ADVANCED EVA NANOCOMPOSITES: DEVELOPMENTS AND NEW OPPORTUNITIES

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ABSTRACT

The paper presents a complete conspectus of ethylene-co-vinyl acetate (EVA) nanocomposites based on different types of nanostructured materials incorporated into EVA polymers. The three types of nanostructured materials, namely zero-dimensional nanostructured materials [(0DNSM) (POSS)], one-dimensional nanostructured materials [(1DNSM) (carbon nanotubes or CNTs, sepiolite)] and two-dimensional nanostructured materials [(2DNSM) (clay)] with EVA are introduced and a detailed discussion is provided on the effect of nanostructured materials on EVA polymer. Simultaneously, we discuss the recent approaches in which CNTs, sepiolite, clay and POSS nanomaterials play a vital role in EVA polymers, in addition to elucidating the influence of composite structures on the thermal, mechanical, and fire retardant properties. On the basis of this review we present the varied and versatile current research on EVA nanocomposites. The whole range of effects on polymer nanocomposite properties is covered. The great progress being made in the preparation of EVA nanocomposites offers fascinating new opportunities for materials scientists.

Keywords: POSS, clay, sepiolite, CNT, EVA

INTRODUCTION

There is currently immense interest in the development of nanostructured materials for a wide variety of applications and these materials offer exciting new challenges and opportunities in all the major branches of science and technology. [1] It is widely recognised that reductions in the size of components influence the interfacial interactions between them and this can, in turn, enhance the material properties to an appreciable extent. [2]

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Consequently, it is also possible to develop materials that are completely discontinuous, i.e. that contain both organic and inorganic phases. Such materials exhibit non-linear changes in properties with respect to composites that are made up of the same phases. This paper focuses mainly on the classification of nanostructured materials such as zero-dimensional (polyhedral oligomeric silsesquioxane or POSS), one-dimensional (CNT, sepiolite) and two-dimensional (clay) nanostructure materials and on the recent developments in EVA nanocomposites (Figure 1.1).
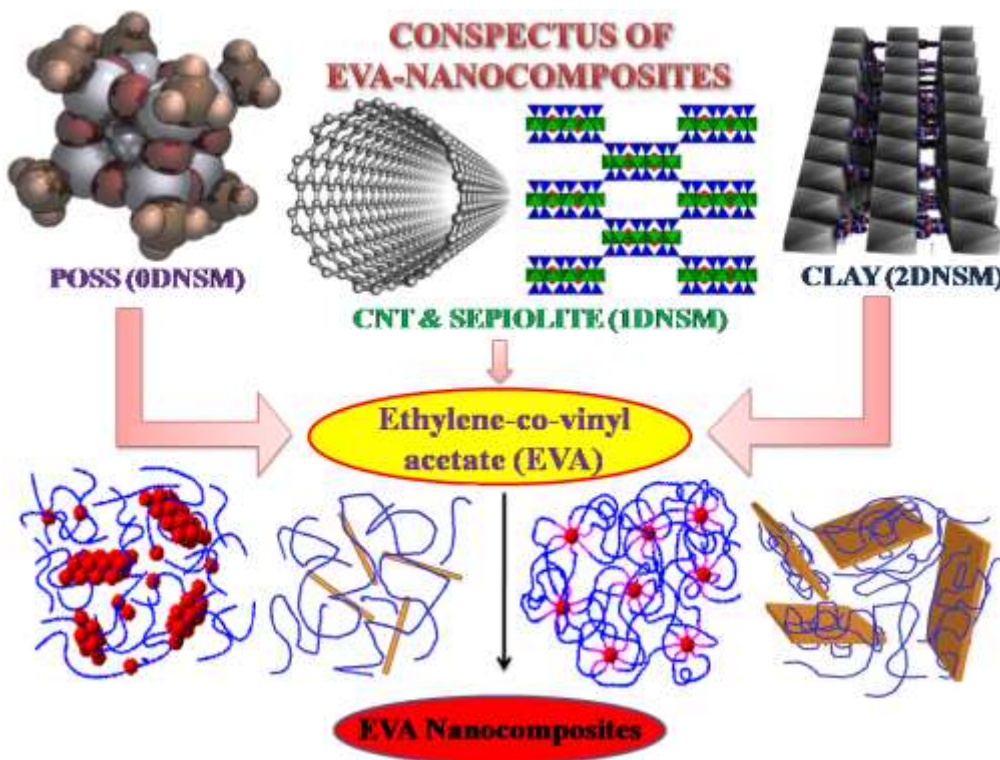

Figure 1.1. Overall theme of this review.

Ethylene-Co-Vinyl Acetate (EVA)

EVA copolymers are among the most important and widely used organic polymers, with a diversity of industrial applications such as electrical insulation, [1] cable jacketing, waterproofing, corrosion protection, packaging of components, [3] photovoltaic encapsulation and footwear. [4] EVA is used in paints, adhesives, coatings, textiles, wire and cable compounds, laminated safety glass, automotive plastic fuel tanks, etc. It is extremely elastomeric and accepts high filler loadings while retaining its flexible properties. [5] However, bulk EVA does not often fulfill the requirements in terms of its thermal stability and mechanical properties in some areas. In order to improve such properties, nanostructured materials are introduced as a reinforcing material. Among several polymeric materials used for polymer nanocomposites, EVA, a copolymer containing repeating units of ethylene as a non-polar and vinyl acetate (VA) as a polar, has been newly adopted for its polymer

nanostructured materials arrangement because of its potential engineering applications in the fields of packaging films and adhesives. [6]

By changing the vinyl acetate content, EVA copolymers can be tailored for applications such as rubbers, thermoplastic elastomers and plastics. [4] The combinations of EVA with nanostructured materials have wide marketable applications and these applications depend on the VA contained in the main chain. As the VA content increases, the copolymer presents increasing polarity but lower crystallinity, and therefore different mechanical, thermal and morphological behaviours. The increasing polarity with increasing VA content is apparently useful in imparting a high degree of polymer nanostructured materials surface interaction, and it has been reported that there is a rise in the Young's modulus and yield strength of EVA polymeric nanocomposites compared with other polymeric nanocomposites. [7]

Classification of Nanostructured Materials (NSMs)

The commencement of research into nanotechnology can be traced back over 40 years, but in the past decade hundreds of NSMs have been obtained across a variety of disciplines. NSMs are low-dimensional materials comprising building of submicron or nanoscale size in at least one direction and exhibiting size effects. [8]
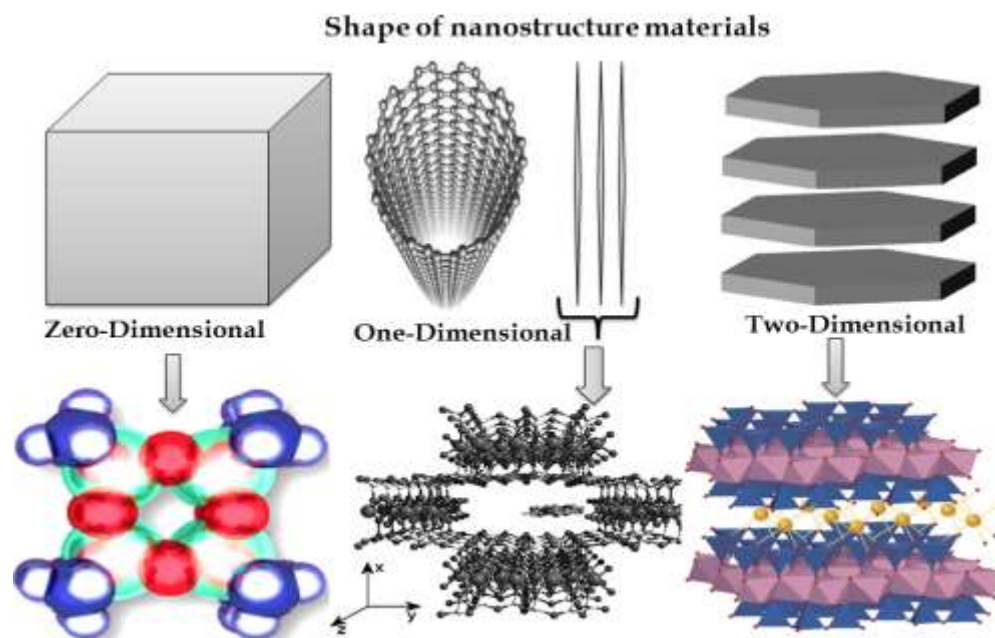

Figure 1.2. Chemical structure and shape of nanostructured materials.

The first part of this review can be classified into the three different types according to the dimensionality of nanomaterials (Fig 1.2), a) 0DNSMs, such as polyhedral oligomeric silsesquioxane (POSS), which are characterized by three nanometric dimensions, b) 1DNSMs (fibrous materials), such as carbon nanotubes and sepiolite, which are characterized by

elongated structures with two nanometric dimensions, c) 2DNSMs (layered materials), like clay (e.g., montmorillonite: MMT), which are characterized by one nanometric dimension.

Zero-Dimensional Nanostructured Materials

Zero-dimensional nanostructured materials (0DNSMs) are those in which all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm). The most common representation of zero-dimensional nanomaterials is nanoparticles.

