

Thermal Degradation of Thermosetting Blends

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Abstract The chapter coalesces literature studies on recent advances concerning the thermal behavior of different thermosetting blends. The introduction debates the general issue concerning polymer blends, that being the occurrence of phase separation phenomena and lists a series of possibilities to overcome these undesired aspects. The introduction section also presents the most common polymers used as crosslinked scaffolds either individual or for different multicomponent polymeric materials. The subchapters that follow are focused on recent studies on the thermal stability and degradation of thermosetting blends, effect of reinforcement and nanofillers on the thermal stability of thermosetting blends and applications and future trends of thermosetting blends, dealing with the latest issues and trying to reveal solutions.

1 Introduction

The beginnings of the polymer industry date back to 1846 when the first polymer blend was patented by Parkes which co-dissolved natural rubber (amorphous *cis*-1,4-polyisoprene) and gutta-percha (semi-crystalline *trans*-1,4-polyisoprene) in CS₂. The blending process yielded a partially crosslinked material. The process was known as co-vulcanization and the interesting aspect of the final blend was that its rigidity could be controlled by composition. Due to this aspect, the blends were used in multiple application domains. What followed was the obtaining of synthetic

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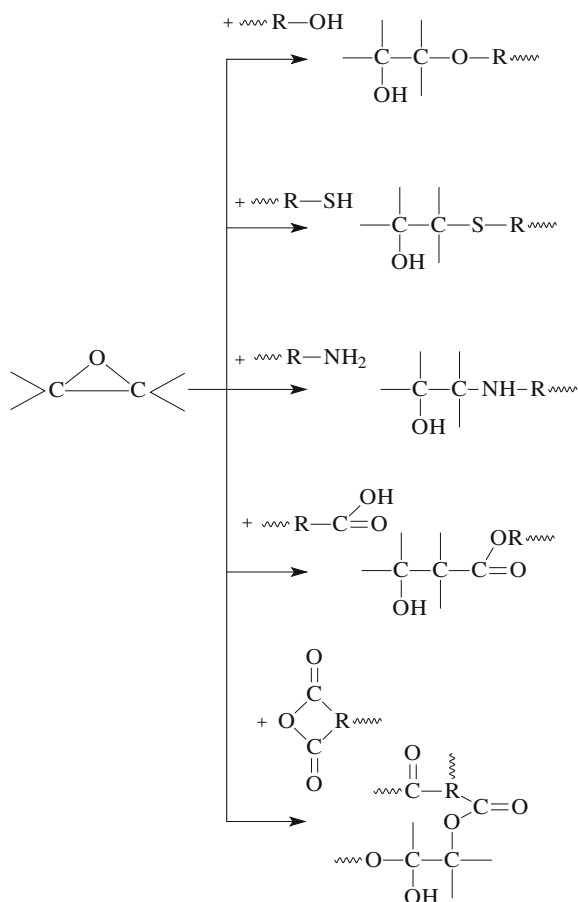
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rubbers, beginning with the first polymerization of isoprene in sealed bottles by Tilden in 1884, and modified natural polymers which included nitrocellulose, cellulose acetate (1926) and cellulose ethers and esters (1927).

Phenol-formaldehyde was reported as the first commercially synthetic polymer (1899) which was introduced as Bakelite™ by Baekeland in 1909. This was the period which marked the dawn for the production of commercial synthetic thermosetting polymers. Other advances in the field included the discovery of urea-formaldehyde resins in 1884 and the beginning of their commercialization as Beetle™ moldable resin in 1928, followed by thiourea-formaldehyde (1920), aniline-formaldehyde (*Cibatine*™ by Ciba, 1935) and melamine-formaldehyde (1937) moulding powders. The year 1909 marked the discovery of epoxy compounds by Prileschaiev, which were not used until World War 2. The first thermoset polyesters, invented by Ellis, date back to 1934 and in 1938 was reported their first use in the forms of glass-reinforced materials [1].

The typical polymers used as scaffolds in thermosetting blends are epoxy (Fig. 1), phenolic (Fig. 2), urea-formaldehyde (Fig. 3) and melamine-formaldehyde resins (Fig. 4), unsaturated polyesters and polyimides [2].

Fig. 1 Crosslinked epoxy resins



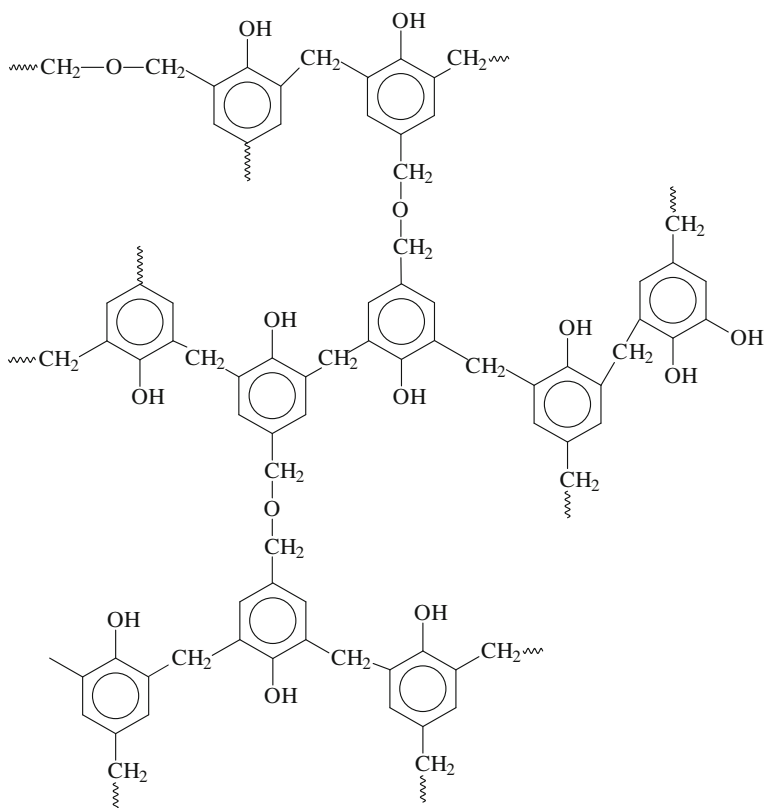
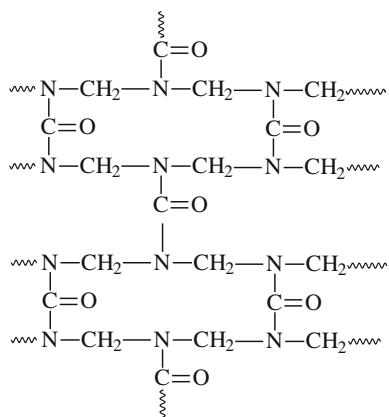


Fig. 2 Crosslinked phenolic resin

Fig. 3 Crosslinked urea-formaldehyde resin



Amongst the outstanding properties of the epoxy resins, their great resistance to chemical agents and corrosion are noteworthy. Other properties include excellent electrical and mechanical behavior, flexibility and moderate toughness, great

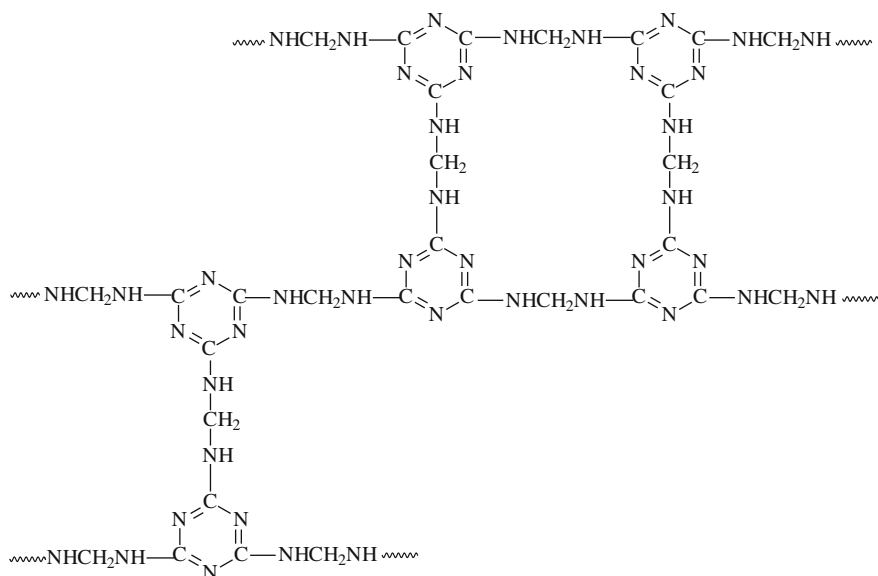


Fig. 4 Crosslinked melamine-formaldehyde resin

abrasion resistance, excellent adhesion to various building materials, low shrinkage during and after curing [2, 3]. Due to such properties, the epoxy resins are used in a wide variety of application domains. Since during World War 2, due to the epoxy resins multiple crosslinking possibilities, their palette of applications has fast and considerably broadened, especially in the civil engineering and building industry sectors where they are used as: structural, general purpose and tile adhesives, crack injecting systems, resistant, laminate and epoxy-tar coatings, floorings, grouts, anchors and antiskid systems (road resurfacing epoxies), mortars and interlayer sealing membranes for bridges [3]. Epoxy resins are also used in special application domains, such as encapsulating materials for miniature components and laminates in the aircraft industry. Carbon fiber reinforced epoxy resin composites are applied for structural modifications in aeroplanes, whilst their aramid fiber based composites are building materials for boats.

