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A Comparative Analysis upon Properties of Styrene Butadiene Rubber Composites

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Abstract – Styrene butadiene Rubber (SBR) based hybrid nanocomposites containing carbon black (CB) and Organo-modified nanoclay (MMT Closite-20A) were prepared. The mixing and compounding at different proportion was done on two-roll-mill and composite sheets were prepared in compression molding. Mechanical properties such as (tensile strength, elongation at break), hardness, Compression set measurement, and ageing properties were studied. The effect of carbon black and organo-modified nanoclay on these rubber hybrid nanocomposites were investigated by Thermal gravimetric analysis (TGA). Morphological properties of composites were evaluated by SEM analysis. The mechanical and thermal properties were found to improve at 5 phr organo-modified nanoclay and further increase in loading of organically modified nanoclay the respective properties found to be decreases due to agglomeration of the organo-modified nanoclay on SBR nanocomposites.

The article presents the effect of attapulgite (ATT) and its synergic action with carbon or silica on the thermal properties and flammability of cross-linked styrene–butadiene rubber. It has been shown that ATT is active filler improving the thermal and mechanical properties of composites containing this aluminosilicate. The decreased flammability of vulcanizates containing ATT compared to that of unfilled vulcanizates results from good insulating properties of the ATT used. The considerable reduction in the flammability of composites containing ATT and carbon nanofiber or silica is connected, first of all, with the formation of a homogeneous boundary layer.

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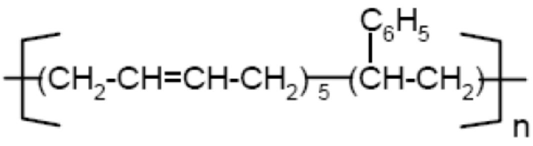
INTRODUCTION

SBR polymers are widely produced by both emulsion and solution polymerization. Emulsion polymerization is carried out either hot, at about 50°C, or cold, at about 5°C, depending upon the initiating system. SBR made in emulsion usually contains about 23% styrene randomly dispersed with butadiene in the polymer chains. SBR made in solution contains about the same amount of styrene, but both random and block copolymers can be made. Block styrene is thermoplastic and at processing temperatures helps to soften and smooth out the elastomer. Both cold emulsion SBR and solution SBR are offered in oil-extended versions. These have up to 50% petroleum base oil on polymer weight incorporated within the polymer network. Oil extension of SBR improves processing characteristics, primarily allowing easier mixing, without sacrificing physical properties.



$$\left[(\mathrm{CH_2{-}CH{=}CH{-}CH_2})_5 - (\overset{\mathrm{C_6H_5}}{\overset{|}{\mathrm{CH}}}{-}\mathrm{CH_2}) \right]_n$$

Styrene-butadiene rubber SBR

SBR was originally produced by the hot emulsion method, and was characterized as more difficult to mill, mix, or calender than natural rubber, as well as being deficient in building tack, and having relatively poor inherent physical properties. Processability and physical properties were found to be greatly improved by the addition of process oil and reinforcing agents. “Cold” SBR generally has a higher average molecular weight and narrower molecular weight distribution. It thereby offers better abrasion and wear resistance plus greater tensile and modulus than “hot” SBR. Since higher molecular weight can make cold SBR more difficult to process, it is commonly offered in oil-extended form. Solution SBRs can be tailored in polymer structure and properties to a much greater degree than their emulsion counterparts. The random copolymers offer narrower molecular weight distribution, low chain branching, and lighter color than emulsion SBR. They are comparable in tensile, modulus, and elongation, but offer lower heat buildup, better flex, and higher resilience. Certain grades of solution SBR even address the polymer's characteristic lack of building tack, although it is still inferior to that of natural rubber.

The processing of SBR compounds in general is similar to that of natural rubber in the procedures and additives used. SBR is typically compounded with better abrasion, crack initiation, and heat resistance than natural rubber. SBR extrusions are smoother and maintain their shape better than those of natural rubber.

SBR was originally developed as a general purpose elastomer and it still retains this distinction. It is the largest volume and most widely used elastomer worldwide. Its single largest application is in passenger car tires, particularly in tread compounds for superior traction and treadwear. Substantial quantities are also used in footwear, foamed products, wire and cable jacketing, belting, hoses, and mechanical goods.

COMPOSITES OF SBR

Composite materials are defined as the materials made up of two or more components, consisting of two or more phases. They are divided into three categories, viz. (i) Particulate filled composites, (ii) Fibre filled composites, and (iii) Interpenetrating network composites.

