore hardness.

Morphology or the state of dispersion of the minor phase in these blends was also studied from the photomicrographs of the cryogenically fractured surfaces of blends etched with xylene at room temperature.

It was seen that SEBS formed the discrete phase and PVC formed a continuous phase. Also the size of domains increased with increase in SEBS content.

Dynamic mechanical thermal analysis studies showed a decrease in softening point of P/S₅ blend. Further increase in SEBS showed no effect on the softening temperature. A β -transition was observed in PVC at -37.6°C . This β -relaxation is due to the torsional vibration of $-\text{C}-\text{Cl}$ group. The β -transition was also observed in blends. Activation energy (ΔH^*) of the β -relaxation process was calculated by recording the DMTA traces at frequencies of 1 Hz and 10 Hz. An increase in ΔH^* was observed in P/S₅ blend (381 kJ/mol). It decreased with further increase in SEBS content.

Chapter III deals with the thermal characterisation of PVC/SEBS blends. Melt Rheological behaviour of these blends such as shear stress, shear rate and apparent melt viscosity were also evaluated. These materials showed a non newtonian pseudoplastic behaviour. At a fixed temperature the melt viscosity decreased with increasing shear stress following the power law. Activation energy (ΔE) for viscous flow was also calculated from Arrhenius plots. An increase in SEBS content in blends resulted in a decrease in activation energy. Some blends were prone to melt fracture above a limit of shear stress called critical shear stress and temperature.

TG and DTG traces were recorded in N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range of $50\text{--}600^\circ\text{C}$. From the TG traces initial decomposition temperature and final decomposition temperature were noted. The temperature of maximum rate of weight loss, (T_{max}) was determined from DTG traces. Thermogravimetric results showed two step decomposition in PVC and PVC/SEBS blends with $T_{\text{max-1}}$ at $298 \pm 3^\circ\text{C}$ and $T_{\text{max-2}}$ at $468.5 \pm 1.5^\circ\text{C}$. In SEBS, a single step degradation was observed. Incorporation of SEBS did not affect the characteristic decomposition temperatures of PVC. However, weight loss decreased in the temperature range of $270\text{--}325^\circ\text{C}$ by increasing SEBS content. From the derivative weight loss curves it was observed that rate of weight loss decreased as SEBS content was increased in blends. However, in second step of degradation, the rate increased with incorporation of SEBS in PVC. The main volatile product i.e. HCl formed during PVC degradation at lower temperature ($\sim 270^\circ\text{C}$) is thus reduced by blending with SEBS, thereby reducing its toxicity.

The heat deflection temperature and Vicat softening temperature of PVC marginally decreased with incorporation of SEBS.

PVC has 56.8% of chlorine and is very effective flame suppressant. Incorporation of SEBS in PVC decreased limiting oxygen index. PVC/SEBS blends still meet many of

the industrial requirements for construction, business machine housings as well as electronic/electrical components.

Chapter IV deals with the preparation of SEBS. SBS triblock copolymer was synthesised by termination free anionic polymerisation of styrene and butadiene monomers using n-butyl lithium as an initiator. A two stage diblock polymerisation was followed by addition of difunctional coupling agent p-xylene dibromide to unite the diblocks and form triblock copolymer. The prepared intermediates and elastomers were characterised by FTIR and $^1\text{H-NMR}$ spectroscopic techniques. Polystyrene and elastomer samples were also evaluated for viscosity average molecular weight using Ubbelohde viscometer. The modification of SBS block copolymer by hydrogenation was accomplished by p-toluene sulphonyl hydrazide (TSH). Attempts to minimize side reactions using free radical scavenger (Irganox-1010) and ionic scavengers (pyridine, KHCO_3 and K_2CO_3) were made. A significant reduction in side products formation was observed when KHCO_3 , Irganox-1010 and TSH were used.

Summary and conclusions highlighting the salient features of the work carried out are given in Chapter V. Suggestions for future work are also made. References are given at the end of the thesis.

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