Owing to their large specific surface area and other properties superior to those of their bulk counterparts arising from the quantum size effect, 0DNSMs have attracted considerable research interest and many of them have been synthesised in the past 10 years. [9-11] It is well known that the behaviours of NSMs depend strongly on their sizes, shapes, dimensionality and morphologies, which are thus the key factors giving rise to their ultimate performance and applications. It is therefore of great interest to synthesise 0DNSMs with a controlled structure and morphology. In addition, 0DNSMs are important materials due to their wide range of applications in the areas of catalysis, as magnetic materials and as electrode materials for batteries. [12] Moreover, the 0DNSMs have recently attracted intensive research interest because the nanostructures have a larger surface area and supply enough absorption sites for all involved molecules in a small space. [13] On the other hand, their having porosity in 3 dimensions could lead to better transport of molecules. [14]
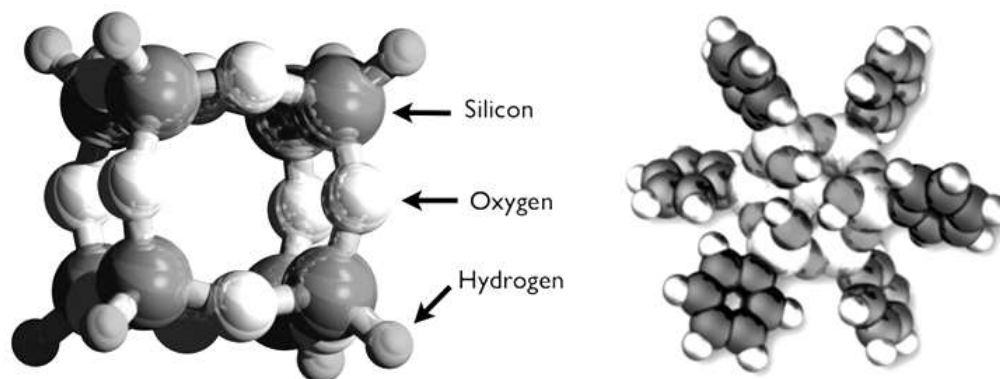

Figure 1.3. Chemical structure of polyhedral oligomeric silsesquioxane.

POSS is a class of organic-inorganic hybrid 0D nanostructure material constituted of an inorganic silica, [15] which consists of a rigid, crystalline silica-like core, have the general formula $(RSiO_{1.5})_a(H_2O)_{0.5b}$, where R is a hydrogen atom or an organic group and a and b are integers ($a = 1, 2, 3, ...; b = 1, 2, 3, ...$), with $a + b = 2n$, where n is an integer ($n = 1, 2, 3, ...$) and $b \leq a + 2$. POSS is unique with regard to size (0.5 nm in core diameter) when compared with other nanofillers and can be functionally tailored to incorporate a wide range of reactive groups. [16] The size of a POSS molecule is nearly 1.5 nm in diameter and about 1000 D in mass; hence POSS nanostructures are approximately equivalent in size to most polymer dimensions and smaller than the polymer radii of gyration. Figure 1.3 shows the chemical skeleton of one of the POSS. POSS systems may be viewed as the smallest chemically

discrete particles of silica possible, while the resins in which they are incorporated may be viewed as nanocomposites, which are intermediate between polymers and ceramics.

POSS derivatives have two unique features: (a) the chemical composition of POSS ($RSiO_{1.5}$) was found to be intermediate between that of silica (SiO_2) and siloxane (R_2SiO), and (b) POSS compounds can be tailored to have various functional groups or solubilising substituents that can be attached to the POSS skeleton.

One of the most popular branches of silsesquioxanes is polyhedral oligomeric silsesquioxanes, including the T_8 cage, T_{10} cage, T_{12} cage and other partial cage structures. Cubic structural compounds (completely and incompletely condensed silsesquioxanes) are commonly illustrated as T_6, T_7, T_8, T_{10} and T_{12} based on the number of silicon atoms present in the cubic structure (Figure 1.4). The silica core of POSS is inert and rigid, whereas the surrounding organic groups provide compatibility with the matrix and processability. However, much more attention has been directed to the silsesquioxanes with specific cage structures designated by the abbreviation POSS. [17] Kudo et al. [18] explored various stages of the most plausible mechanism for the synthesis of POSS, and an entire reaction scheme, including all intermediates, was considered.
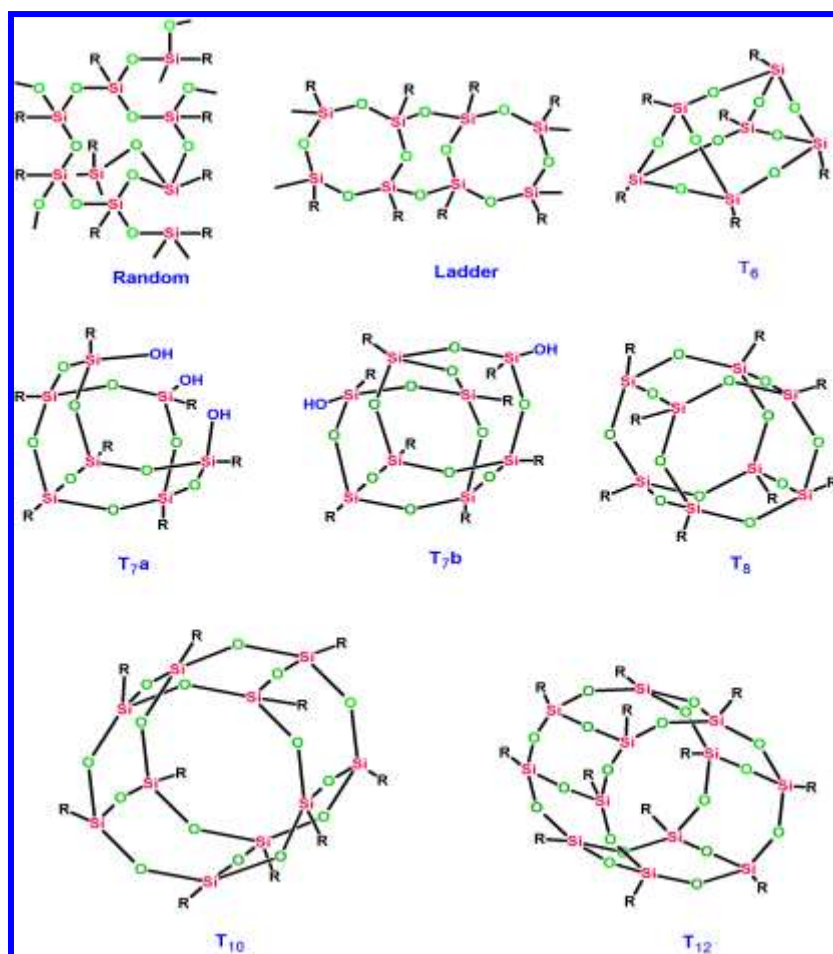

Figure 1.4. Chemical structures of different types of silsesquioxanes

Conceptually, POSS may be thought of as an organic-inorganic hybrid (Figure 1.5). Similarly, POSS is sometimes considered to be filler and sometimes a molecule. For example, POSS is rigid and inert like inorganic fillers, but unlike those conventional fillers, POSS can dissolve molecularly in a polymer.
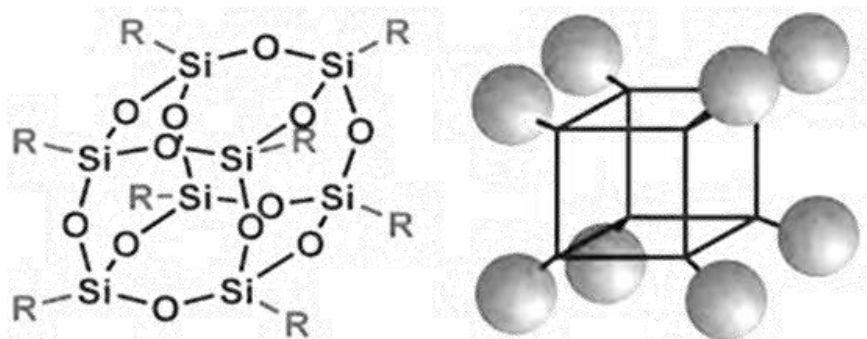

Figure 1.5. Silsesquioxanes Q_8 (Q =$SiO_{2/2}$); R =H, vinyl, epoxy, acetylene and acrylate.

One-Dimensional Nanostructured Materials

Within the various branches of nanotechnology, one-dimensional nanostructures (1DNSMs) have paved the way for numerous advances in both fundamental and applied sciences. One-dimensional nanostructured materials have one dimension that is outside the nanoscale. This leads to needle-shaped nanomaterials. One-dimensional materials, which include nanotubes, nanorods and nanowires, with at least one dimension in nanometre size fall under the category of 1DNSM. Almost all classes of materials, i.e. metals, semiconductors, ceramics and organic materials, have been used to produce 1DNSMs. However, carbon nanotubes (Figure 1.6) have occupied the most significant place and are the most widely studied 1DNSM. [19]

It is generally accepted that 1DNSMs are ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of functional properties. Certain fields of 1DNSMs, such as nanotubes and sepiolite, have received significant attention.
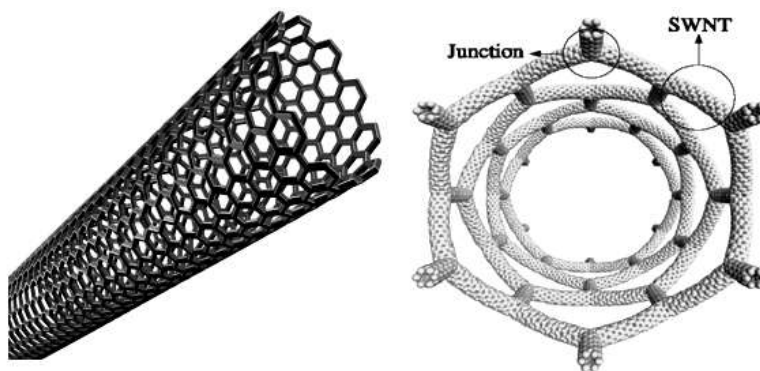

Figure 1.6. Schematic representation of one-dimensional nanostructured CNT.