Unlike epoxy resins, the chemical resistance of phenolic resins is mostly dependent on the type of resin and filler. It has been reported that simple phenol-formaldehyde is affected by NaOH attack, whereas xyleneol and cresol based resins are inert. Due to the high crosslinking degree and interlocking, phenolic mouldings are characterized as insoluble, hard and heat resistant (up to 200 °C) materials. Due to their properties, phenol-formaldehyde mouldings are used for producing telephones, handles, knobs, electrical iron parts, welding tongs and lamp housings, bottle caps and closures. Special applications include compression presses for injection mouldings of thermoplastics and fuse-box covers and distributor heads in the automobile industry.

Urea-formaldehyde resins are applied in the field of electronics. They possess superior electrical insulation properties compared to phenolic resins and are used in the production of mainly sockets, plugs and switches. Urea-formaldehyde resins may come in a wide color range and do not impart taste and odour, thus being also applied in the domestic and sanitary sectors in the making of pot and panhandles and toilet seats. Such resins also exhibit good adhesive properties in the furniture industry for plywood, chipboards and particleboards. A special application of urea-formaldehyde resins consists in the obtaining of foams for placing on airport runways for stopping overshooting aircrafts during emergency landings.

Same as urea-formaldehyde resins, melamine-formaldehyde resins present a wide color range, are track and scratch resistant, possess good electrical properties and superior heat resistance and hardness. The resins excellent adhesive properties make them useful in the furniture industry. Due to freedom from color and the above mentioned properties, urea-formaldehyde resins are employed for laminating. Other applications depend on the nature of different fillers. Electrical applications demand mineral-filled urea-formaldehyde resins, whilst the cellulose-filled resins are used for manufacturing of clock cases and trays. Special applications include flame retardant agents [2].

Unsaturated polyesters present excellent properties for applications in the construction sector, such as: excellent abrasion, chemical, corrosion and heat resistance, high impact and excellent compressive strength and rapid strength gain. Due to these properties, unsaturated polyesters are used as anchoring gouts, coatings, concretes and loop and lighting sealants, amongst other applications. This class of polymers is also used as fiber reinforced materials [3].

Thermosetting polyimides exhibit superior mechanical strength, thermal and thermooxidative stability, are mostly chemically inert and inactive to high energy radiations, thus being suitable for aerospace applications, such as jet engines compressor seals, pressure discs, bearings, friction elements and sleeves [2].

In order for thermosetting polymer blends to be used in different special applications, the thermal stability of such materials, amongst other properties, is a key factor which must be tested and, where the case, improved. For this purpose advanced knowledge on the different thermal decomposition mechanisms and their influence on the miscibility of the comprising polymers are crucial.

2 Recent Studies on the Thermal Stability and Degradation of Thermosetting Blends

The general issue concerning polymer blends consists in the fact that most polymers are highly immiscible and generate phase separation phenomena, this meaning that the free energy change of the mixture is not negative, i.e. the heat of mixing is too high, as previously discussed in this book. According to Hildebrand [4] the heat of mixing can be expressed as:

$$\Delta H = V(\phi_1 - \phi_2)^2 v_1 v_2$$

where V is the total volume, v_1 and v_2 are the volume fractions of the respective components, ϕ_1 and ϕ_2 are the solubility parameters.

$$\phi = \left(\frac{\Delta E}{V} \right)^{1/2}$$

where ΔE is the energy of vaporization (also cohesive-energy density or internal pressure) and V is the molar volume. Hildebrand indicated that a difference in solubility parameters values between the two components of the blend must ideally not exist or be minimal, in order not to increase the positive value of the heat of mixing.

In order to avoid the occurring of phase separation phenomena, a variety of compatibilization methods have been thoroughly discussed in the literature. Phase compatibilization may be achieved by in situ polymerization, introduction of specific groups, crosslinking between phases, polymer-polymer reactions, ternary polymer addition, reactive extrusion, block copolymer addition or obtaining of interpenetrating (IPNs) and semi-interpenetrating polymer networks (SIPNs) [5]. An ideal classification of thermosetting blends can be made as follows [1]:

- thermoset-thermoset blends and IPNs;
- thermoset-thermoplastic blends and SIPNs;
- rubber modified thermosets.

Amongst the above mentioned compatibilization methods, the obtaining of IPNs and SIPNs often proved to be a promising and very efficient route. An IPN is a polymer alloy comprised of two or more chemically crosslinked polymers. The difference between polymer blends and IPNs is that the latter ones swell instead of dissolving in solvents and do not creep or flow. Types of IPNs include sequential, simultaneous, latex and gradient IPNs and may also be thermoplastic (i.e. when physical crosslinks are implied). Thermoplastic IPNs behave as thermosets at ambient temperature, but usually flow when heated at certain temperatures, possess IPN properties and often exhibit dual phase behavior [1].

SIPNs are polymer alloys comprised of one or more linear or branched polymers entangled in one or more crosslinked polymers. The great advantage of obtaining SIPNs is that during such synthesis there occurs a synergism of the individual properties of the components due to a forced compatibilization of the phases. Of course, in not all cases the compatibilization occurs, but rather in limited ones. Whether the occurrence of phase separation phenomena is desired or not, depends on the application domain(s) sought for the future material. However, in most cases phase separation proves to lead to a decline in polymer blends performances, by especially altering their thermal and mechanical properties and thus the occurrence of such phenomena is usually undesired. Another aspect regarding the miscibility of a SIPN is that, in addition to close solubility parameters of the comprising

polymers, the system is also characterized by the existence of a single glass transition temperature domain (T_g) value, which is dependent on the T_g values of the individual components and their weight fractions.

Epoxy resins are excellent coating materials widely used in constructions, due to their high mechanical strength and good adhesion to metals, amongst other properties, as mentioned earlier in this chapter. However, epoxy resins stress crack under impact forces, possess brittleness and usually exhibit stress after curing. One route to resolve this impediment consists in the obtaining of SIPNs with elastomeric polyurethanes which have excellent elasticity, damping properties and abrasive resistance, but in turn do not have the superior properties of the epoxy resins.

Rosu et al. [6] obtained six SIPNs based on a linear aromatic polyurethane and increasing crosslinked epoxy resin (CER) content of 5, 10, 15, 20, 30 and 40 %. Varganici et al. [7] conducted miscibility studies, mostly based on observations of thermal investigations of the six SIPNs, and tried to determine if phase separation phenomenon occurred and at what epoxy resin content value. DSC heating curves showed a single T_g value which increased in the range -33 to 16 °C for the SIPNs containing up to an including 30 % CER content, indicating a good miscibility between the two comprising polymers. For the SIPN containing 40 % CER, the system generated two T_g values, indicating the occurrence of phase separation phenomenon, which was confirmed by scanning electron microscopy and optical microscopy techniques. The evidence of the formation of the SIPNs was made by the reducing in intensities of the melting and crystallization profiles of the polyurethane until their total disappearance with CER content increase. By applying the Fox [8] and Gordon–Taylor [9] equations, authors demonstrated the existence of some specific and strong interactions between the two comprising polymers.

Thermogravimetric (TG) studies indicated that samples thermal stability of the SIPNs depended on the CER concentration. SIPNs containing up to a 10 % CER started decomposing at intermediate temperatures between the ones of the pure comprising polymers. This aspect indicated the existence of some specific weak interactions between the crude comprising polymers. These interactions were also evidenced by thermo-mechanical measurements [10] and miscibility studies [7]. The thermograms and the first derivative curves (DTGs) of the SIPNs and the pure comprising polymers, recorded at a heating rate of 10 °C/min, are given in Fig. 5. The SIPNs containing a higher than 10 % CER content started decomposing at temperatures below that of the polyurethane. The increasing of CER content led to the increase of the strength of interactions of the comprising polymers. The cause may consist in disruption of hydrogen bonding in the pure comprising polymers during the obtaining of the SIPNs. These interactions led to a slight decrease in thermal stability, the findings being in good agreement with the miscibility studies.

