Reinforced Elastomers: Interphase Modification and Compatibilization in Rubber-Based Nanocomposites

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Abstract An extended review is presented on the structure and properties of filler-matrix interface in reinforced elastomeric materials, since the above characteristics are critical for the overall performance of the related products. The current trends for interphase modification in rubber systems containing various fillers, such as Carbon black, Silica, Calcium Carbonate, Clays with emphasis on clay nanofillers, as well as Graphene is discussed. The use of fibrilar reinforcements is also reported, including traditional materials, such as Natural fibres, as well as Aramids and Carbon Nanotubes. On the other hand, the concept of hybrid composites, i.e., those composed of a mixture of matrices or reinforcements, further enhances the versatility of those materials, since it provides new possibilities of extending the area of rubber applications. In fact, the above products combine the property improvement attributed to each one of the system's components and, moreover, they can usually take advantage of their synergistic action. In the same context the role of some other additives, necessary to adjust mechanical properties (e.g. plasticizers) or to promote phase miscibility in complex systems, such as compatibilizers, was investigated. The vulcanization of elastomeric materials is a critical step, with high impact on the properties of final products. In fact, the extent of this reaction, the cross-links density along with the other network parameters, are some important factors controlling the overall behavior of the vulcanized rubber and, therefore, monitoring, control, and modeling of rubber vulcanization are also examined in this work. The above review showed that the main reason for reinforcing rubbers is to improve their mechanical and thermal properties, as well as to reduce cost and sometimes the weight of a construction. It seemed that recent advances in nanoparticles have attracted much attention in manufacturing of rubber nanocomposites, because of the small size of filler and the corresponding increase in the surface area, which leads to the required mechanical properties at low filler loading. Carbon nanotubes and graphene nanoparticles are promising

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materials, offering good electrical properties. Surface treatment of the filler particles with the appropriate coupling agents is often vital, in order to promote proper dispersion and adequate filler/matrix interactions. Also, efficient dispersion of the reinforcement into rubber matrices usually needs the assistance of functionalized polymers, i.e., compatibilizers. Among the different modifying agents, maleic anhydride is the most commonly used and seems to ensure best results at relatively low cost. Finally, the cross-linking parameters must be controlled for an optimal network formation. The newly developed polyblends, based on mixtures of rubbers with polyolefins, require the suitable compatibilization in order to reveal their unique properties. Nanoparticles, being very efficient reinforcing agents even at low concentrations, were also found to play the role of compatibilizer for these mixtures of immiscible polymers.

Abbreviations

3-APE	3-aminopropyl-triethoxy silane
IIR	Butyl rubber
ACM	Acrylic rubber
APTES	Aminopropyltriethoxysilane
ATO	Sb doped tin dioxide
BIMMS	Brominated polyisobutylene-co-paramethylstyrene
BPDA	Benzophenone-3,3′,4,4′-tetracarboxylic dianhydride
BR	Butadiene rubber
Bt	Bentonite
C-8	Octylamine
CB	Carbon black
CNT’s	Carbon nanotubes
C-SEBS	Carboxylated SEBS
DDA	Dodecylamine
DFT	Density functional theory
DSC	Differential scanning calorimetry
EAR	Ethylene acrylate rubber
ENR	Epoxidized natural rubber
EOC	Ethylene-octene copolymer
EPDM	Ethylene-propylene-diene rubber
EPR	Ethylene-propylene rubber
EPR-g-MA	Ethylene-propylene rubber grafted with maleic anhydride
EVA	Ethyl-vinyl acetate copolymer
FGS	Functionalized graphene sheets
FKM	Fluoroelastomer
GIC	Graphite intercalated compound
GF	Glass fibres
GMA	Glycidyl methacrylate
GN	Graphite nanosheets
GO	Graphene oxide
HDPE	High density polyethylene

HDS	Hexadecyltrimethoxy-silanes
HNBR	Hydrogenated acrylonitrile butadiene rubber
HTV-SR	High temperature vulcanized silicone rubber
HXNBR	Carboxylated NBR
Ipp	Isotactic polypropylene
KF	Kenaf fibres
LB	Liquid polybutadiene
LDPE	Low-density polyethylene
MA-g-EPDM	Maleic anhydride grafted EPDM
MA-g-PB	Maleic anhydride grafted 1,2 polybutadiene
MB	Master batch
MDI	Methylene-bis-diphenyl diisocyanate
MG	Modified graphene
MH	Magnesium hydroxide
MMT	Montmorillonite
MPPB	Maleic anhydride grafted propylene-butadiene copolymer
MPTS	3-mercaptopropyltribis(triethoxysilylpropyl)tetrasulfide
MPS	γ-ethacrylopropyltriethoxysilane
MPS	γ-methacryloxypropyltrimethoxy
MRPS	γ-mercaptoproyltrimethoxy
MVMQ	Methyl vinyl silicone rubber
MWNTs	Multiwall nanotubes
NBR	Acrylonitrile-butadiene rubber
NG	Natural graphite
NR	Natural rubber
NR-g-MA	Maleic anhydride grafted natural rubber
NXT, NXT Z	3-octanoylthio-1-propyltriethoxysilane
ODA	Octadecylamine
OMEC	Online measured electrical conductance
OMMT	Organophilic montmorillonite
PMDA	Pyrromellitic dianhydride
PR	Petroleum resin
PU	Polyurethane
PUR	Polyurethane rubber
PA	Poly(amide), nylon
PB	Polybutadiene
PDMS	Poly(dimethyl siloxane)
PE-g-MA	Polyethylene grafted maleic anhydride
Phr	Parts per hundred
PPEAA	Poly(propylnene-eyhylene acrylic acid)
PP-g-MA	Polypropylene grafted maleic anhydride
PSA	Polysulfonamide
RBFMs	Rubber-based friction materials
RFL	Resorcinol fromaldehayde latex

RGO	Reduced GO
RTV	Room temperature vulcanized
RP	Red phosphorus
SACP	Surface-acetylated cellulose powder
SBR	Styrene-dutadiene rubber
SBS	Styrene-butadiene-styrene
SEBS	Styrene-ethylene- butylene- styrene
SEBS-g-MA	Styrene-ethylene- butylene- styrene grafted maleic anhydride
SEM	Scanning electron microscopy
SEP	Poly(styrene-b-ethylene-co-propylene) diblock copolymer
Si69	Bis(triethoxysilylpropyl)tetrasulfide
SRBC	Styrene rubber block copolymer blends
SWNTs	Single wall nanotubes
TEM	Transmittance electron microscopy
TEOS	Tetraethoxysilane
TESPT	1,4-phenylene diisocyanate (PPDI), methylene-bis-diphenyl
T_g	Glass transition temperature
TPNT	Thermoplastic natural rubber
ULM	Ultrasonically assisted latex mixing process
VPR	Butadiene–styrene–vinyl pyridine rubber
WHRA	White rice husk ash
XRD	X-ray diffraction

1 Introduction to Interphase Modification and Compatibilization in Composites

The structure and properties of filler-matrix interface play a major role on the mechanical and physical performance of composite materials. The quality of interface is a dominant factor for fracture toughness properties of composites as well as for their response to aqueous and corrosive environments. In fact, the interfacial area between filler and matrix, is believed to constitute a separate phase, otherwise called interphase or mesophase, with its own characteristics. Composite materials with poor interfacial properties have relatively low strength and stiffness but they display high resistance to fracture, whereas materials with strong interfaces ensure high strength and stiffness, often accompanied with brittleness. In a simple system bonding at an interface is due to adhesion between reinforcement and matrix. Adhesion may be attributed to five main mechanisms which can occur at the interface, either in isolation or in combination to produce the bond: (i) absorption and wetting (ii) diffusion of the polymer molecules on one surface into molecular network of the other surface (interdiffusion) (iii) electrostatic attraction and (iv) mechanical adhesion [1].

The effectiveness of a filler depends on its characteristics, such as particle size and shape and, more significantly, on the strength of polymer-filler interactions. To achieve maximum improvement, strong fibre interaction with the polymeric matrix will be needed because the interface/interphase between fibre and matrix has a large influence on the mechanical properties of the composite. These interactions may also increase the effective degree of crosslinking and such an effect is particularly strong if the particles have some reactive surface groups [2].

A great deal of effort has been directed towards ensuring that the fibre-matrix interface can transfer the stresses efficiently, so that the properties achieved by reinforcing are maintained and not degraded by the environment. The use of coupling agents, i.e. substances chemically reactive with both matrix and reinforcement, and/or chemical modification of the surface of one or more constituents, have been the most successful means of providing reasonably well controlled bond between matrix and the encapsulated reinforcement.

The rapid growth of using multiphase polymer systems (blends and composites) is undoubtedly related to the availability of methods of controlling the physical and chemical interactions at the interface. Compounds acting as interfacial agents are commonly known as “compatibilizers” in blends, or “coupling agents” in composites, and their function is to promote interfacial adhesion and enhance overall properties [3].

In general, compatibilizers reduce interfacial tension and, therefore, are capable of promoting adhesion leading to a finely dispersed morphology that shows stability against gross segregation. Compatibilizers are often based on polyolefins functionalized with acrylic acid [4], maleic anhydride [5] or other thermoplastics with polar groups such as ionomers [6].

2 Current Trends in Interphase Modification and Compatibilization of Rubbers

Rubbers, also called elastomers, are high molecular weight materials which possess very low interchain force, low glass transition temperature, T_g, and predominantly amorphous nature with low strength. The common characteristics of rubbers are their elasticity, flexibility and toughness and their commercial grades can be classified into two types: crosslinked systems and thermoplastic elastomers. Most of the commonly used rubbers are polymeric materials with long chains, which are chemically crosslinked during the curing process. These materials, once formed, cannot be reshaped, softened, melted nor reprocessed by a simple subsequent reheating. Thermoplastic elastomers, on the other hand, are rubbers which act at room temperature in a manner similar to crosslinking materials but are copolymers, with one phase being rubbery and the other crystallizable. Therefore, they can repeatedly shaped upon heating [7]. Rubbers are often compounded with reinforcing fillers to improve their mechanical properties, such as tensile strength, modulus, tear resistance and abrasion resistance and the most usual filler for this reason are carbon black and silica [8].

The performance of a filler in the rubber matrix is controlled by its characteristics, such as particle size and shape, concentration, surface activity, degree of interactions with rubber matrix and structure of the particle agglomerates. Increasing the area of contact between rubber matrix and filler particles seems to be the most important factor for ensuring a strong reinforcement effect and this surface area of the interface is controlled by the size of filler particles and their volume fraction. Furthermore, the magnitude of adhesive bonding between rubber matrix and filler is a key factor in determining the degree of reinforcing.

2.1 Carbon Black/Rubber Composites

Carbon black (CB) is an essential component in many rubber formulations. It is composed of carbon particles solidly fused together by covalent bonds, thus forming aggregates which cannot be broken into smaller sizes during the ordinary processing conditions of the material. The incorporation of CB with high surface area into an elastomer results in a high reinforcing level and gives higher tensile strength, tear strength and abrasion resistance. There are likely both chemical and physical interactions between CB and rubber, resulting in property improvement, but the understanding of the nature of this type of reinforcement is still growing. The close interfacial contact of a rigid solid phase (CB) and a soft phase (rubber) results in chemical or physical absorption of the rubber molecules into the CB surface. The consequence of this absorption is the formation of “bound rubber” on the CB surface. “Bound rubber” is the portion of elastomer which can not be separated from the filler surface when the rubber mix is extracted by one of its good solvents, such as toluene, over a specific period of time at room temperature. The formation of bound rubber structures, is believed to enhance the mechanical and physical properties of CB-filled rubber compounds [9].

The dispersion and distribution of CB in a rubber matrix are important factors to achieve optimum physical properties. Moreover, its structure, wettability by the rubber phase and the related interactions have all major influence on the properties of the rubber compound. It is known that the wettability of a filler particle by a polymer chain can be quantified in terms of surface energy and similar values of this parameters ensure good compatibility.

Non-uniform distribution of CB in a rubber blend is a major problem, especially in the case of dissimilar rubber blends, such as natural rubber/ethylene-propylene-diene rubber (NR/EPDM) or styrene-butadiene rubber/ethylene-propylene-diene rubber (SBR/EPDM). In such blends, CB tends to partition into the highly unsaturated phase leaving the saturated phase less occupied. For this filler, the surface energy is high compared to that of elastomers like SBR, NR and EPDM. Therefore, in order to get an appreciable influence on the dispersion and distribution properties of CB into a rubber blend, a significant reduction of its surface energy is needed. For instance, surface modification of a fullerenic CB by plasma polymerization was successfully carried out by Mathew et al. [10], in an attempt to reduce its surface energy and further compatibilize the filler with various elastomers. The plasma-coated CB shows low filler interaction in the different rubber systems compared to the untreated version. This is due to the low surface energy of plasma-coated carbon black and it was found that the filler/polymer interaction remains unaffected in unsaturated SBR and acrylonitrile-butadiene rubber (NBR) matrices, while in saturated EPDM rubber it decreases. EPDM rubber showed a decrease of tensile properties due to a substantially reduced interaction between the plasma-polymer film and the elastomer because of its saturated nature. In SBR and NBR the properties remained almost unaffected due to possible interactions between some residual unsaturations left in the plasma-polymer layer and the double bonds present in backbone of these rubbers [10].