1DNSMs have had a profound impact on nano-electronics, nanodevices and nanocomposite materials. Carbon nanotubes (CNTs) are long, slender fibres formed into tubes. The walls of the tubes are hexagonal carbon (as shown in Figure 1.6) and the tubes are often capped at each end. [20] CNTs have been found to be effective reinforcing agents for several polymeric materials, apart from their ability to increase the electrical and thermal conductivity of these materials [21, 22]. Since Chaudhary et al. [23] first reported their existence, they have attracted increasing attention because of their high electrical and thermal conductivity, mechanical strength and chemical stability. [24]

Sepiolite is a family of fibrous hydrated magnesium silicates with the theoretical half unit-cell formula $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4 \cdot 8H_2O$. [25] The chemical structure of sepiolite shown in Figure 1.7 is similar to that of the 2:1 layered structure of montmorillonite, consisting of two tetrahedral silica sheets enclosing a central sheet of octahedral magnesia, except that the layers lack continuous octahedral sheets. [26] The discontinuity of the silica sheets gives rise to the presence of silanol groups (Si–OH) at the edges of the tunnels, which are the channels opened to the external surface of the sepiolite particles. [27] The presence of silanol groups (Si–OH) can enhance interfacial interaction between sepiolite and polar polymers. [28]
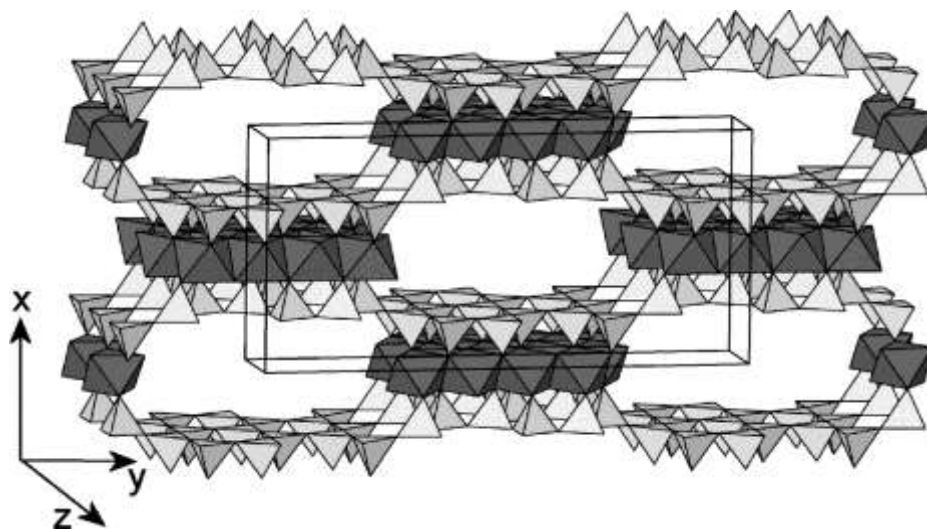

Figure 1.7. Schematic representation of one-dimensional nanostructured sepiolite

Two-Dimensional Nanostructured Materials with Ethylene-Co-Vinyl Acetate

Two-dimensional nanomaterials do not have two of the dimensions confined to the nanoscale, i.e. 2D nanostructures (2DNSMs) have two dimensions outside of the nanometric size. 2D nanomaterials exhibit plate-like shapes and include nanolayers and nanocoatings.

In recent years, 2DNSMs have become a focus area in materials research, owing to their many low-dimensional characteristics which differ from the bulk properties. [29] In the quest for 2DNSMs, considerable research attention has been focused over the past few years on the development of 2DNSMs. 2DNSMs with certain geometries exhibit unique shape-dependent

characteristics and they are consequently utilised as building blocks and key components of nanodevices. [30-32] The 2DNSM of clay is shown in Figure 1.8.
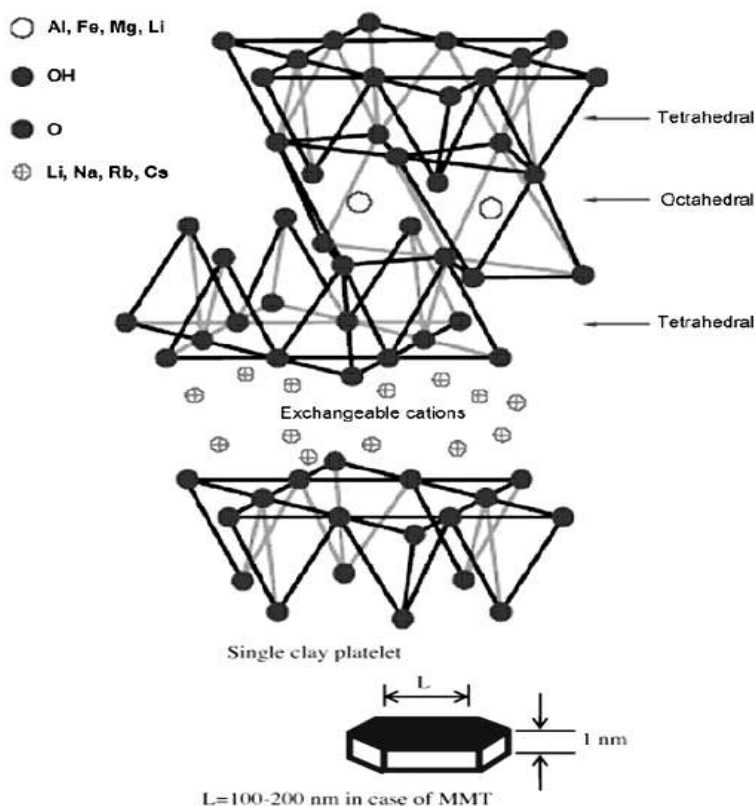

Figure 1.8. Graphical representation of two-dimensional nanostructured clay platelet [33]

POLYMER NANOCOMPOSITES

Nanoscale fillers, which are considered to be very important, include layered silicates (such as montmorillonite), nanotubes (mainly CNTs), fullerenes, SiO_2, metal oxides (e.g. TiO_2, Fe_2O_3, Al_2O_3), nanoparticles of metals (e.g. Au, Ag), POSS, semiconductors (e.g. PbS, CdS), carbon black, nanodiamonds, etc. Clay systems have been well developed, followed by POSS; little work has been performed using graphite-polymer and nanotube-polymer nanocomposites. In addition to clays, nanocomposites have been prepared using POSS, graphites and CNTs. The interest in such systems (organic-inorganic hybrid materials) is due to the fact that the ultrafine or nanodispersion of filler, as well as the local interactions between the matrix and the filler, lead to a higher level of properties than for equivalent micro- and macrocomposites. [34] In a nanocomposite, the clay, or the nanofiller/additive, is well dispersed throughout the polymer. Polymer-clay nanocomposites are a new class of composite materials consisting of a polymer matrix with dispersed clay nanoparticles. In recent years, more attention has been given to incorporating nanomaterials into polymer matrices to obtain high-performance nanocomposites. Clays typically consist of particles with

a high aspect ratio, i.e. their length is much longer than their width. Dispersion of the filler on a nanometre scale generally gives the polymer interesting insulation properties.

POSS Nanocomposites

Due to the great chemical flexibility of POSS molecules, POSS can be incorporated into polymers by co-polymerisation, grafting, or even blending using traditional processing methods and it can lead to a successful improvement of the flammability, thermal or polymer mechanical properties. [2, 35] Unlike traditional organic compounds, most POSS compounds release no volatile organic compounds below 300 ºC, are odourless, non-toxic, and reduce the toxicity of smoke upon Combustion. Apart from this, the problems associated with polymer immiscibility are reduced. In the polymer-POSS nanocomposites, the POSS acts as a nanoscale building block and its interaction with the polymers on a molecular level is believed to be helpful for efficient reinforcement. Polymer-POSS nanocomposites are defined as polymers having small amounts of nanometre-size fillers (POSS) which are homogeneously dispersed by only several weight percentages (Figure 1.9). A polymer-POSS nanocomposite with a filler having a small size leads to a dramatic increase in the interfacial area as compared with traditional composites. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from those of bulk polymer even at low loadings. [36, 37]
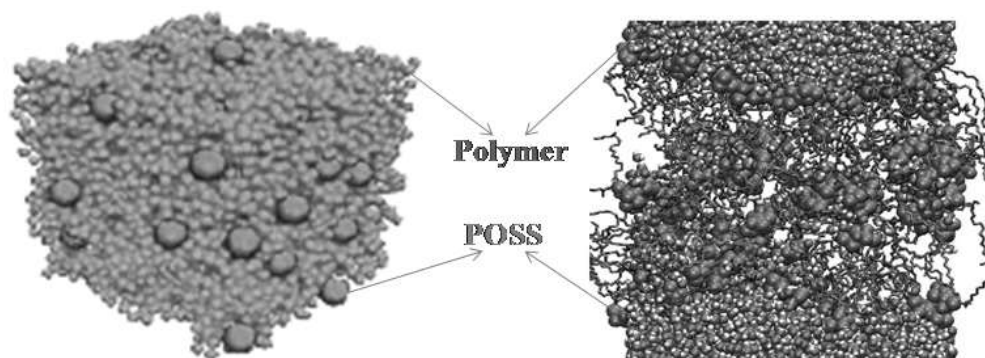

Figure 1.9. Systematic representation of polymer-POSS nanocomposites.

Normal fillers and especially nanofillers suffer from agglomeration. The agglomerates formed when conventional fillers are used lead to weak points in the polymer (stress concentrations) and this gives poor impact resistance and poor elongation to break. As a molecule, POSS dissolves in polymers as 1–3 nm cages and this gives performance advantages not seen with fillers. POSS increases the modulus of elastomers due to the stiffness of the cage and the high cross-link densities attainable using polyfunctional POSS cross-linkers. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance, and decreased flammability. This nature allows them to exhibit properties different from those of conventional microcomposites.

