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A REVIEW ON MODIFIED POLYMERS AND THEIR COMPOSITES

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ABSTRACT

The main objective of this paper is to realise a review on fundamental research regarding the development of new and efficient methods to determine the mechanical, thermal, tribological, and thermo-mechanical properties of composite materials, analysing the results obtained through various graphs and diagrams accompanied by demonstrations and explanations from the specialized literature. Developing new materials or improving the properties of existing materials has been and is a concern of researchers. The chemistry of complex combinations represents one of the most important fields of scientific research, both in terms of theoretical investigations and practical applications. The interest shown towards complex combinations is justified by the contribution brought by the accumulation of knowledge about inorganic chemicals, polymers as well as about epoxy resins and polyvinyl ester, of course also about the design, formation and analysis through mechanical tests (compression, tension, three-point bending), thermal, tribological of composite materials modified with various modifying agents.

KEYWORDS: modified polymers, composites, complex combinations, epoxy resins

1. Introduction

Many current industrial fields are in continuous development, both in terms of products and the materials used to make them. This fact has recently led to the replacement of classic (heavy) materials with modern materials, often plastics or composites [1-6]. Due to some of their higher characteristics, the applications of composite materials are numerous in fields such as: electronics, chemistry, medicine, optics, construction, sports, cars, agricultural machines, automobiles, electrotechnics, etc. Composite materials have some physical and chemical characteristics clearly superior to conventional materials (metals, wood, plastic, concrete), but they also have weak points. Despite the fact that there are factors that could stop the wide use of composite materials such as: high costs, elaborated research, lack of testing standards, the advantages of using these materials, in the long term, will establish, worldwide, a considerable increase in applications created from composite materials. Composite materials became the first to allow researchers to modify their internal structure, both by combining them at the molecular level and in preferential directions with the aim of obtaining clearly superior properties to the original materials [7-9]. Thus, the diversity of composite materials, their properties and behaviours are limited only by the imagination of human nature, giving a multitude of possibilities, of associations, of course, taking into account the performances and costs defined as research objectives [10-12]. Starting with the second half of the 19th century, the chemical modification of natural materials had generated a really boom of the diversity of polymers produced in the laboratory [13-15]. It is difficult to list what exactly around us does not contain polymers, starting with the surrounding objects and ending with aerospace applications [16, 17].

Tuttle M. E., in his work [18], claims that the function of a matrix, of a composite material, is to provide a relatively rigid environment that is able to transfer the effort to the fibrous components of the material. The function of the reinforcement in a composite material is to take the loading stress transferred through the matrix. The load must thus be distributed between the matrix and the reinforcement [19]. The reinforcement is included in the matrix material (via interphase bonds) [20]. In the formation of composites, an important aspect regarding with the choice of matrix and reinforcement is the provision of a high-quality interphase that ensures the transfer of stresses from the matrix to the reinforcement without being directly affected. Technological additions have the role of catalyst, accelerator, flame retardant agents, protection against ultraviolet rays [21]. According to studies, both the matrix and the reinforcement of a composite material can be obtained from different types of materials [22]. The classification of composite materials can be done according to the type of matrix material, reinforcement material, how the composite is made, use, mechanical, physical or chemical properties, etc [23].

2. Polymer matrix

To make the composites, the most common matrices used are metallic, ceramic or polymeric, of which, due to the very low prices, the polymeric ones are the most common, however, the remarkable properties of the ceramic matrix composites (especially those related to thermal resistance) make them preferred for aerospace applications [24]. On the other hand, metal matrix composites are preferred for underwater applications because metals are much easier to treat in terms of corrosion resistance, by painting, coating with various protective layers or chemical passivation, etc. [25]. Regarding polymer matrices, at present, the trends are especially related to obtaining polymers or modified polymers with properties as close as possible to those of metals [26]. The matrix defines the shape of the landmark, protects the reinforcement from the action of external factors and keeps its geometry predefined in the design, so that the functionality of the part is ensured [27]. The choice of matrix type is made according to the technology of forming composite materials [28, 29].

Depending on the type of polymer, composite materials can be formed with thermoplastic or thermoset matrices [30]. If, in the case of thermoplastic materials, all technologies involve bringing the raw material into the melting phase followed by injection, the polymerization being ensured by cooling the material in the mould, in the case of thermoset polymers, the polymerization or polycondensation is ensured by use of catalytic agents, usually called hardeners [31]. Composite materials with a thermoplastic matrix are relatively easy to separate, while composites with a thermoset matrix are extremely stable and the reinforcement or additive can no longer be extracted from the matrix [32].

