Chapter 7
Thermal Stability and Degradation of Polymer Nanocomposites

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7.1   Introduction

The field of polymer nanocomposites shows tremendous application potential and is currently intensively investigated for new materials fabrication and properties evaluation.

In nanocomposites, one of the components has at least one dimension less than 100 Å. As an example of length scale, carbon fibers, commonly used as a reinforcement in sporting goods, are approximately 7 μm in diameter, and the length of a carbon–carbon chemical bond is about 10^{-10} m [1, 2]. Polymer nanocomposites include, e.g., biomaterials with nanohydroxyapatite, nanostructured drug delivery systems, layer-by-layer self-assembled polymer films, nano-reinforced elastomers, and electrospun nanofibers. The presence of nanostructured additives may considerably enhance barrier properties, thermal stability, flame resistance, electro-optical, and antibacterial properties of polymer matrix.

Nanostructured fillers applied as additives in polymer nanocomposites can be divided into:

- Metal oxides
- Carbon nanotubes
- Nanoclays
- Others, e.g., POSS moieties

It is worth mentioning that polymer-based nanocomposites with, e.g., carbon black have been known since decades in chemical technology; however, their characterization at the nanoscale was not possible due to lack of appropriate experimen-

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tal techniques. This has changed at the beginning of 1990s with the first papers on polyamide 6 (PA6)/layered silicate nanocomposites published by Usuki and Okada [3, 4].

As nanofillers can significantly improve various properties of the polymer matrix they are incorporated into, it is of crucial importance to investigate the mechanism of their action. This mechanism may strongly depend on the degree of exfoliation and agglomeration effects of nanoparticulates. It can be clearly seen when considering the thermal and flame retardancy properties of polymer nanocomposites with, e.g., montmorillonite [5–12].

In this chapter, the influence of different types of nanofillers on the thermal stability and decomposition of polymer nanocomposites will be discussed. Mechanisms of thermo-oxidative degradation processes of polymer nanocomposites will be discussed. Although the mechanical reinforcement aspects in the polymer nanocomposites are of the primary interest, thermal stability and flammability resistance get an increased attention. An interesting issue is the search for synergistic actions between the nanofiller and the "classical" thermal stabilizer toward improvement of the final performance of polymer nanocomposites.

7.2 Types of Nanofillers

7.2.1 Nano-oxides

Nano-oxides like metal oxides or nanosilica are spherical particles with diameter in the range of 20–300 nm. Metal nano-oxides, especially titanium dioxide, show photocatalytic properties. Titanium dioxide can be converted by hydrothermal synthesis into titanium nanotubes [13]. These titanium nanotubes have length of 1 μm, an external diameter of 10–20 nm and an internal diameter of 5–8 nm. Nanoalumina spherical particles in sizes from 20 nm are used as fillers with catalytic properties in polymer composites. The use of metal oxides as nanofillers often requires surface functionalization. For instance, Guo et al. have reported the functionalization of nano-oxides by methacryloxypropyl trimethoxisilane [14, 15].

7.2.2 Carbon Nanotubes

Carbon nanotubes (CNT) were discovered by Oberlin and Endo in 1976 [16, 17] and by Iijima in 1991 [18]. The tubes display a nanometric-scale diameter and much larger length in comparison with its diameter. In general, three types of carbon nanotubes are considered:

- Single-walled carbon nanotubes (SWCNT) with diameter between 1 and 2 nm
- Double-walled carbon nanotubes (DWCNT) with diameter between 2 and 4 nm

- Multi-walled carbon nanotubes (MWCNT) with diameter between 4 and 150 nm

  Carbon nanotubes are produced by two methods:

- A catalytic chemical vapor decomposition process at temperature in range of 600–1000 °C
- An electric discharge process under helium at temperature in range of 3000–4000 °C

Both processes yield a mixture of SWCNT, DWCNT, and MWCNT. Some surface defects may occur. The proper dispersion of carbon nanotubes in polymer matrices can be achieved via functionalization or by applying high shear rates [19, 20].

7.2.3 Nanoclays

Layered silicate nanofillers can be natural or synthetic clays of transition metals. The most widely used enhancement is clay due to its natural abundance. Clays used in the synthesis of nanocomposites consists of very thin layers that are usually bound together with counterions [19]. The crystal lattice of 2:1 layered silicates consists of two-dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedra by the tip. In tetrahedral sheets, silicon is surrounded by four oxygen atoms, and in octahedral sheets, e.g., aluminum or magnesium is surrounded by eight oxygen atoms. The layer thickness is around 1 nm depending on the particulate silicate, the source of the clay, and the method of preparation [21–24]. The crystal lattice 2:1 structure with silicon in the tetrahedral sheets and aluminum in the octahedral sheet, without any substitution of atoms, is called pyrophyllite. In case when silicon in the tetrahedral sheet is substituted by aluminum, the resulting structure is called mica. Due to this substitution, the clay is characterized by a negative surface charge, which is balanced by interlayer cations [25]. If in the original pyrophyllite structure the trivalent Al-cation in the octahedral layer is partially substituted by the divalent Mg-cation, the structure of montmorillonite is formed. Then overall negative charge is balanced by sodium and calcium ions, which exist hydrated in the interlayer called gallery [26]. A particular feature of the resulting structure is that the layers are held together by relatively weak forces; water and other polar molecules can enter between the unit layers [27, 28]. Layered silicates are only miscible with hydrophilic polymers, such as poly(vinyl alcohol) and poly(ethylene oxide). In order to render them miscible with other polymers, one must exchange the alkali counterions with a cationic-organic surfactant like quaternary alkyl ammonium sulfonium and phosphonium salts [26, 29]. The application of organically modified layered silicates provides some superior properties of nanocomposite material in comparison with systems containing sodium clay [30]. However, ammonium salts that are the most frequently applied salts [31, 32] suffer from thermal degradation during the fabrication and further processing of nanocomposites. This leads to the changes in surface properties of organoclays resulting in alternation of