Organic-inorganic composite materials have been extensively studied for a long time. These may consist of two or more organic-inorganic phases in some combined form with the

constraint that at least one of the phases or features must be nanosized. Such materials combine the advantages of the organic polymer (e.g. flexible, dielectric, ductile and process able) and those of the inorganic material (e.g. rigid and thermally stable). For these reasons nanocomposites promise new applications in many fields such as for gas separation, [8a, 38] in the aerospace industry, [39] for electrical applications, [40] as mechanically reinforced lightweight components, and in non-linear optics, solid-state ionics, nanowires, sensors, and many others.
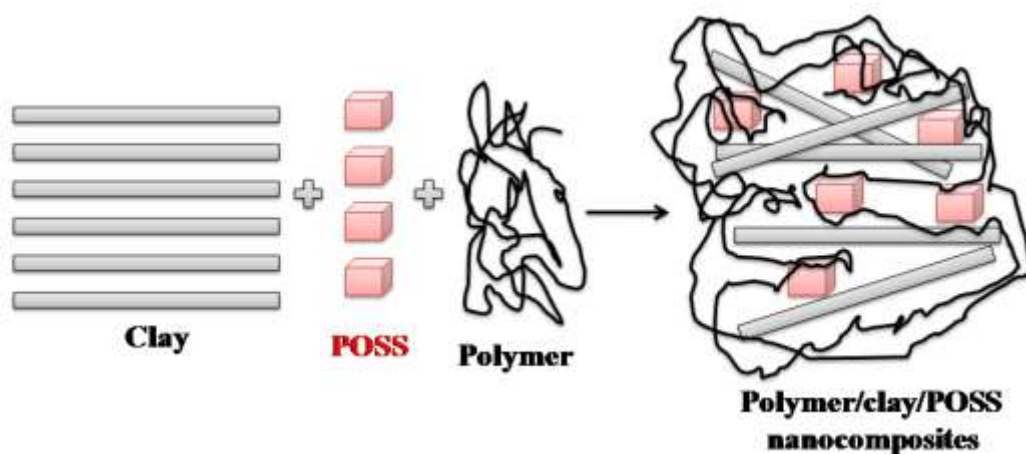

Figure 1.10. Formation mechanism of polymer/clay/POSS nanocomposites.

Fox et al. [41] prepared a POSS tethered imidazolium surfactant and used it to exchange montmorillonite (MMT) for the preparation of polymer nanocomposites in poly(ethylene-co-vinyl acetate) using a melt blending technique. Vaia et al. [42] have suggested that the extent of exfoliation of clay layers in a melt blended polymer composite is a result of two competing factors: enthalpic loss due to unfavourable polymer clay interactions and entropic gain due to increased polymer mobility over confinement within an intercalated clay structure. In addition, the presence of POSS interactions add to the enthalpic barrier to exfoliation, since the POSS crystal domains must be melted. Despite these barriers to exfoliation, polymer composites exhibit small increases in exfoliation and smaller tactoids over unmodified clay. It is conceivable that the more rigid structure of POSS-imidazolium relative to other organic modifiers creates a more permanent barrier between the charged clay surface and more hydrophobic polymer chain. The model reaction of POSS/Clay composite shown in Figure 1.10

Fox et al. [43] reported the synthesis and characterization of 1,2-dimethyl-3-(benzyl ethyl iso-butyl polyhedral oligomeric silsesquioxane) imidazolium chloride (DMIPOSS-Cl) and DMIPOSS modified montmorillonite (DMIP-MT) at several loadings of DMIPOSS-Cl.

To investigated the ability of these clays to exfoliate in poly(ethylene-co-vinyl acetate) systems. In addition, they reported the effects of partial clay loading using only the POSS-modified imidazolium surfactant on the extent of exfoliation and quality of dispersion in polymer.

In addition, Zhao et al. [44] have shown that although the organic groups on POSS do lower the polarity of clay surface, the surface free energy of clay exchanged with

aminopropylisooctyl POSS is reduced by only half, leaving the clay surface still significantly more polar than polymer. Since clay is only partially exfoliated upon incorporation of polymers, regardless of their polarity, it is likely that the propensity for POSS to aggregate and limited space for intercalate polymer chains to move dominate the behaviour in POSS exchanged clays.

CNT and Sepiolite Nanocomposites

The one-dimensional nanostructure of CNTs, their low density, their high aspect ratio, and extraordinary properties make them particularly attractive as reinforcements in composite materials. These studies have been discussed in some excellent reviews. [21, 45] The variation of many parameters, such as CNT type, growth method, chemical pre-treatment as well as polymer type and processing strategy has given some encouraging results in fabricating relatively strong CNT nanocomposites. Since the early preparation of a CNT/epoxy composite by Ajayan [46], more than 30 polymer matrices have been investigated with respect to reinforcement by CNTs. The outstanding potential of CNTs as reinforcements in polymer composites is evident from the super tough composite fibres fabricated by Baughman et al. [24] By now, hundreds of publications have reported certain aspects of the mechanical enhancement of different polymer systems by CNTs.

CNTs have clearly demonstrated their capability as fillers in diverse multifunctional nanocomposites. The observation of an enhancement of electrical conductivity by several orders of magnitude at very low percolation thresholds (<0.1 wt.%) of CNTs in polymer matrices without compromising other performance aspects of the polymers such as their low weight, optical clarity, low melt viscosities, etc., has triggered an enormous activity world-wide in this scientific area. Nanotube-filled polymers could potentially, among the others, be used for transparent conductive coatings, electrostatic dissipation, electrostatic painting and electromagnetic interference shielding applications. A wide range of values for conductivity and percolation thresholds of CNT composites have been reported in the literature during the last decade, depending on the processing method, polymer matrix and nanotube type.

The majority of research in polymer/clay nanocomposites is focused on platelet-like clays, smectite clays such as MMT. Instead of very few works have been focused on fibre-like clays particles (sepiolite). [47] Because of the peculiar shape, these nano-fillers are believed to be good candidates for the preparation of nanocomposites materials. In fact the dispersion of needle-like clays, compared to platelet-like clays, is favoured by the relatively small contact surface area. Moreover, the reinforcement capacity of fibres in polymer nanocomposites is higher than that of platelet for uniaxial composites. These types of special reasons divert and investigate this research to sepiolite based polymer nanocomposites with different types of polymer matrices have been taken into consideration: polypropylene (PP), polyamide 6 (PA6), [48] polyurethane, [49] and acrylonitrile–butadiene–styrene (ABS) [50].

Clay Nanocomposites

Clays have been widely investigated and used as reinforcing agents for polymer matrices. [21, 51-53] They can dramatically enhance the mechanical performance and the barrier

properties at filler loadings as low as 3–5 wt.%, without significantly changing other important characteristics such as transparency or density. In order to enhance their compatibility with polymer matrices, clays are usually modified with organic compounds (e.g. quaternary ammonium salts) but, even in this case, the properties of the polymer matrices are often not significantly improved. [51] Various researchers have reported on properties of nanoclay-EVA nanocomposites. [54, 55]
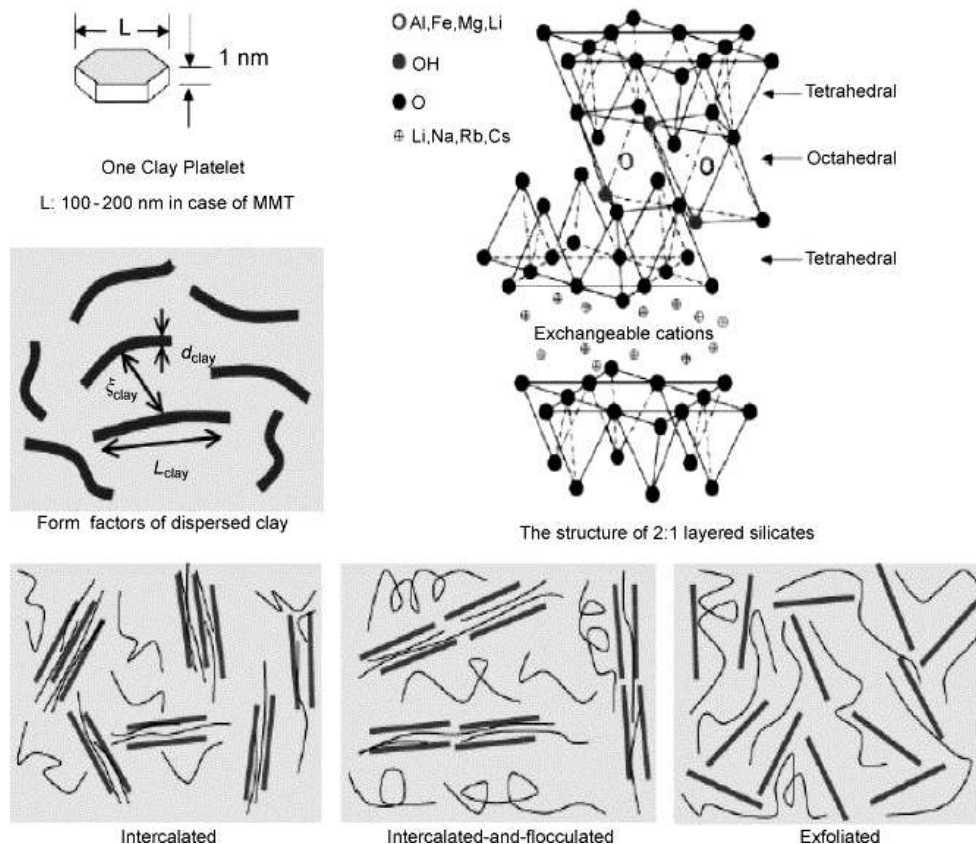

Figure 1.11. Schematic representation of clay with different dispersed phases [51].