The molecular configurations, and the properties manifested by polymers at the macroscopic level, in the liquid or solid phase, depend on the configurations of the molecular chains, and this dependence can be explained on the basis of the low or high mobility of the polymer molecules under the conditions of heating the material, or the external mechanical loading of it [33-35]. If in the case of thermosetting polymers, the chemical bonds that are made between the polymer chains are covalent bonds, in the case of thermoplastic polymers the bonds between the polymer chains are hydrogen bonds or van der Waals bonds [36]. In the case of thermosetting polymers, heating leads at most to the breaking of covalent bonds, which leads to the oxidation of the material and its destruction [37]. The most important difference between thermosetting polymers and thermoplastic polymers is their behavior at temperature and pressure. Thermosetting polymer matrices are hydrothermally sensitive and can degrade at moderately high temperatures (70 °C – 80 °C in the presence of water) by absorbing moisture [17, 38]. An increase in temperature leads to gradual softening of the polymer, up to a certain point, indicating a transition from a glassy behavior to an elastic or elasto-plastic behavior. The temperature at which this transition occurs is called the glass transition temperature Tg, which decreases with increasing humidity [39]. An increase in temperature beyond this transition point causes the polymer to undergo a rapid transition from rigid solid behavior to elasto-plastic or elastic solid behavior. As a result, the dominant properties of the matrix (shear strength and stiffness) are reduced and the material becomes too soft for use as a structural material [40-42].

3. Thermoset matrix

Thermosetting matrices are characterized in particular by: limited life time, long formation cycle – due to the cross-linking times necessary to reach the degree of hardening, the hardening process in the matrix can lead to the appearance of products with small molecules, which causes the appearance of bubbles and pores in the final product, processing waste is not recyclable [43]. The most commonly used thermoset polymers are epoxy, polyester and vinylester resins, and all of them can be single-component systems or two-component systems and are in the liquid phase at room temperature. Resins are heat treated at high temperatures (or sometimes just at room temperature) to obtain the final shape [44]. The formation of composite materials with thermosetting matrix offers the following advantages: very easy processing, because in the initial phase the resin systems are in a liquid state, the wetting of fibres or particles with thermosets is relatively easy, thereby avoiding voids, porosity and dry areas in formed composite materials, the heat and pressure required in the processing of thermosets show lower values than those required in the processing of thermoplastics [45].

Unsaturated polyester resins – properties depend on molecular weight and chemical composition. The increase in molecular mass determines the improvement of the main mechanical properties, the increase in hardness, resistance to temperature and chemical agents [46]. The specific properties of unsaturated polyester resins are [47]: easy acquisition and quick access to raw materials, fast solidification, no production of secondary elements, dimensional durability and positive mechanical properties of the reinforced form, multiple colouring characteristics as well as transparency, high chemical resistance to the action of different non-oxidized acids and alcohols [48]. It is also present the following disadvantages: high shrinkage during the forming process, poor flame behavior, low resistance to hot water and alkalis [49].

Vinylester resins – the mechanical properties of the hardened resins, especially the tensile and flexural strengths, depend on the molecular mass of the epoxy resin used in the synthesis (they are obtained by acid or acrylic reactions with the reactive oxiranic groups in crosslinked epoxy resins under the action of UV radiation), have good dielectric properties, those based on epoxy resins with methacryloid end groups show particular chemical resistance to the action of acids, bases and solvents [50-52].

Epoxy resins – are generally more expensive than polyester or phenolic resins, but have very good mechanical, chemical and electrical characteristics, forming at temperatures between 50 °C and 130 °C, hard materials and dimensionally stable during curing, have structure that ensures good adhesion to most of the reinforcement materials, they are resistant to the action of acids and solvents, very resistant to the action of alkaline substances, very good electrical insulating materials, thermally stable at temperatures up to 260 °C and very little hygroscopic [53-55]. They have mechanical properties dependent on the loading or reinforcing agent, the thermal properties depend on the chemical structure and the hardening method [56]. In the case of epoxy resins, the cross-linking of polymer chains is very important, and leads to improved mechanical performance. This process is carried out by using chemical cross-linking agents, which also contribute to the polymerization and hardening of resins [57]. In the case of an epoxy resin, the polymerization is due to the specific groups (epoxy), the cross-linking of the chains being a consequence of the use of hardeners, for this the mixture recipe must be extremely balanced. Thus, if the hardening-crosslinking agent is a primary or secondary amine, it is necessary that the ratio between the number of mobile hydrogen atoms in the respective amine and the number of epoxy groups has to be 1:1 [58]. This aspect leads to the possibility of controlling the reaction by establishing the amount of the strengthening-crosslinking agent [59]. Most studies of polymer composites are focused on epoxy matrices due to this polymer's versatility and ease of handling. In general, manufacturers deliver it in liquid form (bi-component), they recommend it for use in additive strategies with various agents – especially carbon nanotubes [60].