Many commercial polymeric materials are composites and often useful as compared with individual polymers from which they are made, as the composites exhibit higher strength, stiffness, and dimensional stability. Composites also improve heat distortion temperature and mechanical damping, besides reducing permeability to gases and liquids' All these benefits arc obtained at lesser cost.

In rubber industry, fillers like, calcium carbonate, zinc oxide, mica, and china clay arc used, besides carbon black and silica. It is generally agreed that adhesion caused by van der Waals forces arising between the filler and the matrix phases impart reinforcing effects, but for superior reinforcement, high degree of adhesion between filler surface and the matrix phase, produced by chemical interaction is desirable.

To understand the matrix-filler interaction for elastomeric matrix and inorganic fillers the study has been under taken by selecting SBR and inorganic fillers, such as calcium carbonate, flyash. and barium sulphate. In this paper the effect of particle size and shape, nature of elastomer-filler interaction on the properties like tensile strength, modulus at 100, 200, 300, 400 per cent, elongation at break, and hardness are reported.

SBR BASED ON CARBON BLACK AND NANOCLAY

Carbon black (CB) is the most important reinforcing filler used in the rubber industry. About 90% of the worldwide production of CB is used in the tire industry in which the CB serves as reinforcing fillers for improving tear strength, modulus, and wear characteristics of the tires. As the source of CB is petroleum, the preparation and processing of CB is hazardous. Moreover, CB imparts black colour to rubber. In the past two decades, research was aimed to develop other reinforcing agents to replace CB in rubber compounds such as sepiolite, kaolin, and precipitated silica. These fillers are inorganic in nature and incompatible with organic polymer matrices. Thus, the reinforcing effect of these fillers was much lower than that of CB. However, the layered silicate nano-fillers have already been developed. In those nano-fillers, the silicate layer surfaces have been effectively modified to render them organophilic so that the organically modified nano-fillers can significantly enhance the critical performance properties of polymer–clay composites. The unique properties, imparted by nanoclay (NC) to rubber composites, have opened up a new prospect in developing CB–NC-hybrid nanocomposites via facilitating the possible partial replacement of CB with NC in rubber products without affecting the critical performance properties.

The aim of this work, the unique properties, imparted by nanoclay to rubber composites, have opened up a new prospect in developing carbon black-nanoclayhybrid composite via facilitating the possible partial replacement of carbon black with nanoclay in rubber products without affecting the critical performance properties.

THERMAL STABILITY AND FLAMMABILITY OF SBR

Recent years have witnessed a great interest in polymeric materials with special properties, resistant to the action of considerably lowered or elevated temperature, flameretardant or non-flammable, being characterized by suitable mechanical strength at the same time.

In the making of polymeric materials with increased thermal stability and resistance to the action of fire, one uses various types of mineral fillers, such as calcium carbonate, silica, halloysite, or montmorillonite. From recent literature reports it follows that fibrous aluminosilicate (attapulgite, ATT) can also be active mineral filler.

ATTof chemical formula:Mg5[Al]Si8O20(OH)2–(OH2)4 9 4H2O is characterized by a high sorption capacity ranging from 15 to 30 mval/100 g, showing features of a molecular sieve as zeolites. ATT is widely used as absorbent, catalyst carrier, disinfectant, adhesive agent, food or drug additive as well as filler of polymers. It has a three-level structure.

Single fibrous crystals are the smallest structural unit with a length of 500–2,000 nm and a diameter of 10–30 nm. Each single crystal consists of many laminar units such as tetrahedrons comprising two silicon atoms and two oxygen atoms. Between neighboring layers are five aluminum atoms tetrahedrally combined with five oxygen atoms. Individual structural units are combined with oxygen atoms to form a

crystalline structure in the form of fiber. Particular fibrous nanocrystals are arranged in bundles that undergo agglomeration visible in a micro-scale as large solid particles.

This article presents the results of examining the effect of ATT and its modification procedure on the thermal stability and flammability of styrene–butadiene rubber (SBR) cross-linked by means of an organic peroxide or sulfur. A particular attention was paid to the structure of the rubber combustion residue. The effect of the synergic action of ATT and carbon nanofiber or silica on the properties of cross-linked SBR was also assessed.