nanocomposite structure and related properties [33, 34] and facilitates the occurrence of some unwanted side reactions and contamination of polymeric material with the products of thermal degradation of organic modifier that may be responsible for enhanced thermal degradation of polymer matrix [35], color formation, and accelerated aging [36, 37]. The need to improve the thermal stability of organoclays applied for the preparation of polymer nanocomposites has motivated to search for an organic modifier or stabilizer combining high thermal stability with high efficiency in facilitating dispersion of nanofillers in polymer matrix. In Table 7.1, various natural and synthetic nanoclays available and used as fillers in polymers are presented.

7.2.4   Other Nanofillers

Other nanofillers include, e.g., nanosilver, nanozinc, and nanogold. These metal nanoparticles exhibit catalytic behavior and antibacterial properties at the surface. Of interest are also their electrical and magnetic properties [39–41].

Another large group of nanofillers are silsesquioxanes with formula $R-SiO_{3/2}$ with R typically being alkyl or organo-functional groups. They show three-dimensional symmetry and nanometric size making them suitably building blocks for hybrid materials and nanocomposites. The large number of possible functional groups and chemical stability of the cage allows for design of tailored nano-

Table 7.1 Natural and synthetic nanoclays used as fillers in polymers

Family		Group
Double lamellar hydroxide	Synthetic	Hydrotalcite
Polysilicate	Synthetic	Fluorohectorite
		Zeolite
	Natural	Zeolite
		Silhydrite
		Ilerite
		Kanemite
		Magadiite
		Kenyaite
Phyllosilicates	TO(1:1)	Kaolinite
	TOT(2:1)	Smectite
		Sepiolite
	TOT:O(2:1:1)	Chlorite
		Bentonite
		Saponite

Adapted from [38]

architectures in all three dimensions [42–44]. Special attention is focused on polyhedral oligosilsesquioxanes (POSS) as reinforcement for polymer matrices.

7.3   Synthesis of Polymer Nanocomposites

There are four main methods to prepare polymeric nanocomposites:

- In situ template synthesis
- Intercalation of polymer or prepolymer from solution
- In situ intercalative polymerization
- Melt intercalation

Out of these, melt intercalation technique is widely used because it allows to obtain polymer nanocomposites with high yield using all types of nanofillers.

In situ polymerization was the first method used to synthesize polymer–clay nanocomposites based on polyamide 6. The modified layered silicate is swollen by a liquid monomer or a monomer solution. Then, the monomer migrates to interlayer gap of the layered silicate, so that the polymerization reaction can occur between the intercalated sheets. The reaction can be thermally or radiation initiated or by using an initiator located inside the interlayer [5, 22, 24, 45].

Melt intercalation consists of blending the nanoadditive with the thermoplastic polymer matrix in the molten state. If the filler surfaces are sufficiently compatible with the chosen polymer, the macromolecules can, under appropriate conditions, migrate into the interlayer space and form either an intercalated or an exfoliated nanocomposite [5, 22, 24, 46]. Among the abovementioned techniques, in situ polymerization and melt intercalation are considered as commercially attractive approaches for preparing polymer/layered silicate nanocomposites.

An important from technological point of view aspect is the tendency of nanofillers to agglomerate or aggregate. This effect leads to lowering of mechanical and thermal properties, so proper measures have to be taken to prevent or minimize it. Some solutions include [47–50]:

- Functionalization of nanoparticles
- Mixing at a high shear rate to improve the intercalation and then applying vacuum to remove air bubbles
- Sonication

Nanocomposites containing carbon nanotubes can be produced by different techniques, depending on whether or not pre-fiber mat is used [51, 52]. One of the fabrication methods of nanocomposites containing carbon nanotubes is the casting of a large objects subjected to high stresses. Layered hybrid laminates in thermoset matrix containing carbon nanotubes are manufactured in two steps: carbon nanotubes are isolated and dispersed in the mixture containing the matrix. Next, the suspension of polymer/carbon nanotube is added to a mat of fiber. Depending on the matrix and viscosity of the system used, the incorporation of carbon nanotubes could be performed up to 2 wt% [19, 20].

