BLENDS AND COMPOSITES OF NATURAL RUBBER AND EPDM RUBBER WITH POLAR RUBBERS

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Recent developments in polymer blends and composites from non-polar/polar rubbers are reviewed in this article. Blending of elastomers is frequently used to enhance the performance/processing characteristics of rubber compounds. Many of the elastomer blends are characterized by a two-phase morphology, narrow interface, and poor physical and chemical interactions across the phase boundaries resulting in poor mechanical properties. To overcome this, compatibilizers and reactive blending are generally used which improve the interfacial adhesion and reduce the coalescence between non-polar/polar rubbers. These blend systems are immiscible and the compounding ingredients are nonuniformly distributed in two phases depending on their affinity, rate of diffusion and reactivity to different components.

Keywords: Composites, EPDM rubber, Polar rubbers, Rubber blends

INTRODUCTION

Initially synthetic rubbers, like styrenebutadiene rubber (SBR) and butadiene rubber (BR), were introduced counterparts for natural rubber (NR) during World Wars I and II. Normally, synthetic rubbers provide inferior mechanical properties compared to NR due to the lack of strain-crystallization. Synthetic rubbers, like nitrile rubber (NBR), ethylene-propylene rubber (EPM and EPDM) and chlorinated polyethylene (CM) are widely used for their special properties, such as better ageing, ozone, oil and heat resistance. Along with the developments in synthetic rubbers, new vulcanization systems were also designed to achieve proper vulcanization with good properties.

Blending or mixing of two or more elastomers is carried out for three main reasons: improvement of the technological properties of an elastomer, for better processing behavior and for reducing the compound cost. Blending is thus a method of obtaining optimum properties and performance at a reasonable cost, if the technical properties are satisfied.

Mixtures and blends occur at different hierarchical scales in the material range employed in the rubber industry. Composite products such as tyres, hoses, beltings and air springs are composed of metal wire, textile cord and elastomeric compounds which form a rubber matrix. The rubber matrix itself may be a mixture of elastomers, fillers and plasticizers.

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Fillers, which were originally used to reduce the compound coast, now play an important role in the rubber industry as well. It is known that the incorporation of carbon black (CB) can stiffen and reinforce the amorphous elastomers due to chemical and physical interactions between the filler and the polymers. Replacement of CB by silica was another important development in rubber technology in the late 20th century (Baranwal et al., 2001). With the development of a silane coupling agent, silica started to be used widely in elastomeric compositions to reduce the rolling resistance of tyres, which will subsequently reduce the consumption of fuel.

Rubber blends, based on the miscibility of constituent polymers, can be divided into three broad classes: miscible, partially miscible and immiscible blends. A miscible blend is essentially a new single phase rubber obtained by the molecular level mixing of two or more rubbers. Such blends have the advantage of stability, easy mixing etc. Most of the properties of such blends will be a weighted average of the constituent rubbers. A totally immiscible polymer blend on the other hand will be a heterogeneous polymer blend with poor mechanical properties due to poor adhesion between the distinct phases. So, a partially miscible or compatibilized rubber blend will be the most attractive one from a practical view point.

Compatibilization is the modification of the interface in immiscible polymer blends in order to refine and stabilize their phase structure. The better the compatibility between two phases in the blend, the smaller are the dispersed phase domains.

In non-polar/polar rubber blends often a cure mismatch can occur. This is due to the difference in solubility of the curatives in the constituent rubbers of the blend, as well as different reactivity of the rubbers with the curatives employed. In this way an imbalance in crosslink densities of the different rubber phases in the blends can occur. In such cases lack of optimum crosslink densities in the constituent phases result in poor mechanical and dynamic properties. However, if the blend and the compounding ingredients are selected carefully, blending of different rubbers is an effective and economic method to achieve a desired combination of properties. Potential merits of rubber blends are; improved solvent resistance, improved processability and manufacturing flexibility along with improved productivity.

Concerning the morphology of phase separated rubber blends, the main factors governing the structure of the entire system are (1) the interfacial tension, which influences the size of the phases; (2) the viscosity of the matrix; and (3) the shear stress. Co-continuous blend morphology is observed only for rubbers with similar viscosities. The relative mixing viscosities of the components affect the size and the shape of the domain zones. Generally, the matrix is formed by the phase with lower viscosity, while the one with higher viscosity forms the dispersed phase. Homogeneity of mixing can be controlled either by using proper mixing conditions or by the addition of compatibilizers.

Dielectric measurement (Azima *et al.*, 2001) is an important tool to investigate the compatibility of different polymer blends. The dielectric properties of heterogeneous blends are affected by interfacial phenomenon, which arises due to phase separation in polymer blends. This type of phase separation has been detected by dielectric relaxation technique (Fujimoto *et al.*, 1968). Recently a number of works have been conducted by measuring dielectric

constants in order to describe the compatibility of different polymer blends (Azima *et al.*, 2001).

Blending of elastomers having different polarity is always a challenge due to the incompatibility, which is further aggravated by non-uniform distribution of fillers (Hess *et al.*, 1967) and curatives (Gardiner, 1968) in the constituting elastomeric phases. It is expected that this technique would produce blend vulcanizates having improved physicochemical properties.

Studies with non-polar/polar rubber blends have demonstrated that these materials have a range of properties which make them suitable for the production of several products.