IUPAC defines a composite as "a multicomponent material comprising multiple different (non-gaseous) phase domains in which at least one is a continuous phase". Polymer-clay composites can be prepared in three different ways, namely by in situ polymerisation, [56, 57] by solution intercalation and by dispersion through melt processing. Three organoclay nanocomposite microstructures are possible, i.e. phase separated, intercalated and exfoliated. The outcome is determined by which one of the interfacial interactions is favoured in the system. The three main interactions are polymer-surface, polymer-surfactant and surfactant-surface. [58] The consensus is that, for thorough clay sheet dispersion, highly favourable polymer-surface interactions are essential. [58] A greater degree of exfoliation and better dispersion of layered double hydroxides (LDHs) were obtained in more polar matrices. Polyolefin nanocomposites are difficult to prepare as the low polymer polarity does not provide effective interaction with LDHs. Addition of the maleic anhydride grafted polyethylene as compatibiliser improves, to some extent, the dispersion of clays in non-polar

matrices during melt compounding. [59] The dispersed form of clay platelets is shown in Figure 1.11. It is well established that the dispersion of particles with high aspect ratios, such as fibres and platelets, in polymeric matrices improves mechanical stiffness as well as some other properties.

However, good interfacial adhesion and a homogeneous dispersion are prerequisites. [60] Nanostructured clays are ideal for the preparation of polymer-clay nanocomposites that possess improved gas barrier properties, better mechanical properties, [61] enhanced flame retardancy, [62] UV stabilization [63] or enhanced photodegradation, [64] and so forth.

ETHYLENE-CO-VINYL ACETATE NANOCOMPOSITES

POSS-EVA Nanocomposites

EVA represents a considerable portion of the polymers currently marketed and has a wide range of applications, e.g. in non-scratch films, hoses, coatings and adhesives. [65] It is commonly used in blends with polyolefins in order to improve the mechanical strength, processability, impact strength and insulation properties. The demands for specific polymer properties for new applications have increased, including their use at higher temperatures and greater resistance to oxidation. The polymer industry has been able to keep abreast of these market demands through the use of additives, fillers and polymer blends. More recently, the diverse and entirely new chemical technology of POSS nanostructured polymers has been developed. [16, 66] This technology affords the possibility of preparing plastics that contain nanoscale reinforcements directly bound to the polymer chains.

The incorporation of POSS cages into polymer materials may result in improvements in polymer properties, including increased temperature of usage, oxidative resistance and surface hardening, resulting in better mechanical properties as well as a reduction in flammability and heat evolution. [67] In nanocomposites the addition of POSS nanoparticles can lead to the thermal stabilisation of polymers during their decomposition. [68] However, in this regard the effect of the nanoparticle content is very crucial. In most cases the thermal stability enhancement takes place at a low loading (4–5 wt.%) of POSS nanoparticles, while at higher contents thermal stabilisation becomes progressively lower. This is because at higher concentrations nanoparticles can form aggregates and thus the effective area of nanoparticles in contact with polymer macromolecules is lower. In this case microcomposites may be formed instead of nanocomposites and thus the protective effect of nanoparticles becomes lower.

In EVA systems the presence of 1 wt.% of POSS slightly increases the values of the stabilised and totalised torque and specific energy. This suggests that the viscosity is higher, probably due to an increase in the extent of entanglement caused by the incorporation of POSS into the polymer matrix. [69] A decrease in these values for a POSS content of 5 wt.% was also observed, suggesting that, in high concentrations, POSS forms aggregates, which are not incorporated into the polymer, leading to a decrease in viscosity. However, for EVA systems there is an increase in the stabilised and totalised torque and in the specific energy with an increase in the POSS content.

XRD analysis was carried out in order to verify the crystal structure of the POSS and of the polymer matrix. The XRD diffractograms of the POSS and the systems under study are shown in Figure 2.1. For pure POSS, Figure 2.1 shows peaks at $2\theta = 8°$, $8.8°$, $10.9°$, $11.7°$, $18.3°$ and $19.7°$, which are characteristic of its crystalline structure. The EVA copolymer (Figure 2.1, 0 wt.% of POSS) shows broad peaks (2θ ranging from $21°$ to $25°$) related to the polyethylene structure of the EVA copolymer. For the other systems (Figure 2.1) these peaks appear for POSS concentrations of 1 wt.% and above, indicating that the presence of EVA in the composite leads to the appearance of POSS aggregates at lower concentrations, probably due to the increase in the polarity of the polymer matrix.
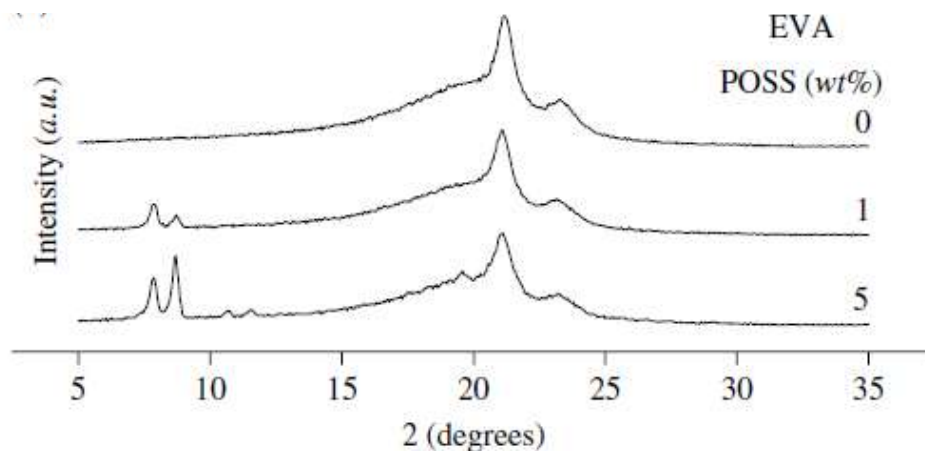
Figure 2.1. XRD patterns of POSS and of the composites [70].

Figure 2.2. SEM (left) and Si mapping (right) of the composites with 1 wt.% of POSS [70].

The morphology and thermal properties of EVA composites with POSS nanostructures were analysed and compared with those of the pure polymers. The POSS underwent aggregation at higher concentrations during composite processing, indicating a solubility limit of around 1 wt.%.The presence of EVA in the composite favours POSS aggregation due to

the increase in the polarity of the polymer. These aggregates were observed in Si mapping and were characterised by the presence of a melt peak of POSS.

Further, these aggregates indicate that the polarity of the polymeric matrix plays a major role in the composite's morphology, even for immiscible systems. Figs 2.2 and 2.3 show SEM and Si mapping of 1% and 5% of POSS in EVA nanocomposites respectively.

The differential scanning calorimetry (DSC) curves of the second heating for the systems are shown in Figure 2.4. EVA has Tm values of 84 °C. The EVA systems with 5 wt.% of POSS also show a third melt peak, at approximately 56 °C, which is characteristic of POSS. In the system with 1 wt.%, the POSS appears to be homogenously dispersed in the polymer matrix, minimising the size of the domains in the samples. However, at a concentration of 5 wt.%, aggregation of the POSS takes place, which is characterised by the melt peak.
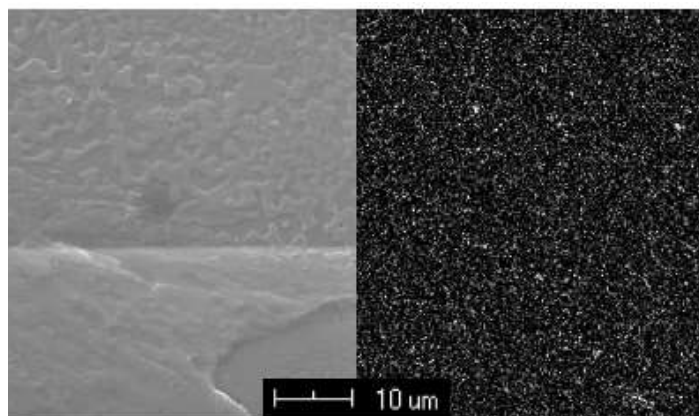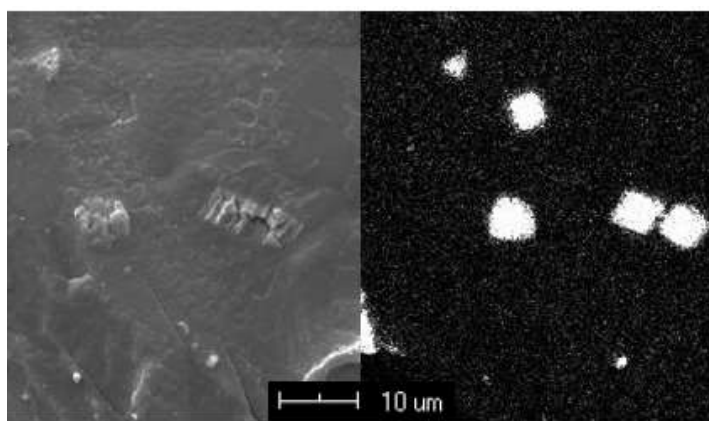

Figure 2.3. SEM (left) and Si mapping (right) of the composites with 5 wt.% of POSS [70].
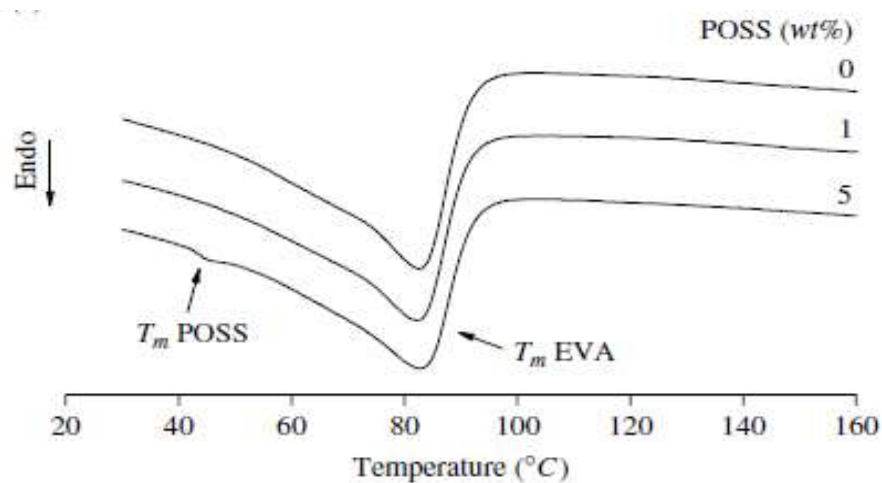

Figure 2.4. DSC curve of EVA–POSS nanocomposites [70].

