STUDIES ON GRAFTING OF NATURAL RUBBER AND ITS BLENDS WITH POLY (STYRENE -co- ACRYLONITRILE)

By

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copolymers

For
My Wife Sisy and Our Kids Rohit & Diya

CERTIFICATE

This is to certify that the thesis entitled "**STUDIES ON GRAFTING OF NATURAL RUBBER AND ITS BLENDS WITH POLY (STYRENE-co-ACRYLONITRILE)**" being submitted by **Mr. Benny George** 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. Benny George 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.

This work has 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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ABSTRACT

Graft copolymers of synthetic rubbers such us polybutadiene (PB), styrene butadiene (SBR), EPDM rubbers have been extensively used as impact modifiers for brittle thermoplastics. Acrylonitrile butadiene styrene (ABS) plastics, one of the most successful toughened plastics, is prepared by blending poly (styrene-co-acrylonitrile) (SAN) with varying ratios of PB-g- SAN. Numerous publications and patents are available on the preparation of these copolymers and structure property analysis of the blends with SAN. However, very little is published about the preparation of NR-g-SAN and its use as toughening agent for SAN. The present thesis reports the synthesis of NR-g-SAN and NR-g-PMMA (core-shell latex particles) and evaluation of the mechanical properties of their blends with SAN with special emphasis on impact strength.

Graft copolymers of SAN with NR were prepared by γ- rays initiated emulsion polymerization of styrene/acrylonitrile (in varying ratios) in prevulcanised NR latex. The NR: monomer ratio (NR: M) was varied from 60:40, 50:50, 40:60 and 32:68 while the styrene: acrylonitrile (S: AN ratio) in the monomer feed varied from 92:08, 85:15, 78:22, 70:30 and 60:40. Two different dose rates ~1kGy/h and ~2 kGy/h) were used for the polymerization.

A linear relationship between % conversion was observed up to 90% conversion. The rate of polymerization (%conversion/h) was evaluated from this initial slope. The rate of polymerization was not affected by a change in NR: M ratio while an increase in AN content in the monomer feed increased the rate of the polymerization till 30% AN content. The increase in dose rate, though increased the rate of polymerisation, the maximum conversion attained was lower at higher dose rate.

The percent grafting (PG) and grafting efficiency (GE) was determined by extracting ungrafted SAN copolymer using methyl ethyl ketone (MEK). PG increased with decrease in NR:

M ratio while GE decreased. At fixed NR: M ratio, increase in AN content increased the PG and GE. At equivalent percent conversion, lower dose rate gave higher PG. Bulk preparation of graft copolymer was done by using a total dose of 10 kGy and a dose rate of ~1kGy/h.

The NR-g-SAN copolymers were characterized using IR and TGA. The presence of absorption bands at 2237 cm^{-1} ($\nu_{C\equiv N}$) and 1603 cm^{-1} (aromatic skeletal vibrations) confirmed the grafting of acrylonitrile and styrene on to NR chain. Similarly, the free SAN extracted was also characterized. The TGA studies of the copolymers showed a two-step degradation pattern for the graft copolymers at lower AN content. The first step mass loss was attributed to the degradation of NR. An increase in AN content in the monomer feed resulted in an increase in the $\overline{Mw}$ and $\overline{Mn}$ of the ungrafted SAN (GPC study).

Blends of NR-g-SAN with SAN were prepared by melt blending at 170^0C in a Haake rheocord and samples were prepared by injection molding at 220^0C. The mechanical properties of the blends were evaluated. At constant S: AN ratio in the feed and at constant rubber content in the blend, impact strength increased with PG, reached a maximum and then decreased. Thus at a rubber content of 20% and S: AN ratio 78:22 in the monomer feed, the impact strength of the blends increased from 5.1, 14.0, to 22.7kJ/m^2 when PG increased from 34.2, 49.0 to 65.0% respectively. Further increase in PG to 85% decreased the impact strength to 19.2kJ/m^2. Similar trend was observed when rubber content in the blend was increased at a constant PG and S: AN ratio. The impact strength increased systematically from 2.4 to 22.7kJ/m^2 when rubber content was increased from 0 to 20%(PG= 65%, S: AN = 78:22). Further increase in rubber content to 25% decreased the impact strength to 22.45kJ/m^2. At a constant NR: M ratio, the change in AN content in the monomer feed (which changes the AN content in the grafted chain too) also had a profound influence on the impact strength of the blends up to a S: AN ratio 70:30 and further increase in AN content did not influence the impact properties.