At least three stages of thermal decomposition were evidenced for the SIPNs, from the DTGs. The polyurethane and CER thermally decomposed in four and one stage, respectively [11, 12]. The DSC thermograms, recorded simultaneously with the TG ones, were in good agreement with the DSC thermograms recorded for the miscibility studies [7], indicating a melting profile around 200 °C for the polyurethane, with

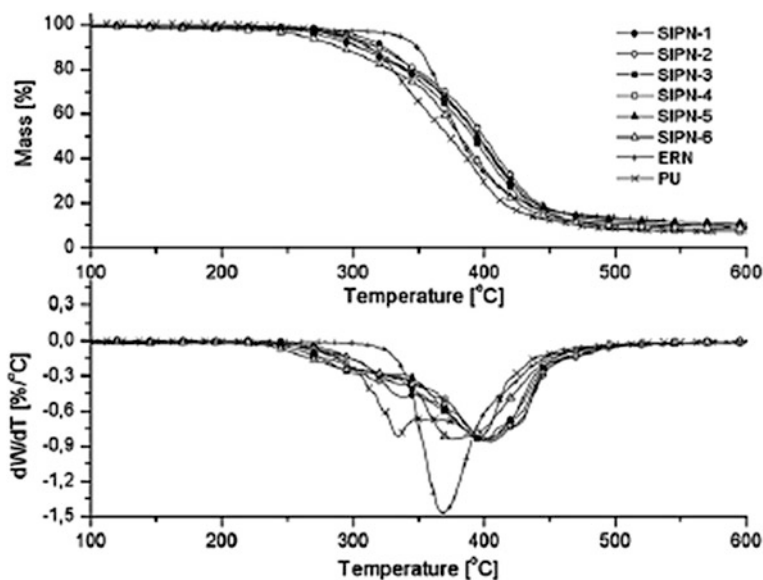
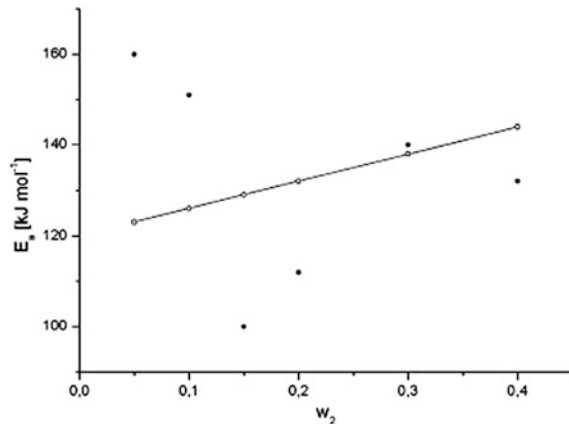


Fig. 5 TG and DTG thermograms recorded at 10 °C/min (reproduced with kind permission from Elsevier—License no. 3280641074690)

reducing intensity until disappearance, and also three endothermic processes, corresponding to each individual thermal decomposition stage.

The global kinetic parameters values of the thermal decomposition process were determined for the structure containing 20 % CER, since the other SIPNs presented similar thermal behavior, by applying the differential and integral isoconversional methods of Friedman and Ozawa, Flynn and Wall (OFW) [13, 14]. In both cases activation energy (E_a) values increased with the conversion degree (α), suggesting a complex thermal decomposition mechanism through successive and/or parallel reactions [15]. A three consecutive stage thermal decomposition mechanism was proposed. The OFW imposes a first order reaction model (i.e. $1 - \alpha$) in describing the thermal decomposition process. If the process is indeed characterized by a first order reaction model, then the straight lines of the OFW graph should respect the same parallelism, however, in this case, this condition was not met. Authors tested 14 kinetic models, detailed in the literature [16], by multivariate non-linear regression method, in order to find the real form of the conversion function which best characterized the global thermal decomposition process and to determine the values of the kinetic parameters (E_a , pre-exponential factor (A) and reaction order (n)) characteristic to each individual stage of the thermal degradation, corresponding to each DTG curve peak. A good correlation between simulated and experimental data was found for an n -th order reaction model (i.e. $(1 - \alpha)^n$) for all studied SIPNs. The first stage of thermal decomposition of SIPNs containing 5 and 10 % CER content were characterized by values of $n > 2$, indicating that mass loss occurred through scission and intermolecular transfer phenomena [17]. For higher

Fig. 6 E_a variation as function of CER content for the first stage of thermal decomposition min (reproduced with kind permission from Elsevier—License no. 3280641074690)



than 10 % CER content $n \approx 1$, suggesting that mass loss occurred by random scission of the polyurethane main chain [17].

Two instances can be observed from Fig. 6, which shows a comparison between E_a experimental values and those calculated with the additivity rule in Eq. (1), for the first stage of thermal decomposition of the SIPNs, where E_{a1} and E_{a2} are the E_a values of the polyurethane and CER, and y_1 and y_2 are their corresponding weight fractions:

$$E_a = y_1 E_{a1} + y_2 E_{a2} \quad (1)$$

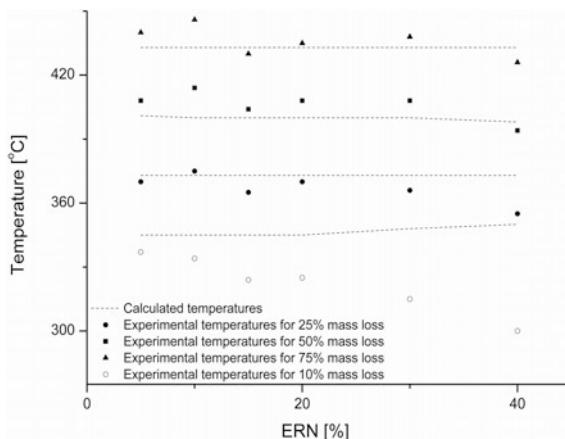
In the first instance, the SIPNs containing 5 and 10 % CER were characterized by E_a values higher than the calculated ones, aspect attributed to the high mobility of the polyurethane chains in the melt states, thus increasing the probability of recombination reactions occurrence between macroradicals generated during thermal decomposition [18].

In the second instance, the experimental E_a values of structures containing 15 and 20 % CER content were lower than the calculated ones, due to the enhanced stiffness of the SIPNs induced by the increasing CER content which reduced the macroradicals deactivation probability by diffusion processes and increased the thermal decomposition rate [18]. For the structure containing 30 % CER content, the experimental E_a value exceeds the calculated one due to a maximum crosslinking density and afterwards phase separation phenomenon occurred and the E_a value of the SIPN containing 40 % CER becomes lower than the calculated value [19].

A comparative study between experimental and calculated temperatures values corresponding to 10, 25, 50 and 75 % weight loss is shown in Fig. 7, where ERN is the epoxy resin content.

The occurrence of specific interactions between the two comprising polymers is confirmed by the experimental values which are lower than the calculated ones for a 10 % mass loss and which decrease with CER concentration. The existing specific interactions are lower for a CER concentration up to 10 % and become more intense

Fig. 7 Temperatures corresponding to a specific mass loss, as a function of epoxy resin content concentration (reproduced with kind permission from Elsevier—License no. 3280641074690)



with CER concentration increase up to 40 %. It can also be observed that experimental and calculated values start approaching at mass loss values higher than 25 %.

The evolved gas analyses were conducted on FTIR and mass spectroscopy (MS) devices, coupled to the TG apparatus. The main volatile compounds released below 350 °C were carbon dioxide and water vapours, which increased during the whole thermal decomposition process. Alcohol traces and aromatic structured compounds were also identified. Volatile structures containing carbonyl groups were found in the gaseous mixture at temperature values above 350 °C. Ammonia evolution was also found in the gaseous mixture. The MS spectra were in good correlation with the findings from the FTIR spectra data.

Shojaei and Faghihi [20] studied the effect of different concentrations of organoclay on styrene-butadiene rubber and phenolic resin blends prepared by two-roll mill. Thermogravimetric studies indicated that the organoclay enhanced the thermal stability of styrene-butadiene rubber vulcanizate, whilst manifesting a catalytic behavior in presence of the phenolic resin.

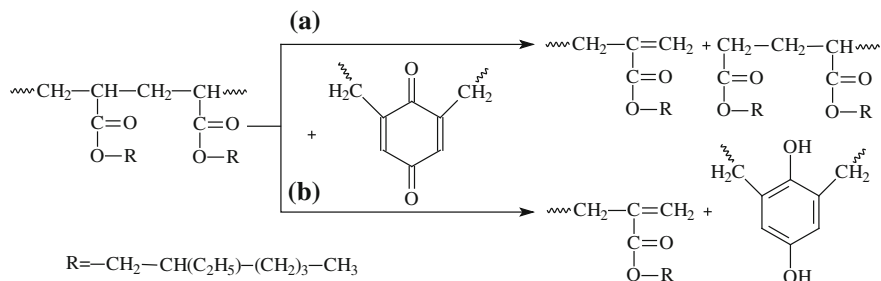
Varshney et al. [21] prepared oxazolidone modified epoxy blends by cycloaddition reactions of diglycidil ether of bisphenol A and tolylene 2,6-diisocyanate, forming linear thermoplastic polymers. The obtained polymers were cured with benzophenone tetracarboxylic dianhydride, leading to the obtaining of thermosets by the crosslinking reaction of the epoxy chain ends. The oxazolidone concentrations varied in the range 5–50 %. All blends exhibited high thermal stability in nitrogen atmosphere and in the onset temperature range 373–384 °C. Char yields increased with the increasing number of heterocyclic oxazolidone moieties in the blends. It was concluded that 15 % oxadiazole in the blend was an optimum concentration value in yielding the highest thermal stability.

Phenolic-acrylic IPNs have been extensively studied due to their excellent mechanical and thermal properties [22–26]. It was reported that such IPNs exhibited lowering of T_g values owed to an enhancement of toughness, but weak thermal stability in comparison to pure phenolic resin. This aspect was explained by the

occurring of certain chemical reactions between the IPNs components at certain temperature values [27]. The decreasing in T_g values related to the toughening of phenolic–acrylic IPNs was attributed to novolac resin possible curing reaction occurrence in the presence of the acrylic polymer. In order to correlate this possible reaction with the thermal behavior, a quantitative evaluation of both global thermal decomposition parameters and T_g s of phenolic–acrylic IPNs is necessary. For this purpose, Goswami and Kiran [28] obtained sequential IPNs and SIPNs based on novolac resin and poly(2-ethyl hexyl acrylate) in varying ratios and studied their thermal decomposition behavior and kinetics in nitrogen atmosphere. All structures showed a good miscibility by exhibiting a single T_g value which shifted to lower temperature domains with the increase of acrylate concentration. Activation energy values of the T_g s decreased for all samples, and were lower for the SIPNs compared to IPNs which had both components crosslinked. All structures thermally decomposed in two stages with the SIPNs exhibiting lower thermal stability than the IPNs. A thermal decomposition mechanism of the phenolic resin in the absence and presence of the acrylate network interpenetration was reported by Chakrabarty and Goswami [29] (Scheme 1).