2.2 Silica/Rubber Composites

Synthetic silicon dioxide (silica) can be produced either by precipitation or by pyrogenic (thermal) process and, therefore, this filler can be classified into two groups; namely precipitated and pyrogenic (fumed) silica. It is the most important filler competing CB in the area of rubber technology. However, in the early stages of silica usage, their uses as reinforcing filler instead of CB were limited due to a number of problems:

- Silica-filled compounds show higher viscosities
- They are more difficult to mix and process
- There is a concomitant increase in vulcanization time
- Silica-filled compounds often show lower crosslinking density

Surface silanol groups of silica have received keen interest in recent decades, because of their important role of interfacial interactions in several applications, such as the reinforcement of synthetic or natural elastomers. The silanol groups show strong filler–filler interactions and cause the absorption of the polar materials such as curatives on the surface. Such absorption of curatives results in a reduction in the crosslinking density and delay of the scorch time of the silica filled rubber compounds.

The main concern in using silica as a reinforcing filler for elastomeric matrices is the difficulty of obtaining a very efficient dispersion of silica particles, due to the filler's surface behavior, dominated by the chemistry of the terminal silanol groups, which can be isolated, vicinal or germinal. Silanols make the surface of hydroxylated silicas hydrophilic, inducing strong interactions between silica particles and leading to a poor dispersion of the filler in the conventional natural or synthetic non-polar type elastomer. Dispersion of silica can be enhanced by either, reducing the polarity of the filler particles or sterically avoiding their aggregation. For example, silane coupling agents containing sulfur are widely used in the tire industry to increase dispersibility of silica into elastomeric matrices, thus promoting the formation of covalent bonds between the phases.

The strength of chemical interactions between silica of different chemical characteristics and NBR, was studied by infrared spectroscopy measuring the increase of $C \equiv N$ fundamental vibration frequency and by the density functional theory (DFT) [11]. The results showed that functional groups on the silica's surface (after modification with electron donors, alkaline and acidic groups), play an important role on the compatibility of immiscible blends of NBR copolymers, as they strongly interact with the rubber phase.

In the field of saturated elastomers, Hui et al. [12] explored the effect of pristine silica nanoparticles on a model low-density polyethylene (LDPE)-ethyl-vinyl acetate copolymer (EVA) thermoplastic rubber blend. It was observed that the blend properties were strongly affected by the sequence of addition of nanofillers during the composite preparation. The addition of a silane coupling agent (Si-69) to the formulation of silica-filled polymer blends leads to significant increase of tensile strength, modulus, extensibility and dynamic properties of the blends. Also, morphological studies clearly indicated that the differential properties of these mixtures primarily stemmed from the extent of dispersion and alternation of crystalline morphology, which in turn was a strong function of preferential incorporation in the LDPE or EVA matrix and the agglomeration tendency of nanofillers.

It has been suggested that partial or complete chemical modification of silica surface, which can be achieved by the reaction of the surface hydroxyl groups with coupling agents such as organosilanes, affords more or less significant changes in the thermodynamic properties of surface. This, in turn, will influence the silica/silica interactions and, furthermore, its dispersibility into a polymeric matrix.

Some silanes, such as bis(triethoxysilylpropyl)tetrasulfide (TESPT) and 3-octanoylthio-1-propyltriethoxysilane (NXT and NXT Z silanes), have been proposed for use as coupling agents. TESPT displays bifunctionality, which permits it to react both with silanol OH groups present on the silica surface and with the elastomer during vulcanization by sulfur.

Bertona et al. [13] prepared a new type of filler starting from precipitated silica modified with alkoxysilane coupling agent (sb1), obtained by grafting 3-mercaptopropyltrimethoxysilane (MPTS) onto polybutadiene oligomer chains. Styrene-butadiene copolymer was used as matrix and TESPT was the reference modifier of silica. The above authors found that the best tensile properties were obtained with TESPT-modified silica. The properties of the compound loaded with sb1-pre-grafted silica were scantily lower than those corresponding to the other compounds and this was attributed to higher crosslinking density given by the sulfur deriving from TESPT decomposition during vulcanization process.

A better understanding of the impact of physical characteristics of the filler-rubber interface and the resulting interphase on the macroscopic mechanical performance of rubber composites was attempted by Stöckelhuber et al. [14]. The rubber matrix consisted of a solution of styrene-butadiene copolymer, filled with 20 or 40 phr pyrogenic or precipitated silicas, with different surface modifications by silanes, as well as with a CB sample as a reference. The "layered fibre model" was proposed, based on the hypothesis that during deformation of composites, the polymer chains slip off from the polymer interphase around the filler particles into the gaps between filler particles, where uniaxially oriented, high-strength polymer fibres are formed. The results of experiments with cured vulcanizates at its operating temperature, support the assumption of an immobilized layer of absorbed polymer molecules in the vicinity of the filler particle interface.

Some more sophisticated processing techniques have also been adopted for special product requirements. Thus, sol–gel techniques generating in situ silica from the sequential hydrolysis and condensation reactions of tetraethoxysilane (TEOS) have been adopted to synthesize transparent rubber-silica hybrid nanocomposites from polar rubbers, like acrylic rubber (ACM) and epoxidized natural rubber (ENR) [15]. It is mentioned that polarity of the host rubber matrix is significant in determining the structure distribution of the silica particles.

2.3 Calcium Carbonate/Rubber Composites

Calcium carbonate ($CaCO_3$) is one of the most inexpensive and recyclable natural resources, with the highest reserves on earth and is widely used in polymer processing. $CaCO_3$ nanoparticles were used for reinforcement of PP/SEBS and PP/carboxylated SEBS (C-SEBS) blends [16]. The composite with SEBS showed morphology with the SEBS domains and $CaCO_3$ particles independently dispersed within the PP matrix. On the other hand, the composite with C-SEBS showed a core-shell structure.

To use $CaCO_3$ as reinforcing agent, surface treatment with coupling agents or organic acids is absolutely necessary. Song et al. [17] studied the factors affecting the mechanical properties of styrene-butadiene-styrene (SBS) block copolymer composites filled with $CaCO_3$, after its surface treatment with liquid polybutadiene (LB). The above authors, concluded that the mechanical properties of SBS can be improved remarkably through reinforcing with $CaCO_3$ subjected to the above surface treatment, proving the filler surface with high content of 1,2-double bonds. When SBS, $CaCO_3$ and LB were directly blended, secondary aggregation of $CaCO_3$ took place and the mechanical properties of the composite were significantly lower. In the integral blend method, LB was shown to function as a plasticizer.

Coating of $CaCO_3$ with stearic acid leads to significant decrease of its surface tension, which results in decreased interactions and, hopefully, contributes to limited aggregation [18]. The phase separation of ternary phase composites is influenced by the melt rheology of the system, the compounding techniques, as well as by the surface characteristics and mutual wettability of the fillers and polymer components. In PP/EPDM/$CaCO_3$ composites, the surface treatment of filler was found to result in separate dispersion of phases (EPDM and $CaCO_3$), whereas encapsulation occurred when untreated calcium carbonate was used.

To promote the adhesive bonding between polymer and filler particles, functionalization of polymer phases was carried out. In Polypropylene/Ethylene-propylene rubber (EPR)/filler systems, it was shown that incorporating PP functionalized with maleic anhydride resulted in separate dispersions of elastomer filler. The use maleated EPR and non-functionalized PP was said to give a filler encapsulation structure [19, 20].

In another related work [21], the properties of PP/EPR/coated nano-$CaCO_3$ composites, with and without compatibilizers, were studied. The results indicated that good dispersion of nanoparticles in PP/EPR depends on their surface coatings of stearic and other fatty acids. In both cases, the final morphology is the core-shell structure, in which EPR acts as the shell part encapsulating coated $CaCO_3$. The use EPR-g-MA copolymer does not improve the interface between PP/EPR and nanoparticles but propylene ethylene (PEP) copolymer should be preferentially localized at the interface of PP and EPR/nano-$CaCO_3$ phases generating an improved adherence, which will ensure a better cohesion of the whole material. It is believed that the synergistic effect of both, EPR elastomer and $CaCO_3$ nanoparticles, should account for the balanced performance of the ternary composites.

2.4 Clay/Rubber Composites

Rubber-clay nanocomposites exhibit outstanding properties, at low loading levels of clay, as compared with unfilled rubber compounds or conventional filled composites. In general, the preparation methods for rubber-clay nanocomposite can be divided into four major groups, according to the processing technique:

- In situ polymerization
- Intercalation of rubber via solution blending
- Direct melt intercalation method
- Intercalation of rubber via latex compounding

The main objective of preparing organoclay nanocomposites is to achieve high degree of dispersion of organoclay aggregates within the polymer matrix, which can yield very large surface area. The efficient dispersion of organoclay platelets in the polymer matrix leads to improvement of the overall properties of the polymer.

Clay minerals have hydrophilic character and hence a nanometric dispersion into a hydrophobic polymer is hard to achieve, particularly through solution and melt blending methods. To obtain a homogeneous dispersion in a hydrocarbon matrix, the alkaline-earth cations of pristine clay minerals are replaced by hydrophobic organomodifiers, typically ammonium cations bearing long alkyl chains a compensating cations. The role of the alkyl ammonium cations is to lower the host's surface energy and thereby improve wetting-out by the polymers. The obvious outcome of the polymer-organoclay interactions is improved strength characteristics because of the strong interfacial interactions between silicate layers and the polymer chains. By appropriate choice of the alkyl ammonium cation, the interactions between the host layers and the intercalated polymer chains can be tailored to synthesize new organic–inorganic hybrids.

Montmorillonite is the most commonly used layered silicate for preparation of nanocomposites because of its high aspect ratio, large surface area, and surface reactivity. Some typical nanocomposite systems owing rubber matrix are the following:

2.4.1 Clay/SEBS Nanocomposites

SEBS block copolymer is one of the widely used thermoplastic elastomers, which exhibits elasticity and easy processability, good thermal stability etc. To further improve rubber properties clay nanoparticles were studied as reinforcing additive. Chang et al. [22] recorded increased tensile strength of SEBS/clay hybrids, at 10 phr clay concentration with 5–20 phr compatibilizer of SEBS-g-MA.

The effect of blending sequence on the microstructure of ternary nanocomposites composed of nylon 66/organoclay/(SEBS-g-MA) was studied by Dasari et al. [23], who also studied the microscale and nanoscale deformation behavior of nylon 66/organoclay/SEBS-g-MA ternary nanocomposites.

Lai et al. [24] prepared SEBS block copolymer/clay (Cloisite 20A) nanocomposites via melt mixing technique, using two types of maleated compatibilizers: SEBS-g-MA and polypropylene grafted maleic anhydride (PP-g-MA) in order to improve dispersion of organoclay. PP-g-MA compatibilizer system conferred higher tensile strength and tear strength than SEBS-g-MA compatibilized system, mainly due to its semi-crystalline nature. At fixed content of compatibilizers, the above mechanical properties were improved with increasing clay content as well.

Martín et al. [25] studied the intercalation capability of SEBS in nanocomposite systems prepared by melt blending, consisted of isotactic PP with 5 % organically modified montmorillonite (Cloisite 20A). They found that organoclay is not in direct contact with the PP phase because the clay is always located inside the elastomer domains. The elastomer surrounds the nanoclay, hindering the clay exfoliation and preventing its dispersion in the PP matrix. On the other hand, the presence of nanoclay causes a decrease in the coalescence of rubbery phase. There is a reduction of the size of SEBS domains in comparison with binary PP/SEBS systems and these domains are better distributed in the PP matrix.

2.4.2 Clay/Propylene-Butadiene and SBR Nanocomposites

Maleic anhydride grafted propylene-butadiene copolymer (MPPB) was investigated as compatibilizer for a composite of PP/SBS/organophilic montmorillonite (OMMT) [26]. In the presence of 10 phr MPPB, the impact strength of the composite was improved by about 20 %. TEM images showed that the OMMT was better dispersed in the matrix upon inclusion of MPPB. A better distribution of the rubber phase and a rugged fracture surface were observed in SEM images as the MPPB content increased.