7.4 Degradation Process of Polymer Matrices

The service life of polymer matrices is restricted by their degradation, which can be caused by a number of environmental factors such as humidity, impurities, irradiation, mechanical load, microorganisms, and temperature. Degradation is in most cases an undesired process in the majority of polymer composites applications as it generally leads to changes in the chemical and physical structure of the matrix–nanofiller system resulting in the loss of many useful properties, such as polymer molecular weight [53], color [54], mechanical strength [55], and impact resistance [56]. The understanding of degradation mechanisms of polymer nanocomposites is further complicated by factors such as morphology, diffusion processes, and interactions of nanofillers. The physical behavior of thermoplastic composites in high temperatures is dependent on the degree of crystallinity of polymer matrices. For crystalline matrix-based nanocomposites, there exists a well-defined melting temperature. At the glass transition temperature, the composite material starts a transition toward a soft and rubbery state. For materials requiring stiffness and compressive strength, the glass transition temperature is an upper limit for practical use [57]. Interestingly, numerous polymer matrices could not achieve a viscous state because they begin undergoing thermal decomposition before the material melts (Fig. 7.1). Thermosetting or thermoplastic-based composite materials produce carbonaceous char during the thermal decomposition. It play an important role in stabilization of polymer matrix by inhibiting the flow of heat from the gaseous combustion zone back to the condensed phase and by hindering the access of oxygen [59, 60].

The thermal degradation of polymer nanocomposites could begin with start of oxidative processes that are often auto-accelerated. Oxygen molecules can penetrate the layers well below the surface of polymer matrix [61, 62].
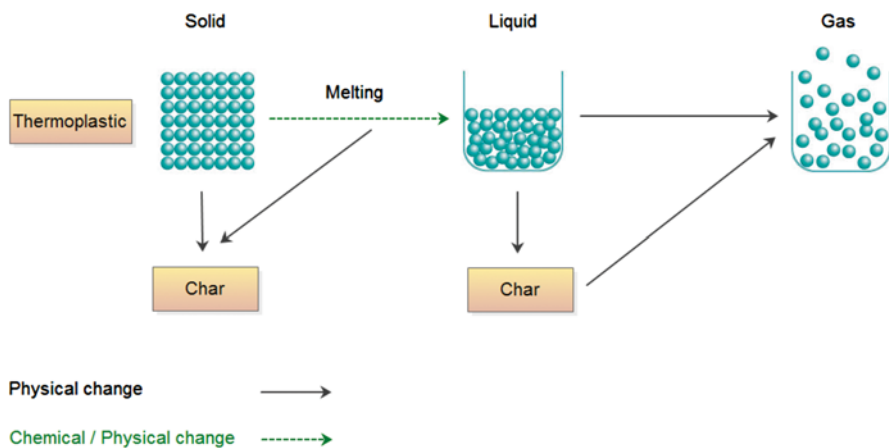

Fig. 7.1 Physicochemical changes during thermal degradation of polymer matrix [58]

Initiation			
	Polymer	$\rightarrow$	$P^\bullet + P^\bullet$
Propagation			
	$P^\bullet + O_2$	$\rightarrow$	$POO^\bullet$
	$POO^\bullet + PH$	$\rightarrow$	$POOH + P^\bullet$
Chain branching			
	$POOH$	$\rightarrow$	$PO^\bullet + {}^\bullet OH$
	$POOH + POOH$	$\rightarrow$	$PO^\bullet + POO^\bullet + H_2O$
	$PH + {}^\bullet OH$	$\rightarrow$	$P^\bullet + H_2O$
	$PH + PO^\bullet$	$\rightarrow$	$P^\bullet + POH$
Termination			
	$P^\bullet + P^\bullet$	$\rightarrow$	Non-radical product
	$P^\bullet + POO^\bullet$	$\rightarrow$	Non-radical product
	$POO^\bullet + POO^\bullet$	$\rightarrow$	Non-radical product + O_2

Fig. 7.2 Auto-oxidation scheme based on free radical chain reaction theory

A number of properties affect the thermal and oxidative degradation of thermoplastic polymers, such as average molecular weight, thermal history, and the presence of weak linkages or irregular structures [63–66].

Oxidation is one of the most important degradation processes and has been thoroughly investigated [67–70]. Oxidation processes may occur in every step of the life cycle of a polymer nanocomposite: during processing, storage, and the service life. In the oxidation process, different polymer decomposition products are formed, e.g., acids, alcohols, aldehydes, esters, ketones, lactones, peracids, peresters, and peroxides [71]. In the presence of impurities or irregular structures, such as branches, functional groups, or unsaturations, the rate of oxidation usually increases. During processing by extrusion or injection/blow molding, peroxy radicals are formed under high temperature and mechanical shear [72]. When certain concentration of hydroperoxides is reached, accelerated oxidation reactions start immediately [72]. The auto-oxidation scheme based on free radical chain reaction theory is shown in Fig. 7.2.