It was demonstrated that the thermal decomposition of phenolic resin followed a first order kinetic model due to only one reactant evolving during the rate determining step, whilst the thermal decomposition of phenolic–acrylic IPNs was described by a second order reaction model due to parallel evolvement of formaldehyde and poly(2-ethyl hexyl acrylate) in the second thermal decomposition stage. Global thermal decomposition activation energy values decreased with the increasing of acrylic concentration in the IPNs and reaction order values remained unmodified, indicating that the 2-ethyl hexyl acrylate molecules facilitate phenolic resin decomposition.

Honmote et al. obtained IPNs based on polyaniline and poly(vinyl alcohol) as thin films with different concentrations of aniline through oxidative polymerization of aniline by using ammonium persulphate as oxidant [30]. All IPNs exhibited similar thermal behavior in nitrogen atmosphere, presenting the features of both comprising polymers. The structures thermally decomposed in three stages, exhibiting dopant release in the first stage (30–100 °C), covalently linked water in



Scheme 1 Thermal decomposition of polyacrylate: **a** in absence and **b** in presence of novolac resin

the second stage (180–240 °C) and decomposition of both comprising polymers leading to polyene entities and volatile compounds in the temperature range 410–450 °C. The structures yielded char residue values of 26, 25 and 21 % at the end of the thermal decomposition process.

IPN membranes based on poly(dimethyl siloxane) with vinyl terminations and increasing concentrations of aromatic polyimide (5, 10, 15 %) for methanol and toluene azeotrope separation were obtained and their thermal stability was studied in both nitrogen and air atmospheres [31]. The blends were first cured at 300 °C, which is the temperature for optimum imidization process. In both atmospheres the structures exhibited thermal stability higher than 400 °C which increased with the polyimide content due to electrostatic attraction between silicone moieties and polyimide molecules. The blend components each decomposed following identical pathways. The thermal stability of all structures slightly decreased in air compared to nitrogen atmosphere and in both situations it was higher than that of neat poly(dimethyl siloxane). The thermal decomposition processes of the IPNs and the pure comprising polymers followed similar first order kinetics. Activation energy values increased in both atmospheres with the polyimide content due to its shielding mechanism which protected the poly(dimethyl siloxane) during thermal decomposition. Char yields values at 800 °C varied in the range 46–56 % in nitrogen atmosphere and in the range 0–49 % in air atmosphere.

Pielichowski and Janowski obtained a series of SIPNs based on polyurethane and poly(vinyl chloride) by prepolymer method using partially polymerized diphenylmethane-4,4'-diisocyanate, polyoxypropylenediol and 1,4-butanediol as chain extender. The networks were thermally characterized in order to gain new insights in further understanding of the flame retardant effect of poly(vinyl chloride) in different polymer based blends [32]. All structures thermally decomposed in three stages in argon atmosphere. The first stage ranged between 313 and 503 °C with a mass loss value of 12 % and was explained by decomposition initiation. The second stage was found in the interval 503–693 °C with a mass loss value of 50 % and was attributed to main thermal degradation during which the decomposition rate was the fastest. The third thermal decomposition stage occurred in the range 693–863 °C with a mass loss value of 14 % and was attributed to the end of the decomposition process leading to the formation of solid residue due to crosslinking processes [33]. Authors reported the occurrence of a decrease of maximum thermal decomposition rate (i.e. DTG peak maximum) for poly(vinyl chloride) in comparison to the crude polyurethane because of hydrogen chloride evolution which retards the burning process by playing a scavenger role for free radicals [34]. Furthermore, the amount of solid char remained after thermal decomposition process exhibited an increase with molecular mass of polyoxypropylenediol increase, due to the multiphase morphology of the polyurethane. The polyoxypropylenediol comprises the soft segments creating a flexible matrix scattered between hard segments domains which physically crosslink to form a complex temperature dependent morphology with phase separations.

Merlin and Sivasankar obtained SIPNs based on low (1000 Da) and high molecular weight (2000 Da) biocompatible polyurethane incorporated in poly

(acrylamide) and studied their thermal decomposition characteristics in nitrogen atmosphere [35]. Both SIPNs thermally decomposed in two stages in comparison to pure poly(acrylamide) which decomposed in three stages. The first stage of thermal decomposition occurred in the range 180–210 °C for pure poly(acrylamide), 120–257 °C for the low molecular weight based SIPN and 250–380 °C for the high molecular weight based SIPN and was attributed to the decomposition of poly(acrylamide) by ammonia loss to form imide group via cyclization reactions. The second stage of thermal decomposition occurred in the range 250–450 °C for the low molecular weight based SIPN and 390–490 °C for the high molecular weight based SIPN and may describe the decrosslinking of the network structure. The second stage of thermal decomposition of pure poly(acrylamide) ranged between 284 and 314 °C and was due to loss of bonded water and ammonia, whilst the third occurred in the range 381–425 °C when the degradation of the cyclized products was observed.

An earlier study by Mathew et al. reports the obtaining and thermal stability studies of natural rubber and polystyrene SIPNs and IPNs with varying components ratios (30/70, 50/50, 70/30), initiators and crosslinking agents types and concentrations for both components [36]. The IPNs were obtained sequentially by first crosslinking the natural rubber with dicumyl peroxide followed by the polymerization and crosslinking with divinyl benzene of styrene. Authors investigated the effects of the different initiating system (1 % benzoyl peroxide, 1 % dicumyl peroxide or 0.5 % azo-bis-isobutyronitrile), composition and crosslinking density on the thermal stability of the obtained IPNs and SIPNs. The uncrosslinked polystyrene and vulcanized natural rubber presented similar thermal stability up to 280 °C in nitrogen atmosphere and decomposing until 400 °C. Both homopolymers thermally decomposed in one single stage. Natural rubber decomposed by yielding a mixture of isoprene, dipentene and p-menthene, whilst polystyrene decomposed by yielding a mixture of styrene, toluene and methyl styrene. The IPNs and SIPNs exhibited superior thermal stability compared to the homopolymers. All network structures started decomposing after 300 °C and exhibited approximately 90 % mass loss around 450 °C. It was observed that the increase of natural rubber concentration led to a decrease in thermal decomposition temperatures. The IPNs showed higher thermal stability than the SIPNs, presenting a 30–50 % mass loss at 400 °C compared to a mass loss of 60–80 % at the same temperature, due to the higher crosslinking density reducing the bond cleavage in the IPNs. Up to a 4 % of polystyrene crosslinking agent content proved to contribute to the enhancement of all the networks thermal stability. The change in the initiating system had no influence on the thermal stability of the samples.

Boonpoo-nga et al. obtained SIPNs based on poly(4-styrenesulfonic acid) and crosslinked poly(acrylic acid) for proton-conducting membranes in fuel cell applications [37] and studied the influence of the crosslinking degree on the membranes water and thermal stability and hydrophilicity properties. The membranes were obtained by mixing the comprising components solutions in different ratio and crosslinked afterwards by maintaining those 2 h at 120 °C. All structures were thermally stable up to 200 °C in nitrogen atmosphere and afterwards decomposing in three stages. The first mass loss occurred below 200 °C and was

attributed to absorbed water removal. The second mass loss occurred in the temperature range 200–340 °C and was due to the thermal decomposition of polymeric side chains. The last thermal decomposition stage occurred in the temperature range 340–480 °C and was attributed to main chains degradation. Authors observed a slight increase in the thermal decomposition rate with lower crosslinking degree values. By comparison to the membranes with the same crosslinking degree, the membrane with higher content of poly(4-styrenesulfonic acid) exhibited a larger weight loss in the first thermal decomposition stage. This aspect was explained by the strong hygroscopic character of poly(4-styrenesulfonic acid).

Huang et al. synthesized a class of thermosetting poly(2,6-dimethyl-1,4-phenylene oxide)s containing pendant epoxide groups [38]. The procedure was conducted by bromination reaction of poly(2,6-dimethyl-1,4-phenylene oxide) in halogenated aromatic hydrocarbons to yield polymers with different bromination values (50, 35 and 26 %). The obtained compounds were afterwards submitted to a Witting reaction to obtain vinyl-substituted polymer derivatives. The obtained vinyl-substituted polymers, with vinyl ratios of 38, 31 and 23 %, were treated with *m*-chlorobenzoic acid to yield epoxidized poly(2,6-dimethyl-1,4-phenylene oxide) with different pendant epoxide molar ratios (35, 28 and 20 %). The thermal stability of the brominated polymers in nitrogen atmosphere decreased slightly with the increase of bromo substituent quantity and the char yield increased up to 45 % at the end of the measurements (800 °C). The structures thermally decomposed in two stages. The first stage, in the range 250–340 °C with a mass losses of 2–20 %, was attributed to side chain decomposition due to weaker C–Br bond dissociation energy compared to that of C–H benzylic bond. The second stage of thermal decomposition occurred in the range 420–500 °C and was attributed to backbone scission [39]. A similar thermal decomposition trend was followed by the vinyl-substituted polymers. The increase of the degree of functionalization led to a slight decrease in thermal stability, due to the greater disorder in the structural conformation introduced by the vinyl group. The char yield increased in the range 33–50 %. The epoxidized compounds exhibited an intense exothermic peak in the range 257–267 °C attributed to the curing reaction of the epoxy groups during heating. The curing process led to a significant increase in the thermal stability of the cured compounds in comparison to the epoxy analogues. The thermal decomposition temperature corresponding to 5 % mass loss shifted from within the range 250–256 to 340–355 °C, with tolerable increase in char yield.