In another work, SBR and OMMT were directly mixed to obtain nanocomposites, which have shown intercalated and partly exfoliated structure with improved viscoelastic and mechanical properties [27]. Also, SBS/MMT nanocomposites were successfully prepared by in situ living anionic polymerization with n-BuLi initiator [28]. The results from the kinetic study and ^{1}H NMR indicated that the addition of OMMT did not change the living copolymerization as well as the components of copolymer, when OMMT content was lower than 3 wt%. The result from TEM and X-ray diffraction revealed that a completely exfoliated structure existed in the nanocomposite with 25 wt% styrene units and OMMT content from 1 to 4 wt%, and styrene played an important role in expanding the OMMT layers. Moreover, nanocomposites possessed higher glass-transition temperature, thermal stability, tensile strength and elongation at break than SBR when the OMMT content ranged from 2.5 to 4 %. Regarding the type of nanofiller, Sadhu and Bhowmick [29] studied the preparation and properties of different nanoclays based on sodium montmorillonite, bentonite and potassium montmorillonite, and organic amines of varying lengths in the SBR matrix. The tensile strength of SBR nanocomposites increased with increasing chain length of amine. Among the examined clays, modified Na^+-MMT exhibited better mechanical properties than either bentonite or K^+-MMT in accordance with X-ray data. The incorporation of amine governs the organophilicity of the clay. This in turn leads to better polymer-filler interaction and hence better strength of nanocomposites. The higher polymer-filler interaction explained the shift of the glass transition temperature (T_g) in the positive direction as measured from DSC experiments.

2.4.3 Clay/NR Nanocomposites

Magaraphan et al. [30] mentioned that MMT clays treated with long primary amines led to much more improved mechanical properties when incorporated into NR matrices, than those treated with quaternary amines of the same number of carbon atoms. The length of hydrocarbon in the alkylamines had no effect on the curing time, whereas the nanocomposites prepared with long quaternary amine showed comparatively faster cure time.

Varghese et al. [31] prepared NR, polyurethane rubber (PUR) and NR/PUR-based nanocomposites from the related lattices by adding 10 phr pristine synthetic sodium fluorohectorite. It was observed that, in blends composed of polar PUR and apolar NR, the silicate layers were preferentially embedded in the polar PUR phase in well a intercalated/exfoliated stage. The properties of the PUR/NR-based nanocomposites were similar to those containing plain PUR. This result was claimed to be of great economic significance as NR latex is cheaper than PUR latex.

In an attempt to produce rubber nanocomposites based on NR or SBR, an innovative organoclay containing polybutadiene chains was prepared. It was obtained by reacting a maleinized polybutadiene oligomer with the $–CH_2CH_2OH$ moieties present in the ammonium cation of a commercially available organoclay (Cloisite 30B). A second organoclay was prepared in situ during melt blending by reacting Na^+Mt with dialkyl dimethylammonium chloride (Mt-2HT). Satisfactory exfoliation and dispersion of the innovative organoclay in both rubber matrices were obtained, not far from those observed in systems containing Mt-2HT.

In both NR and SBR, Mt-PB4 promoted a fast crosslinking reaction and a lower crosslinking density, with respect to Mt-2HT. It was observed that Mt-PB4 seems recommended to promote reinforcement of rubber compounds, without exceedingly increasing their rigidity and sacrificing their ultimate properties. It was confirmed that the enlargement of the basal spacing in a layered clay mineral, thanks to the use of a long chain hydrophobic substituent of the ammonium cation, is a positive strategy to achieve both exfoliation and dispersion of the organoclay [32].

The organically modified material is polar, hence it may not ensure an efficient dispersion upon direct incorporation in non-polar rubbers like SBR and EPR. Therefore, a polar rubber, which is compatible with the matrix polymer can be used as a compatibilizer.

Epoxidized natural rubber (ENR), obtained by epoxidation of 1,4-polyisoprene, has a higher glass transition temperature, polarity and superior compatibility with SBR and EPR. Rajasekar et al. [33] studied the effect of dual fillers on the properties of SBR and EPR compounds prepared using ENR as a compatibilizer. ENR-organically modified nanoclay (Cloisite 20A) composites were prepared by solution mixing and the obtained composite was incorporated in SBR and EPR matrices along with carbon black. The morphological studies proved the intercalation of nanoclay platelets in ENR and further incorporation of EC in SBR and EPR matrices leads to partial exfoliation of nanoclay platelets. A curing study demonstrated faster scorch time, cure time and increased maximum torque for the compatibilized SBR and EPR nanocomposites containing a dual filler system compared to control. Dynamic mechanical thermal analysis showed an increase of storage modulus for SBR and EPR compounds containing dual fillers as compared to compounds containing pure and single filler. The same compounds showed substantial improvement of mechanical properties.

2.4.4 Clay/EPDM Rubber Nanocomposites

EPDM rubber is a widely used engineering elastomer with outstanding resistance to ozone degradation, combined with high thermal stability and, therefore, EPDM/clay nanocomposite materials have attracted special attention. However, this elastomer does not have any polar groups in the backbone and, therefore, strong interactions between EPDM chains and clay layers can hardly be achieved, unless a suitable compatibilizer is used.

EPDM/montmorillonite (MMT) composites were prepared through a melt process and three kinds of surfactants with different ammonium cations were used to modify MMT and thus, to alter the morphology of composites [34]. In fact, the morphological configuration is dependent on the alkyl ammonium salt length, that is, the hydrophobicity of the organic surfactants. Organophilic montmorillonite (OMMT), modified by octadecyltrimethyl ammonium salt and distearyldimethyl ammonium salt, was intercalated and partially exfoliated in the EPDM matrix, whereas OMMT modified by hexadecyltrimethyl ammonium chloride exhibited a morphology with the clay nanoparticles existing as a common filler. Ethylene-propylene-diene rubber grafted with maleic anhydride (MA-g-EPDM) was used as compatibilizer and greatly affected the dispersion of OMMT. When OMMTs were modified by octadecyltrimethyl ammonium chloride and distearydimethyl ammonium chloride, the EPDM/OMMT/MA-g-EPDM composites (100/15/5) had an exfoliated structure and they showed good mechanical properties and high dynamic moduli.

Gatos et al. [35] studied the characteristics of EPDM/organoclay nanocomposites, resulting from different processing conditions and formulations. The change in the rubber polarity was attained by replacing half of EPDM rubber by maleic anhydride (MA)—and glycidyl methacrylate (GMA)-grafted EPDM. It was shown that incorporation of grafted EPDMs strongly improves the strength and stiffness of nanocomposites containing 10 phr organoclay.

EPDM-g-MA was used as compatibilizer in EPDM/OMMT nanocomposites prepared by melt compounding [36]. XRD analysis indicated that matrix chains were intercalated into the gallery space of OMMT effectively. An almost complete dispersion was obtained when the compatibilizer-filler ratio was three. In the samples containing less EPDM-g-MA, strong flocculation of the stacked dispersed clay particles was evidenced. Better dispersion of silicate layers was obtained in EPDM matrices with a higher Mooney viscosity, as they exert higher shearing during mixing. Also, the linear polymer chains can be more intercalated into OMMT galleries than long-branch EPDM chains.

2.4.5 Clay/NBR Nanocomposites

Rubber-clay nanocomposites have been prepared by modification of the naturally occurring Na montmorillonite clay followed by mixing with rubber in solution. Intercalation and/or exfoliation of the clay layers has been observed in SBR, NBR, butadiene rubber (BR), brominated polyisobutylene-co-paramethylstyrene (BIMS), EOC and thermoplastic elastomers.

The resulting structure and orientation of clay particles in the matrix depend on the nature of both rubber and clays. Usually nonpolar rubbers are better compatible with the organoclays where long aliphatic amine chains are present, whereas some polar rubbers have better attraction towards unmodified clay. When rubber and clay are compatible, more uniform dispersions of clay are obtained when the width of the clay layers is thinner than in the case of lower compatibility [37].

Kim et al. [38] prepared nanocomposites of octadecylamine-modified (ODA) MMT and NBR in an internal mixer using 3(-mercaptopropyl)trimethoxysilane as a coupling agent. No change in the maximum torque values were observed with the addition of coupling agent thereby proving that the coupling agent took no part in the crosslinking, at 180 °C with a sulfur curing system. The above authors reported enhanced thermal stability of the organo-MMT/NBR nanocomposite in the presence of the coupling agent, which was attributed not only due to the difference in chemical structure but also due to the restricted thermal motion of macromolecules in the silicate layer. It was observed that incorporation of below 5 phr coupling agent in the organoclay/NBR nanocomposites enhanced the tensile strength and modulus while above 5 phr content these properties were decreased. The improvement was explained by the authors due to a better interaction between organoclay and NBR whereas the decrease was attributed to the excessively added silane compound existing as a nonreactant after curing which form multimolecular layers between the boundaries of organoclay and NBR, thus causing a defect in the nanocomposites.

The effect of clay modification on organo-MMT/NBR nanocomposites was further studied by Kim et al. [39]. The alkylamines used for modification were octylamine (C8), dodecylamine DDA (C12), and ODA (C18). It was found that the mechanical properties increased in the order C8-MMT< C12-MMT< C18-MMT, depending on the length of the alkyl chain in the alkyl ammonium. With increasing organo-MMT content, the organo-MMT/NBR nanocomposites showed substantial improvement of mechanical properties compared with unfilled NBR. This high reinforcement effect implied a strong interaction between the matrix and the clay interface, which was attributed to the nanoscale and uniform dispersion of the silicate layers in the NBR matrix.

Study of the vulcanization reaction showed that as the chain length of the modifier increased the rheometric torque decreased and the optimum curing time were shortened [40]. They also observed the extent of swelling in methyl ethyl ketone (MEK) clearly decreased with increase in organo-MMT loading. Thus the organo-MMT/NBR nanocomposites have excellent barrier properties compared with vulcanized NBR.

2.5 Carbon Nanotubes/Rubber Composites

Carbon nanotubes (CNT) can be visualized as graphene layers rolled into cylinders consisting of planar hexagonal arrangement of carbon–carbon bonds. During their growth, depending on the synthesis methods, they can assemble either as concentric tubes (multiwall nanotubes, MWNTs) or as individual cylinders (single wall nanotubes, SWNTs). They attracted enormous attention for their fundamental behavior and for their use in a wide variety of applications in nanoelectronic devices, probe tips for scanning probe microscopes or in the automotive and aerospace industries for the dissipation of electronic charges. The extensive interest in CNTs arises from their unique structural and physical properties: their small size in the nanometer scale, their unique electronic behavior, their exceptional properties of ballistic transport, their extremely high thermal conductivity and high optical polarizability, as well as their unparalleled mechanical properties such as high elastic modulus and tensile strength.

One of the biggest challenges in the preparation of polymer composites, is to obtain a homogeneous dispersion of carbon nanotubes in a polymer matrix because van der Waals interactions between individual tubes often lead to significant aggregation or agglomeration, thus reducing the expected property improvement of the resulting composite.

Different techniques intended to optimize the nanotube dispersion within the polymeric medium have been used. These include oxidation [41] or chemical functionalization [42] of the tube surface and use of surfactants [43]. The above methods intend to promote adhesion between nanotubes and polymer, thus enabling effective stress transfer at the polymer–filler interface.

CNTs treated with 3-aminopropyltriethoxysilane improved the mechanical properties of NR composites, through the stronger polymer-filler interactions between reinforcement and rubber matrix [44].

Composites based on MWCNT and block copolymer SBS with two different contents of styrene have been investigated and their electrical conductivity and mechanical properties have been evaluated [45]. According to the results of dynamic mechanical analysis, the MWCNTs interact with both phases of the copolymer acting as reinforcing filler, whereas the dispersed agent acts as plasticizer. However, it was shown that the reinforcing effect of MWCNTs is dominant, resulting in an overall improvement of mechanical properties of the composites.

MWCNTs were used in SBR-based rubber compound for partial replacement of carbon black and with high content of plasticizers [46]. By the increase of their apparent shape factor it was shown that the oil permits better dispersion and alignment in the rubber matrix. The reinforcing effect of MWCNTs has been studied for both, sulphur-vulcanized and radiation cured nanocomposites. In those cases, a strong reinforcing effect has been recorded at low elongations, but the extra-reinforcement tends to disappear at high elongations due to the poor interaction between the nanotube surface and rubber matrix, The incorporation of plasticizer permits to partially reduce the fast heat build up and, hence, the strong mechanical hysteresis normally observed in nanocomposites prepared with MWCNTs.

In another work [47], it was found that the addition of 1 phr MWCNT to SBR leads to 45 % increase of modulus and 70 % increase of tensile strength. On the other hand, TEM analysis of composites has revealed poor dispersion. The large decrease of equilibrium swelling in toluene with MWNT content was not ascribed to filler-matrix interfacial interactions but to the occlusion of rubber into the aggregates.

2.6 Graphene/Rubber Composites

Graphene possesses similar mechanical properties as CNTs, but has superior electrical and thermal properties and larger surface area because of its 2-dimensional crystal structure. This material as well as its derivatives as fillers for polymer matrix composites, have shown a great potential for various important applications. The interface between the dispersion layers and the matrix plays a crucial role in determining the structure and properties of nanocomposites. Surface functionalization, including non-covalent or covalent modification of nanoparticles, is an effective method for improving the interfacial interactions between nanoparticles and polymer matrix [48].