The basic stages include free radical initiation, propagation, chain branching, and termination. At high degree of oxidation, secondary reactions may play important role [73]. During polymerization reactions, catalysts, radical initiators, impurities in monomers, and minute amounts of oxygen could react and form peroxy radicals POO• which separate hydrogen from the polymer chain and form an alkyl radical and hydroperoxides. These hydroperoxides decompose when heated or irradiated to free radicals that initiate auto-oxidation processes [70, 72, 74, 75]. Because the formation reaction of hydroperoxides has a high activation energy, an increase in temperature of oxidation process will increase the rate of reaction, which leads to increase in the number of propagation cycles [76–79]. Chain branching reaction occurs when hydroperoxides undergo thermolysis to produce alkoxy and hydroxy radicals [78]. Termination of the propagation cycle take place, when two radicals recombine to yield non-radical products [80–83] – Fig. 7.3.
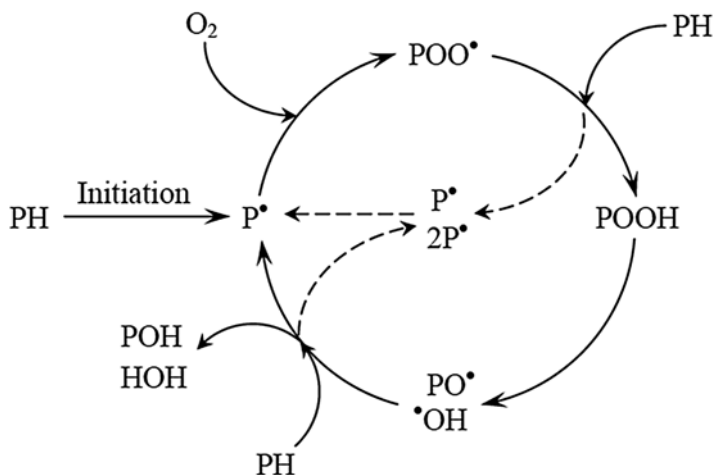
Fig. 7.3 The auto-oxidation cycle of polymer matrix

7.5 Thermal Stability of Polymer Nanocomposites

7.5.1 *Polymer/Nano-oxide Nanocomposites*

The increase in the thermal stability of polymer/metal or metal oxide nanocomposites is explained by the formation of polymer–nanoparticle network by physical cross-linking of polymer chains through metal particles, which stabilizes the whole system by restriction of the thermal motions of polymer chains. The examples of such systems are polyacrylate/ZnO [84] or polyurethane/TiO$_2$ [85] nanocomposites. A decrease in the thermal stability, often reported for hybrid materials, could be linked with metal-catalyzed oxidative degradation processes [86, 87].

The inclusion of the ceramic nanofiller into the more flexible polymer matrix with lower thermal resistance can substantially improve its stiffness and thermal stability [88, 89]. The nano-sized silica or alumina particles without any chemical modification could be incorporated into the polymer matrices such as poly(ether ether ketone). The mechanisms of thermal stability enhancement of polymers by silica oxide are referring to molecular dynamics [90], physical cross-linking, and specific interactions between the components. The experiments on the polymaleimide/colloidal silica nanoparticles nanocomposites show that the inorganic networks chemically bound to polymaleimides work for improving the thermal resistance of the nanocomposites [91]. In some cases, incorporation of nanoparticles into polymer matrix causes physical or chemical cross-linking increasing thus the initial decomposition temperature.

7.5.2 Polymer/Carbon Nanotube Nanocomposites

The dispersion of carbon nanotubes in polymer matrix can be improved by functionalizing the surface of nanofiller, which improves the interfacial interactions with the matrix [19]. There are three possible ways of functionalization:

- Chemical functionalization
- Physical functionalization
- Surface deposition

Several mechanisms of thermal stability enhancement have been considered for carbon nanotubes and nanofibers. Retardation of mass loss in inert atmosphere is likely to be a result of physical adsorption effect of the macromolecules on the nanotube surfaces that causes slower volatilization of polymer without change in initial degradation temperature [92] or absorption of free radicals generated during polymer degradation [93, 94]. Another scenario is a reduction of mobility of the macromolecules in the presence of CNTs. Although carbon nanotubes do not tend to show an intercalation phenomena, the stabilization effect of carbon nanotubes could be rationalized, similarly to the effect of layered silicates [94, 95]. This effect is clear in inert atmosphere and is displayed by the shift of degradation onset temperature [96]. Marosfői research group found out that the thermal stabilization effect of carbon nanotubes could be attributed to the increased interfacial interactions between the nanoadditive and polymer matrix, which leads to an increase of the activation energy of degradation [97]. They demonstrated that the presence of multi-walled carbon nanotubes slightly delayed thermal volatilization without modification of the thermal degradation mechanism, whereas thermal oxidative degradation in air was delayed by about 100 °C, independently from multi-walled nanotubes concentration [98, 99]. The stabilization effect was ascribed to the formation of a thin protective film of multi-walled carbon nanotubes/polyaromatic carbon char generated on the surface of the nanocomposites. This char was composed by a network of homogeneously dispersed multi-walled nanotubes entangled to form a nonwoven math-like structure [95]. Chipara et al. have shown that the thermal stability of polymer/carbon nanotube nanocomposites is strictly related to the nanoadditive content. They pointed out at an important role of interactions between macromolecular chains and carbon nanotubes that contribute to the formation of polymer–filler interface with enhanced thermal stability [100]. However, carbon nanoparticles could also play an accelerating role at the initiation of polymer decomposition, especially under oxidative conditions [101]. Most of the explanations attributes this effect to the remaining traces of inorganic elements [102]. The degradation behavior of polymer/carbon nanotube nanocomposites strongly depends on the type of modification that carbon nanotubes are subjected to [103, 104]. These reactive chemical modifications can substantially change degradation pathway and offer the increase of the thermal stability due to finer dispersion of nanoparticulates. For instance, the plasma-modified carbon nanotubes with maleic anhydride improved the thermal stability of polyimide nanocomposites through enhancing the dispersion and enabling the modified carbon nanotubes to bond chemically or physically interact with the polymer matrix [105]. Carbon nanotubes modified using amine groups cause significant improvement of thermal stability when covalently bonded to the epoxy matrix [106].