3 Effect of Reinforcement and Nanofillers on the Thermal Stability of Thermosetting Blends

Reinforced thermosets are used in a wide variety of applications, some of which involve the exposure to high temperatures. In these cases thermal stability of such thermosetting materials is investigated by thermogravimetric analysis. The char

yield of these materials is correlated to their flame retardancy; the increased char yield can limit the production of combustible gases and inhibit the thermal conductivity of the material [40].

In the last years, natural fibres were investigated as reinforcement materials in polymer composites instead of synthetic fibres, due to their properties such as low cost, high specific strength, low weight, good thermal and acoustic insulation properties or lack of toxicity for human health. Alamri et al. investigated the effect of reinforcement with recycled cellulose fibres and nanoclay platelets (Cloisite 30B) on the thermal behavior of epoxy systems [41]. The presence of cellulose fibres and nanoclay slightly increased the rate of nanocomposites thermal degradation at low temperatures. However, at higher temperatures the char yield of the nanocomposites was significantly higher than that of the pure epoxy and epoxy reinforced only with cellulose fibres. This means that nanoclay acted as a barrier and hindered the diffusion of volatile decomposition products from the nanocomposites.

Shih studied the thermal behavior of an epoxy resin reinforced with water bamboo husks fibres and powders [42]. The char yield increased from 8.9 % for the epoxy resin to 10.1–13.6 % for the composites containing 10 % bamboo fibres or powder. The results showed that the addition of bamboo powder or fibres to epoxy systems would raise the char yield of the sample, therefore could improve the flame retardancy of these materials. Similar results were obtained in the case of *Phormium tenax* fibres reinforced epoxy composites, containing 20 % fibres. The presence of plant fibres determined an increase of the composites thermal stability, due to the improved fibre-matrix interactions [43].

Kenaf fibres were used as reinforcing materials for an epoxy resin [44]. The maximum degradation temperature was shifted to higher values in the case of composites. The remaining residue at 500 °C, after thermal degradation, was the lowest in the case of neat epoxy and increased for the composites containing modified fibres with NaOH and for the composites with unmodified fibres. The composites containing modified fibres had a lower char yield than those containing unmodified fibres due to the removal of lignin by alkalization treatment, lignin being responsible for the char production in natural fibres. It was concluded that the thermal stability of kenaf fibres/epoxy composites depends on the composition of the fibres.

The thermal stability of composites containing natural fibres may also depend on the nature of the matrix. In the case of composites containing unsaturated polyester or unsaturated polyester modified with acrylic acid reinforced with jute fibres it was shown that the composites with modified polyester matrix were more resistant to temperature than the ones with unmodified polyester matrix. The reason for this enhanced thermal stability was the presence of acrylic acid as modifier [45].

Cellulose nanocrystals were used as reinforcing filler for waterborne epoxy resin matrix [46]. In the case of nanocomposites, the onset temperature of thermal degradation decreased compared to neat epoxy. The same trend was obtained for the temperature of maximum weight loss for the first degradation step, while the temperature corresponding to the second step of degradation was slightly increased with increasing the cellulose nanocrystals content in the nanocomposites. The

results of this study revealed that the addition of cellulose nanocrystals to the epoxy matrix improved the mechanical properties without compromising the neat matrix properties.

The thermal behavior of the composites based on raw and surface modified *Grewia optiva* particle fibres reinforced unsaturated polyester matrix was studied [47]. The fibres were modified by mercerization, silanation, benzoylation and graft copolymerization. The thermal stability of the composites containing modified fibres was improved compared to the unsaturated polyester matrix and to the composites containing untreated fibres. This was a consequence of the additional intermolecular bonding between fibres and matrix induced by the surface modification. The highest thermal stability was obtained by the composites based on silanated fibres due to the formation of strong covalent bonds between silanes and cellulose.

Due to properties such as high tensile strength, high modulus and high chemical resistance, glass fibres are also used as reinforcement materials for thermosetting matrices. Epoxy resin modified with poly(styrene-co-acrylonitrile) was reinforced with glass fibres [48]. The thermal stability of these composites was improved, their decomposition starting at higher temperature than that of the neat epoxy. Also the temperature at maximum weight loss was increased in the case of composites. Moreover the char residue was around 60 % for composites, while for the neat epoxy was only 6.6 %. This behavior was a consequence of the presence of thermally stable glass fibres. Glass and aramid (aromatic polyamides) fibres were used as reinforcement for epoxy foams [49]. All composites exhibited improved thermal stability compared to the neat epoxy. However, samples reinforced with glass fibres exhibited higher thermal stability than those reinforced with aramid fibres. The ash content was of 95 % for the samples reinforced with glass fibres, while the ash content of the samples containing aramid fibres was 45 %. This proved that the addition of glass fibre produced epoxy foams with improved thermal stability.

In the last years the thermal behavior of carbon fibre reinforced epoxy resins has been investigated by different research groups [50]. Régnier et al. performed a kinetic study on the thermal degradation of carbon fibre/epoxy composites, both in air and in inert atmosphere. The thermal degradation of the composites occurred in three stages [51]. The presence of vapour-grown carbon nanofibres into the epoxy resin matrix did not influence the thermal stability of the resin. The decomposition temperatures in the case of composites were almost the same with the decomposition temperature of epoxy resin [52].

Huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$) was used as reinforcement for an unsaturated polyester resin [53]. A content of 3 % huntite had a reinforcing effect for the resin, which caused an improvement of the mechanical and thermal properties. Regarding the thermal behavior, the onset temperature of composites thermal degradation was increased with approximately 50 °C, while the maximum degradation temperature was improved with 16 °C, compared to the polyester matrix.

The properties of a composite material can be changed with the particle size or distribution, dispersion state and geometric shape. The incorporation of nanometer sized fillers has become an important strategy for the enhancement of polymers

physical and mechanical properties. The obtained nanocomposites have properties different than the pure polymers due to the small size of the filler and increased surface area [54, 55]. The literature data showed that the performances of different nanocomposites are difficult to compare because the same filler can produce different effects, depending on the matrix, or in the same matrix can induce different effects, depending on the processing conditions [56]. For example, different results were reported regarding the effect of nanoclay incorporation on the thermal properties of thermosetting matrices.

The incorporation of montmorillonite (MMT) nanoparticles in different epoxy resins caused an enhancement of the nanocomposites thermal stability, which was more significant in the first stage of degradation. In this case, the MMT nanolayers acted as a barrier and prevented the volatilization of the epoxy polymer matrix. Moreover, the segmental motion of the polymer network was restricted in the presence of clay layers, which was reflected in an increased thermal stability, compared to the systems without MMT [57]. Similar results were obtained when commercial Cloisite 25A organoclay was used [58]. Both degradation steps were shifted to higher temperatures in the samples filled with nano-organoclay, compared to neat epoxy resin. Also, the activation energy for the first step of degradation was higher for the nanocomposite system because of the inorganic clay thermal resistance, which increased the energy demand for thermal degradation of the resin.

The thermal properties of the nanocomposites of diglycidyl ether of bisphenol A epoxy resin containing different montmorillonite nanoclays depends on the surface modifications of the nanoclays. Moreover, the addition of nanoclays improved the thermal properties of the nanocomposites, compared to the neat epoxy [59].

Brnardic et al. studied the thermal stability of nanocomposites based on organically modified MMT and an epoxy resin [60]. Compared to the neat resin, small changes in the thermal stability were observed in the case of nanocomposites. The interlayer organic ions in organically modified MMT were more prone to degradation than the neat epoxy resin, causing a slight decrease in the onset temperatures of nanocomposites thermal degradation. The nanocomposites containing 5 % nanoclay had a thermal stability equal to that of the epoxy resin in the absence of nanoclay. An increase of the nanoclay content, up to 10 % determined a slight decrease in the thermal stability of the nanocomposites [61].

Phenolic resin/montmorillonite nanocomposites were prepared by intercalative polymerization of phenol and formaldehyde in the presence of organo-modified montmorillonites [62]. The nanocomposites thermal stabilities were higher than that of the neat phenolic resin. The highest thermal stability was observed for the nanocomposites containing MMT treated with quaternary ammonium salts containing benzene ring. This effect was attributed to the enhanced chemical affinity between the resin and the modifiers containing benzene groups. The favorable interactions promote the exfoliation and homogenous distribution of the MMT into the phenolic resin matrix.