Non-polar/polar rubber blends

NR/NBR blends

Nitrile rubber (NBR) is a copolymer of acrylonitrile and butadiene manufactured by emulsion polymerization. This rubber is one of the most widely used commercial rubbers for manufacturing technical rubber goods. By selecting appropriate acrylonitrile content, the properties of the rubber can be tailor made in order to use NBR for different applications like roll covers, hydraulic hoses, conveyor belting, oil resistant packers, seals for all kinds of plumbing and appliances. It has excellent temperature resistance properties with a wide short- and long-term temperature ranges (as much as -40 °C to +125 °C). Like most unsaturated thermoset elastomers, NBR requires formulating with added ingredients, and further processing to make useful articles. Additional ingredients typically include reinforcement fillers, plasticizers, weather protectants and vulcanization agents (El-Nashar, 2003).

Because of the structural dissimilarity, NR and NBR are immiscible, and compatibilizers are used during their blending. Chloroprene rubber (CR) as a compatibilizer for NBR/NR blend has been reported (Shaji *et al.*, 2012). Also, CR has many advantageous like good oil resistance, toughness, dynamic flex life and adhesion capacity. Thomas *et al.* (2005) have studied the properties of 20:80 NR–NBR blends with CR as compatibilizer. The tensile strength, tear resistance, and abrasion resistance of the gum vulcanizates of the blend were improved by the compatibilizing action of CR up to 5 parts per hundred parts of rubber.

A new class of membranes were developed from blends of nitrile rubber (NBR) and epoxidized natural rubber (ENR) and their morphology, miscibility, mechanical, and viscoelastic properties were discussed (Asha et al., 2005). The morphology of the blends indicated a twophase structure in which the minor phase is dispersed as domains in the major continuous phase. The performance of NBR/ ENR membranes has been studied from the mechanical property measurements. The viscoelastic behavior of the blends has been analyzed from the dynamic mechanical data and various composite models have been used to predict the experimental viscoelastic data. The homogeneity of the system was further evaluated by Cole-Cole analysis. Finally, a master curve for the modulus of the blend was generated by applying the time-temperature superposition principle. The tensile strength of the blend lies between that of pure components. Among the blends studied, the NBR/ENR 50/50 composition showed the highest strength due to its co-continuous morphology.

The detailed investigations of the transport behavior of a series of aromatic solvents through crosslinked nitrile rubber/

epoxidized natural rubber blend membranes were carried out (Asha et al., 2005). This work focuses mainly on the diffusion and sorption behavior of organic solvents through crosslinked NBR/ENR blends. The effects of blend composition, temperature and nature of penetrants on the diffusion process have been studied. The solvent resistance of the blend increases as the volume fraction of NBR increases. The equilibrium solvent up-take decreases as the temperature increases because of the leaching out of additives from the rubber compound. The diffusion and permeation coefficient values decrease with an increase in the molar volume of the penetrants. The scanning electron micrographs of NBR/ENR blends are shown in Figure 1. It is seen that in 30/70 blend, NBR phase is dispersed in the continuous ENR matrix. In 50/50 blend, both ENR and NBR form continuous phases leading to a co-continuous morphology. In 70/30 blend, ENR phase is the dispersed phase in the continuous NBR phase. Because of the dispersed nature of ENR phase in 70/30 blend, the continuous, NBR phase restricts the transport process.

Hanafi et al. (2001) studied the curing and mechanical properties of nitrile and natural rubber blends. Two series of blends were prepared, *i.e.*, NBR/NR and NBR/ENR 50 blends. Results indicate that the scorch time and cure time increase with increasing NBR content in both blends. In NBR/ENR 50 blend the increasing content of NBR increases the maximum elastic torque, torque difference, tan δ and viscous torque. However, in NBR/NR blends the reverse trend is observed for maximum elastic torque and torque difference. In both blends modulus at 100 and 300 per cent elongations increases with increasing NBR content, whereas tensile strength and elongation at break show a decreasing trend.

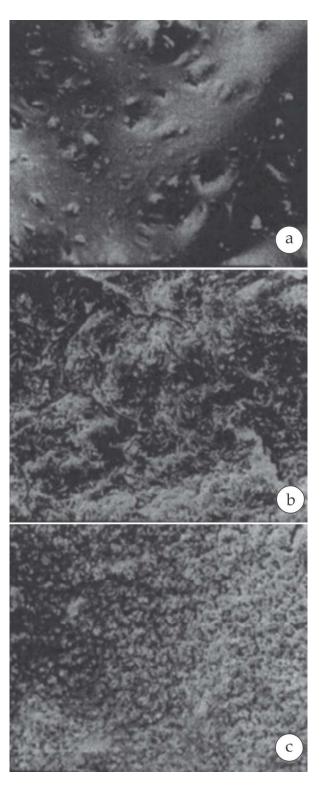


Fig. 1. SEM photographs of (a) 70/30 NBR/ENR, (b) 50/50 NBR/ENR and (c) 30/70 NBR/ENR blends

Carboxylic functional groups have been introduced into rubbers in order to crosslink the polymer chains or to attach them to other molecules or surfaces. Also, the group is added to significantly improve the abrasion resistance of NBR while retaining excellent oil and solvent resistance. XNBR compounds provide high tensile strength, toughness, abrasion resistance and good physical properties at high temperatures. Also, XNBR generally exhibits poor hysteresis properties and reduced cold temperature flexibility. However, chemical resistance of XNBR is considerably superior (Brown *et al.*, 1957).

NR is known to exhibits numerous outstanding properties, and reinforcing fillers are necessarily added into NR in most cases in order to gain the appropriate properties for speciûc applications. A wide variety of particulate fillers are used in the rubber industry for various purposes, of most important which the reinforcement, reduction in material costs, and improvements in processing (Waddell et al., 1996). In most applications, carbon black (CB) and silica have been used as the main reinforcing fillers. In general, a CBreinforced rubber has a higher modulus than a silica-reinforced one. However, silica provides a unique combination of tear strength, abrasion resistance, ageing resistance, and adhesion properties (Hashim et al., 1998). In tyre treads, silica provides a lower rolling resistance at equal wear resistance and wet grip than CB (Brinke et al., 2003). However, NR exhibits a limited ozone resistance and a high dependence of dynamic properties with temperature (T_a) (Arroyo et al., 2007).