These results indicate that the rubber content in the blend, percent grafting and AN content in the grafted chain are the three major factors influencing the toughening of these blends. The percent grafting and AN content control the dispersion of the rubber particles in the SAN matrix and provide sufficient adhesion between the rubber particles and the matrix which is essential for the efficient transfer of stress. Though increase in rubber content increased the impact strength by inducing multiple crazing in the matrix, rubber content above an optimum level, however terminate the craze growth at a correspondingly earlier stage and thus reduce the total energy absorbed during impact.

The morphology of fractured surface of these blends was examined using scanning electron microscopy. The PG, AN content and the rubber content in the blend influenced the morphological features of the fractured surface. The blends which had high impact strength showed cavitation of rubber particles followed by plastic flow of the matrix and craze induced matrix deformation.

At constant rubber content in the blend, the tensile and flexural strength were only marginally influenced by PG and AN content. The yield stress increased from 24.1MPa to 26.1 MPa when the PG was increased from 34.2 to 85.9% at 20% rubber content and at S: AN ratio 78:22. Flexural strength also showed similar trend.

Dynamic mechanical scans of these blends showed transitions due to rubber phase and SAN confirming the two phase nature of the blends. At constant rubber content, increase in PG of rubber in the blend decreased the Tg of rubber as well as the height of the tanδ peak. This may be attributed to the better adhesion between the rubber particles and the matrix (e.g. SAN).

Melt rheological behavior of SAN/NR-g-SAN was studied as a function of rubber content, temperature, PG and AN content. The melt viscosity of both SAN and the blends at different rubber content (10 and 20%) decreased with increase in shear rate and shear stress confirming psuedoplasticity. At lower shear stress (3.1 x 10^4 Pa) and shear rate (< $50s^{-1}$), the viscosity of SAN remained constant while that of the blends showed a tendency to increase. The melt elasticity was higher at higher rubber content. At shear rates above $3200s^{-1}$, the melt elasticity of the blends having various rubber content was similar. The temperature dependence of the melt viscosity was studied at 200, 210 and 220^0C. The activation energy at constant shear stress ($E\tau_{\omega}$) remained constant while activation energy at constant shear rate $E\gamma_{\omega}$ decreased by increasing shear rate from $10s^{-1}$ to $100s^{-1}$ and then remained constant. This implies that the rubber modified SAN is less sensitive to temperature changes at high shear rates and shear stresses.

The PG of rubber in the blend did not affect the viscosity at higher shear rates and shear stresses. However, at lower shear rates (<$100s^{-1}$) or shear stresses (<2.4 x 10^5 Pa) the viscosity was higher at lower PG (34.2%) and decreased as the PG increased to 49%. Further increase in PG (65% and 85.9%) increased the viscosity. Same trend was observed in the MFI of the blends. However, the AN content in the grafted chain did not influence melt viscosity.

The emulsion polymerization of MMA in NR latex was also carried out in a semi-continuous manner using a bipolar redox initiator consisting of cumene hydroperoxide and tetraethylene pentamine to promote core-shell morphology. The effect of various reaction conditions like the type of surfactants, cross-link density of the NR seed, NR: MMA ratio and mode of addition of the monomer on particle morphology was evaluated using TEM.

Three surfactants, i.e. oleic acid, SDSS (sodium dioctyl sulphosuccinate) and NPEO (nonyl phenyl ethylene oxide condensate with 100 ethylene oxide) were investigated at a minimum concentration required to prevent the coagulation of the latex during polymerization. Use of oleic acid led to the formation of a large crop of free PMMA by secondary nucleation, while NPEO and SDSS gave predominantly core-shell morphology. NPEO gave smoother and uniform shell compared to SDSS. Therefore, NPEO was used for further studies. The shell was smoother and more uniform at higher cross-link density of the rubber core. At low MMA concentration, the smaller particles were coated heavily than larger ones. Batch mode of addition of the monomer showed increased tendency for secondary nucleation of PMMA.

The mechanical properties of the blends of SAN/NR-g-PMMA were studied as a function of cross-link density of the rubber, PG and rubber content. The cross-link density of the rubber core was varied from 0- 4.92 x 10^{-5} mol cm^{-3}. The highest impact strength of 15.6 kJ/m^2 was obtained when cross-link density of NR was 2.003 x 10^{-5} mole cm^{-3}. At constant cross-link density and rubber content, impact strength increased with PG while at constant PG and cross-link density of rubber, impact strength increased with increase in rubber content and maximum value was obtained at 20% rubber content.

The PG and cross-link density of rubber had only marginal influence on the tensile strength; modulus and elongation at break of the blends at constant rubber content. However, both yield stress and modulus decreased systematically with increase in rubber content.

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