REINFORCEMENT OF STYRENE-BUTADIENE RUBBER WITH SILICA

Silica is an important filling materials in rubber industry. The application in rubber process was restricted by its less processability compared with carbon black once a time. The first application of composite polymer materials silane coupling agents in real process was in 1947 by Ralph. He made the polyester complex material from fiberglass cured with propenyl-trimethoysilane. Double intensity of the material was obtained. It was found that the silane coupling agents can enhance the consistency between silica and rubber, and improve processability and mechanical property of rubber. In 1970s, the application of silica in rubber process increased remarkably. At the same time, the research and development of the silane coupling agents expanded rapidly. The study of mechanism of the silane coupling agents was begun in 1960s. The four step reaction model of the process was put forward by Arkles. In this model, there was usually only one bond from each silica to the substrate surface, and the other two silanol groups were present either in condensed or free form. The relative stability of the organosilane bonded to silica-surface with Schiffs base was measured. The interaction of triethoxysilane (TES) and bis[3-triethoxysilylpropyl]-tetrasulfane (TESPT) with silica was studied by means of IR spectroscopy. The spectral features of Si—O bonded were identified. The IR spectra showed that the treatment of silica with TES (or TESPT) strongly decreased the amount of adsorbed water, whereas two Si—O—Si bridges were formed between TES (or TESPT) and the silica surface. Now, more analytic instrument is brought to get the surface information of material and study the reinforce ageing process of complex material. The chemical bond theory has been put forth to explain the mechanism of the silane coupling agents .

Quantum chemistry deals with atoms and molecules based on their electronic structure and motion, and unveil the relationship between the property of materials and the strange quantum effects. By quantum chemistry, general conclusions can be drawn at the level of electrons. Then the vital prediction of chemical activities can be acted as the guidance for further investigation. In this paper, quantum chemistry computation is employed to investigate the difference of chemical bonds formed by different silane coupling agents, silicon and styrene-butadiene rubber (SBR). The correlation between the mechanical property and the chemical bonds is analyzed on the basis of the differences.

ADHESION PROPERTIES OF SBR

Recently, we have carried out several investigations on the viscosity, tack, peel and shear strength of natural rubber (NR) and epoxidized natural rubber (ENR). It has been shown that the viscosity and tack of natural rubber-based adhesive increases with resin content due to the concentration effect of tackifier resin. The peel strength generally increases with resin content, an observation which is attributed to the wettability of substrates.

On the other hand, shear strength of the adhesive decreases gradually with increasing resin content as a result of decreasing cohesive strength of adhesive as resin loading is increased. For a fixed resin content, shear strength increases with increasing coating thickness suggesting that shear strength is thickness-dependent. With regard to ENR-based pressure-sensitive adhesives, results show that peel strength passes through a maximum at 40 phr of tackifying resin. However, the shear strength indicates a gradual decrease with increasing resin loading due to the decrease in cohesive strength of adhesive. ENR 25 consistently exhibits higher peel strength and shear strength than ENR 50. The viscosity and loop tack of ENR-based adhesive increases with increasing zinc oxide concentration.

For the peel strength, it increases with zinc oxide concentration up to 30–40 phr of filler and drops after the maximum value. However, with respect to the effect of rubber blending on the adhesion property of pressure-sensitive adhesives, there is no study reported so far. We have thus carried out a systematic investigation to evaluate the effect of % SBR on the viscosity, tack and peel strength of SBR/SMR L-based pressure sensitive-adhesive.

The rubbers were masticated on a 2-roll mill for 10 minutes. Different blend ratios of SBR/SMR L corresponding to 0, 20, 40, 60, 80 and 100% SBR were prepared. For each adhesive formulation, 5 g of the rubber blend was used. The rubber blend was then dissolved in 30 ml of toluene. The rubber solution was kept in a conditioned room for 24 hours before the addition of phenol-formaldehyde resin.

In order to study the effect of phenol-formaldehyde concentration on the adhesion properties, three different weights i.e. 2, 4 and 6 g corresponding to 40, 80 and 120 parts per hundred parts of rubber [phr] of resin were added to the rubber solution to prepare the adhesives. After the addition of resin, constant stirring with glass rod was carried out to ensure a homogeneous adhesive was formed. The adhesive was left for at least 3 hours prior to testing.

PROPERTIES OF SILICA-FILLED STYRENE-BUTADIENE RUBBER COMPOSITES THROUGH PLASMA SURFACE

Since the beginning of polymer technology, the improvement of polymer properties has been a subject of common interest. In the case of amorphous elastomers like styrene-butadiene rubber (SBR), which do not undergo strain-induced crystallization, the use of filler can improve the processibility, mechanical properties and reduce cost of the rubber articles.

Carbon black is considered as an unbeatable and universal reinforcing filler in weak elastomers like SBR. But in an effort to obtain the required properties and to reduce the cost, several new materials have been tried as fillers. Several research has reported on the substitution of carbon black with other fillers like mica without adversely affecting the mechanical properties. But silica is gaining more importance compared to carbon black in the reinforcement of elastomers, especially in the tire industry where carbon black was playing the main role. This is because of the low hysteresis, leading to lower rolling resistance at equal wear resistance and wet grip shown by the silica filled vulcanizates compared to black filled cases.