Polyfurfuryl alcohol (PFA) nanocomposites were obtained by in situ polymerization of furfuryl alcohol in the presence of MMT (natural and organomodified) or cellulose nanowhiskers [63]. Below 400 °C, the temperatures at the onset of

degradation were increased for the nanocomposites, compared to pure PFA. The highest increase was obtained for nanocomposites containing cellulose whiskers, due to a stronger matrix-nanoparticle interaction as compared to the nanocomposites containing MMT. Above 400 °C the nanocomposites containing organo modified MMT exhibited superior weight retention, compared to the nanocomposites containing cellulose nanowhiskers or to pure PFA. This increase was attributed to the complete exfoliation of the clay in the nanocomposites.

In the case of Novolac phenolic resin, the incorporation of highly dispersed organoclays containing cationic pillaring agents, did not improved the thermal stability of the resin [64]. Upon reaching the resins decomposition temperatures, the clay surfaces may provide some catalytic activity which promotes decomposition. The thermal stabilities of the nanocomposites, expressed by their 5 and 10 % weight loss temperatures, were established for the initially cured samples (80 °C/2 h) and for the samples which were additionally cured at 100 °C for 0.5 h. These temperatures were higher for the samples cured than for the nanocomposites partially cured. Moreover, the char yield at 900 °C was higher for the totally cured nanocomposites.

The effects of Cloisite loading on the thermal decomposition behavior of an epoxy resin were reported by Ingram et al. [65]. It was shown that the addition of Cloisite in the systems improved the thermal stability of the epoxy resins which underwent an initial cure at 180 °C. However, when the nanocomposites were post cured at 220 °C, the nanoclay incorporation induced a decrease in the thermal stability of the systems. This behavior may be attributed to the dissociated alkyl chains, which destabilize the thermal properties after being subjected to high temperatures [66]. Therefore, a careful selection of cure and post cure temperatures must be made in order to obtain nanocomposites with improved physical properties and with enhanced thermal stability.

The thermal stability of some thermosetting nanocomposites obtained by thermal cationic cure of diglycidylether of bisphenol A and γ -valerolactone using rare earth metal triflates (trifluoromethanesulfonate) as initiators and containing different types of Cloisite was studied. The addition of clay into the polymeric matrix was found to increase the thermal stability, acting as a superior insulator and mass transport barrier to the volatile products evolved during thermal decomposition [67].

In the case of phenolic resin/organic expanded vermiculite nanocomposites (a mica-type silicate) the thermal behavior was investigated in both air and nitrogen atmosphere [68]. The onset temperature of thermal degradation, as well as the temperature of 15 % weight loss showed a significant increase in the presence of vermiculite. Also, the mass loss rate of the resin was higher than that of the nanocomposites. These results were obtained for the experiments carried out in both atmospheres. The addition of 1.5 % vermiculite in the nanocomposites determined an increase in the temperature of 15 % weight loss from 476 to 511 °C, in nitrogen atmosphere and from 422 to 467 °C in oxidative conditions. The improvement of thermal stability in the case of nanocomposites was attributed to a uniform dispersion of the exfoliated platelets of vermiculite into the polymer matrix.

These platelets acted as superior insulator and as barrier for oxygen transport and volatilization of the products resulted after the thermal degradation.

The incorporation of 5 % organically modified sepiolite, which is a micro-crystalline-hydrated magnesium silicate, in a bisphenol A-based epoxy resin has no significant effect over the thermal stability of the epoxy resin, due to the poor dispersion of the clay and poor diffusion of the resin between fibres [69]. The effect of attapulgite (magnesium aluminium phyllosilicate) over the thermal properties of hyperbranched polyimides was studied. The presence of this silicate in the nanocomposites significantly improved the thermal stability of the neat polyimide [70].

Ollier et al. reported the effects of modified and unmodified bentonite loading on the decomposition behavior of unsaturated polyester thermosets [71]. It was shown that the addition of bentonite increased the thermal stability of the resin. Furthermore, the clay modification did not significantly influence the degradation temperatures of the nanocomposites.

The incorporation of other type of nanoparticles, such as CuO, TiO₂, silsequioxanes was found to affect the thermal degradation of the thermosetting materials. The thermal stability of the epoxy resin/cupric oxide (CuO) nanocomposites in air atmosphere was improved by the presence of CuO nanoparticles. Furthermore, the presence of these nanoparticles affected the degradation mechanism of the epoxy resin [72].

Cupric oxide unmodified and functionalized with methacryloxypropyl trimethoxysilane was used to obtain vinyl-ester resin polymeric nanocomposites [73]. The resistance to thermal degradation was improved for the nanocomposites with and without postcuring, compared to the pure cured resin. The thermal stability of the nanocomposites containing functionalized CuO was higher than that of the nanocomposites containing the unmodified CuO nanoparticles. The presence of the coupling agent prevented the intimate contact between CuO and vinyl-ester resin, passivating the particle surface, and thus increasing the thermal stability of the nanocomposites with functionalized CuO nanoparticles. Similar results were obtained in the case of vinyl-ester resin nanocomposites with iron oxide nanoparticles (un-modified and functionalized with the same coupling agent) [74, 75].

In the case of Ni–La–Fe–O/epoxy nanocomposites, the thermal degradation showed a more complicated behavior than the neat epoxy resin, with two peaks in the 300–475 °C temperature range. Moreover, the thermal stability of the resin decreased in the presence of Ni–La–Fe–O nanoparticles, due to the fact that these nanoparticles may act as catalysts to degrade the epoxy matrix [76].

The thermal stability of epoxy resin/TiO₂ nanocomposites was found to be dependent on the nanoparticles loading, as well as on their dispersion state [77]. At a very low TiO₂ loading into the matrix, the nanoparticles were dispersed uniformly and formed a barrier to heat and oxygen, due to their ceramic nature. When the content of the nanoparticles was increased, they tended to agglomerate into lumps, which were non-uniformly distributed into the matrix. In this case the nanoparticles were less effective in blocking the heat and oxygen, but still more effective than the neat epoxy resin.

The incorporation of the hybrid TiO_2 – SiO_2 nanofillers into an epoxy resin increased the thermal stability of the neat resin [78]. Also the char yield increased from 0 % for the neat resin to 25 % for the nanocomposites. These phenomena are a consequence of the hybrid nanoparticles which acted as thermal stabilizers for the epoxy resin.

When SiO_2 was incorporated into poly(furfuryl alcohol) thermosetting matrix, the thermal stability of the furanic matrix was enhanced [79]. The thermal decomposition temperature corresponding to 10 % weight loss increased with 30 °C in the presence of SiO_2 . Also in the early stage of degradation the rate of thermal degradation decreases significantly. These results were a consequence of the interconnections which appeared between the furanic end groups and silica, reducing the possibility of unzipping the furanic chain. This meant that the chain scission predominated and high molecular weight compounds with low volatility were formed. Above 400 °C the rate of degradation was the same for the systems with or without silica, suggesting that the silica network had no influence on the latter stages of poly(furfuryl alcohol) thermal degradation.

Silsesquioxanes are Si–O–Si networks with organic substituents attached to each Si atom, which can improve the compatibility with the polymer matrix. The materials containing silsesquioxanes have improved thermal stability because char formation is promoted and the diffusion of gases into the material is retarded [80]. Nagendiran et al. studied the thermal degradation behavior of epoxy/polyhedral oligomeric silsesquioxane (POSS) nanocomposites [81]. The thermal stability of the nanocomposites containing octa-aminophenyl silsesquioxane (OAPS) was improved compared to the pure epoxy resin, with a retarded mass loss rate and an enhanced char yield. The increased OAPS concentration and the nanoscale dispersions of POSS into the epoxy matrices contributed to the enhanced thermal stability. The high char yield implied that fewer volatiles were released during nanocomposites thermal degradation, suggesting that the flame retardancy of the materials was increased.

Epoxy acrylate/vinyl POSS nanocomposites were obtained by in situ polymerization and UV-curing method [82]. The thermal degradation mechanism of epoxy acrylate was not modified by the presence of vinyl-POSS and the thermal stability of the nanocomposites was improved with the increasing of POSS loading. The temperatures corresponding to 50 % mass loss increased in the case of nanocomposites, compared to the neat epoxy acrylate. Also the char yield was increased because of SiO_2 yield which was produced by POSS thermal degradation.

Schutz et al. studied the thermal properties of a phenolic resin nanocomposite containing silsesquioxanes [80]. The thermal oxidative stability of the nanocomposites was improved, as compared to that of the pure resin. This effect may be a consequence of the formation of a protective layer of SiO_2 during silsesquioxanes pyrolysis at the surface of nanocomposites, which retarded the thermal oxidative degradation. The temperatures characteristic to thermal degradation processes were higher in the case of nanocomposites, compared to the pure resin matrix.

In the case of a resole phenolic resin, the presence of trisilanophenyl POSS markedly increased the thermal stability of the phenolic nanocomposites. The

temperatures corresponding to 5 and 50 % mass loss increased with 34 and 90 °C, respectively, for the maximum amount of POSS used (10.4 %) [83].