Blending of elastomers has been often used to obtain an optimum physical properties, processability and cost. NR shows very interesting physical properties

because of its ability to crystallize under stretching. The blend vulcanizates thus produced exhibit enhanced physical properties by judicious selection of the NR: XNBR ratio (Naskar *et al.*, 2001).

Pal *et al.* (2008) have examined XNBR and NR blends having various compositions. It is found that the XNBR plasticize the NR during its mastication. Vulcanizate properties of NR such as modulus, abrasion resistance and compression set are improved at a blend ratio of 80:20 XNBR/NR.

Naskar et al. (2001) studied the successful use of bis (diisopropyl) thiophosphoryl trisulphide (DIPTRI) and bis (diisopropyl) thiophosphoryl tetrasulphide (DIPTET) as a novel coupling agent and accelerator, respectively, to covulcanize an elastomer blend comprising polar carboxylated nitrile rubber (XNBR) and non polar natural rubber (NR). These compounds are capable of forming a chemical link between these dissimilar rubbers to produce technologically compatible blend. The blend vulcanizates thus produced, exhibit enhanced physical properties that can further be improved by adopting a twostage vulcanization technique and also by careful selection of the NR: XNBR ratio.

NR/CR blends

Chloroprene rubber (CR) is well known for its high gum vulcanizate strength arising from strain-induced crystallization. It has excellent physical properties like weather resistance, thermal resistance and low temperature properties. Owing to the presence of halogen in the rubber molecule, CR exhibits better flame resistance than other hydrocarbon rubbers.

Natural rubber is widely known to possess good mechanical properties such as high tensile and tear strengths due to its

ability to crystallize upon stretching. The elasticity and dynamic properties of NR are also excellent. However, due to the existence of numerous reactive double bonds on the molecular backbone, NR is highly susceptible to degradation by thermal ageing and ozone attack. In addition, oil resistance of NR is relatively poor, compared to polar synthetic rubbers such as CR or NBR. To overcome such shortcomings, NR is frequently blended with synthetic rubbers such as NBR or CR. Recently, blends of NR/CR have been extensively studied (Saad et al., 2001; Helaly et al., 2002; Das et al., 2005). The incorporation of CR into NR helps to improve oil and thermal resistance of NR. As CR and NR are cured using different curatives, careful adjustment of the cure system is essential in order to avoid nonuniform distribution of crosslinks within the phases. Cure system of NR/CR blend therefore generally includes sulphur, with thiourea derivatives other conventional accelerators (Hofmann, 1989). Apart from the curing system, the difference in polarity of the blend partners could also bring about high interfacial tension which is detrimental to the mechanical properties of the blend (Tinker et al., 1998).

The use of silica as reinforcing filler in CR/NR blend and the effect of blend ratio on properties of silica-filled CR/NR blend was investigated (Sae-oui et al., 2007). The mechanical properties as well as the resistance to ageing, oil and ozone of the blends were focused. Silica was selected as a reinforcing filler due to its unique interaction with CR. The results reveal that, due to the better filler dispersion and the greater crosslink density, the silica-filled CR possesses lower compound viscosity and better mechanical properties, compared to the silica-filled NR. The ageing properties, oil and ozone resistance of the silica-filled CR are also significantly better than those

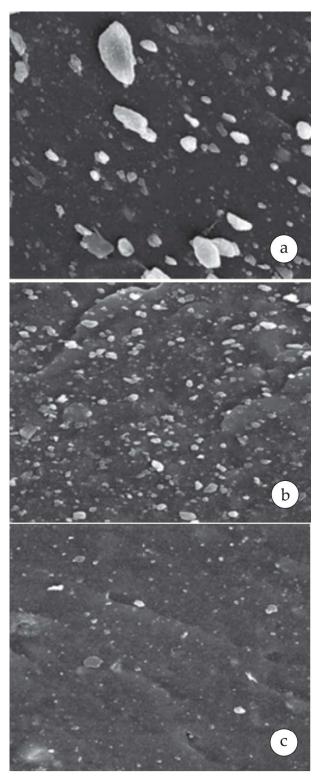


Fig. 2. SEM photographs of (a) silica filled NR, (b) silica filled 50/50 NR/CR blend and (c) silica filled CR

of the silica filled NR. The mechanical properties and the resistance to degradation of the silica-filled CR/NR blends are mainly governed by the blend morphology (Fig. 2). It is found that good mechanical properties in association with adequately high resistance to degradation from thermal ageing and oil are obtained when CR remains in the blends. Even though the ozone cracks are found in all blends, the results reveals that considerable improvement in ozone resistance is achieved with increasing the CR content.

CR is generally blended with other diene rubbers for improving the oil resistance, ageing resistance and flame resistance of the blend vulcanizates. When it is blended with diene rubbers like NR (Gaczynski et al., 1974), EPDM (Sutton, 1964) etc. the physical properties of the vulcanizates are greatly affected. In a blend of elastomers, which differ in polarity, there occurs a concentration gradient for the fillers and the curatives which further leads to diffusion of curatives from less polar diene rubber to more polar chloroprene rubber. Earlier researchers reported several studies regarding the cure behavior of CR/EPDM (Ishitobi et al., 1971; Younan et al., 1998) blend systems.