Graphene oxide (GO) is oxygenated graphene possessing abundant oxygen-containing functional groups including epoxide, hydrpoxyl and carboxyl groups on the edges and surfaces. It has attracted increasing interest as a filler for polymer nanocomposites due to its high dispersive capacity, long coherence length and the barrier property. The improvement of mechanical properties of GO/polymer composites was attributed to its high elastic modulus ($\sim$650 GPa) and the efficient stress transfer through the polymer matrices to GO. This enhancement of mechanical properties mainly depends on two factors: filler dispersion and interfacial adhesion. It also should be noted that the oxygen-containing groups of GO assist its dispersion into polymer matrices and form strong hydrogen-bonding interactions especially with polar polymer matrices [49].

Bai et al. [50] successfully prepared, by a modified Hummers method, chemical exfoliated GO nanosheets with high aspect ratios. Such nanosheets were well mixed with carboxylated NBR (HXNBR) by a simple solution-mixing method and produced GO/HXNBR composites. The addition of 0.44 vol.% of GO nanosheets enhanced the tensile strength and modulus at 200 % elongation of HXNBR by more than 50 and 100 %. This was claimed to be due to strong interfacial interactions between the oxygen-containing functional groups of nanosheets and the carboxyl groups present in HXNBR. This speculation is further supported by the increase of the glass transition temperature of HXNBR from −23.2 to −21.6 °C, at a GO content of 1.3 vol.%. The results indicated that GO efficiently reinforced HXNBR due to the good dispersion and strong interfacial interactions.

In another work, butyl rubber (IIR) nanocomposites based on modified graphene (MG) sheets, were fabricated by solution processing followed by compression molding. MG was prepared from natural graphite (NG) through graphite oxide route [51]. X-ray diffraction showed that the exfoliated MG was homogeneously dispersed in the IIR matrix with doping levels of 1–10 wt% as evidenced by the lack of the characteristic graphite reflection in the composites. In contrast, the graphite retained its stacking order and showed the sharp characteristic peak in the NG-IIR composites. Scanning electron microscopy images of the fracture surfaces of the IIR matrix showed that MG nanofillers exhibited better compatibility than NG. The mechanical properties of MG-IIR nanocomposites were significantly improved due to the efficient distribution of the large surface area MG sheet.

Well-dispersed GO/EPDM/petroleum resin (PR) composites were successfully prepared by Chen et al. [52], via the combination of solution mixing and two-roll mill processing. The matched surface energy as well as low interfacial energy of EPDM and GO probably contributed to the good dispersion of EPDM/PR composites. These results would provide valuable guidance for evaluating the dispersion of GO in polymer matrices through surface energy and interfacial energy. Furthermore, the addition of 0.5 wt% GO increased the tensile modulus, tensile strength and elongation at break of the GO/EPDM composite. Low GO loading improved the damping properties of EPDM/PR matrices, which seemed to provide a novel approach to prepare damping materials. However, the thermal stability of EPDM/PR mildly decreased with low GO loading.

Ozbas et al. [53] demonstrated the use of functionalized graphene sheets (FGS) as multifunctional nanofillers to improve mechanical properties, lower gas permeability, and impart conductivity of several elastomeric matrices. Sixteen times higher loadings of traditional carbon black (CB) fillers are required to obtain the same stiffness as FGS. All these elastomers showed similar and significant improvements of mechanical properties with FGS, indicating that the mechanism of property improvement is inherent to the FGS and not simply a function of chemical crosslinking. FGS slightly accelerates the curing rate of NR, but the insensitivity of the increase of modulus to the polymer type suggests that the major mechanism of reinforcement does not arise from increased crosslinks density but from the FGS nanofiller geometry. The decrease of gas permeability was attributed to the high aspect ratio of the FGS sheets. This creates a tortuous path mechanism of gas diffusion; fitting the permeability data to the Nielsen model yields an aspect ratio of $\sim$1000 for the FGS. Electrical conductivity is demonstrated at FGS loadings as low as 0.08 % in poly(dimehtyl siloxane) (PDMS) and reaches 0.3 S/m at 4 wt% loading in NR. This combination of functionalities imparted by FGS is shown to result from its high aspect ratio and carbon-based structure.

An interesting technique of preparing nanocomposites of reduced GO (RGO) platelets with NR, was based on the co-coagulation of NR latex and RGO followed by compounding in order to incorporate the curing system, by one of two methods: solution treatment or two-roll milling [54]. It was demonstrated that property improvements were strongly dependent upon the processing history and nanocomposite morphology. Solution treatment (implantation of peroxide curing agent by swelling the NR in toluene) preserved the segregated filler network morphology produced by the co-coagulation procedure, whereas the milling process destroyed this network and generated a homogeneous dispersion of RG-O platelets in the NR matrix. The segregated network morphology was shown to be advantageous for conductivity properties and greatly increased the stiffness of the composite versus neat NR, but also significantly reduced the elongation to break of the samples. The milled nanocomposites also exhibited enhanced stiffness and strength while maintaining a high elongation to break. On the other hand, reinforcing effect in the solution-treated nanocomposites was attributed to the formation of a sample-spanning network of strongly interacting RGO platelets, located in the interstitial regions between latex particles, whereas in the milled nanocomposites, reinforcement is due to simple mechanical restraint along with promotion of strain-induced crystallization by the high aspect ratio RGO platelets.

2.7 Aramid Fibre/Rubber Composites

Natural rubber (NR) is one of the most important elastomers characterized by excellent elasticity and flexibility. This type of elastomer contains small amounts of fatty acids and proteinaceous residues, acting as accelerators to sulfur curing, which is the main route used in industry to vulcanize natural rubber. Because of the double bonds in its macromolecular backbone, it displays poor oil and ozone-resistance due to oxidative or thermal degradation. Moreover, loss of mechanical properties, such as low tensile strength and poor tear resistance, are also some drawbacks of NR. Many techniques were investigated in order to improve these disadvantages, such as reinforcement with various particulate fillers (e.g. carbon black, ultra-fine calcium carbonate and modified montmorillonite).

Aramid fibres were also used as reinforcement for rubbers, because they combine high specific strength and modulus, high thermal resistance, chemical inertness and low electrical conductivity compared with metallic fibres. There is, however, a recognized problem of poor interfacial adhesion between aramids and the usual rubber matrices and, therefore, various methods have been used to modify their surface. The application of chemical treatment like N-alkylation, RFL dipping, plasma treatment and polymer grafting to improve surface roughness and to bring various functional groups on the fibre surface is highly required for these kinds of fibres to improve adhesion with the elastomeric matrix [55–58].

In order to improve aramid-rubber interactions, these fibres have been treated with resorcinol formaldehyde latex (RFL). Previous studies have shown that the aramid-NR interaction was improved by the introduction of RFL treatment on the fibre surface [59].

Similar attempts in the past, have used di-isocyanate treatment of the aramid fibre surface, for its subsequent incorporation into polyurethane elastomers [60].

The use of a reactive compatibilizer like maleic anhydride grafted polymer with a non polar part having a structure similar to polymer matrix is also used to promote fibre-matrix interactions in aramid fibre reinforced composite [61].

Thermoplastic compounds of natural rubber and high density polyethylene, at a ratio of 70/30, were reinforced with aramid fibres [62]. The incorporation of graft-co-poly(ethylene/maleic anhydride) (PE-g-MA) as compatibilizer significantly improves the mechanical properties of composites with an optimum corresponding to 20 % fibre loading.

Short aramid fibres coated with RFL were studied by Shibulal and Naskar [63] as reinforcement for ethylene-octene copolymer (EOC), a new generation metallocene catalyzed thermoplastic elastomer which has been implemented successfully as an impact modifier of PP. Significant improvement was observed in the low strain (10 %) modulus and modulus at 100 % elongation by tensile tests, as well as in the storage modulus at the low strain region by rheological analysis. Improvement in tensile strength coupled with elongation at break and good fibre dispersion particularly at high fibre loaded composite were achieved with the incorporation of low molecular weight maleic anhydride grafted 1,2 polybutadiene (MA-g-PB), which indicates that it acts as an interface modifier through compatibilization between the fibre and the EOC matrix, being a good dispersing agent at the same time. SEM photomicrographs of the fractured surfaces of the composite with MA-g-PB revealed sticking of polymer traces on the pulled out fibre surface and further support the evidence of compatibilizing action of MA-g-PB.

Another simple chemical treatment reported in the literature for aramids is surface hydrolysis. Improvement of the interfacial adhesion of aramid fibre to styrene-ethylene-butylene-styrene (SEBS), a thermoplastic block terpolymer, was obtained by slightly hydrolyzing the fibre with sodium hydroxide solution to increase the number of reactive amino end groups and then mixing with the matrix and maleic anhydride grafted SEBS (MA-g-SEBS), acting as compatibilizer [64]. The tensile strength of the compatibilized composite was found to increase for compatibilizer concentration up to 5 % wt.

2.8 Natural Fibre/Rubber Composites

Over the past decade there has been growing interest in the use of lignocellulosic fibres, as reinforcing elements in elastomers. Compared with other fillers, cellulose owns a series of advantages, such as its renewable nature, low cost, low density, ease of chemical modification and biodegradability. Natural-fibre reinforced polymer composites are used as an alternative low cost sustainable material for structural and non-structural applications, such as building products, automotive applications, packaging, furniture and consumer goods [65–67].

It is well known that different surface properties between fibre and matrix, i.e. the former is highly polar and hydrophilic while the latter is, generally, non-polar and relatively hydrophobic, make necessary the suitable modification, in order to improve fibre/polymer compatibility and their interfacial adhesion.

Several strategies of changing the surface profile were developed, including chemical or physical treatment, the use of compatibilizers and surface modifications techniques. Alkali treatments, acetylation, graft co-polymerization or the use of maleic-anhydride-propylene co-polymer are some techniques appropriate to adjust the surface polarities between the natural fibre and polymer matrix [68].

In addition, the chemical modification using coupling agents bearing two reactive groups, one of which being likely to react with the OH function at the fibre surface, whereas the other one is left to copolymerize with the matrix, constitutes an interesting way allowing the establishment of covalent bonding between fibres and matrix, thus leading to materials with high mechanical properties.

For instance silane coupling chemicals present three main advantages: (i) they are commercially available in a large scale (ii) at one end, they bear alkoxysilane groups capable of reacting with OH-rich surface, and (iii) at the second end, they have a large number of functional groups which can be tailored as a function of the matrix to be used. The last feature ensures, at least, a good compatibility between reinforcing element and the polymer matrix or even covalent bonds between them.

Regarding the study of elastomeric composite systems, cellulose fibres were incorporated in low density polyethylene and natural rubber after chemical modification involving three silane coupling agents, namely γ-methacryloxypropyltrimethoxy (MPS), γ-mercaptoproyltrimethoxy (MRPS) and hexadecyltrimethoxysilanes (HDS). Composites reinforced with cellulose fibres treated with MPS and MRPS displayed good mechanical performance [69]. On the other hand, with HDS treated fibres only a modest enhancement on composite properties was observed.

Varghese et al. [70] reported that the surface of sisal fibres modified by acetylation treatment could increase its adhesion properties to natural rubber. Also, Martins and Joekes [71] observed an improved performance of rubber composites after surface acetylation of cellulose fillers.

In another work [72], wood fibres were subjected to mechanochemical reaction with acetic anhydride to prepare surface-acetylated cellulose powder (SACP) through pan-milling in the solid state at ambient temperature. Curing characteristics indicated that NR compounds filled with SACP possessed better processability and scorch safety. The mechanical properties of vulcanizates, i.e. tensile strength, tear strength and modulus at 100, 200 and 300 % elongation, increased with SACP, but elongation at break and hardness were less as compared to those of pristine cellulose fibres filled composites. They attributed this improvement in better filler dispersion and increase filler-matrix interfacial adhesion.

The use of particulate cellulose fillers, obtained from natural fibres, was also investigated. In fact, cellulose particles were successfully modified using different coupling agents, such as pyrromellitic dianhydride (PMDA), benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BPDA), 1,4-phenylene diisocyanate (PPDI), methylene-bis-diphenyl diisocyanate (MDI), γ-mercaptopropyltriethoxysilane (MRPS) and γ-ethacrylopropyltriethoxysilane (MPS) [73]. The stiff backbone of these grafted agents ensures that the one reactive group is preserved and directed outwards from the fibre surface. Grafting and preservation of the second function were proven by several techniques. These functionalized fibres were exploited in the preparation of cellulose-reinforced composites based on OH- or C=C rich matrices such as NR.

Similarly, the treatment of cellulosic agro-based fillers (sorghum stalk) for rubber reinforcement with alkali, glyceride oil, and cationic agents indicated that glyceride oil further inhibited adhesion between filler and matrix [74]. The alkali treatment was aimed at cleaning the surface of the cellulosic filler by removing its natural admixtures, such as lignin, pectines and some fats and oils. However, it is believed that some surface roughening will also be imparted. Improvement in tensile strength, hardness and density was observed in comparison with untreated fibre composites. The cationic treatment was designed to offer a positive potential to the filler as a prelude to trigger electrostatic attraction with rubber. It was found that this objective was fulfilled, the cationic filler composite was dense and for some low loadings it had the highest strength and hardness.