Aflori et al. synthesized POSS-based hybrid nanocomposites with methacrylate units containing titania and/or silver nanoparticles (POSS-AgTi and POSS-Ag) and tested these materials as antibacterial/antifungal coatings for monumental stones [84]. The thermal decomposition of the nanocomposites presented different stages (93–260, 260–285, 384–456, 456–550 °C for POSS-Ag; 78–156, 156–230, 300–435 °C for POSS-AgTi) and residues of 51.22 % for POSS-Ag and 27.7 % for POSS-AgTi, respectively, at 600 °C in nitrogen atmosphere. The first decomposition stage of POSS-Ag corresponded to residual isopropyl loss and dehydration, with a secondary condensation process between Si–OH groups in the range 85–175 °C, loss of AgO and decomposition of dodecylamine surfactant (around 220 °C). A similar thermal behavior was observed for POSS-AgTi up to 230 °C, the degradation processes occurring during the succession of two decomposition stages and with similar mass loss (6 %). POSS-AgTi exhibited a lower initial temperature corresponding to solvent loss compared to POSS-Ag, probably due to the rigid network structure which did not trap the solvent molecules inside the polymer chains. The second thermal decomposition stage (260–285 °C) of POSS-Ag occurred with a small mass loss (3.35 %) due to chain-end initiation phenomena from end double bonds around 277 °C. For POSS-AgTi, the presence of titania delayed the degradation of the end double bonds, up to 300 °C. Within the temperature range 300–550 °C, the mass loss corresponding to random polymeric chain scission was lower for POSS-AgTi (21.64 %), compared to POSS-Ag (45.68 %). The improvement of the thermal stability of POSS-AgTi was correlated with the fact that this hybrid nanocomposite with silsesquioxane and titania content might act as a cage, trapping free radicals generated during thermal degradation. Furthermore, the influence of titania-catalyzed oxidative decomposition of the polymer matrix was negligible, thus it was concluded that titania nanoparticles were wrapped within the silica components. This observation led to the state that the silsesquioxane-based coating protected the polymer scaffold from catalytic degradation.

The thermal behavior of nanocomposites films based on poly(triazole-imide) reinforced with neat and modified SiC nanoparticles was investigated [85]. The nanocomposites decomposition temperatures increased with SiC content, indicating an enhancement of the thermal stability in the presence of SiC. Moreover, the char yield increased from 58 % for the poly(triazole-imide) to 85 % for the nanocomposites containing 10 % SiC. The nanocomposites containing SiC nanoparticles functionalized with epoxide-end groups showed a lower thermal stability compared to the nanocomposites containing neat SiC.

Carbon nanotubes (CNTs) can be used as nano-modifiers in the thermosetting matrices due to their attractive mechanical, thermal and electrical properties. Nevertheless, the incorporation of CNTs into these matrices has not had remarkable effect on the polymers thermal properties, with some exceptions [86]. The effect of CNTs over the thermal stability of thermosetting polymers depends on some factors such as CNTs type and content, aspect ratio and dispersion, the interactions

between CNTs and the polymer matrix. The addition of multi-walled carbon nanotubes (MWCNTs) leads to a decrease of the thermal stability of epoxy matrices [87, 88]. This effect is caused by the increase of the polymer thermal conductivity as a consequence of MWCNTs addition. It was also reported that the nanotubes length and modification with amino groups has no significant influence on the thermal stability of MWCNTs/epoxy nanocomposites. The activation energies of the thermal degradation reactions were calculated using the method proposed by Flynn-Wall-Ozawa. For all studied nanocomposites, the activation energy had lower values, for all conversion degrees, compared to the neat epoxy. This proved that the addition of MWCNTs to the epoxy matrix increased the materials degradation efficiency. MWCNTs have high thermal conductivity properties, facilitating heat transportation in nanocomposites and implicitly decreasing the activation energy [89]. Similar results were reported in the case of single-walled CNTs [90].

Nanocomposites containing functionalized CNTs exhibited increased thermal stability, compared to the neat epoxy resin. In this case the functionalized CNTs had a better affinity for the polymeric matrix than the un-functionalized CNTs [91]. Kuan et al. reported that the incorporation of the MWCNTs functionalized with vinyltriethoxysilane into an epoxy resin increased its thermal stability [92]. The same effects were obtained in the case of MWCNTs grafted with triethylenetetramine [91] and MWCNTs functionalized with silane [88].

The thermal stability of nanocomposites containing cyanate ester/MWCNTs was found to be dependent on the surface modification of CNTs [93]. The results showed that the presence of unmodified MWCNTs in the nanocomposites produced a decrease of the initial decomposition temperature and a char yield similar to the neat resin. On the contrary, the initial decomposition temperature increased with 20 °C in the presence of modified MWCNTs. Moreover, the char yield of the nanocomposites containing modified MWCNTs was much higher than that of the cyanate ester resin. These results proved that the nature of carbon nanofiller is important for developing new nanocomposites with enhanced thermal properties.

The nanocomposites obtained from phenolic resin and carboxylated MWNTs showed an improvement of the thermal stability than the neat phenolic resin. The highest thermal stability was obtained in the case of the nanocomposites obtained by in situ polymerization, due to the quality of dispersion of the functionalized MWCNTs [94]. An enhancement of the thermal stability was also obtained in the case of nanocomposites containing boron phenolic resin and MWCNTs modified with nitric acid, 4,4'-diaminodiphenyl methane and boric acid. This effect was ascribed to better interfacial interactions between modified MWCNTs and the resin matrix [95].

The effect of carbon nanofibres on the thermal behavior of phenolic resins was studied by Bafekrpour et al. [96]. The presence of carbon nanofibres produced an increase in the thermal stability of the nanocomposites, compared to the neat phenolic resin. Thus, the decomposition temperature was shifted to higher values with an increase of the nanofibres content. The same trend was obtained for the nanocomposites char yield.

Faraz et al. obtained new composites from carbon nanofibres (CNFs) and bismaleimide, using a thermokinetic mixing method [97]. The addition of CNFs slightly improved the thermal stability of the nanocomposites. The presence of CNFs caused the formation of more char residue, but this char was thermally unstable and it degraded faster compared to the char formed in the case of pure resin.

Graphene is a new type of nanofiller, with two-dimensional structure and with excellent mechanical, thermal and electrical properties [98]. The addition of two kinds of nanofillers: graphene and magnetic graphene (graphene nanosheets coated with iron core iron oxide shell nanocomposites, $\text{Fe}@\text{Fe}_2\text{O}_3$) to an epoxy resin matrix caused a decrease of the thermal decomposition temperatures. This effect was attributed to the spatial obstruction of the nanoparticles on the formation of highly cross-linked epoxy structure. The nanocomposites containing magnetic graphene showed a much lower weight loss compared to the pure epoxy and epoxy matrix containing graphene, due to protruding $\text{Fe}@\text{Fe}_2\text{O}_3$ nanoparticles on the surface of graphene, which favored the char formation during the thermal degradation process [99]. Wang et al. reported an improvement in the thermal stability of epoxy nanocomposites containing 0.1 % graphene oxide nanoparticles [100].

The presence of graphene oxide slightly changed the thermal stability of the polyurethane/graphene oxide/epoxy nanocomposites. In the case of these nanocomposites, a content of 0.033 % graphene oxide caused a slight increase of the degradation temperatures [101]. Isocyanate-treated graphene oxide and cyanate ester resin were used to prepare nanocomposites by a solution intercalated method. The composites presented a higher char residue than the cyanate ester resin, as a result of the interactions between graphene oxide and the resin matrix. Also the degradation temperatures slightly increased with increasing the graphene oxide content and the decomposition rates significantly decreased [102].

New materials can be developed by using interpenetrating polymer networks (IPN) as matrices for various nano-reinforcing agents. Polyhedral oligomeric silsesquioxanes (POSS) was used for the reinforcement of dimethacrylic/epoxy IPN. The addition of POSS to the neat resin caused a slightly decrease of the onset temperature of degradation and no change in the maximum weight loss rate. Moreover, the presence of POSS did not influence the thermal stability of the IPN [103].

The thermal decomposition of polyurethane/epoxy resin interpenetrating polymer network (IPN) nanocomposites containing organophilic montmorillonite was found to be a complex, two-stage process. The thermal stability of these nanocomposites was improved by the presence of nanoclay [104]. Potassium titanate whiskers were used as reinforcement of polyurethane/epoxy resin IPN [105]. The incorporation of the whiskers enhanced the thermal stability of the polyurethane/epoxy resin IPN. The temperatures for 20 and 80 % mass loss were increased compared to the IPN in the absence of potassium titanate whiskers. Moreover the residual weight at 600 °C increased from 11.13 % for the IPN to 19.27 % for the IPN containing 5 % potassium titanate whiskers. When carbon nanotubes were used as reinforcement for these polyurethane/epoxy resin IPNs, the thermal stability decreased slightly. This was caused by the CNTs high thermal conductivity [106].

4 Applications and Future Trends of Thermosetting Blends

There are several emerging domains incorporating a great deal of research from multidisciplinary fields and from which great expectations arise for the future. Such continuous evolving domains include the obtaining of new construction materials, drug delivery systems, biomaterials, fuel cells [107], cells for solar energy capture, renewable resources for biofuels, biodegradable polymer systems and smart materials which are covered in a series of recent reviews [108–110].