EPDM/NBR blends

Elastomers based on more network precursors have become technologically important material for their diverse applications. Their physical and chemical properties recommend them as engineering materials for chemical industry, automotive and aircraft production and in many other areas. The blending of NBR and EPDM rubber was performed to achieve the best properties from each component. Blending EPDM with NBR can improve the disadvantages of EPDM because polar NBR

exhibits excellent solvent resistance and adhesion properties. NBR has high resistance to swelling in oils and solvent but suffers from poor ozone resistance and heat ageing properties (Mohamed et al., 1998). EPDM is a saturated, nonpolar rubber (*i.e.*, very low -C=C- content). EPDM exhibits several properties, including balanced heat stability, ageing resistance, low temperature flexibility and water resistance; therefore, EPDM is widely applied in many rubber products. The application of EPDM is restricted due to its poor solvent resistance and adhesion properties (Ismail et al., 2003). The blend of such two polymers attracts the attentions of many researchers to tailor a blend which withstands ozone, heat ageing, oil and solvents swelling with desirable mechanical characteristics. It could be used for the production of automotive brake hoses, automotive radiator hoses, motor mounts, transmission belts, conveyor belts, sheets and rolls. Jovanovic et al. (2012) studied cure kinetics, mechanical properties, morphology and thermal stability of composites based on carbon black reinforced NBR/EPDM rubber blends. The maximum and minimum torque increases with increase in CB loading, but the cure rate index (CRI) decreases. Two separate T_g values for CB reinforced composites based on EPDM/NBR rubber blends were observed. The energy of activation, E_a for the NBR/EPDM/CB rubber blend composite is lower (45.1 kJ mol⁻¹) compared to E₂ for the rubber based on NBR (156 kJ mol-1) and EPDM (75 kJ mol⁻¹), which indicates easier formation of blend (Jovanovic et al., 2013).

The rheometric characteristics, curing kinetics, mechanical properties before and after thermal ageing and morphology of nanocomposites based on various network precursors were reported. (Jovanovic *et al.*, 2012). The results obtained demonstrated a correlation between the calculated

activation energies of cross linking (E_{ac}) and reversion (E_{ar}) with mechanical properties. EPDM/NBR (20/80) blend showed maximum tensile strength values and synergism.

Grafting of maleic anhydride (MAH) on olefinic polymers has been carried out in the presence of initiators (Norbert *et al.*, 1990). The MAH residue attached to EPDM rubber has been determined (Coutinho *et al.*, 1994). Moulded composites having good water, impact and heat age resistance, have been made from blends of polyamide and polyester resins and EPDM rubber modified with MAH (Thomes *et al.*, 1988). Botros *et al.* (2006) prepared of MAH-g-EPDM and evaluated its performance as a compatibilizer in EPDM/NBR elastomer

blend. The effect of blend ratio on heat resistance and stability against UV radiation of compatibilized blends were also discussed. In order to overcome the problem of in-homogeneity between EPDM and NBR a polar group was introduced into EPDM via grafting with MAH.

The effect of carbon black fillers *viz.*, semi reinforcing furnace (SRF), high abrasion furnace (HAF) and intermediate super abrasion furnace (ISAF) blacks on the cure, swelling and mechanical properties of 70/30 EPDM/NBR blend have been investigated (Manoj *et al.*, 2011). The maximum torque values have been increased with increase in filler loading. Filled systems were found to exhibit a

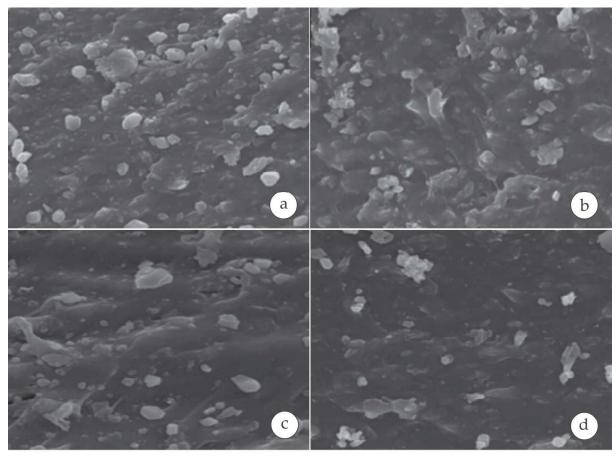


Fig. 3. SEM photographs of 15 phr carbon black filled 70/30 EPDM/NBR blend (a) pure blend, (b) SRF, (c) HAF and (d) ISAF

reduced solvent uptake compared to the unfilled sample. Blends loaded with ISAF exhibited the lowest toluene uptake among the carbon black filled systems due to the better filler reinforcement. A more uniform morphology has been observed for ISAF-filled samples compared to the other samples and is shown in Figure 3. The improvement in the mechanical properties has been observed to be the highest for ISAF-filled samples followed by HAF and SRF filled systems. This could be attributed to the smaller particle size of ISAF black.

To enhance the physical properties of blends, it is important to understand the microstructure and interactions between the two phases of the blends. There exist many physical probes for characterizing the structure and properties of polymer blend (Liu et al., 1995). However, only a limited number of probes are available for characterizing free-volume properties because of the small size. Positron annihilation spectroscopy is a sensitive probe for detecting free-volume holes in polymeric materials at an atomic scale (Peng et al., 1994). The effect of silica on the freevolume properties of an EPDM/NBR (75/25) blend were also examined with positron annihilation spectroscopy and doppler broadening of annihilation radiation.