The thermogravimetric analysis (TGA) curves of the systems are shown in Figure 2.5. The first weight loss is observed in the temperature (T_1) range of 356 to 374 °C, which is

related to the elimination of the acetic acid in EVA and the degradation of POSS. In all systems, as the POSS content increases, the values of the onset temperature for degradation decrease due to the lower POSS thermal degradation temperature (285 °C). Fina et al. [66] obtained similar results for the thermal degradation of polypropylene/POSS nanocomposites.
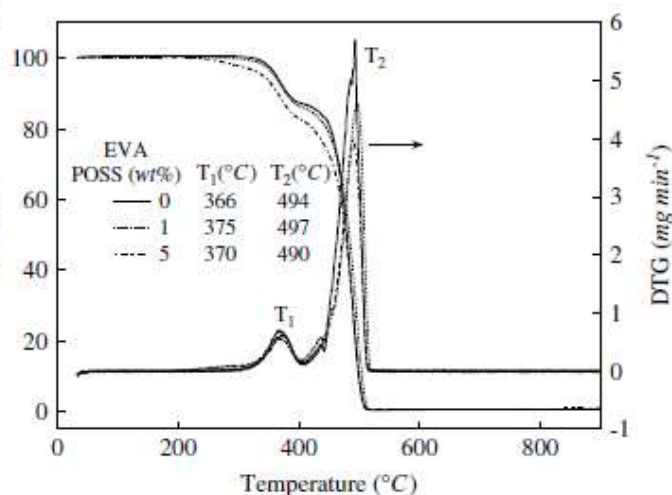

Figure 2.5. TGA curves of EVA-POSS nanocomposites [70].

CNT-EVA and Sepiolite-EVA Nanocomposites

The CNT is one of the stiffest materials produced commercially, having excellent mechanical, electrical and thermal properties. The reinforcement of rubbery matrices by CNTs was studied for EVA. George et al. [71] investigated the tensile strength of EVA-CNT and showed that it increased greatly (to 61%), even for very low fibre content (1.0 wt.%). The introduction of even a small number of CNTs can lead to improved performance of EVA. At 4 wt.% CNT loading, both the modulus and the tensile strength of the nanocomposite increased substantially. However, similar improvements were not observed at higher (8 wt.%) nanofiller loading due to filler agglomeration. George and Bhowmick[3] explained the effect of nanofillers and the VA content on the thermal, mechanical and conductivity properties of nanocomposites. They showed that polymers with high VA content have more affinity towards fillers due to the large free volume available, which allows easy dispersion of the nanofillers in amorphous rubbery phase, as confirmed from morphological studies. The thermal stability of nanocomposites is influenced by type of nanofiller.

Beyer [72] studied the flame retardant EVA-CNT nanocomposites and was synthesized by melt-blending. Fire property measurements by cone calorimeter revealed that the incorporation of CNT into EVA significantly reduced the peak heat release rates compared with the virgin EVA. Peak heat release rates of EVA with CNT were slightly improved compared with EVA nanocomposites based on modified layered silicates. There was also a synergistic effect by the combination of carbon nanotubes and organoclays resulting in an overall more perfect closed surface with improved heat release values. Carbon nanotubes are highly effective flame retardants; they can also be more effective than organoclays. There was

a synergistic effect between organoclays and nanotubes; the char formed during the degradation of the compound by a cone calorimeter was much less cracked compared with those from the single organoclay or carbon nanotube based compounds.

Huang et al. [56] prepared EVA-sepiolite composites and observed a remarkable change in the Young's modulus when only a small amount of sepiolite was incorporated. The fact that sepiolite has little effect on the elongation at break of the EVA/MH/SP composites, but a distinct effect on the Young's modulus, can probably be ascribed to the complex interactions between the polar EVA and the silanol groups of the high-aspect-ratio sepiolite. Hydrogen bonding may also be expected to occur between the ester groups of EVA and the characteristic silanol groups.

Clay-EVA Nanocomposites

Melt intercalated nanocomposites of EVA with layered silicates have been studied over the last decade. [4, 6, 8b, 23, 57, 73-81] The method is an alternative to in situ polymerisation and solution intercalation in the preparation of polymer nanocomposites. It is the most environmentally friendly method of all, versatile and compatible with current processing equipment.

Melt intercalation consists of blending molten polymer matrices with silicates. Polymer chains may diffuse from the matrix into the silicate interlayer. Conventionally, polymer chains should first intercalate into the silicate interlayers. Subsequently, the chains may push the silicate platelets further apart. Individual silicate particles may thus exfoliate into the polymer matrix. Sufficient compatibility between the surface energy of the silicate layers with that of the polymer chains is required. Silicate layers are hydrophilic, tending to be compatible only with polar polymers. Non-polar polymers appear to exhibit interfacial adhesion with organosilicates. However, compatibility between the polymer matrix and the surfactant chains of organosilicates is indispensable. It maximises the freedom of the organosilicate chains in the polymer matrix configurationally. Hence, organosilicate chains gain entropy, which balances entropy loss owing to polymer chain confinement. It has been shown that only polar polymer chains are attached to silicate platelets, whereas non-polar chains protrude into the bulk melt. Therefore, the interfacial adhesion with organosilicates is insufficient to yield thermodynamically stable nanocomposites.

Delaminating silicate platelets and achieving exfoliation requires strong shear forces. [82] These are attained during nanocomposite processing. Exfoliated structures are those in which the clay platelets are delaminated and individually dispersed in the polymer matrix. In exfoliated nanocomposite structures, silicate platelets are extensively interspaced. Such extensive interlayer separations disrupt coherent layer stacking and the resultant ordering of the clay platelets is not sufficient to produce a scattering peak. Hence, a featureless XRD diffraction pattern is recorded. Conversely, intercalated nanocomposites are those in which polymer chains and silicate layers alternate, in a well-ordered multilayer arrangement, with a well-defined and well-preserved interlayer distance.

Exfoliation is a key requirement for improving polymer properties. These include mechanical, thermal, barrier, flame retardant and optical properties. Exfoliation can lead to a very large surface area for the interaction of stiff silicate particles with polymer chains. EVA, $-(CH_2CH_2)_n[CH_2CH(OCOCH_3)]_m-$, is a somewhat polar copolymer due to its VA units. A

higher content of VA, $-CH_2CH(OCOCH_3)-$, affords polarity for interaction with (OH groups of) pristine silicates. [77a] Good surface affinity between EVA and silicates alone is not enough to achieve exfoliation – prior break-up and expansion of intrinsic silicate stacks is required. This is accomplished through organic intercalation, using ion-exchange reactions. The stacks intrinsic to silicates are explained as follows: layered silicates comprise particles with thicknesses in the nanometre range; their aspect ratio is very large, exceeding two hundred; there is a propensity for aggregation of such particles due to the large packing area.

Generally, mechanical shear forces break up intrinsic silicate stacks. Subsequently, intercalation of large organic species expands the silicate interlayers. This expansion facilitates the diffusion of polymer chains into the layers. This, in turn, promotes the exfoliation of silicate platelets in polymer matrices. Ultimately, a large interfacial area for interaction between polymer chains and silicate particles is thus created. Intercalation may further alter the silicate surface chemistry. The changing nature of the silicate layers from hydrophilic to organophilic renders them compatible with hydrophobic polymers. To date, the preparation of fully exfoliated EVA-layered silicate nanocomposites remains a challenge. The use of different types of processing equipment and varying conditions has yielded disparities between nanocomposite structures and properties. This has resulted from the use of EVA with diverse features, silicates and organic modifiers of different types, modifiers with several chain lengths and different polarities, all intercalated into silicates in dissimilar amounts. It is therefore necessary to understand the influence of materials, instruments and processing conditions on the properties of created composites.

The transmission electron microscopy (TEM) shows the composites structures. Structures probed solely by X-ray diffraction analysis (XRD) are not completely certain. When no XRD peak is observed, it could be deduced that exfoliation has taken place, whereas the presence of a small number of ordered stacks may also yield a featureless XRD diffractogram. Moreover, the presence of a high number of non-uniformly dispersed clay stacks likewise yields a featureless pattern or interlayer variations. In turn, the presence of any homogeneous distribution of the clay nanoplatelets could be interpreted as intercalation. Further, the presence of few silicate stacks could be deemed to indicate conventional microcomposites. Certainly, the presence of recalcitrant XRD reflections confirms the occurrence of intercalated or unmodified silicate regions. However, exfoliated regions may perhaps co-exist and even predominate. TEM is critical since it gives direct evidence of composite structures. However, it may also fall short when a few samples not representative of the whole material are used. The research work reviewed below has probably been subject to this dilemma.

