Modification of Natural Rubber using Grafting Technique

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Introduction

With growing demands for new products and technologies there has been continued interest in the field of modification of rubber. A considerable amount of published information is available on the modification of synthetic and Natural Rubber (NR). Further, with increase in price of products based on petroleum, some of the synthetic rubbers which were commercially available subsequently replaced by modified natural rubbers.

Carboxylated synthetic rubbers mainly Nitrile Butadiene Rubber (NBR) and Styrene Butadiene Rubber (SBR) exist in the market. Main advantage of introducing extra carboxylic link on the synthetic rubber could be explained in terms of mechanical and physical properties of the final product.

The aim of this project was to introduce such a system (extra carbonyl group) to natural rubber, which is not available at present. The properties of natural rubber have been modified by several methods. These include, either change the chemical nature of the rubber molecule or alter its structure. A useful method of modification involves the grafting of monomers on to natural rubber backbone.

This study is based on the graft copolymerization of Methyl Methacrylate (MMA) and acrylic acid on to NR by emulsion polymerization using Tertiary Butyl Hydroperoxide(TBHP)/ Tetra ethylene Pentamine (TEP) and Potassium persulfate/ Sodium thiosulfate initiator systems, respectively. Introduction of COOH groups using monomers on to the main back bone of the polymers would create new sites for cross links to be formed by metal oxides (ZnO, MgO etc.) or any other chemicals present in the formulation. Those new cross links formed in the system would enhance mechanical properties of the final product compared to C-S-C cross links formed by conventional sulphur vulcanization.

Methodology

Methyl Methacrylate Grafted Rubber (MG rubber)

The monomer emulsion was prepared by first mixing the monomer with TBHP (0.25% on rubber), Oleic acid (1.0% on monomer) and then with water (1/2 volume) containing ammonia (0.8% on water). Vigorous agitation was needed to form a good emulsion. Then the monomer emulsion was added slowly to the latex while stirring and the stirring was continued for fifteen minutes.TEP solution was then added slowly to the mixture and stirring was continued for a further ten minutes. The mixture was left for at least eighteen hours to permit completion of polymerization; during this time, the latex was stirred as gently as possible. Finally MG rubber extracted using acetone and petroleum ether.

Acrylic acid grafted rubber

Cationically, stabilized latex (Positex) was used during grafting of acrylic acid on to natural rubber. Potassium persulfate/ Sodium thiosulfate initiator systems and nonionic surfactant

was used to initiate above grafting reaction. Grafted rubber was extracted using distilled water in order to remove un- grafted monomers and homopolymer from the system.

Analysis

The effect of grafting monomers on to NR back bone was investigated by FT-IR spectroscopy. The FT-IR spectrum of MG film after extraction was compared with the spectrum of NR film. The FT-IR spectrum of acrylic acid grafted rubber was compared with the FT-IR spectrum of positex film.

MG rubber was chosen to blend with natural rubber in the latex stage in order to improve strength and aging properties. The cast films prepared using the above blend were air dried and aged at 70 ^{0}C. Then mechanical properties of the cast films were determined using Hounsfield Tensile Testing machine. The physical properties of MG /NR blended films were compared using tensile strength, tare strength and modules values.

Results and discussion

The polymerization reaction is an exothermic reaction and the temperature of the MMA grafted mixture increased during polymerization up to 42^0 C but temperature increment could not be observed for acrylic acid grafted system.

The presence of extra carbonyl group in the spectrum provides the evidence for grafting of MMA on to NR (Figure 1). However, presence of carboxylic link has not appeared in the FTIR spectrum of acrylic acid grafted rubber (Figure 2).

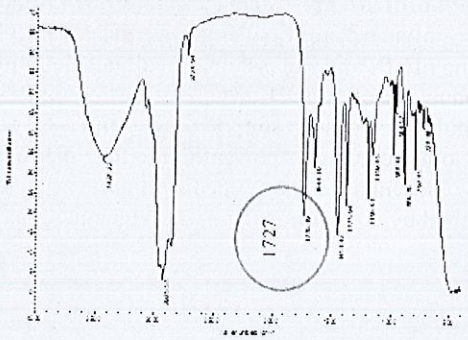

Figure 1: FI- IR spectrum of MG rubber after extraction

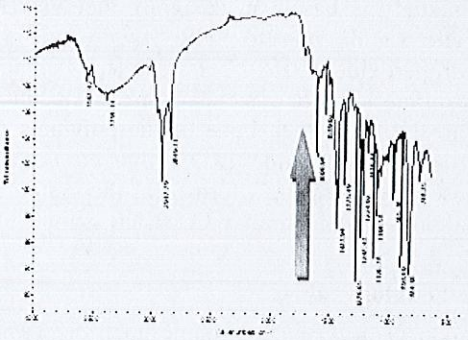

Figure 2: FT- IR spectrum of acrylic rubber after extraction

Only the homopolymer formation was succeeded using hydrophilic initiator system (Potassium persulfate/ Sodium thiosulfate) in acrylic acid grafting. During that reaction temperature has increased rapidly as expected from the polymerization reaction. Simply it means acrylic acid grafting on to NR could not be achieved using the grafting conditions applied during this research because acrylic acid monomers have failed in entering in to the rubber particles in the presence of said initiator system. However, copolymerization reaction has occurred outside of the rubber phase. Therefore, it is essential to explore another method to initiate this grafting reaction.

Mechanical property analysis of the MG/NR blend revealed that NR: MG, 60:40 blend has very good physical properties. This blends with optimized elastic and plastic properties from NR and MG rubbers, respectively. As MG rubber provides polar properties to the blend, mixing of compounding ingredients (especially accelerators) will be very effective. Additional reinforcement from MG rubber will decrease the filler loading of the compound.

Further, many advantages could be achieved through the MG/NR blend. Natural rubber latex prepared with NR: MG, 60:40 blends will give extra stiffness to gloves that are used for industrial purposes. Adhesive made from this blend will enhance bonding properties of the substrates made out with textiles. Hence this could be used in textile supported glove industry and shoe manufacturing industry.

Conclusions

MMA grafting on to natural rubber was achieved using hydrophobic initiator system. Mechanical property analysis revealed that NR: MG, 60:40 blend has very good tensile and tare properties.

The both initiator systems (hydrophilic and lipophilic) that were used in grafting of acrylic acid on to natural rubber were not effective. Main drawback of this grafting reaction was the difficulty in entering acrylic acid monomer into the natural rubber phase as acrylic acid is hydrophilic in nature.

However, using hydrophilic imitator system acrylic acid was homopolymerised. Hence further studies on this system have to be done to investigate suitable mechanism to graft natural rubber with hydrophilic acrylic acid monomer.

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