The physical properties of the cured blends are influenced by vulcanization and filler distribution. Normally, rubbers are vulcanized by cure systems based on sulphur or peroxide. The common feature of these systems is that they all require activation energy in the form of heat. The extremely high cure temperatures (~150–180 °C) have the disadvantage that the final properties of the finished product may be affected by a variety of uncontrolled side reactions, happened during vulcanization. On the other hand, radiation curing is a

process that differs form thermal curing, as it is carried out at ambient temperature under controlled conditions. Radiation can produce crosslink densities similar to that obtained by sulphur curing, but the net effects are not identical. The type of crosslink formed in this method (–C–C–) give rise to better mechanical properties at higher temperature (Coran *et al.*, 1994). This might be reflected in better high temperature performance as improved hot tear strength. Also, it can lead to greater abrasion resistance (Bohm *et al.*, 1972) and superior ozone resistance (Basfar *et al.*, 1994).

Filler distribution in the blend affects the properties, as it is controlled by the molecular weight of the polymer and filler dispersion in each phase and chemical interaction between polymer and filler (Bandyopadhyay *et al.*, 1995). Radiation degradation of polymer blends containing NBR/EPDM was studied by DSC (Traian, 2001).

Both NBR and EPDM rubbers are categorized as predominantly radiation crosslinkable polymers which would account for the increase in tensile strength (TS) values with radiation dose up to 150 kGy (Woods et al., 1994). Degradation may predominate at doses higher than 150 kGy (Banik et al., 1999). High stress transfer between the rubber matrix and filler particles is expected to take place in a strong rubber-filler interface. Moreover, the different types of group that exist on filler surface participate in physical as well as chemical bond formation at the interface between the filler and rubber matrix, on irradiation (Franco et al., 2001).

Magda et al. (2007) studied a blend of NBR and EPDM (50/50) loaded with different concentrations of HAF cured by gamma irradiation. The mechanical, physical, electrical and thermal properties of these blends have been studied with respect to filler

loading as well as irradiation dose. In general, blends of NBR/EPDM loaded with HAF carbon black may be suitable for industrial applications requiring high strength, semiconductivity with oil resistance.

EPDM/CR blends

CR is an extremely versatile synthetic rubber with more than 75 years of proven performance in a broad industrial spectrum due to its unique combination of properties

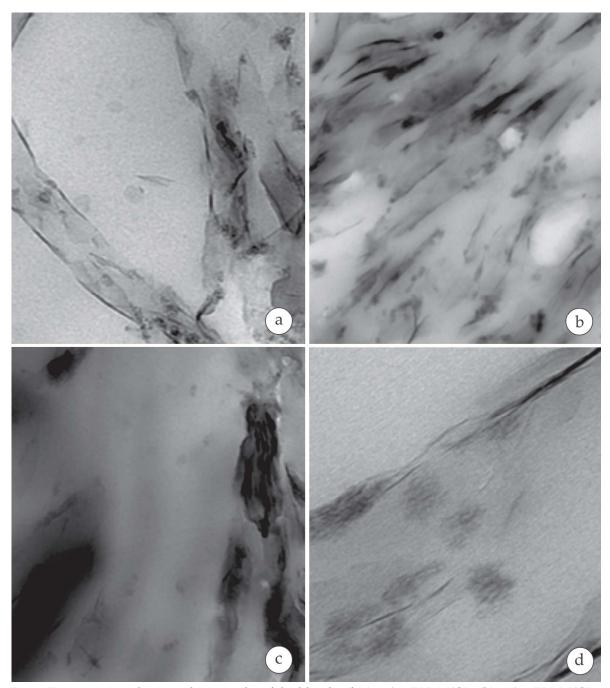


Fig. 4. Transmission electron photographs of the blends of (a) 25/75 EPDM/CR, (b) 50/50 EPDM/CR, (c) 75/25 EPDM/CR and (d) 25/75EPDM/CR filled with 10 phr nanoclay

such as ozone resistance, oil resistance, toughness, dynamic flex life, good adhesion to other materials and heat resistance up to 100 °C (Das *et al.*, 2004). This rubber has been the material of choice for mouldings for different and extrusions type like reinforced

hoses, roll covers, belting, air spring bellows, cable sheathing and insulation for low-voltage cables, sponge rubber, corrosion-resistant linings and numerous other applications. To meet these emerging needs and also for new material development for

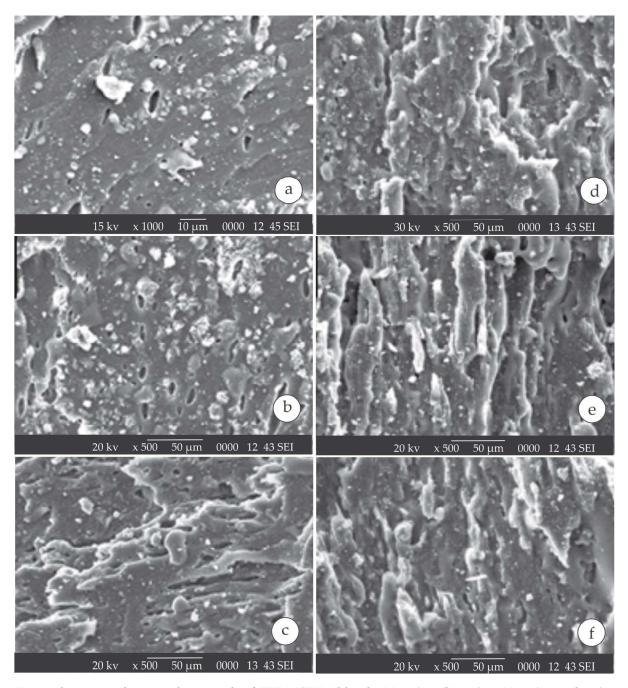


Fig. 5. Scanning electron photograph of EPDM/FKM blends (a) 80/20, (b) 60/40, (c) 50/50 and 50/50 blends containing (d) 2.5, (e) 5, (f) 10 phr MA-g-EPDM

more demanding applications, improvements in heat resistance and cut growth resistance are very desirable. The above requirement for CR products could be satisfied by blending with polyolefin elastomers such as ethylene–propylene rubber (EPR) or EPDM, which have better resistance to heat, ozone, and cut growth (Deuri *et al.*, 1987). However, these CR/EPR or EPDM blends are incompatible (Ramesan *et al.*, 2001).