EFFECT OF EQUIPMENT, TYPES OF CLAY AND EVA ON NANOCOMPOSITES

Effect of Processing Equipment and Conditions on Dispersion of EVA Nanocomposites

A co-rotating twin-screw extruder is considered the most effective shear device for the dispersion of silicate platelets. This is because the screws rotate in the same direction, intermesh and pass resin over and under one screw to another. The material is thus subjected

to identical amounts of shear and unlikely to become stagnant. Chaudhary et al. [23] and Pistor et al. [79b] reported similar EVA nanocomposite structures. Partial intercalation and exfoliation were the predominant characteristics reported in both communications. It was further stated that all the samples contained small tactoid fractions. [23, 79b] However, the processing equipment and conditions employed by these researchers were different.

La Mantia et al. [78a] prepared equivalent samples using two different extruders. They reported similar EVA nanocomposite structures comprising intercalated silicate domains, as detected by XRD. The d_{001} was slightly increased for samples compounded in a twin-screw extruder. [78a] Similarly, Chaudhary et al. [23] and Pistor et al. [79b] found that, overall, nanocomposite structures seemed independent of processing equipment. In addition, all nanocomposites appeared to be insensitive to different processing temperatures and shear forces.

Effect of Silicate Type on Dispersion of EVA Nanocomposites

The effect of the silicate type on the dispersion of EVA composites was investigated by Zanetti et al. [73b], Riva et al. [74a] and Peeterbroeck et al. [77b]. EVA matrices were melt blended with hectorite (HT), fluorohectorite (FH), magadiite [80] and montmorillonite (MMT), all organically modified. The dispersion of hectorite-type clays was found to be better than that of MMT clays. This may be attributed to the large interfacial area available for the interaction of polymer chains with hectorite-like minerals. The interaction of silicates with a high surface area with polymer chains yields excellent dispersion. [23] Hectorite has an aspect ratio of approximately 5000, while that of MMT is < 1000. Magadiite did not yield nanocomposites, only microcomposites.

Effect of Organic Modification of Silicates on Dispersion of EVA Nanocomposites

Nanocomposite creation was found to depend on the type of silicate modification. [73] Suitable modification should render the silicate compatible with the polymer matrix. Silicates modified with ammonium cations bearing carboxylic acid moiety yielded conventional microcomposites, independent of the co-vinyl acetate content of EVA matrices. In contrast, organosilicates with non-functionalised alkyl ammonium tails (one and two) displayed affinity towards EVA chains. They yielded nanocomposites whatever the VA content (12, 19 and 27 wt.%) of the matrix. Exfoliated silicate sheets were observed, together with stacks of intercalated and unmodified silicates. The nanocomposite structures were considered to be intercalated/exfoliated. [73] Higher numbers of stacks were observed in EVA12 nanocomposites. These authors speculated that such a small extent of exfoliation was due to the low polarity of the EVA12 matrix.

Similarly, organosilicates with one long alkyl chain yielded nanocomposites with relatively high numbers of stacks. Riva et al. [74a] used MMT modified with $(CH_2CH_2OH)_2N^+CH_3$(tallow) and EVA19. The polarity of MMT was increased, further improving its affinity towards polar EVA matrices. An exfoliated structure was reported for the nanocomposite based on EVA19. In addition, stacks of unmodified silicates were

observed. [74a] Zhang et al. [8b] increased the number of long alkyl chains used to modify MMT up to three. They anticipated that such an increase would decrease the organo-MMT polarity. Nevertheless, they found it necessary in order to yield wider organo-MMT basal spacing.

The aim was to obtain a proper balance between the two as this would facilitate the migration and penetration of EVA chains into the silicate layers. The morphological features of the EVA-MMT nanocomposites were then examined. They were found to depend on the basal spacing of the organically modified MMT and the polarity of the EVA. Increasing both promoted better dispersions. The chains of EVA diffused more easily into the MMT layers. Two long alkyl chains were found sufficient to yield organosilicates with wider basal spacing. [8b] These authors recorded further marginal expansion of d_{001} for triple-tailed organoclay.

Effect of VA Content on Dispersion of EVA Nanocomposites

The effect of changing the matrix VA content on the dispersion of the EVA composites was assessed by several authors [4, 6, 23, 73, 74b, 76, 79a, 83]. Increasing the EVA polarity lowers the thermodynamic energy barrier for polymer interaction with silicates and therefore the polymer chains diffuse more easily into the silicate layers. Increased matrix amorphousness (with increasing VA units) further facilitates the stabilisation of polymer chains within the silicate galleries. [23] These authors claimed that higher amorphous content prevents recrystallization of polymer chains during annealing. Therefore, the chains remain diffused within the silicate layers. [23]

Whatever the VA content, organosilicates with OH groups along the alkyl N substituents appeared to be well dispersed.

They may be due to strong intermolecular interactions between the OH groups of the organic modifier and the acetate functions of the EVA matrix. [77b] Increasing the VA content improved the degree of organosilicate dispersion, independent of the type of silicate modification.

When the number of long tails was the same, organosilicates with higher chain lengths dispersed better.

This may be related to the interlayer spacing of the organosilicate. Densely packing modifier into the silicate did not aid dispersion. Chaudhary et al. [23] claimed that this reduces the number of EVA chains penetrating the interlayer spaces.

Zhang and Sundararaj [6] investigated the extent of dispersion of some double-tailed organosilicates in EVA matrices with five VA contents (6, 9, 12, 18 and 28 wt.%). It was found that all EVA matrices further expanded organoclay interlayers. Increasing the VA content from 6 to 12 wt.% expanded the silicate interlayers considerably. Above such VA contents, no further interlayer expansion was recorded.

An intercalation-limiting effect of the polarity after a certain critical VA content was revealed. [6] This critical VA content was found to be approximately 15 wt.%. The degree of intercalation of EVA into double-tailed organoclay increased only at VA contents up to about 15 wt.%. Thereafter the expansion of basal spacing ceased.

The interlayer expansion was attributed to increased diffusion of EVA. Polymer diffusion depends strongly on how well it flows. The latter is determined by the melt flow index (MFI).

Effect of MFI on Dispersion of EVA Nanocomposites

The propensity of EVA with a higher VA content to diffuse into the silicate interlayers has been established. [8b] Zhang and Sundararaj [6] examined the influence of MFI on the structure of nanocomposites. They used five EVA28 matrices with different MFIs (3, 6, 25, 43 and 150 g/10min). The effect of the MFI on the intercalation-limiting effect of EVA polarity into double-tailed organoclay was investigated. Lowering the MFI from 150 to 25 did not cause any detectable change in the basal spacing. However, further decreasing the MFI to 6 did expand the silicate interlayer. Below this MFI, the silicate interlayer collapsed. It was then concluded that effective polymer diffusion requires a suitable conjugation between its mobility and its shear force. [6] The shear force should (i) create shear tensions during nanocomposite processing; (ii) aid the breaking up of organosilicate agglomerations; (iii) disperse silicate platelets or a few tactoids throughout the matrix; and keep the silicate platelets or tactoids apart. With regard to polymer mobility, it should be sufficient to promote the diffusion and penetration of polymer into the silicate layers before layer restacking. The existence of an intercalation-limiting effect of EVA into double-tailed organoclays was confirmed, although it appears to be dependent on the MFI of the matrix rather than on its VA content. Zhang & Sundararaj 2004 recorded increasing interlayer distances with increasing VA content from 3 to 15 wt.%. No further expansion was recorded for organo-MMT intercalated by EVA22 with different MFIs (2 and 3 g/10 min). Zhang and Sundararaj [6] also recorded increased interlayer spacing when the MFI of EVA28 was lowered from 25 to 6. Thus it is speculated that EVA resins conjugating good mobility and sufficient shear force will have an MFI in the range of 3–25. Marini et al. [79a] agreed that matrix viscosity is the driving force for polymer chain mobility within clay lamellae. In addition, imposed shear tension is also responsible for causing lamellae slippage and clay dispersion. Adequate affinity between polymer matrix and organosilicate was thus confirmed as indispensable.

EFFECT OF EVA NANOCOMPOSITE STRUCTURE ON ITS PHYSICAL PROPERTIES AND PERFORMANCE

Influence of Composite Structure on its Mechanical Properties

The effect of VA content on the mechanical properties of EVA/Mg layered double hydroxide nanocomposites has been studied by various groups. [8b, 83, 84] As expected, various nanocomposites exhibit a much higher storage modulus than pure EVA grades, especially at low temperatures, given the reinforcing effect of nanofillers on the matrix. In addition, the presence of the fillers enables the matrix to sustain high modulus values at high temperatures. Also, various nanocomposites show a reduction in tan δ peak height as compared with the heights of the respective neat elastomers. This is due to the restriction in polymer chain movements imposed by the filler-polymer interactions. The enhancements in dynamic mechanical properties indicate that the more elastomeric (VA content) matrix is, the more easily the nanofillers are dispersed due to the higher free volume.

Typically, silicate particles have higher tensile moduli than polymer matrices. With increasing concentration of nanofiller, there is an increase in the Young's modulus (stiffness)

of the nanocomposites. Alexandre and DuBois [85], using 5 wt.% MMT, prepared nanocomposites with double the Young's modulus of pure EVA27. It was found that EVA19 and EVA12 increased the Young's modulus by 50%. The variation in the modulus of nanocomposites was explained on the basis of their different structures. The dispersion of individual clay platelets responsible for the large increase in modulus was higher in the EVA27 nanocomposite. [85] Apart from polymer polarity, silicate modification with a surfactant having non-functionalised chains compatible with polymer matrices was similarly critical. The ductility of the EVA27 nanocomposite decreased only slightly compared with that of the pure polymer. This was in spite of a large increase in nanocomposite stiffness.