7.5.3 Polymer/Clay Nanocomposites

The current literature concerning thermal stability of polymer/clay nanocomposites gives inconsistent conclusions on clay efficiency in improving thermal stability. For instance, Vaia's experimental work revealed that char resulted in an order-of-magnitude decrease in the mass loss rate compared to the pristine polymer matrix, even for as little as 2 wt% of exfoliated layered silicate [107]. In turn, Tidjani [108] reported that the presence of the clay in poly(propylene-*graft*-maleic anhydride)/layered silicate nanocomposites exerted only a minor effect on the thermal degradation and the nanocomposites hardly showed any additional residue. Numerous divergences in results indicate the occurrence of effects of chemical nature that, unlike the physical effects, are different for each polymer–nanofiller system. Thus, the role of the dispersed nanoclay in thermal degradation of a polymer depends critically on the specific mechanisms associated with the polymer degradation reaction as well as chemical properties of nanoadditive [4]. Systematic studies concerning the thermal stability of a number of polymers have put forward the idea that the clay does not only quantitatively but also qualitatively affects the polymer degradation. Great differences in efficiency of clay in improving the thermal stability of various polymeric matrices have been considered in terms of the complexity of degradation mechanisms or in terms of radical stability [109–112]. One can assume that if the stability of free radicals produced during thermal degradation of polymer is high and they exhibit longer lifetimes, the probability that they will undergo secondary intermolecular reactions is also high. The presence of organoclay leads to prevent mass transport from the bulk and to permit radical recombination reactions, exerting thus a stabilization effect in the polymer/layered silicate nanocomposite [113–115]. It should be noted that the free radical trapping model successfully explains why the degradation of polymer/clay systems is slower, but they do not offer direct ways of explaining the changes in the thermal effect. Blumstein reported that the one proposed in literature mechanisms of thermal stability improvement in polymer/layered silicate nanocomposites is the reduction of molecular motions and physical processes in the condensed phase [116]. Recent research works confirm changes in molecular dynamics of macromolecular chains stick to the filler surface that result in, for instance, an increase of glass transition temperature. Since the macromolecular mobility is the major factor that contributes to the transport of reactive species within the polymer matrix, these nanomaterials could have lower reactivity and greater chemical and thermal stability than pristine polymer [117–119].

Montmorillonite is extracted from the bentonite by a process of sedimentation in water and then activated by sodium cations to improve clays swelling. Unmodified sodium montmorillonite exhibits good thermal stability in the temperature range of 20–500 °C, evolving physically adsorbed water at temperatures up to 120 °C, and the water from hydrated ions which is lost in the temperature range of 80–180 °C. The dehydroxylation of crystal lattice of clay was observed at temperatures above 500 °C, at which most of commercial polymers have already decomposed [120–122]. As it was noted, two of the main parameters of nanocomposites that are the dispersion of the nanoadditives and their interaction with the matrix play an important role in thermal stability of polymer nanomaterials [33, 123–126].

Incorporation of appropriate organic links between the matrix and the filler by functionalization improves the intercalation of polymer chains between the layers [49]. These cations reduce the surface energy of organoclay and facilitate macromolecule access between the layers of clays. Hence, the inclusion of layered silicates in a thermoplastic melt needs the exchangeable cations from the clay to be replaced by organophilic cations such as commonly used quaternary ammoniums. In Fig. 7.4, commonly used cations for polyolefin-based and polyamide-based nanocomposites are shown.

Considering the interaction between the nanofiller and the matrix at the nanometric scale, three scenarios are possible, which affect considerably the properties of the polymer composite material:

- The nanofillers are not intimately mixed in the matrix but form regions.
- The macromolecules enter between nanofillers' plates.
- The nanofillers are totally exfoliated and dispersed.