Das et al. (2011) studied the reinforcement and migration of nanoclay as filler in CR/EPDM rubber blends. With the incorporation of less than 9 wt. per cent nanoclay, the dynamic storage modulus of such a blend increases from 2 to 54 MPa. This tremendous reinforcing as well as the compatibilization effect of exfoliated nanoclay platelets in the interface of CR and EPDM was observed in TEM (Fig. 4). Das et al. (2011) suggested a method for compatibilization of incompatible rubber blends. The compatibilizing action of the pristine montmorillonite clay was investigated which showed the presence of clay at the interface of the non-polar/polar rubber blends (Essawy et al., 2004).

EPDM/FKM rubber blends

commercially important One fluorocarbon rubber (FKM) is made by copolymerizing the fluorinated analogs of ethylene and propylene. This rubber has a density of 1.85 g cm⁻³ and has a service temperature exceeding 200 °C. Fluoroelastomers are widely used in many industrial applications due to their excellent resistance to heat, oil and solvents (Kader et al., 2003). The increasing use of such polymers in automobile, aerospace, off shore, and energy-related industries imposes stringent product performance under high temperatures and in hostile chemical environments. The

disadvantage of fluoroelastomer is its lack of low-temperature resistance (Ghosh *et al.*, 2001).

The blending of fluoroelastomers with rubbers having low glass transition temperature (T_a) may enhance the low temperature properties of fluoroelastomer (Chawdhury *et al.*, 2006). Ethylene propylene diene monomer rubber (EPDM) is the material that has excellent performances in low-temperature flexibility, thermal stability, weatherability and oxidation and ozone resistance (Deniz et al., 2007). Blending EPDM with fluoroelastomer can be a potential method to prepare the materials with better overall properties. However, the incompatibility and non-covulcanization between FPM and EPDM make this task difficult (Mathew et al., 2001). Fluorocarbon elastomer (vinylidenefluoride-co-hexafluoro propylene) can be vulcanized by nucleophiles such as bisphenols. A polyphenol hydroxyl EPDM (PHEPDM) with phenol hydroxyl groups can act as crosslinking agent for FPM. Thus the molecules of FPM and PHEPDM are connected through chemical bond which imparts speciûc properties to the vulcanized materials. The vulcanization procedure, low-temperature resistance, behavior, thermal degradation behavior and mechanical properties of the FPM/ PHEPDM reactive blends have been reported (Wang *et al.*, 2009).

EPDM and fluoroelastomer (FKM) blends with and without compatibilizer (MA-g-EPDM) were prepared by two-roll mill mixing. The effect of blend ratio and amount of compatibilizer on mechanical properties and thermal stability were investigated (Nair *et al.*, 2012). The tensile properties of all the composites, especially

those with higher proportion of FKM increased with ageing. Swelling of the blends was reduced after ageing. The incorporation of FKM rubber improved the thermal stability of EPDM rubber. The morphology of blends was investigated using SEM and is shown in Figure 5. In compatibilized blends, a finer and more even dispersion of the elastomer particles were observed. Morphology studies of the blend samples are in good agreement with the variation in mechanical properties.

CONCLUSIONS

Cure characteristics and mechanical properties of non-polar/polar blends are discussed as a function of blend ratio and the concentration of compatibilizer. The

addition of compatibilizer improves the mechanical properties of the blends. The dynamic mechanical properties of blends are also discussed as a function of the concentration of filler. It is observed that upon the addition of nano-filler the storage modulus increases, due to the better interaction between rubber and the filler. However, at higher concentrations the modulus is found to decrease owing to the agglomeration of filler particles. The morphology indicates a two-phase structure in which, the viscosity decreases from its high value with the increasing concentration of the compatibiliser and finally, levels off at higher concentrations, which indicates an interfacial saturation.

REFERENCES

- Arroyo, M., Lopez-Manchadoa, M.A., Valentina, J.L., and Carretero, J. (2007). Morphology/behaviour relationship of nanocomposites based on natural rubber/epoxidized natural rubber blends. *Composites Science and Technology*, **67**: 1330-1339.
- Asha, E. M. and Thomas, S. (2005). Morphology, mechanical and viscoelastic properties of nitrile rubber/epoxidized natural rubber blends. *Journal of Applied Polymer Science*, **97**: 1561–1573.
- Azima, L.G. and El-Sabbagh, S. (2001). Compatibility studies on some polymer blend systems: Electrical and mechanical techniques. *Journal of Applied Polymer Science*, **79**: 60-71.
- Bandyopadhyay, S., De, P.P., Tripathy, D.K. and De, S.K. (1995). Dynamic mechanical and spectroscopic studies on the miscibility of polychloroprene epoxidized natural rubber blend in presence of carbon black ûller. *Polymer*, **36**: 1979–1984.
- Banik, I. and Bhowmick, A.K. (1999). Inûuences of electron beam irradiation on the mechanical properties and crosslinking of fluorocarbon elastomer. *Radiation Physics and Chemistry*, **54**: 135–639.