Sisal fibre/NR composites were prepared with filler loading 10–30 phr [75]. fibre treatment (alkalization) and addition maleic anhydride grafted natural rubber (NR-g-MA) were followed to improve interfacial adhesion of fibres to NR. Composites of alkali treated sisal fibre and NR exhibited higher tensile properties and hardness than those containing untreated fibres at all fibre concentrations, due to the improved adhesion between treated fibre and NR matrix through the mechanical interlocking mechanism. The addition of NR-g-MA into composites increased their mechanical properties but prolonged scorch time and cure time. NR-g-MA provided to the composite a more effective improvement of mechanical properties when compared to fibre alkalization.

2.9 Rubber Reinforcements for Special Uses

As already stated, EPDM, an elastomeric terpolymer consisting of ethylene, propylene and unsaturated diene, has become one of the most popular synthetic rubbers, because of its unique properties. However, due to the copolymerization of ethylene with propylene, EPDM possesses low crystallinity and cannot reinforce itself like NR or polychloroprene. There are two traditional methods to reinforce EPDM: incorporation of filler (carbon black, silica, clay minerals) and blending with crystal resin.

Sammarium borate ($SmBO_3$) and Sb-doped SnO_2 (ATO), due to their special electric and magnetic properties, were used to reinforce EPDM composites. However the tensile strength of those EPDM composites is not satisfactory, therefore blending with crystalline polymers, such as polyolefins, was proposed. Su et al. [76] used three types of ethylene-olefin copolymer (POE) in order to reinforce EPDM/$SmBO_3$ and EPDM/Sb-doped SnO_2 (ATO) compounds.

EPDM composites reinforced with polysulfonamide (PSA) short fibres were prepared and compared with those contaning aramid fibres [77]. It was found that the ablation rate and thermal conductivity of PSA/EPDM composites were lower, whereas their thermal degradation temperature and limiting oxygen index were higher. Dynamic mechanical thermal testing and morphology observations revealed that strong interfacial bonding between fibre and matrix was developed and this was beneficial for improving the ablation properties of the composites.

Manjhi and Sarkhel [78] reported an enhancement of filler-matrix bonding and filler dispersion in EPDM/kaolin systems with the incorporation of MA-g-EPDM as compatibilizer.

Maleic anhydride grafted EPDM (MA-g-EPDM) was used as compatibilizer to enhance miscibility in EPDM/bentonite (Bt) composites [79]. The addition of 10 parts per hundred (phr) of MA-g-EPDM into EPDM/Bt composites results in significantly improved tensile properties and solvent resistance, as compared with composites without compatibilizer. The cure and scorch time, maximum torque and minimum torque of compatibilized composites were increased upon addition of MA-g-EPDM. Finally, SEM micrographs of tensile fractured surfaces of compatibilized EPDM/Bt composites showed better dispersion of Bt and interfacial adhesion between EPDM and Bt as compared with uncompatibilized composites.

Pasbakhsh et al. [80] reported similar results, claiming that the incorporation of MA-g-EPDM promotes compatibilization by creating an interphase between the EPDM matrix and halloysite nanotubes, which produces stronger interfacial interactions and also improves the dispersion of nanotubes in the rubber matrix.

In the field of rubber composites suitable for special applications, poly(dimethyl siloxane) (PDMS) elastomers are a class of materials of prime importance. In fact, PDMS is a highly recommended elastomer for a variety of applications including those of medical, electronic, automotive and aerospace industries. However, these grades of elastomers are characterized by poor mechanical properties and, therefore, reinforcing fillers must be added to overcome this drawback. PDMS is commonly reinforced by fumed silica in a significant proportion to form high performance composites. The use of such large amounts of silica significantly increase the opacity of the resulting materials as well as their specific weight. Alternatively, fillers with large specific area and aspect ratio, such clay nanoplatelets, could bring better mechanical performance, improved barrier properties and thermal stability, keeping the material transparent and lightweight. In spite of their similarities in structure, montmorillonite does not naturally delaminate in PDMS matrix. In order to achieve the expected properties of nanocomposites, stacked clay platelets must be dispersed and strong interactions between the polymer and mineral phase must be promoted. Due to its hydrophilic nature, clay is generally modified by quaternary ammonium surfactants to increase the intergallery spacing and to achieve enough hydrophobicity, which will readily promote miscibility with the polymer matrix.

Successful treatments of the reinforcement include that of Burnside and Giannelis [81], who studied PDMS/OMMT nanocomposite systems, using melt intercalation. The organosilicate was prepared by ion exchanging Na^+-MMT with dimethyl ditallow ammonium bromide. The prepared nanocomposites exhibit decreased solvent uptake and increased thermal stability.

In another work, organosilicate was also prepared by ion exchange Na^+-MMT with hexadecyltrimethylammonium bromide and the silicone rubber/OMMT hybrids were prepared by simple mechanical mixing [82]. It was observed that the mechanical properties and thermal stability of hybrids were very close to those of aerosilica-filled silicone rubber.

A novel kind of OMMT was successfully prepared by Wang et al. who used *N,N*-di(2-hydroxyethyl)-*N*-dodecyl-*N*-methylammonium chloride as intercalation agent [83, 84]. Exfoliated nanocomposites were prepared using addition type silicone rubber via solution intercalation. The enhanced mechanical and physical properties demonstrated the efficient reinforcing and thermal stability properties of OMMT.

In a more recent work, Kim et al. [85] used bis(3-triethoxysilylpropyl)tetrasulfide (TESPT) to functionalize two commercially available clays, sodium montmorillonite and Cloisite 25A. Incorporation of the tetrasulfide group-containing clays was found to be effective for the enhancement of interfacial interaction between PDMS and clay, by possible chemical reaction of tetrasulfide groups with vinyl-terminated PDMS. According to the results obtained by swelling in toluene, the crosslinking density was lower than that of neat PDMS, indicating that the observed improvement in mechanical properties arise from enhanced compatibility between the constituents and not from increased crosslinking density.

Poly(dimethylsiloxane) (PDMS)/clay nanocomposites have also been produced by Labruyère et al. [86, 87] by the use of ω-ammonium functionalized oligo-PDMS surfactant [PDMS-$N^+(CH_3)_3$]. The clay ion-exchanged by PDMS-$N^+(CH_3)_3$ has been compared to nanocompositions prepared with PDMS and either non-exchanged sodium MMT and to two organoclays modified by using either alkyl ammonium cations ($C_{38}H_{80}N^+$) or hydroxyalkyl ammonium ($C_{22}H_{48}ON^+$) cations. The authors observed that nanocomposites based on PDMS-$N^+(CH_3)_3$ exhibit the best filler dispersion and significantly higher viscosity due to better intercalation of PDMS chains into clay galleries. Increase of stiffness with increasing the content of treated clay in PDMS was also recorded, but no significant differences between the different organo-modifiers were detected. Regarding the transport properties for organic vapours, the sorption is not influenced by the presence of organically modified clay, whereas the diffusion parameter is significantly affected in the range of sorbed vapour 0–4 % for acetone and 0–7 % for *n*-hexane [87].

Regarding the characteristics of the elastomeric matrix, recent studies try to investigate the related effects. Takeuchi and Cohen [88] published on systems of organo-montmorillonite and PDMS networks prepared from hydroxyl- or vinyl-terminated precursors. No improvement in the modulus of networks synthesized from vinyl-terminated precursors was obtained. The authors concluded that enhancement of the modulus was obtained only for non-optimal networks formed with hydroxyl-terminated precursor chains in contrast with vinyl-terminated chains. Their results indicate that reinforcing effect of these elastomers can be attributed to the anchoring of the hydroxyl end group to the silicate filler that dramatically reduces the soluble fraction and binds pendent chain ends.

The preparation procedure is also very critical for proper filler dispersion. A two step process was reported for the preparation of exfoliated/intercalated polymer/MMT nanocomposites, which included preparation of MMT solution via in situ polymerization of dimethyldichlorosilane inside the galleries of layered silicate hosts and, then, after separating most of the PDMS amount, the treated–MMT solution was blended with several polymers [89]. Bokobza [2] made a series of silicone/nanoclay composites from organically modified montmorillonite and addition cured PDMS. Nanoclay platelets were mixed with hydride terminated PDMS, subsequently cross-linked by 1,3,5,7-tetravynil-1,3,5,7-tetramethylcyclotetrasiloxane via a chemical reaction catalyzed by platinum divinyl-tetramethylsiloxane. Unfortunately, the process demands cure time of 12 h, making impractical the application of this method in a continuous molding process. Moreover, only minor improvements in tensile properties were reported. A new strategy to prepare disorderly PDMS nanocomposites was developed by Ma et al. [90]. More specifically, a quaternary ammonium-containing polysiloxane surfactant was adopted to modify the clay. The slurry of modified clay was then mixed with commercial RTV silicone rubber by hand and exfoliation was achieved as it was confirmed by TEM and XRD analysis. The resulting silicone/nanoclay composites presented significant improvement of their mechanical properties.

In order to overcome difficulties during preparation of high temperature vulcanized silicone rubber (HTV-SR) nanocomposites, Wang and Chen prepared a master batch of the above modified montmorillonite (OMMT-MB) by solution intercalation [91].

From the study of a multi-system, it has been shown that for nanocomposites based on silanol-terminated PDMS and alkylammonium modified layered-silicate fillers, there are two factors controlling silicate dispersion:

(i) the presence of the appropriate number of long ammonium-bound alkyl chains and
(ii) the presence of the appropriate number of polar functional groups. Therefore, dispersion is not a function of the molecular weight or of the differences in processing viscosity induced but it is rather influenced by the silanol end-group concentration [92].

Masterbatches of MMT and OMMT with siloxane-polyether surfactant were used for the preparation of high molar mass poly(dimethylsiloxane)-gum nanocomposites [93]. The incorporation of 5 phr OMMT into PDMS matrix, via masterbatch compounding, improved the tensile strength as much as that obtained with composites loaded with 3 phr OMMT clay by direct addition of the clay to PDMS.

Organoclay nanocomposites show increased versatility regarding their performance properties. Yang et al. [94] prepared flame-retardant methyl vinyl silicone rubber (MVMQ)/MMT nanocomposites by the solution intercalation method, using magnesium hydroxide (MH) and red phosphorus (RP) as synergistic flame-retardant additives, accompanied by aero silica as synergistic reinforcing filler. The above researchers claim that this kind of silicone rubber nanocomposites may be a promising flame-retardant polymeric material.

Liu et al. [95] examined the changes of diffusive properties, due to the incorporation of organo-modified MMT clay into a silanol terminated PDMS matrix, cross-linked with TEOS using 2-ethylhexanote. A cure time of 12 h was required and the study focused on the effect of deformation on diffusion rates. However, a notable reduction in the gas permeability of the silicone/OMMT samples with increasing filler loading was observed in the absence of external deformation.

Siloxane modified MMT nanoclays and commercially available organo-modified nanoclays were combined with liquid silicone rubber (LSR) matrix [96]. The morphologies of the LSR/nanoclay composites were analyzed by SEM and TEM, and partial exfoliation of the clay platelets was observed. Up to 20 % reduction of water permeability was achieved, as well as a 24 % improvement of tear strength and 40 % improvement of compression.

HTV-SR/OMMT-MB-20 % nanocomposites demonstrate enhanced tensile and thermal properties in comparison with HTV-SR/OMMT-20 %. In a recent work [97], this type of hyperbranched OMMT was directly added in HTV-SR system. The enhanced tensile properties suggest an efficient reinforcing agent because of the good dispersion of nanosilicate layers and the resulting "anchor" effect of the hyperbranched macromolecules in the composite.

Incorporation of aminopropyltriethoxysilane (APTES) to silicone rubber by copolymerization enhanced the adhesion properties of silicone rubber [98]. Stability of the silicone rubber against thermal degradation was examined through Thermogravimetric analysis. The tests revealed that compounding with Cloisite 30B boosted up the thermal stability of silicone rubber, much more efficiently than carbon black.

In an attempt to correlate silicate dispersion with the resulting mechanical properties in the PDMS/layered silicate nanocomposites, a systematic study was performed of the mechanical properties, equilibrium swelling and sol fraction measurements of cross-linked silanol-terminated PDMS networks as a function of the type and content of nanofiller as well as of the composition of base resin [99]. In montmorillonite systems, in particular, it was observed that equilibrium solvent uptake and mechanical properties are independent of dispersion state, which suggests that edge interactions play a more significant role than the degree of exfoliation.

The effect of intercalation agent for organic modification of MMT in the mechanical properties of condensation type polysiloxane was studies by Tarantili and Vasilakos [100]. It was observed that the incorporation of Cloisite 20A showed higher reinforcing capacity in PDMS in comparison with Cloisite 30B hybrids due to its higher content organic modification, which results in increased interlayer distance of clay platelets and, therefore, facilitates intercalation and further exfoliation processes.