Typically, clays used in polymer nanocomposites have a double catalytic effect on the thermal degradation of organic molecules. If the temperature in inert atmosphere is increasing, carbon–carbon bond scission is accelerated by the clay, which comes in competition with acceleration of carbon–hydrogen bond scission in the presence of oxygen. Consequently, thermal degradation leads to volatiles, whereas thermo-oxidative dehydrogenation leads to unsaturated moieties evolving thermally stable charred nanomaterial [127]. The char formation due to the presence of dispersed montmorillonite layers is suggested as a mechanism of thermal stability improvement; however, under oxidative conditions, exfoliated clay nanoparticles may catalyze the hydroperoxide decomposition [128–132]. It has been shown that nanoadditive induced degradation reactions before the onset of thermal decomposition of the neat polymer. Consequently, charring process slows down the rate of mass loss in a subsequent stages of degradation [132–134]. The catalytic activity of organoclay toward degradation of polymer is also observed during nanocomposite compounding and aging in the thermal oxidative environment [135]. Xie and coworkers showed [136] that quaternary alkyl ammonium organoclays decompose
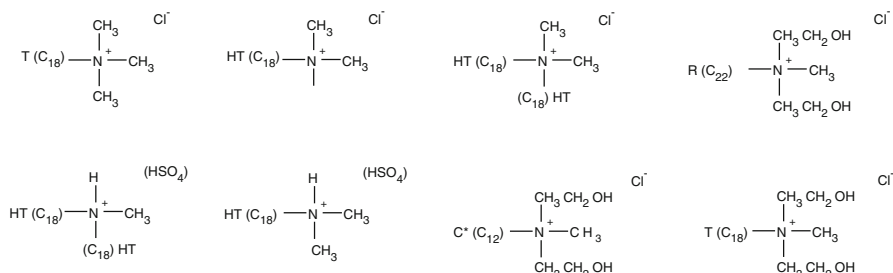

Fig. 7.4 Commonly used cations for polyolefin-based and polyamide-based nanocomposites. The symbols: *T,* tallow (predominantly composed of chains with 18 carbons ($\approx$65 %)); *HT*, hydrogenated tallow; *R*, rapeseed (consisting largely of chains with 22 carbons ($\approx$45 %)); *C**, coco (product made from coconut oil, consisting predominantly of chains with 12 carbons ($\approx$48 %)); *H,* hydrogen designates the substituents on the nitrogen [34]
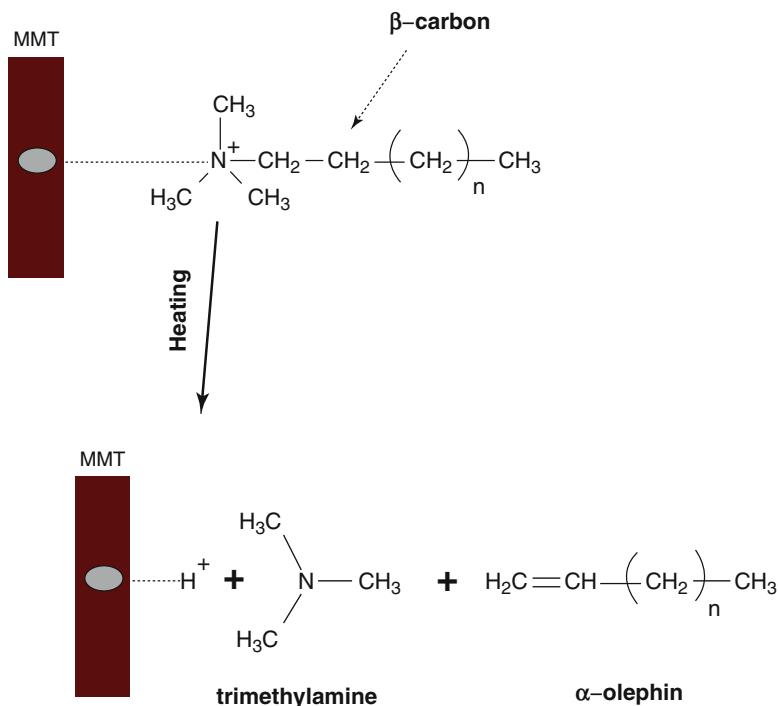
Fig. 7.5 Hofmann elimination reaction for quaternary ammonium compounds [37]

between 200 and 300 °C to produce α-olefins and amines, which is in agreement with Hofmann elimination mechanism [137–142]. This mechanism generally appears when a quaternary ammonium hydroxide or chloride, under high temperatures, is converted into an alkene and an amine, as it is presented in Fig. 7.5.

In the case of organoclays, elimination of the ammonium modifier could result in a substitution of the ammonium linkage on the clay with a hydrogen proton on the β-carbon. Ultimately, the α-olefin intermediates produced in this reaction could attack the polymer [35, 99, 143]. Davis research group also reported a significant level of PA6 degradation during high-temperature melt processing at 300 °C of in situ formed nanocomposites. Authors suggested that the degradation was largely due to hydrolysis caused by water originating from the clay. These authors also proposed other mechanisms – a catalytic degradation caused by unexchanged sodium cations on the surface of the clay [99]. The increased degradation of polymer in the presence of organoclay is often explained in terms of the catalytic activity of acidic sites formed due to the Hofmann degradation of onium compound. It should be emphasized that not only organic modifier and products of its degradation appears to have a catalytic effects on polymer degradation but also acidic sites inherently present on the mineral surface [144]. Several research works evidenced that the metal ions such as Fe^{3+} or Cu^{2+}, naturally present in clay minerals act as catalytic sites increasing the degradation reactions. On the other hand, cations of

some transition metals promote the molecular cross-linking and an increase in the amount of charred residue [145–149].