- Baranwal, K.C. and Stephens, H.L. (2001). Basic Elastomer Technology. *Meeting of the Rubber Division of the American Chemical Society*, New York.
- Basfar, A.A. and Silverman, J. (1994). Improved ozone resistance of styrene butadiene rubber cured by a combination of sulfur and ionizing radiation. *Polymer Degradation and Stability*, **46**: 1–8.
- Bohm, G.G.A. and Dole, M. (1972). The radiation chemistry of macromolecules, Academic Press, New York.
- Botros, S. H. and Tawfic, M. L. (2006). Synthesis and Characteristics of MAH-g-EPDM Compatibilized EPDM/NBR Rubber Blends. *Journal of Elastomers and Plastics*, **4**: 349-365.
- Brinke, J.W.T., Debnath, S.C., Reuvekamp, L.A.E.M. and Noorermeer, J.W.M. (2003). Mechanistic aspects of the role of coupling agents in silicarubber composites. *Composite Science and Technology*, **63**: 1165-1174.
- Brown, H. (1957). Carboxylic elastomers. *Rubber Chemistry and Technology*, **30**: 1347-1386.
- Chawdhury, R., Banerji, M.S. and Shivakumar, K. (2006). Development of acrylonitrile-butadiene

- (NBR)/polyamide thermoplastic elastomeric compositions: Effect of carboxylation in the NBR phase. *Journal of Applied Polymer Science*, **100**: 1008–1012.
- Coran, A.Y., Mark J.E, Erman, B. and Eirich. (1994). Vulcanization. In: Science and Technology of Rubber. New York: Academic Press.
- Das, A., Mahaling, R.N., Stöckelhuber, K.W. and Heinrich, G. (2011). Reinforcement and migration of nanoclay in polychloroprene/ethylene–propylene–diene-monomer rubber blends. *Composites Science and Technology*, **71**: 276-281.
- Das, A., Ghosh, A. K. and Basu, D. K. (2005). Evaluation of physical and electrical properties of chloroprene rubber and natural rubber blends. *Kautschuk Gummi Kunststoffe*: **58**: 230–238.
- Das, A., Naskar, N. and Basu, D.K. (2004). Thiophosphoryl disulphides as crosslinking agents for chloroprene rubber. *Journal of Applied Polymer Science*, **91**: 1913-1913.
- Deniz, V., Karaagac, B. and Ceyhan, N. (2007). Thermal Stability of Butyl/EPDM/Neoprene Based Rubber Compounds. *Journal of Applied Polymer Science*, **103**: 557–563.
- Deuri, A.S. and Bhowmick, A.K. (1987). Aging of rubber. *Journal of Applied Polymer Science*, **34**: 2205–2222.
- El-Nashar, D.E. and Turky, G. (2003). Effect of mixing conditions and chemical crosslinking agents on the physicomechanical and electrical properties of NR/NBR blends. *Polymer Plastics Technology and Engineering*, **42**: 269–284.
- Essawy, H. and El-Nashar. (2004). The use of montmorillonite as a reinforcing and compatibilizing filler for NBR/SBR rubber blend. *Polymer Testing*, **23**: 803–807.
- Franco, C., Pitro, R. and Pandalai, S.G. (2001). Effects of combined action of radiation and sulfphur curing on the physical properties of a NR/SBR rubber compound. *Material Science*, **2**:253–61.
- Fujimoto, K. and Yoshimiya, N. (1968). Blends of *cis*-1, 4-polybutadiene with natural and styrene butadiene rubber. *Rubber Chemistry and Technology*, **41**: 669-667.
- Gaczynski, R., Parasiewicz, W. and Ciechanowicz, L. (1974). *Polymery Tworzywa Wielkoczastecskowe*, **19**: 249.
- Gardiner, J.B. (1968). Curative diffusion between

- dissimilar elatomers and its influence on adhesion. *Rubber Chemistry and Technology*, **41**: 1312-1328.
- Ghosh, A., Naskar, A.K., Khastgir, D. and De, S.K. (2001). Dielectric properties of blends of silicone rubber and tetrafluoroethylene/propylene/ vinylidene fluoride terpolymer. *Polymer*, 42: 9849– 9853
- Hanafi, I., Tan, S. and Poh, B. T. (2001). Curing and Mechanical Properties of Nitrile and Natural Rubber Blends. *Journal of Elastomers and Plastics*, **33**: 251-262.
- Hashim, A.S., Azahari, B., Ikeda, Y. and Kohjiya. S. (1998) The effect of *bis* (3-triethoxysilylpropyl) tetrasulfide on silica reinforcement of styrenebutadiene rubber. *Rubber Chemistry and Technology*, **71**: 289-299.
- Helaly, F. M. and El-Sabbagh, S. H. (2002). Bone meal waste and Ca (HPO)₂ as reinforcing filler for NR and CR and their blends compared with conventional white filler. *Journal of Elastomers and Plastics*, **34**: 335–348.
- Hess, W.M., Scott, C.E. and Callan, J.E. (1967). Carbon black distribution in elastomer blends. *Rubber Chemistry and Technology*, **40**: 371-384.
- Hofmann, W. (1989). Rubber Technology handbook. *Hanser Publishers*, Munich.
- Ishitobi, T. (1971), 38th Annual Meeting Society of Rubber Industry. Japan.
- Ismail, H., Jaffri, R.M. and Rozman, H.D. (2003). The effects of filler loading and vulcanization system on properties of oil palm wood ûour–natural rubber composites. *Journal of Elastomers and Plastics*, **35**: 181–92.
- Jovanovic, V., Jovanovic, S. S., Simendic, B.J. Gordana, Markovic, G. and Cincovic, M.M. (2012). Composites based on carbon black reinforced NBR/EPDM rubber blends. *Composites: Part B*, **45**: 333-340.
- Kader, M.A. and Bhowmick, A.K. (2003). Acrylic rubber fluorocarbon rubber miscible blends: Effect of curatives and fillers on cure, mechanical, aging and swelling properties. *Journal Applied Polymer Science*, 89: 1442–1452.
- Liu, J., Jean, Y. C. and Yang, H. (1995). Free-Volume Hole Properties of Polymer Blends Probed by Positron Annihilation Spectroscopy: Miscibility. *Macromolecules*, **28**, 5774.