2.10 Hybrids

Another alternative to conventionally reinforced elastomers is the use of a mixture of two or more fillers of different morphologies, which produces a composite called "hybrid". Wang [101] showed that vulcanizates filled with CB and silica, without coupling agent, display a weaker Payne effect than that resulting from direct addition of two single fillers. This suggests a less developed filler network in the filler blend compounds due to a weaker interaction between silica and CB aggregates than between two aggregates of any single filler.

One of the most important commercial hybrid fillers is carbon–silica phase dual filler, produced by pyrolizing petroleum based feedstocks with silicon containing feedstocks, by a unique co-fuming technology developed by Cabot Corporation [102]. This material, which consists of individual composite aggregates containing carbon and silica phases, was shown, when added to hydrocarbon rubber, to have stronger polymer-filler interaction compared to a blend of silica and carbon black of equivalent rubber.

Bokobza et al. [103] used spherical silica particles, generated in situ via sol-gel process and nanofibres of sepiolite for reinforcing NR. In a more recent work, composites of SBR filled with mixtures of pyrogenic silica combined with a silane agent and fibres of organophilic sepiolite were studied. It has been demonstrated that composites filled with mixtures of these fillers exhibit improved characteristics with regard to single filler materials. The morphologies, mechanical and swelling properties reveal synergistic effects arising by the incorporation of these two types of fillers.

As mentioned above, the major problem during preparation CNTs-elastomer composites is poor distribution and dispersion of CNTs in the elastomer phase. Many researchers have reported the use of hybrid systems instead of CNT alone. Bokobza et al. [104] used this approach for the investigation of reinforcing SBR with mixtures of CB and MWCNTs. The results revealed an improvement of mechanical properties and electrical conductivity with lower percolation threshold than that obtained with composites filled only with CNTs. Through a combination of the benefits of each type of filler, these hybrid composites could potentially exhibit improved characteristics with respect to single-filler systems. On the other hand, the dilution of expensive CNTs with a cheaper reinforcing component, without compromise of the mechanical properties of the resulting material, would have an economic impact as it would reduce the cost of nanotube-based composites [47].

Similarly, MWCNTs and silica were used as hybrid fillers in NR nanocomposites [105]. The results of this study showed that scorch and curing time decreased as the MWCNT content increased in the silica/MWCNT mixture and the maximum torque was increased about 30 %. Furthermore, the tensile strength, elongation at break and fatigue also increased up to a certain filler content and then decreased because of the agglomeration of both fillers, which reasonably results in reduction of their reinforcing capabilities. As the concentration of MWCNT increased, agglomeration became dominant and reduced the combined reinforcing effect. These results imply that silica/MWCNT hybrid presented better properties and created a synergistic effect for the nanocomposites.

Many researchers investigated the synergistic effect of different fillers, in order to achieve a balance between properties and cost. Although graphene and CNTs are similar in chemical composition, different topology distinguishes carbon nanotubes from graphene and offers them unique properties. One major advantage of graphene over CNTs lies in the precursor of graphene-graphite, which is natural abundant [106]. This is essential for industrial applications in the field of composites, since high yield production as well as cost effective and scalable process is allowed [107].

In comparison to graphene, the dispersion of MWCNTs into silicone rubber matrices was found extremely difficult, although both the above possess similar physical structure, whereas it is much easier for MWCNTs to be dispersed into the matrix with the aid of graphene. The strong interactions between graphene and silicone rubber, as well as between graphene and MWNTs, account for the good dispersion of MWNTs. Graphene also behaves as a compatibilizer, as it was observed that the addition of graphene provides a simple route to disperse carbon nanotubes and the synergistic effect facilitates fabrication of high performance polymer composites [108].

A new hybrid nanofiller (MWNTs/OMMT) has also been used as reinforcement for thermoplastic natural rubber (TPNR) composites, by incorporation into the rubber system via the melt blending method. TPNR is a blend of PP, liquid natural rubber (LNR) as a compatibilizer, and NR at the percentage of volume ratio 70:10:20, respectively [109]. The total reinforcement content was fixed at 4 wt%, so a compound of TPNR with 4 wt% OMMT, 4 wt% MWNTs, and hybrid 2 wt% OMMT 2 wt% MWNTs was compounded using the internal mixer. The results showed that the tensile strength and Young's modulus of the composite were improved by using the hybrid nanofillers. However, the elongation at break considerably decreased with the above hybrid fillers. The effect of MWNTs, OMMT, and hybrid MWNTs–OMMT was also confirmed by DMA. The results suggest that the storage modulus, loss modulus, and glass transition temperature (T_g) also increased for all samples reinforced with nanofillers. TEM micrographs revealed the interfacial adhesion between the fillers and the matrix, which contributed significantly to the improvement of the properties.

Elastomeric hybrids consisting of graphene oxide (GO) sheets were fabricated by utilizing butadiene–styrene–vinyl pyridine rubber (VPR) as the host through co-coagulation process and in situ formation of an ionic bonding interface [110]. The VPR/GO composites with a normal hydrogen bonding interface were also prepared. The mechanical properties and gas permeability of these hybrids with an ionic bonding interface were obviously superior to those of the composites with a hydrogen bonding interface. With the ionic interfacial bonding, inclusion of 3.6 % v/v of GO in VPR generates a 21-fold increase in glassy modulus, 7.5-fold increase in rubbery modulus, and 3.5-fold increase in tensile strength. The very fine dispersion of GO and the strong ionic interface in the hybrids are responsible for such unprecedented reinforcing efficiency of GO towards VPR.

Recently, studies of the synergistic effect of natural fibres and particulate fillers compounded with different polymeric matrices on the physicochemical properties of hybrid composites have been reported [111]. These studies revealed interesting results, showing the improvement of specific properties together with additional environmental and cost benefits.

Anuar et al. [112] prepared hybrid composites of thermoplastic natural rubber (TPNR) reinforced with *Hibiscus cannabinus* L fibre (kenaf fibre: KF) and short glass fibre (GF) via melt blending using internal mixer. The effects of coupling agents, silane and maleic anhydride grafted polypropylene (PP-g-MA) on the tensile properties were also investigated. The results on tensile strength have shown that the increasing in kenaf fibre content substantially reduced the tensile strength and modulus. Incorporation of silane coupling and PP-g-MA has enhanced the mechanical properties of the systems and the fibres were coated by the TPNR, subsequently reduced the formation of void as observed in SEM micrographs for untreated systems.

It is anticipated that the combined use of both short natural fibres and silica will combine the beneficial effects of individual reinforcements for the development of materials with desirable properties. NR based hybrid composites were prepared by incorporating cellulose fibres and silica in a laboratory two-roll mill and, in order to modify the surface properties of the fillers, a silane coupling agent [bis(triethoxysilylpropyl)tetrasulfide, Si69] was used [113]. It was found that silane treatment of both fillers had significant effect on the processability but offered little benefit as rubber reinforcement. It was also found that treated fillers were better dispersed into the composite matrix and their compatibility with NR increased with silane treatment. The above study showed that these hybrid fillers when combined with Si69 silane coupling agent, could be used as substitutes for silica to improve the processability of the products with the environmental advantage and acceptable performance for rubber applications.

Shojaei et al. [114] studied the effect of carbon and cellulose fibres on the tribological characteristics of rubber-based friction materials (RBFMs). They observed that the maximum attainable drum temperature caused by the friction-induced heat containing carbon fibres is lower than that of composites reinforced with cellulose fibres. CB influence slightly the coefficient of friction, due to the lubricating role of this material as well, but considerably improve wear resistance and fade behavior. Cellulose fibres offered high friction coefficient but it was found to be destructive for fade behavior and wear rate point, due to its weak thermal stability.

3 Crosslinking

The vulcanization of elastomeric materials is a complex process, which has a high impact on the properties of the final product. In fact, the extent of this reaction, the crosslinks density along with the other network parameters are some critical factors controlling the overall behaviour of the vulcanized rubber. Therefore, it is important to monitor and control this crosslinking reaction. Several articles on the kinetics of vulcanization of various rubbers are available in the literature and especially in silicone rubbers, which is the material with very interesting curing paths. However, there are only a few reports on the vulcanization kinetics of rubber nanocomposites and the changes in rheological and thermal behaviors during the network formation by the addition of nanofillers. It has been reported that curing behavior of organomodified rubbers conflicts as strong acceleration, no change or retardation effects.

Mathew et al. reported that the addition of organoclay accelerated the cure rate of ethylene acrylate rubber (EAR) and lowered the activation energy for curing reaction calculated from the autocatalytic model [115]. The pristine clay-filled EAR composite showed a similar trend, but much smaller effect.

Monsanto rheological measurements on NR reinforced with octadecylamine-modified bentonite have shown that the organoclay accelerates vulcanization reaction and gives rise to a marked increase of torque, indicating that the elastomer becomes more densely cross-linked [116]. These results are in agreement with those from swelling experiments and from the study of vulcanization reaction with thermal analysis, where an appreciable increase of the involved heat from curing reactions has been observed. Moreover, thermodynamic parameters have shown an increase in the structural order of the nanocomposite [116]. Also, the effect of incorporation of bentonite on the vulcanization kinetics of NR was investigated by means of both cure-meter and DSC under dynamic and isothermal conditions [117]. A marked decrease in the induction time and optimum cure time of the elastomer were observed in the presence of organoclay. Although octadecylamine itself accelerated the vulcanization process, the octadecylamine-modified clay gave rise to a further significant increase of vulcanization rate, due to a synergistic effect between filler and amine. Moreover, in the presence of organoclay, a dramatic increase of the torque value was recorded, because of the formation of higher number of cross-links, which could be attributed to the confinement of the elastomer chains within the silicate galleries and consequently, to better interactions between filler and the rubber.

In another work, the influence of inorganic nanoparticles on the cross-linking mechanism of NR nanocomposites has been evaluated by applying the tube model on equilibrium statistical mechanics. The obtained results have shown that a highly ordered structure with a huge amount of entanglements, wherein the polymer is nanoscopically confined, is formed by the addition of nanoparticles [118].

Carretero-González et al. studied the influence of nanoclay on the morphological and microstructural changes of NR network based on the results from broadband dielectric spectroscopy and in situ synchrotron wide-angle X-ray diffraction [119]. It was found that nanoclay introduces a dual crystallization mechanism, due to the alignment of nanoparticles during stretching. Moreover, the strong interfacial adhesion between nanoparticles-rubber matrix can induce an early promotion and enhancement of overall crystallization of NR chains under uniaxial stretching. The above authors reported that the organoclay does not affect the extent of curing and the observed increase in modulus was attributed to: (a) the hydrodynamic effect of the clay and (b) the formation of physical cross-links due to the presence of clay.

Cataldo observed that the addition of organo-modified montmorillonite in a NR/SBR mixtures causes an increase in the cure rate and this effect was explained by the high concentration of ammonium cations present in the exfoliated clay [120].

Very interestingly, differential scanning calorimetry was established as a useful analytical tool for the determination of the energy required during rubber vulcanization. Analysis through DSC is based on the assumption that the heat of reaction is only due to a single curing reaction and is proportional to the extent of the reaction [117, 121–124]. Therefore, in isothermal curing conditions, the degree of curing (a) can be calculated from the heat-flow peak of a DSC curve by the following equation:

$$a = \frac{\Delta H_t}{\Delta H_\infty} \tag{1}$$

where ΔH_t is the accumulated heat evolved to time t and during vulcanization, and ΔH_∞ is the total amount of heat generated during the reaction.

The dynamics of the vulcanization reaction are modeled by means of a differential equation with regard to time, where the influence of the temperature and vulcanization rate are separated. Thus, the equation expressing the vulcanization rate may be written as follows [125]:

$$\frac{da}{dt} = K(T) * f(a) \tag{2}$$

where t is the time, T is the temperature, and K is the kinetic constant.

The function K(T) is related to the activation energy according to the Arrhenius expression:

$$K(T) = K_0 * \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where K_0 is the preexponential factor, E_a is the activation energy and R is the universal gas constant.

For solid-state transformations, combination of Eqs. (2) and (3) gives:

$$da/dt = K_0 e^{-Ea/RT} f(a) \tag{4}$$

In curing reaction the function f(a) may get different forms depending on the reaction mechanism. In our study, a model given for autocatalytic reaction with two reaction orders, known as Ŝesták-Berggren equation was adopted to simulate vulcanization process [126]:

$$f(a) = a^m * (1 - a)^n \tag{5}$$

where m and n denotes reaction order.

The choice of model depends on the type of chemical reaction. In the autocatalytic reaction, the maximum rate of cure is given for a conversion degree other than zero, because the reaction is promoted by the same products of the reaction.