Zhang and Sundararaj [6] recorded ever-increasing Young's moduli of EVA nanocomposites with increasing concentration of nanofiller. In parallel, they proposed the existence of a "platelet saturation effect". Such an effect reduces the extent of platelet dispersion in the polymer matrix. The saturation effect is explained as follows: layered silicates have a large aspect ratio, exceeding 300; interaction between them is quite strong because of the large packing area; exfoliation and dispersion of silicate layers depend mainly on two factors: EVA-silicate interaction (ε_{es}) and silicate-silicate interaction (ε_{ss}); when $\varepsilon_{es} > \varepsilon_{ss}$, exfoliation of silicate layers is possible; conversely, when $\varepsilon_{es} < \varepsilon_{ss}$, exfoliation is impossible; an increase in clay content leads to a larger ε_{ss}; this is due to a shorter distance between the silicate aggregates. [6] The effect of the interplay between EVA polarity (amorphicity) and silicate concentration (wt.%) on the Young's modulus has been evaluated. It has been accepted that platelet "randomisation" characterises exfoliated nanocomposite structures. Typically, the effective dispersion of nanosilicates suppresses the ability of the matrix to absorb energy at lower VA content in the EVA matrix. [23] Nanosilicates increase spatial hindrance for polymeric chain movement. They impart rigidity to the polymer matrix, creating a "rigid" amorphous phase. Platelet-polymer and platelet-platelet interactions tend to create a flexible silicate network structure in the matrix. Owing to polymer entanglement, such a network increases the initial resistance of polymeric chains moving under stress. The initial deformation energy is then absorbed by the silicate network. Simultaneously, the flexible network increases the modulus of the nanocomposite. With increasing VA content, the flexibility of the silicate network increases. Consequently, the resistance of the polymeric chains to movement is lowered. Thus, a "mobile" amorphous phase develops, and the network's ability to absorb deformation energy decreases. This occurs in spite of platelet-polymer and platelet-platelet interactions in the flexible silicate network. Stress is then partially transferred to the polymer chains, allowing them to absorb higher deformation energy. Hence, the modulus appears to be dominated by the extent of matrix crystallinity/amorphousness rather than by the silicate network.

Rigidity may also be imparted without the formation of a silicate network structure. There will be good interaction between silicate platelets or clusters of tactoids with the matrix where they are dispersed and suitably oriented. However, tensile strength is likely to be reduced. [6] Favourable interactions at the polymer/silicate interface are critical for efficient stress transfer. Tensile strength does not increase when polymer-clay interactions are sufficiently developed. The strength of the nanocomposite reduces with increasing flexibility of the silicate network structure. Increasing matrix polarity tends to maximise extent of diffusion of EVA into silicate layers. A higher specific surface area becomes available for polymer-silicate interactions. [23]

Influence of Composite Structure on its Steady Shear Rheological Properties

The degree of dispersion of silicates in a polymer matrix affects the rheological behaviour of nanocomposites. Measurement of complex viscosity by oscillatory testing is useful to estimate the degree of exfoliation of composites. The viscosity of highly dispersed nanocomposites, with an exfoliated structure, increases considerably when the shear rate is changed. Conversely, the viscosity of poorly dispersed nanocomposites increases only moderately with the shear rate. At a low shear rate, exfoliated nanocomposites have the propensity to display solid-like behaviour. This has been attributed to the formation of a network structure by dispersed silicate layers. [77a] Polymer chains are entrapped within the network. Because there are unable to flow, the viscosity rises. High zero-shear viscosities indicate that the network of dispersed layers remains unaffected by the imposed flow. Interactions between silicate layers and polymer chains are more pronounced in exfoliated systems than in fully intercalated ones. At the same silicate concentration, the elastic modulus is higher for exfoliated structures than for intercalated ones. [74a] Hence, solid-like behaviour occurs at higher silicate loading in the latter systems. This leads to a slower relaxation of polymer chains. [77a]

High shear rates breakdown the silicate network and orient the platelets in the direction of flow. For this reason nanocomposites exhibit shear thinning behaviour. The slope of curves, the so-called "shear thinning exponent", is used to estimate the extent of nanocomposite exfoliation. It has been accepted that higher absolute values of the exponent indicate higher rates of exfoliation [77a, 78b]. However, Marini et al. [79a] suggested that a significant increase in viscosity in the low shear region indicates strong matrix-organosilicate interactions rather than exfoliation. Both well-dispersed intercalated and/or exfoliated silicates can lead to a huge increase in zero-shear viscosity. [79a]

La Mantia and Tzankova Dintcheva [78a] stated that the intensity of matrix-organosilicate interactions increases with silicate interlayer spacing. When the basal spacing increases, the surface area available for contact with the polymeric chains also increases. Moreover, due to the larger inter platelet distances, the volume concentration of the silicate increases. [78a] High interactions between the organosilicate and the polymer chains are critical for nanocomposite creation. However, they are not sufficient on their own to guarantee effective clay dispersion and exfoliation [6, 79a] Strong matrix-organosilicate interactions are indicated by a significant increase in zero-shear viscosity, rather than simply high zero-shear viscosity. Marini et al. [79a] recorded large rheological differences between EVA nanocomposites, depending on the matrix viscosity. High-viscosity EVA12 (MFI = 0.3 g/10 min) and EVA19 (MFI = 2.1 g/10 min) consisted of fairly well dispersed compact tactoids and had higher zero-shear viscosity than their respective EVA matrices. However, such viscosities were of the same order of magnitude or were only one order of magnitude different. Further, pure matrices also displayed pseudoplastic behaviour. Absolute values of the "shear thinning exponent" calculated for EVA12 nanocomposite and its matrix were high. Similarly, nanocomposites produced with low-viscosity EVA18 (MFI = 150 g/10 min) and EVA28 (MFI = 25 g/10 min) exhibited higher zero-shear viscosity than their respective EVA matrices. However, such viscosities were more than one order of magnitude different. Moreover, pure matrices exhibited Newtonian behaviour. It was then concluded that organosilicate dispersion was dependent on EVA matrix polarity and viscosity. [79a] On its own, a high "shear thinning exponent" does not guarantee a higher rate of exfoliation.

Likewise, a high zero-shear viscosity of the nanocomposites does not, on its own, guarantee strong matrix-organosilicate interactions.

Influence of Composite Structure on its Fire Properties

The effect of several parameters (nature of clay and clay loading) on the fire retardancy of the nanocomposite has been investigated. It has been observed that the nature of the cations, which compensate for the negative charge of the silicate layers, affects the fire performance, even though the fire properties were improved for both the montmorillonite-type fillers investigated. The clay loading also affects the fire properties. [75] The Stanton Red croft Cone Calorimeter was used to carry out measurements. The conventional data, namely time to ignition (TTI, s), heat release rate (HRR, kW/m^2), peak of heat release (PHRR, kW/m^2), i.e. maximum of HRR, total heat release (THR, MJ/m^2) and weight loss (WL, kg) were supplied by Polymer Laboratories software.

Huang et al. [56] explained the synergistic flame retardant effects between sepiolite and magnesium hydroxide in EVA matrices. In the light of the positive results from the loss on ignition (LOI) and UL-94 tests, not only did the cone calorimeter test data indicate a reduction in the HRR and MLR, but also a prolonged TTI and a depressed smoke release (SR) were observed during combustion. Simultaneously, the tensile strength and Young's modulus of the system were also improved by the further addition of sepiolite due to the hydrogen bonds between silanol attached to sepiolite molecules and the ester groups of EVA.

Cárdenas et al. [86] studied the mechanical and fire retardant properties of EVA/clay/sepiolite nanocomposites. Their results suggest that the synergistic effect is greater for bentonite with silica and with sepiolite than for bentonite with ATH. This is an expected effect in the case of bentonite with sepiolite taking into account that both inorganic fillers are phyllosilicates and have analogous chemical composition. However, the differences between the pHRR may also be influenced by the specific combustion mechanism of the different inorganic fillers used (silica, sepiolite). It is worth noting that EVA-sepiolite showed the lower THR among the other composites, confirming the synergistic effect between bentonite and sepiolite explained above. In the EVA-sepiolite composite, a uniform and rigid layer was formed, so the contribution of sepiolite to forming a more rigid layer of char was very clear, possibly due to the fibril structure of this type of clay. Consequently, it is possible to conclude that a nanostructure enables better fire performance to be achieved than a microstructure. In fact the presumed "diffusion effect", which leads to such improvements, occurs in a nanostructure but not in a macrostructure.

CONCLUSION

Detailed accounts of the different types of nanostructured materials (NSMs) to enhance the novel properties of pristine EVA have been covered in this review. The review has been systematically structured to give a clear and detailed insight into the materials. In the introduction we reviewed recent papers on the subject and classified the NSMs into three categories according to their dimensions: 0DNSM (POSS), 1DNSM (CNT, sepiolite), and 2DNSM (clay) with EVA. Next we presented a detailed discussion on the effects of POSS,

various types of silicate structure and various organic modifiers on EVA nanocomposites. In the third section we discussed recent approaches to NSMs such as CNT, sepiolite, clay and POSS.As NSMs play a vital role in EVA nanocomposites, we also elucidated the influence of composite structures on their thermal, mechanical, and fire retardant properties.

With great progress being made in the preparation of EVA nanocomposites, there are fascinating new opportunities for materials scientists. While considerable attention is being paid to particular aspects of nanostructures (for instance 0DNSM, 1DNSM and 2DNSM), future progress will hinge on a better understanding of EVA nanocomposites, their composition, size and morphology, which affect the activity of 0DNSM, 1DNSM and 2DNSM. In addition, as greater knowledge is acquired about the physical and chemical properties of 0DNSM, 1DNSM and 2DNSM, there will be more opportunities to exploit individual characteristics in thermal, electrical, mechanical and fire retardant-based applications. Moreover, the development of 0DNSM, 1DNSM and 2DNSM will help to improve our old technologies, and further research will produce more impressive results that will benefit various industries and society. Finally, it is important to note that new types of cubic silica (POSS) nanoparticles have recently been reported and their ability to form nanocomposites with enhanced properties has been proposed.

ACKNOWLEDGMENTS

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