Magda, M. and Abou. Zeid (2007). Radiation effect on properties of carbon black filled NBR/EPDM rubber blends. *European Polymer Journal*, **43**: 4415–4422.

- Manoj, K. C., Kumari, P. and Unnikrishnan, G. (2011). Cure Characteristics, Swelling Behaviors, and Mechanical Properties of Carbon Black Filler Reinforced EPDM/NBR Blend System. *Journal of Applied Polymer Science*, **120**: 2654–2662.
- Mathew, A.P. and Thomas, S. (2001). Studies on the thermal stability of natural rubber/polystyrene interpenetrating polymer networks: thermogravimetric analysis. *Polymer Degradation and Stability*, **72**: 423–439.
- Mohamed, G. M., Abd-El-Messieh, S. L., El-Sabbagh, S. H., Younan, A.F. (1998). Electrical and mechanical properties of polyethylene rubber blends. *Journal of Applied Polymer Science*, **69**: 775–83.
- Nair, A. B., Kurian, P. and Joseph, R. (2012). Ethylene– propylene–diene terpolymer/hexa fluoropropylene–vinylidinefluoride dipolymer rubber blends: Thermal and mechanical properties. *Materials & Design*, **36**: 767-778.
- Naskar, N., Debnath, S. C. and Basu, D.K. (2001). Novel method for preparation of carboxylated nitrile rubber–natural rubber blends using *bis* (diisopropyl) thiophosphoryl polysulfides. *Journal of Applied Polymer Science*, **80**: 1725–1736.
- Norbert, H., Guenther, S., Hans, G. and Rainer, W. (1990). Grafting Polyolefin Blends and use of the Graft Copolymer Blends as an Adhesion Promoter and for the Preparation of Ionomers, *US Patent* 4906690, 1990-03-06 [C08F255/04, C08F287/00].
- Pal, K. Das, T., Pal, S.K. and Das, C.K. (2008). Use of carboxylated nitrile rubber and natural rubber blends as retreading compound for OTR tyres. *Polymer Engineering and Science*, **48**: 2410-2417.
- Peng, Z. L., Wang, B., Li, S. Q., Ng, S. J., Liu, H. and Xie, H. Q. (1994). Investigation of ionic conductivity of polymeric electrolytes based on poly (ether urethane) networks using positron probe. *Physics Letters A*, **194**: 228-234.
- Ramesan, M.T, Mathew, G., Kuriakose, B. and Alex, R. (2001). Role of dichlorocarbene modified styrene butadiene rubber in compatibilisation of

- styrene butadiene rubber and chloroprene rubber blends. *European Polymer Journal*, **37**: 719–728.
- Saad, A. L. G. and El-Sabbagh, S. (2001). Compatibility studies on some polymer blend systems by electrical and mechanical techniques. *Journal of Applied Polymer Science*, **79**: 60–71.
- Sae-oui, P., Sirisinha, C. and Hatthapanit, K. (2007). Effect of blend ratio on aging, oil and ozone resistance of silica-filled chloroprene rubber/natural rubber (CR/NR) Blends. *EXPRESS Polymer Letters*, 1: 8–14.
- Shaji, P. T., Mathew, E.J. and Marykutty, C. V. (2012). Nanomodified Fillers in Chloroprene-Rubber Compatibilized Natural Rubber/Acrylonitrile– Butadiene Rubber Blends. *Journal of Applied Polymer Science*, 124: 4259–4267.
- Sutton, M.S. (1964). Blends of Royalene with other polymers, *Rubber World*, **149**: 62-68.
- Thomes, Y.U. and Thomas, D.J. (1998). Blends of Polyamides, Polyesters and Maleic Anhydride Modified EPDM Rubbers, *US Patent EP0282153*, 1988-09-14 [C08L77/00].
- Tinker, A. J. and Jones, K. P. (1998). Blends of natural rubber: Novel techniques for blending with speciality polymers. *Chapman & Hall Ltd.*, London.
- Traian, Z. (2001). Thermodynamic assessment of cirradiated NBR/synthetic elastomer blends. *Nuclear Instruments and Methods in Physics Research section*, *B*, **185**: 136–139.
- Waddell, W.H. and Evans, L.R. (1996). Use of nonblack fillers in tyre compounds, Rubber Chemistry and Technology, 69: 377-423.
- Woods, R.J. and Pikeav, A.K. (1994). Applied radiation chemistry: radiation processing. New York: John Wiley & Sons.
- Wang, Y., Liu, L., Luo, Y. and Jia, D. (2009). Aging behavior and thermal degradation of fluoroelastomer reactive blends with poly-phenol hydroxy EPDM. *Polymer Degradation and Stability*, 94: 443–449.
- Younan, A.F., Abd-El-Messieh, S.L. and Gasser, A.A. (1998). Electrical and mechanical properties of ethylene propylene diene monomer–chloroprene rubber blend loaded with white and black fillers. *Journal of Applied Polymer Science*, **70**: 2061.