Kong's group suggested a scheme of successive reactions leading to the formation of char during degradation of hydrocarbon polymers in the presence of Fe-organoclay [150, 151]. Probably the presence of metal species in the clay structure could catalytically enable the oxidative cleavage of alkene substituents in alkyl ammonium compounds to produce aldehydes at high temperatures of processing [136, 152]. Alkylammonium salts which have shown catalytic activity toward degradation reactions are able to create other possible schemes of subsequent events such as an unsaturated and conjugated bond formation, cyclization, aromatization, fusion of aromatic rings, turbostratic char formation, and, finally, graphitization [153–155]. The char formation during the thermal degradation process of polymer nanocomposite is an indication of enhanced flame resistance of material. This is the reason why the thermo-oxidative stability of polymer nanocomposites is often investigated in relation to the fire retardancy [156].

7.5.4 Polymers Reinforced with Other Types of Fillers

Some research studies suggested that gold nanoparticles promote the thermal degradation of the polymer due to its catalytic ability. Metal-containing nanocomposites are more resistive to pyrolytic degradation, but increased mass losses are expected in these nanocomposites under oxidative atmosphere due to the catalytic effects toward oxidation reactions [157–160]. Due to graphite highly anisometric shape of elemental particles and its intrinsic heat resistance, physical barriers for heat and diffusing gases could be produced. Unmodified graphite basically does not interfere with chemical pathways of polymer degradation but operates in a physical mode of action [161, 162]. The commonly performed oxidation of graphite via chemical oxidation enhances the formation of polar groups on the graphite layers [163, 164]. The use of oxidized graphite is better in terms of barrier structure formation leading to improvements in the thermal properties as compared to the pristine graphite [165, 166].

Polyhedral oligomeric silsesquioxane nanoadditives find numerous applications as, e.g., surface modifiers, coating reinforcements, catalysts supports, and membrane materials. Inorganic–organic hybrid materials with POSS possess attractive properties such as better flame and heat resistance, higher glass transition temperature, and increased thermal stability and melt strengths which occur even at low POSS contents [167, 168]. POSS offer versatility both as reaction platforms to which other nanobuilding blocks could be attached and as robust and chemically stable nanostructured silica cages. Multifunctionalized POSS molecules, such as octa(aminophenyl)silsesquioxane, can react with diepoxides or dianhydrides to yield high cross-link density materials with good thermo-oxidative stability and increased compressive strengths [169, 170].

7.6 Synergy Between Stabilizers and Nanofillers

It is well established that the thermophysical properties of polymer nanocomposites depend strongly on the nature, amount, morphology, and dispersion degree of nanofillers. The thermal properties of polymeric nanocomposites are usually different from these of "classical" composites containing fillers of larger size which confirms the importance of the size/shape of filler particles. For fire retarded products, polymeric nanomaterials often require the use of other additives such as stabilizers or antioxidants which help to meet performance criteria against fire. On the other hand, incorporation of nanofillers can become an interesting alternative to traditional flame retardation methods [171–174]. Among numerous studies on the thermal properties and flammability of polymeric nanocomposites, investigations on epoxy resin/carbon nanotube nanocomposites demonstrate an increase in thermal conductivity. However, the addition of multi-walled carbon nanotubes into epoxy resins had no significant effect on the nanocomposites decomposition temperature [175]. Biercuk et al. suggest that epoxy resin reinforced with single-walled carbon nanotubes show an increase in the thermal conductivity of nearly 125 % at room temperature [176]. A larger amount of carbon nanotubes caused a decrease in the thermal conductivity, probably due to poor dispersion of nanotubes at high concentrations [177]. Other studies refer to the thermal properties of nanocomposites with clays and their influence on the initial decomposition temperature and glass temperature [178–180].

A synergy between classical flame retardants or stabilizers and nanofillers could be a desirable effect leading to the decrease in the usually large amounts of flame retardant that need to be applied and better mechanical properties [181, 182]. For instance, organoclay nanoparticles lower the flammability properties of the polymer matrix through formation of a compact layer during the exposure to flames. This layer blocks oxygen access to the fire zone and hinders emission of volatiles. The formed char shield reduces the heat transfer between the flame and the material and lowers the radiative flux by diffusing it into gas phase [130, 183].

In the presence of nanoparticles, the molecular mobility of degradation products and macrochain fragments is lowered which may contribute to the thermal stability of polymer nanocomposites. The incorporation of nanoparticles also causes an increase in viscosity of the melt, which restrict the heat transfer during processing.

The successful flame retardancy effect is obtained by combining the nanoparticles with conventional stabilizers such as metal hydroxides, phosphorous, or halogenated compounds, which mode of action is based on physical or chemical mechanisms [184]. However, during combustion, a portion of nanoparticles may be released to the environment causing some risks [185]. The use of double-layered hydroxides is an alternative to the use of modified organoclays for making nanocomposites with good fire and thermal properties. Our observations suggest that combination of montmorillonite with a phosphorus-based stabilizer leads to major improvements in the thermal and fire properties of polymer nanocomposites. Among different compositions of classical stabilizers and nanoparticulates showing possible synergetic effects, one can select:

- Carbon nanotubes in combination with metallic hydroxides
- Nano-hydroxides and nano-oxides in combination with phosphorous compounds
- Organoclays in combination with metallic hydroxides
- Organoclays in combination with phosphorous compounds to form intumescent structure [181, 182].