Paduraru et al. obtained cryogels based on crosslinked poly(vinyl alcohol) and increasing quantities of microcrystalline cellulose (10, 30, 50 %) and conducted *in vitro* tests for the release of vanillin (4-hydroxy-3-methoxybenzaldehyde), an antimicrobial and antioxidant agent, from poly(vinyl alcohol)/cellulose matrices [111]. The tests yielded good results due to the increased release percent of bioactive agent with cellulose content increase in the cryogels and also shortening of the half and maximum release time. Prior to the *in vitro* tests authors conducted thermal stability studies of the cryogel supports. Varganici et al. conducted thermal decomposition kinetics and evolved gas analysis of the cryogels in nitrogen atmosphere as background to industrial processing of the future bioactive formulations for wound dressings [112]. According to the two latter literature reports, pure microcrystalline cellulose exhibited one thermal decomposition stage in the range 30–124 °C with a 2.1 % mass loss, corresponding to physical dehydration. This was followed by a main and major decomposition stage with a maximum temperature at 345 °C, characterized by the highest mass loss (86.09 %), due to the unzipping of cellulose chains and levoglucosan formation with char and volatile products yield. Pure poly(vinyl alcohol) thermally decomposed in four stages, generating water loss, partial dehydration of poly(vinyl alcohol) together with polyene formation, decomposition of the polyenes formed in the second stage together with destruction of macroradicals followed by advanced degradation of the polymeric backbone and scission reactions in the last stage. The highest mass loss occurred in the range 306–419 °C for poly(vinyl alcohol). These temperature values shifted to lower domains for the cryogels and remained situated between those of the pure components. The second thermal decomposition stage (217–306 °C) characteristic to poly(vinyl alcohol) disappeared due to the cellulose influence over the cryogels. An increase of the residual mass with cellulose content increase was also observed, from 3.4 % for the poly(vinyl alcohol) to 11.18 %. The evolved gas analysis indicated that the major volatile thermal decomposition products were water, carbon dioxide and carbonyl and olefin structures.

Other excellent wound healing accelerators consists in various materials based on modified chitosan. The modification of chitosan is necessary, due to its poor solubility in common organic solvents and water, thus inhibiting its utilization. Various modification methods, such as chemical grafting, physical blending or crosslinking have been reported in the literature [113–116]. Rodkate et al. obtained SIPN hydrogels based on polydimethylsiloxane (PDMS)/polyethylene glycol (PEG) modified chitosan by interpenetrating 20 wt% of PDMS and PEG into the

chitosan hydrogels crosslinked with 10 wt% hexamethylene-1,6-di-(aminocarboxylsulfonate) (HDA) [117]. Thermogravimetry in inert atmosphere was used to investigate the effect of PDMS and PEG on the thermal stability of the hydrogels. For PDMS-chitosan SIPNs the mass loss became retarded in comparison to HDA crosslinked chitosan without PDMS, indicating an enhanced thermal stability after addition of PDMS. A slight enhancement of thermal stability was also observed in PEG-chitosan SIPNs. In both cases, the PDMS/PEG-chitosan SIPNs decomposed in two stages, ranging between 230–300 and 380–410 °C, as opposed to HDA-crosslinked chitosan (without PDMS or PEG) which thermally decomposed in a single step.

Another example of biocompatible polymer hydrogels for controlled drug release, tissue engineering, artificial muscles, biosensors, etc. consists of dextran based materials. Dinu et al. obtained hydrogels based on polyacrylamide and dextran, tuned by the synthesis temperature, via free radical crosslinking copolymerization in aqueous solution at three temperatures (–18, 5 and 22 °C) [118]. Dextran decreased the hydrogels thermal stability compared to the corresponding polyacrilamide gels, indicating that the dextran chains interdiffuse and are physically entangled in the crosslinked polyacrilamide. The hydrogels thermal stability did not depend on preparation temperature. Dextran thermally decomposed in two stages, whilst the hydrogels and polyacrilamide gels in three stages, irrespective of the preparation temperature. The first mass loss was attributed to evolvment of water and other volatiles. The dextran chain degradation also explained the lower second stage onset temperatures of the hydrogels and polyacrilamide gels. The hydrogels underwent a higher mass loss in the third stage compared to the cross-linked polyacrilamide matrix which decomposes mainly at higher temperatures. The presence of dextran in the gels led to an increase in char quantity.

Another expanding research field consists in the obtaining of polymers from renewable resources for reducing global warming by replacing of petroleum-based resins. For this purpose, vegetable oils represent very promising raw materials. A favorite candidate is soybean oil because it may be ‘genetically engineered’ for such applications. ‘Functionalization’ of vegetable oils is necessary because double bonds from fatty acids in triglycerides are not very reactive in free radical cross-linking compared to those situated in terminal positions.

Grishchuk and Karger-Kocsis obtained a series of hybrid thermosets from vinyl ester resin and acrylated epoxidized soybean oil by free radical-induced cross-linking, with ratios varying from 75/25 to 25/75 % and the 50/50 % hybrid was modified with different amounts of phthalic anhydride (1, 5 and 10 %) [119]. The thermal stability of the hybrid materials in nitrogen atmosphere increased in comparison to the individual comprising polymers. This aspect was explained by the synergistic effects within the IPN structures, slowing decomposition and volatilization and diffusion of the degradation products. The incorporation of phthalic anhydride was expected to yield even better results, due to a higher molecular confinement induced by the grafts. However, the incorporation of phthalic anhydride led to a decrease in thermal stability. An explanation may be correlated with a

surplus of uncoupled phthalic anhydride in the synthesis or phthalic anhydride acting as initiating site during thermal degradation.

Wang and Schuman [120] synthesized glycidyl esters of epoxidized fatty acids derived from soybean (EGS) and linseed oil to gain higher oxirane content for the purpose of enhancing reactivity and lowering the viscosity compared to epoxidized soybean (ESO) or linseed oil. The EGS and ESO were characterized individually and in blends of different ratios with diglycidyl ether of bisphenol A (DGEBA) and obtaining of thermosetting resins with epoxy monomers and 1,2-cyclohexanedicarboxylic anhydride or BF_3 as catalyst. ESO-DGEBA and the EGS-DGEBA blends presented similar thermal stability profiles. Thermogravimetric analysis results in inert atmosphere showed that all cured resins were stable up to 300 °C. EGS-DGEBA blends led to a slight lowering in thermal stability, compared to ESO-DGEBA blends. All structures thermally decomposed in two stages. The first stage occurred in the range 300–450 °C and was attributed to unreacted 1,2-cyclohexanedicarboxylic anhydride decomposition, hydroxyl groups dehydration and crosslinked epoxy resin network degradation. The second stage ranged between 450 and 600 °C and was correlated to the complete degradation of smaller fragments such as aromatic or cyclized decomposition byproducts as shown by a decrease in char residue with EGS component increase.

Mustata et al. investigated the influences of different amounts of ESO on the curing kinetics and thermal properties of DGEBA cured with p-aminobenzoic acid (p-ABA) by dynamic thermogravimetry in inert atmosphere, amongst other methods [121]. All resins, except crosslinked ESO, exhibited similar thermal behavior and decomposed in a single stage, unaffected by the ESO content, due to the networks structural similarity. All structures started decomposing at approximately 370 °C, with a major mass loss (around 50 %) in the range 370–440 °C. Sample ESO/p-ABA decomposed at a lower temperature in comparison to DGEBA/p-ABA, due to the presence of aromatic ring in the DGEBA molecular structure, which cannot be easily broken. Activation energy values of thermal decomposition decreased with ESO content increase for the DGEBA/p-ABA/ESO samples, due to their chemical structures containing several ester groups, introduced by ESO, which decompose more facile.

The majority of thermal applications of different thermoset blends related to the construction domains consist of thermosetting adhesives. Such adhesives may also be used for circuit boards manufacturing. This may be achieved by the dispersion of a powder of cured heat resistant resin soluble in an acid into a matrix of heat resistant resin which is uncured and hardly soluble in the same acid. One of the phases is cured whilst the other is not, this way forming an adhesive layer. For example, the obtaining of marine adhesives implies the using of polyaromatics which contain reactive end groups and a thermoset resin. This is done by using a reactive catalyst which contains a Lewis acid bearing amine functionality. After the curing process, the amine reacts with the polymer generating an adhesive which is curable at high temperatures and with environmental resistance and excellent mechanical properties. Cocontinuous structures may also be used in combination

with curable thermosets. Such structures give great heat resistance and toughness to circuit boards, good adhesion to copper wiring and little thermal deformation. They also make fine patterns formation possible [122].

5 Conclusions

Most developments in the field of polymer blends have aimed at improving materials final properties. Amongst other plastics, thermosetting polymer blends continue playing a significant role in the development and application of polymer based materials because of their advantageous overall cost-performance relation and their capacity to improve the performance of single resins. Although in the majority of cases thermosetting polymer blends provided great combination of properties to single resins, blending techniques require a rich interdisciplinary knowledge, including surface and phase phenomena characteristics, thermodynamic principles of miscibility, morphology, processing, and performance. It is a known fact that the vast majority of commercial blends are not in a thermodynamic equilibrium state, thus occurring the possibility of generating phase separation phenomena. The selection of adequate processing method determines the product performance. With the continuous improvement of fundamental knowledge and research grows the demand for materials with enhanced performances, making the role of blending more and more important. Processability is also improved by blending. Blending may lead to a reduction in viscosity which is of crucial importance to processing. Since the final properties of the blends are dictated by the properties, composition and morphology of the individual components, processing must be very carefully examined.

Different special applications of thermosetting blends require different processing techniques of such materials, thus their thermal stability, along with other properties, is very important in proving the miscibility of the phases and settling the threshold temperatures for the processing of the future materials. It is for such purposes that fundamental knowledge must be gained on the different thermal decomposition mechanisms and their influence on the miscibility and morphology of the comprising polymers.

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