The surface of silica contains hydroxyl groups which makes the silica surface polar. According to Wolff and Wang, the surface energies of silica are characterized by a lower dispersive component and a higher specific component.

The lower dispersive components cause weak rubber–filler interactions while higher specific component leads to strong interactions among the silica particles. According to transmission electron microscopy (TEM) observations of silica surface, silica with low silanol number, N, (number of silanol groups per unit surface area of silica particles), i.e. N<0.1 (0.1nm^2), cannot form aggregates and/or agglomerates. Also, the number of the average size of the agglomerates which was formed without rubber matrix increased with the increase in N value of silica. Therefore, silica can interact very well with polar elastomers. But at the same time, the polar surface of silica enhances filler–filler interactions also resulting in strong intermolecular hydrogen bonds between the hydroxyl groups of silica. The polar surface leads to the adsorption of curatives and delay the cure time, scorch time and reduce the cure torque of rubber compounds containing silica. Due to such strong intermolecular interactions, it can aggregate tightly resulting in its poor dispersion in the rubber compound. Owing to these reasons, the silica surface should be modified by coating with some materials. This can be done either with some coupling agents or by coating the filler surface with some monomer followed by polymerization of the coated monomer. The commonly used coupling agent is bifunctional organosilanes like bis(triethoxysilylpropyl)-tetrasulfide (TESPT). The silane coupling agent reacts with silanol groups on the surface of silica and form a siloxan bond. The silane molecule on silica can react with the rubber molecule to form a crosslink between silica and the polymer.

The use of plasma polymerization was first practiced in the microelectronic industry for the deposition of thin films and isnowbeing used for the modification of surfaces. The advantage of the technique is that the surface modification can be done without modifying any bulk properties of the material. Plasma state can be produced by supplying high energy dose which can produce ionization of gas molecules giving a mixture of electrons, charged particles, free radicals, and excited atoms/molecules. UV radiation also will be produced due to the inelastic collisions between particles that exchange their energy. By the application of plasma to a surface, four main effects are produced. These are surface cleaning, surface ablation, surface crosslinking and surface chemical modification. So, it is clear that plasma chemistry creates a new world of possibilities for the effective modification of polymer/material surface. It is considered as an alternative to silane coupling treatment which is common in the rubber industry. This is because of the environmentfriendly nature of plasma polymerization technique.

Research publications relating to plasma polymerizations are extensively available in the literature. Among them, the studies conducted by Akovali and Ulken16 on the plasma polymerization coating to carbon black are noteworthy. They have reported improved mechanical property such as tensile strength. However, publications relating to the effect of plasma polymerization coating of silica on its dispersion and mechanical properties in elastomers are relatively rare.

This article deals with the by plasma polymerization coating of acetylene on silica surface for its modification. The surface modified silica was then used as a filler in SBR and performance of the composites with unmodified and silane treated silica was compared. The optimization of plasma treatment was carried out by changing the treatment time and various plasma parameters such as plasma power and gas pressure. The plasma modification on silica surface was characterized by the specific surface area determination and fourier transform infrared spectroscopy (FT-IR). The cure curves of filled rubber compounds were analyzed for the cure kinetics and also for the assessment of filler reinforcement, by calculating Woolf reinforcing parameter. Scanning electron microscopy (SEM) was used to analyze the silica filler dispersion in the SBR matrix.

CONCLUSION

SBR hybrid nanocomposites have been studied by different proportion of CB and NC. The optimum loading of carbon black was found to be 20 phr. SBR-carbon black-clay hybrid composites with 20 phr HAF and 5 phr Nanoclay were shown in excellent mechanical properties, thermal stability and further loading of organo-modified nanoclay the respective properties found to be decreases due to agglomeration of the organo-modified nanoclay on SBR nanocomposites. Since, there is high amount agglomerate in high filler dosage composites; these agglomerates played the role of an obstacle to molecular chain movement of the SBR, thereby initiating failure under stress.

A considerable increase in the resistance of cross-linked SBR and its reduced fire hazard result to a large extent from the structure of the boundary layer formed during the combustion of polymeric materials.

The performance of filled composites based on SBR and silica was analyzed giving emphasis to the cure reaction kinetics, reinforcement parameter af and mechanical properties. Regardless of the surface modification given to the silica filler, the cure reactions of all the rubber compounds followed first-order kinetics. A deactivation in the cure of the rubber compounds containing silica filler was observed compared to that of unfilled rubber, as indicated by the cure reaction rate constants.

The properties of SBR reinforced by modified silica was measured. Quantum chemistry computation was employed to investigate the difference of chemical bond formed by different silane coupling agents, silicon and SBR.

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