The use of modified nanofillers increases the flame retardation efficiency of the hybrid system at constant load of stabilizer. Improving the fire and thermal behavior of polymer materials using nanoparticles is associated with barrier effects but also with radicals scavenging ability. Application of nanoadditives could advantageously be combined with the use of reactive antioxidants. Appropriately selected stabilizers, adsorbed on nanofiller surface, could be added either before or during processing to inhibit the oxidation processes of polymer matrices. Antioxidants are added to the polymeric hybrid systems mostly in order to react with species formed during oxidation in an attempt to suppress the autocatalytic oxidation reactions.

Scavenging antioxidants are mainly used to trap free radicals formed in polymer nanocomposites during decomposition. These types of antioxidants are usually referred to as chain-breaking acceptors and chain-breaking donors [71]. Chain-breaking acceptors are effective at scavenging carbon-centered radicals under oxygen-deficient conditions. Therefore, they are most useful during high-temperature processing of polymeric materials or for the stabilization of the polymer composites [186]. However, they are not effective when molecular oxygen attacks carbon-centered radicals in a very fast reaction. In this case, H-donors such as hindered phenols and aromatic amines could be successfully used [187–190]. Synergistic effects could be achieved if hindered phenols are mixed with a phosphonate as they are preferred hydroperoxide decomposers in, e.g., polyamide nanocomposites stabilization [71]. Phosphonates are able to suppress the chain branching reactions in the auto-oxidative cycle by decomposing hydroperoxides to non-radical products. The hydroperoxides are reduced to an alcohol, while the phosphonate is oxidized in a stoichiometric reaction to phosphates (Fig. 7.6).

7.7 Conclusions and Perspectives

Polymer nanocomposites have considerably application potential in the area of novel advanced materials with improved properties. It is generally agreed that nanofillers can significantly improve various properties of polymer matrix they are incorporated into, but it is of paramount importance to elaborate the mechanism of their action. This is also true for thermal degradation and stabilization actions which mechanism depends strongly on the type of nanofiller, morphology, and polymer–filler interactions. Undesirable effects, such as agglomeration of nanoparticles, may play an important role, too. The results of the research works done so far lead to conclusions that the increase in the thermal stability of polymer/metal or metal
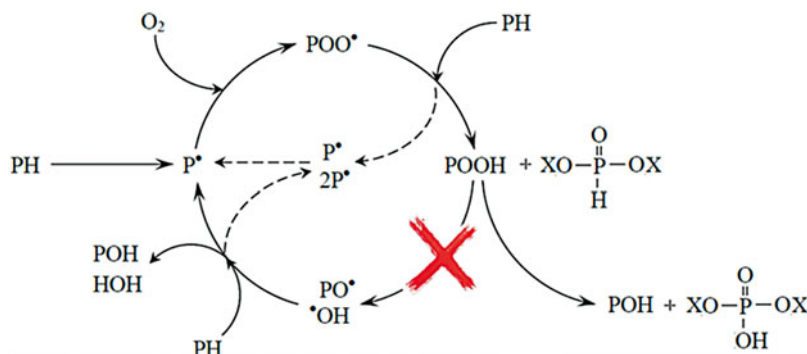
Fig. 7.6 Mechanism of the phosphonates' auto-oxidative cycle

oxide nanocomposites can be explained by the formation of polymer–nanoparticle network by physical cross-linking of polymer chains through metal particles, which stabilizes the whole system by restriction of the thermal motions of polymer chains. The mechanisms of thermal stability enhancement of polymers by silica oxide include slowing down of molecular dynamics, physical cross-linking, and specific interactions between the components. Several mechanisms of thermal stability enhancement have been considered for polymer composites with carbon nanotubes and nanofibers. Retardation of mass loss in inert atmosphere is likely to be a result of physical adsorption effect of the macromolecules on the nanotube surfaces that causes slower volatilization of polymer without change in initial degradation temperature or absorption of free radicals generated during polymer degradation. Another scenario is a reduction of mobility of the macromolecules in the presence of CNTs. For vastly applied polymer/clay nanocomposites, the barrier formation due to the presence of dispersed montmorillonite layers is suggested as a mechanism of thermal stability improvement; however, under oxidative conditions, exfoliated clay nanoparticles may catalyze the hydroperoxides decomposition.

In future developments, a synergy between classical flame retardants or stabilizers and nanofillers could be sought leading to the decrease in the usually large amounts of flame retardant that need to be applied and better mechanical properties of the nanocomposite. Another promising route is surface modification and functionalization of nanoadditives to enhance their dispersion in the polymer matrix or to form covalent bonds in hybrid materials, such as in those with POSS. Other promising area for future research is the use of cheap and abundantly available recyclable polymeric matrices and reinforcing nanomaterials of natural origin. However, materials obtained from renewable raw materials often lack sufficient thermal stability and flame retardancy, so there is a need for novel thermal stabilizers and flame retardants dedicated for this promising class of environmentally friendly nanostructured materials.

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