By substitution of Eq. (5) in (4) the change of degree of conversion da/dt with temperature is given by [124]:

$$\frac{da}{dt} = K_0 * \exp\left(-\frac{E_a}{RT}\right) * a^m * (1 - a)^n \tag{6}$$

Parameters of curing process such as K(T), m, n were calculated by non-linear regression analysis plots of da/dt versus a.

Activation energy was calculated graphically, form the Arrhenius expression (Eq. 3), from the slope ($-E_a/R$) of linear regression of lnK versus 1/T:

$$\ln(K(T)) = \ln(K_o) + \left(-\frac{E_a}{R}\right) * \frac{1}{T} \tag{7}$$

In the case of non-isothermal experiments, i.e. when the sample temperature changes at a desired and constant heating rate, $\beta = dT/dt$, the calculation of activation energy of vulcanization reaction can be made from plots of the logarithm of the heating rate versus the inverse of the temperature at maximum reaction rate T_{max} while d(da/dt)dt = 0, by the Kissinger [127] method using the equation:

$$E_a = -R\frac{d\ln\left(\beta/T_{max}^2\right)}{d(1/T_{max})} \tag{8}$$

From a plot of $\ln\left(\beta/T_{max}^2\right)$ versus $1/T_{max}$, and fitting to a straight line, the activation energy E_a can be calculated from the slope.

The Ozawa method [128] can also be used through the following equation:

$$E_a = -R\frac{d\ln\beta}{d(1/T_{max})} \tag{9}$$

The activation energy for different heating rates can be determined from $\ln\beta$ versus $1/T_{max}$ plot.

In a recent paper [129] the curing mechanism and the related kinetics of montmorillonite/vinyl terminated polysiloxane nanocomposites was followed by the above described method and the effect of commercial unmodified montmorillonite as well as two different types of organically modified products, namely: Nanofil 116, Cloisite 20A and Cloisite 30B was recorded. It was found that Cloisite 20A/PDMS systems showed increased reaction rate at the early stages followed by a retardation of rate and extension of the curing time, in comparison with pure PDMS. On the other hand, Cloisite 30B seemed to decrease the curing rate of PDMS during the whole process, whereas a significant increase of this parameter was recorded in the case of unmodified clay/PDMS nanocomposites. This effect was attributed to physicochemical interactions between the cross-linking system and organoclay particles. In the attempt to further evaluate the obtained results, it was found that the autocatalytic model showed good fitting with the experimental data.

More specifically, for isothermal experiments, the increase of temperature increases, also the curing rate, as shown by the shifting of the exothermic peak to lower time values. Furthermore, the peak becomes narrow and vulcanization is completed faster. Also, the shape of conversion curve is dependent on the temperature. At low temperatures, the change in conversion is more gradual, but as the temperature increases the peak height of the conversion rate curve also increases with a shift of the peak position to higher values. The reaction rate was found to increase rapidly and after reaching a maximum it gradually slows down toward zero and this trend was observed for all the examined PDMS systems.

The incorporation of organoclay nanoparticles into the PDMS matrix affects the vulcanization reaction mechanism of the elastomer. The obtained data show that with increasing organoclay load the time required for completion of vulcanization slightly increases, in comparison with that necessary for unfilled PDMS. The reaction rate for the Cloisite 20A/PDMS systems is high at the beginning of vulcanization. A second stage is observed, where cross-linking proceeds slower, in comparison with the pure elastomer. Therefore, an inhibition during the second stage of the process, might be possible due to organoclay nanoparticles and leading to longer vulcanization time.

A stronger effect on the curing time was observed with PDMS nanocomposites reinforced with Cloisite 30B organoclay, where a significant delay of the vulcanization rate was observed, especially for hybrids reinforced with 5 and 8 phr loading. Therefore it seems that this type of reinforcement, containing hydroxy groups in the intercalation agent, increases to a higher extent the curing reaction time.

Further investigation, in order to elucidate the effect of the intercalation agent, included the study of the effect of another type of reinforcement, i.e. the unmodified montmorillonite Nanofil 116.

From the comparative study of effect of the examined montmorillonite reinforcements in the vulcanization of elastomeric matrix at 60 °C, it was observed that Cloisite 30B increases significantly the vulcanization time of vinyl terminated PDMS, followed by Cloisite 20A. However, the opposite effect was observed for the unmodified reinforcement, where the reaction was completed in shorter time and the maximum rate was achieved at shorter time, than that corresponding to pure elastomer. Curing retardation can be attributed to interactions between the catalyst system and organic moiety (quaternary ammonium compound) of the modified clay, which inhibits catalytic action [130].

In addition to the above, the consumption of a part of the cross-linker for chemical reactions with the active sites of the intercalation agent might be possible and this, would lead to a decrease of the extent of curing reaction especially at high loadings. Moreover, absorption of the cross-linking system into the montmorillonite nanoparticles would reduce the active concentration required for the cure reaction. The enhanced inhibiting effect, observed for hybrids of Cloisite 30B can also be related with the action of radical scavenging of OH groups of the intercalation agent of this type of organoclay. However, the unmodified montmorillonite seems to have a synergistic effect on the vulcanization process of the examined vinyl terminated PDMS leading to faster cure.

Contradictory results were reported in the literature regarding the effect of inorganic nanoparticles on elastomer's curing reaction. The chemistry of vulcanization reaction and the chemical activity of incorporated nanoparticles play a major part on the reaction mechanism.

Investigations of high temperature vulcanized silicone elastomers, filled with superconductive carbon blacks, have shown curing retardation, because of the radical scavenging effect of phenol-OH groups existing in filler surface [131].

On the other hand, Mathew et al. [123] reported an accelerating effect on the curing of ethylene acrylate rubber, introduced by quaternary ammonium ions, present in the organoclay modification medium. The same effect was observed during the vulcanization process of filled fluoroelastomer nanocomposites [124].

Secondary reactions with silane groups of the cross-linker have also been reported [117]. More specifically, it was claimed that the degree of cross-linking was strongly dependent on the amount of silane groups present. This effect was attributed to competitive oxidation/hydrolysis secondary reactions of the silane groups, leading to the formation of Si–OH groups, via reaction with other compounds such as moisture and O_2.

In addition to the above mentioned secondary reactions, in case of polysiloxane nanocomposites the introduction of clay nanoparticles must be taken into account. According to Takeuchi and Cohen [132] silicate oxygen groups on the surface of clays and hydrogen groups along the edge of these clay particles may enhance these secondary reactions.

In the macroscopic level, the properties of nanocomposites prepared with room temperature-vulcanized silicone rubber (RTV-SR) reinforced with MMT modified with di(2-oxyethyl)12-alkane-3 methyl-amine chloride, were explained taking into consideration incomplete curing of the whole system due to reactions of alkoxyl silicane catalyst not only with the hydroxyl containing base but also with the intercalation agent [133].

A decrease of the gel fraction (GF) with increasing clay content was observed by Kong et al. in silicone rubber nanocomposites reinforced with Fe-MMT and Na-MMT, which were modified with cetylthimethyl ammonium bromide [134]. The decrease in GF values was due to the additives of clay having the action of blocking free radicals at the formation of a three dimensional network structure.

Schmidt and Giannelis from their study on silicate dispersion and mechanical reinforcement in polysiloxane/layerd silicate nanocomposites reported that increased nanoffiller content lead to lower swelling, given that compatible nanofillers should increase the (physical) cross-link density [99]. The effectiveness of nanofillers in increasing physical cross-link density is dependent on the effective interfacial area and interfacial interaction strength.

The vulcanization kinetics of fluoroelastomer (FKM) filled with unmodified and organo-modified clay, were studied by Kader and Nah [124] with both, oscillating disc rheometer and differential scanning calorimetry under isothermal and dynamic conditions. The organo-modified clay enhanced the curing procedure through the accelerating effect of quaternary ammonium salt used in the clay modification, while the unmodified clay showed cure retardation due to the absorption of curative by the clay for in situ clay modification. The kinetic analysis showed the suitability of autocatalytic model for cure characterization. The determined kinetic parameters were in good agreement with the experimental values. The result indicated that the organoclay was efficient in reducing the energy requirement for the cure process.

4 Compatibilizing Agents, Plasticizers

4.1 Properties of Interphase Modified/Compatibilized Elastomeric Composites

The combination of different polymers is a fascinating and practical channel to get new materials with novel functions that individual components do not process. Thermoplastic elastomers not only exhibit the conventional properties of elastomeric materials at room and service temperatures but can also flow at elevated temperature and again solidify when the temperature returns, which behave like thermoplastic. However, usually due to mismatch of polarity, melt viscosity, and molecular weight the interface adhesion of rubber and thermoplastic polymer is poor, leading to an inferior mechanical property which limits the application. Therefore it is necessary to improve the compatibilization of two phases.

Compatibilization is a process of modification of the interfacial properties in an immiscible polymer blend that results in formation of the interphases and stabilization of the morphology, leading to the creation of a polymer alloy [135]. According to Utracki [136], a compatibilization process must accomplish three tasks: (i) reduce the interfacial tension, thus finer dispersion (ii) stabilize the morphology against thermal and rheological effects during the processing steps and (iii) provide interfacial adhesion in the solid state. This definition means that apart from decreases in the phase domain size and stabilization of the morphology against thermal and rheological effects, a compatibility additive must also improve the interfacial adhesion between two phases. Improved adhesion should be manifested macroscopically as improved tensile strength and modulus and perhaps as increased impact strength as well.

Elastomer blends are widely used for a variety of reasons, like improved physical properties, service life, easier processing, complex demand for the performance and reduced product costs.

In the previous years, the reactive compatibilizers have been increasingly introduced into blends. Reactive compatibilization can also provide for a degree of control over morphology development in multiphase polymer blends via manipulation of the interfacial energies within the system, which allowed the formation of a composite dispersed phase during melt blending process via encapsulation of one dispersed phase by another. With chemical reaction occurring between the functional group and the blends, the interfacial adhesion would be greatly increased and the interfacial tension would be sharply decreased.

Elastomeric composite materials consisting of cross-linked polymers and nanostructured solid fillers have become increasingly important. The interaction of the polymer molecules with the solid surface of filler particles is crucial in controlling on the performance of these elastomeric nanocomposites.

In recent years, it was reported that the anisotropic nanofillers which have a large specific surface area and high aspect ratio such CNTs and organoclay, can also be used as potential compatibilizers to improve the compatibility of mixtures of immiscible polymers. In immiscible multiphase polymer blends, one component forms the discrete phase, and it is dispersed in the host component, which act as a continuous phase. Generally, new properties are achieved through this dispersed phase, which can exist in the form of droplets, fibrils, lamellae, or even co-continuous structures after blending. The state of distribution and dispersion of filler particles between the two phases, the extent of interaction of the filler surface with either of the polymeric phases, and the resultant final phase morphology are believed to be the most important factors affecting the overall properties of the final blends. These include the affinity of the filler toward the polymeric phases, the viscosity ratio of the polymers, and the feeding routes. In the case of polymer blend nanocomposites, the nanoscale filler distribution and crystalline structure could dictate the resultant properties of the composites.

To understand the compatibilizing effect of inorganic fillers, two possible mechanisms were proposed. Mechanism I (thermodynamic compatibility): with a large specific area and high aspect ratio, anisotropic inorganic nanofillers can absorb the polymers chains on its surface to gain stabilizing energy which make the overall free-energy of mixing (ΔG_m) negative and thermodynamically driven compatibility between the immiscible components [137]. Mechanism II (kinetic compatibility): the selective localization of nanofiller in the polymer interface decreases the interfacial tension and prevents the coalescence of the domains during melt mixing which kinetically improves the compatibility between the binary phases [138].

Therefore, the addition of anisotropic nanofillers may bring about the reinforcing and compatibilization effects for an immiscible blend system simultaneously, which is a new approach to achieve high performance of polymer blend nanocomposites.

Recently rubber blends with layered silicate nanoparticles have received significant attention because of the remarkable improvements of some mechanical properties, enhanced barrier properties and reduced flammability. However, the efficiency of nanoclay with regard to improving the solid-state properties of rubber blends is extremely dependent on the degree of clay dispersion, i.e. intercalation and exfoliation as well as the distribution of the exfoliated platelets and the phase specific clay distribution, respectively. Several studies of polymer/clay systems indicated that a compatibilizing effect of clay in heterogeneous blends exists. Several studies of polymer/clay systems indicated that a compatibilizing effect of clay in heterogeneous blends exists. The droplet size of dispersed phase in NBR/styrene butadiene rubber (SBR) [139], PA6/ethylene propylene rubber (EPR) [140] was drastically reduced by addition of clay.

One of the explanations was attributed to the diminished molecular mobility, which prevents the phase separation of the components [141, 142]. Fisher et al.

[143] proposed another mechanism by which clay can form in situ grafts by absorbing large amounts of polymer, which in turn are very effective for reducing the interfacial tension and inducing compatibilization in blends from highly immiscible components.

A new method of the online measured electrical conductance (OMEC) has been successfully applied by Ali et al. [144] for the characterization of morphology development and kinetics of clay distribution in rubber blends during the mixing process. It was found that the release of the ionic surfactant from the clay galleries during the mixing was the main reason for the electrical conductance of rubber-organoclay composites. Based on the results received at mixing of pure hydrogenated acrylonitrile butadiene rubber (HNBR) with NR-clay masterbatch, the apparent clay migration from NR phase to the HNBR phase was ascribed to the different interactions with polymers and clay. Because in the clay galleries both NR and HNBR molecules can intercalate the bi-intercalated clay tactoids act as compatibilizing agent like a block copolymer. Therefore the refinement of blend morphology is caused by the compatibilizing effect of clay.

Hwang et al. [145] have successfully prepared butadiene rubber (BR)/organosilicate nanocomposites that have intercalated and partially exfoliated structures by using a two-stage melt blending method. As a result of counteracting the polarity effect and compatibility effect, the tensile properties and tear strengths of these nanocomposites increased substantially, relative to those of the neat BR, upon increasing the amounts of incorporated compatibilizer and organosilicates that contain a low weight percent of layered silicates. They attributed these results to the significantly improved compatibility and the strong interactions among the polar layered silicates, compatibilizer, and nonpolar molecular chains of the BR. The BR molecules can interdiffuse into the intergallery space of the layered silicates more readily with the aid of the compatibilizer and result in an intercalated/exfoliated structure. Additionally, these nanocomposites exhibit higher thermal stabilities and dynamic storage moduli than those of the neat BR. The relative water vapor permeabilities of the BR nanocomposites containing 10 parts of organosilicate, both in the presence and absence of the compatibilizer, were reduced to 20 % of that of the neat BR.

Being a two dimensional layered carbon nanomaterial, graphene oxide (GO) has gained much attention due to its unique structure and properties in recent years. Normally, it is oxidized from natural flake graphite and consisted of parallel pseudo two-dimensional lamellaes. The GO layers consist of randomly distributed unoxidized aromatic regions and hexahydric aliphatic regions attached with polar groups, such as hydroxyl, epoxide, ether, and carboxylate groups, as a result of oxidation. Compared to clay, GO, as one of lamellar fillers possesses much higher mechanical properties and has a larger specific surface area, which can maximize the interfacial contact between polymer and fillers and, thus, it has the potential to be effective reinforcing filler and compatibilizer.

The GO-filled natural rubber (NR)/high density polyethylene (HDPE) thermoplastic vulcanizates were successfully prepared by an ultrasonically assisted latex mixing process (ULM) [146]. GO was dispersed into NR latex by ultrasonic irradiation and followed by latex coagulation to obtain NR/GO master-batch, which was further mixed and diluted with HDPE and NR via a dynamic vulcanization process to obtain NR/HDPE/GO composites. It was found that the stacked GO platelets were successfully exfoliated and have good compatibilization efficiency for the immiscible NR and HDPE. The stacked GO platelets enhance the interfacial adhesion and phase compatibility, which results in an increase in mechanical property of NR/HDPE blends. The change of HDPE crystallinity due to the incorporation of GO is small and was not the main reason for the improvement in the mechanical properties. It was found that GO is mainly dispersed in NR phase and the interphace, which act as an obstacle to inhibit the coalescence of the NR phase.

Graphite nanosheets (GNs) have gained great interest because of their high flexibility, large surface area, and lower cost compared with other nanofillers such as nanotubes and nanowires. When natural graphite is intercalated by small molecules, such as sulfuric acid, the spacing between graphite nanolayers is increased and the resulting product is called graphite intercalated compound (GIC).

Impact and water resistant electrically conductive polyurethane (PU) foam nanocomposites with radio frequency wave absorbing characteristics were prepared by impregnation of PU foam in a designed solution of room temperature vulcanizing silicone rubber and conductive graphite nanosheets (GN) called doping solution [147]. Incorporation of bifunctional surfactant into the composition of the doping solution was found to have profound role in improving the dispersion state of GN platelets throughout the silicone rubber as well as PU matrix. Extent of GN particles and hence percolation threshold exhibited to be affected by the functionality of the compatibilizer. All PU/SR/GN nanocomposites generated from bifunctional compatibilizer exhibited higher electrical conductivity with enhanced permittivity implying enhanced formation of conductive networks by GN platelets.

Chlorinated polyethylene (CPE) was found to be an efficient compatibilizer for EPDM rubber/nylon (PA) blends, due to the interactions taking place between CPE and PA [148]. The cold milling of molten EPDM/PA/CPE blend was found to cause the formation of in situ fibril rubber compound, which display magnificently improved tear strength. It was also mentioned that small amount of PA fibril (i.e. 10 %) actually enhanced the mechanical properties of the matrix. In rubber composites reinforced with short fibres, however, that low concentrations of fibre are deleterious for the properties of the matrix rubber. This was explained by the fact that in rubber composites containing “in situ” fibrils, the polarity-matched rubber/plastic blend, the finer dispersed particles and high elongation of PA, make dispersed particles easier to stiffen or constrain the matrix rubber and permit effective load transfer across the hard-soft interface, than in the case of rubber composites containing short fibres.

Ismail and Mega [149] studied the effect of a compatibilizer, poly(propylnene-eyhylene acrylic acid) (PPEAA) and a silane coupling agent, 3-aminopropyl-triethoxy silane (3-APE), on the properties of polypropylene (PP)/natural rubber

(NR) blends reinforced with white rice husk ash (WHRA). The incorporation of WRHA in PP/NR blends increased tensile modulus, stress at yield and elongation at break of the composite system. However, the WRHA filled PP/NR blends treated with 3-APE and PPEAA showed better tensile strength, stress at yield and tensile modulus compared to similar untreated composites. SEM micrographs revealed better filler dispersion and better filler-matrix interaction as a result of the treatment with 3-APE and PPEAA.

In order to improve the compatibility between natural fibres and polypropylene (PP) and polypropylene-ethylene propylene diene terpolymer (PP-EPDM) blends, the functionalization of both matrices with maleic anhydride (MA) was attempted by López Manchado el al. [150]. The morphological observations carried out by scanning electron microscopy show that the incorporation of small amounts of functionalized polymer considerably improves the adhesion at the fibre-matrix interface. In these cases, the fibres are perfectly embedded in the matrix in relation to the composites prepared with the pure homopolymers, and a significant increase in the composite strength is also observed, particularly, after the incorporation of both modified polymers (MAPP and MAEPDM). Thus, it is possible to correlate better interfacial adhesion with the improvement of mechanical properties. It is assumed that the functionalization of the matrix reduces interfacial stress concentrations and may prevent fibre–fibre interactions, which are responsible for premature composite failure. It was also observed that both flax fibre and rubber behave as effective nucleant agents, accelerating PP crystallization. Moreover, these results are particularly relevant when the grafted matrices are added to the composite.

If rubber and plastic are blended to produce a thermoplastic elastomer (TPE), their technical properties are inferior because of the presence of a week rubbery phase and an interface dispersed in a continuous plastic matrix. This limitation can be circumvented by preferential reinforcement of the rubber phase and the interface with the plastic matrix by fillers and/or the addition of crosslinks in the rubbery phase via dynamic vulcanization without the processing characteristics being sacrificed. Pukanszky [151] proposed that the dimensions of the interface and strength of the interaction significantly influence the ultimate tensile properties of composites. The sequence of addition of the individual polymers and fillers plays an important role in determining the properties of polymer blends [152].

Ternary composites consisting of PP, an elastomer and a filler are becoming attractive materials because they possess both, high modulus and high impact strength. It has been explained that the mechanical properties of such ternary composites are strongly influenced by both the composition and the morphology. The morphology is strongly dependent on both, the interfacial interaction between the components and the mixing method. Two different morphologies are expected to form in PP/elastomer/filler ternary composites. One is the morphology with the elastomer and filler particles dispersed independently in the PP matrix, whereas the other has a core-shell type particles consisting of a filler particle core and an elastomer shell. When no functional group is introduced into the elastomer, the elastomer and the filler particles are dispersed independently in the PP matrix because there is no interaction between them. On the other hand, when the functionalized elastomer is reinforced with filler, the aforementioned core-shell structure should be formed.

Denac et al. studied the crystallization process in blends of isotactic polypropylene (iPP), with styrene rubber block copolymer blends (SRBC), as well as in their composites reinforced with talc [153, 154]. Talc crystals, homogeneously incorporated into the iPP matrix, accommodated mostly plane-parallel to the surface of samples and strongly affected the crystallization process of iPP matrix, disturbing well-developed sperulitic morphologies, Both SEBS and SEBS-g-MA block copolymers encapsulated talc crystals, thus forming core-shell morphology at significant higher extent than poly(styrene-b-butadiene-b-styrene) triblock (SBS) and poly(styrene-b-ethylene-co-propylene) diblock copolymer (SEP) in iPP/talc composites. The observed differences between the effect of SEBS and SEBS-g-MA on mechanical properties could be explained by the higher molecular weight and different miscibility with the iPP chains of the SEBS than SEBS-g-MA elastomer, as well as by the higher extent of encapsulation and disorientation of talc crystals by SEBS-g-MA than by SEBS copolymer.

5 Future Prospects

Nowadays rubber technology has become an important part in industry. Because the essential modulus and strength of neat rubber is low, it is necessary to introduce an additional reinforcing phase to achieve optimal properties required in their applications.

The expansion of the polymer industry and the continuous demand for new composites with improved properties and lower particle content are some of the new challenges in this area.

The use of nanomaterials for the reinforcement of rubber composites is a new technology that gives high expectations because it has shown enhancement in the composites properties, such as modulus of elasticity, gas-barrier property, electrical conductivity, magnetic susceptibility, hardness, abrasion resistance, scratch resistance and ultraviolet protection.

Carbon nanotubes or exfoliated graphite/graphene offers substantial opportunities in the electrical/electronics/optoelectronics areas as well as potential in specific engineering technologies. Conductive elastomer nanocomposites can be applied as artificial muscles, electromechanical actuators, touch control switches, and shape-memory polymers, etc.

Graphene oxide is another interested nanomaterial that can act as both the effective reinforcing nanofiller and the compatibilizer in the immiscible rubber-based blends in order to produce high performance, ultralight vulcanizate.

Recently, one area that has come under intense inspection is the role of nanoparticles as potential compatibilizer in immiscible polymers. The combination of two different fillers in preparation of rubber nanocomposites is an interesting tool that can present synergistic effect and gives the potential for preparing new engineering materials with specific and improved properties. There are reports in the synergistic effect of different fillers to make balance between properties and cost. A good example is the combination of CNTs with graphene.

Currently, the demand for reinforcing fillers from renewable resources, such as plant-based natural fibre, for the production of biosustainable "green-composite" materials is increasing in research area and manufacturing because of their ease of processing, low cost, low density, biodegradability and good mechanical properties. Natural fibres provide with interesting properties the final composite such as their capacity to be recyclable, renewable raw material, and less abrasive and harmful behavior.

6 Conclusions

Elastomers represent a class of natural and synthetic materials of profound scientific, technological and commercial interest. Due to the high versatility in their composition and structure, rubber products are capable of satisfying almost any requirement and standard of use. In addition, the incorporation of additives that produce reinforcing effect to the elastomeric matrix and further improve the properties, such as physicomechanical, electrical, endurance etc., greatly increases the spectrum of applications.

The reinforcing fillers commonly used in elastomers are carbon black, silica, clay particles and glass fibres. However, advanced technology reinforcements, such as aramids, might be recommended for special applications.

Hybrid composites provide new possibilities of extending the area of rubber applications, as they combine selected filler properties taking advantage of their synergistic effect.

The main reason for reinforcing rubbers is to improve the mechanical and thermal properties as well as to reduce cost, and sometimes weight of the compounds. The recent advances of nanoparticles has attracted much attention in manufacturing of rubber nanocompositres because of the small size of the filler and the corresponding increase in the surface area allowing to achieve the required mechanical properties at low filler loading. Carbon nanotubes and graphene nanoporticles are promising materials as rubber reinforcements offering good electrical properties.

Since the filler/matrix interfacial characteristics (including wetting, adhesive bonding etc.) are of prime importance for an efficient reinforcing effect, surface treatment of the filler particles with the appropriate coupling agents is necessary in order to promote proper dispersion and adequate filler/matrix interactions.

In order to improve dispersion of reinforcement in rubber matrices the use of the respective functionalized polymer, otherwise called compatibilizers, might be necessary. Among the different modifying agents, maleic anhydride is the most commonly used and seems to ensure best results at relatively low cost.

The newly developed polyblends based on mixtures of rubbers with polyolefins, require the suitable compatibilization in order to reveal their unique properties. Nanoparticles, being a very efficient reinforcing agent even at low concentrations, were also found to play the role of compatibilizer for these mixtures of immiscible polymers.

The incorporation of reinforcing fillers along with some other additives into the elastomeric matrices, often leads to very complex systems and, therefore, the influence on the crosslinking parameters must be carefully studied in each specific case, since the network characteristics are critical for the overall performance of final products.

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