4. Composites with polymer matrices

Polymer matrix composites contain a wide variety of long, short fibres and powders fused through and within a polymer matrix. Unlike ceramic matrix composites, in which reinforcements are used to increase fracture resistance, in the case of polymer composites reinforcements are used to increase mechanical strength and material persistence [61]. Composites with a polymer matrix are created so that the mechanical loads of the structures exposed to the loads are taken over by the reinforcements, and the role of the matrix is to bind the fibres or other reinforcing elements and to transfer the loads between them [62-64]. Polymer matrix composites are often grouped into two broad categories: reinforced plastics and advanced composite materials [65]. Here the difference is made based on the level of mechanical properties (e.g., strength and stiffness), although this is not a sufficient criterion for the delimitation process of these materials [66]. The most used properties of composite materials with polymer matrix are: low density, high mechanical strength along the reinforcement (long, ordered reinforcing fibres) [67].

Recently, these materials have been studied with increased attention that can be applied to the construction of structures for the aircraft industry (military, at first, and civil). Their cost, often very high, still remains an important obstacle in expanding the area of use in commercial fields [68]. The most advanced polymer composites are created by a complicated way of adding layer by layer (lay-up) [69]. Ceramic composites, compared to polymer composites, show performance results in production (especially military aircraft) [70]. In some cases, it could even be concluded that technology has surpassed the scientific understanding of these materials and their behavior [71].

In order to create more efficient versions of materials and for an effective design, studies are needed in the field [72]:

1. Materials processing - new cheaper ways like, cost and knowledge of how the forming method adjusts the final characteristics of the materials;
2. Increasing the impact resistance of polymer composite materials in order to ensure the effectiveness and durability in service of the structures [73];
3. Increasing the resistance to the delamination process, the studies that have already been carried out confirm the conclusion that this process is the only one that can lead to the destruction of these materials [74].

5. Nanomaterials and nanostructures

Nanotechnology is the science of designing, manufacturing and applying nanostructures or nanomaterials. Also, nanotechnology studies the relationships between the physical properties and dimensions of materials [75]. Nanotechnology operates with materials or structures of nanometric scalar order [76]. We call nanotechnology any technology that results in a nanometric product: fine particles, microlithography [77]. If we take into account the increasingly close collaboration between engineering and medicine in the nanotechnological field, we inevitably come to the conclusion that nanotechnology represents an important link in the development process of humanity in the years to come [78].

Among the main components of the science of nanomaterials and nanotechnology, the following can be highlighted: fundamental studies of the properties of materials at the nanoscale level, the development of nanotechnology both for the intentional creation of nanomaterials [79], as well as the search for the use of natural objects with nanostructured elements [80], the creation of finished products using nanomaterials and the integration of nanomaterials and nanotechnologies in various branches of industry and science, the development of tools and methods for studying the structure and properties of nanomaterials, as well as methods of control and certification of semi-finished products for nanotechnology [81]. The term nanotechnology was first proposed by N. Taniguchi in 1974 [82].

6. Applications of composite materials

Mishra *et al.* [83], stated that many researches are ongoing to improve the mechanical and tribological properties of these engineered biocomposites by filling the appropriate amount of inorganic nanoparticles such as ZrO_2, SiO_2, CuS, ZnO, CuO and TiO_2 in polymer matrices. The analysis revealed that the incorporation of inorganic nanoparticles into a natural fiber reinforced polymer composite improved the mechanical and tribological properties, also improved the thermal stability and flame resistance, and reduced the water absorption capacity of the biocomposites.

Chuan Li, *et al.* and his work [9], fabricated phase change composite materials using inorganic salts for thermal energy storage at medium and high temperatures. It was concluded that the performance of the selected salts in various aspects directly influences the thermal loading/discharging behavior and also the thermal energy storage capacity of the composite. In cases where heat transfer is viewed as a restriction, thermal conductivity additives are required to improve heat transfer in salt-based composites.

In [84], a new type of functionalized silicone polymer was designed and synthesized. The DMA test showed that the functionalized silicon polymer preserved the heat resistance of the epoxy composite material to a certain extent while strengthening the epoxy. SEM images of the fracture surface of the composites confirm that the novel silicone polymer PSOL-(N-TMSPrVaC) is uniformly dispersed in the epoxy resin. The impact resistance reaches the highest value with 3.0 phr PSOL-(N-TMSPrVaC), the percentage was increased by 18.2% compared to pure epoxy resin.

Polymer matrix composites were produced from type I collagen fibers as reinforcement and epoxy matrices with varying fiber volume fractions, namely 10%, 20%, 30% and 40% [85]. The obtained results were tabulated and the following conclusions were drawn: the specific wear rate of the composites decreased as the percentage content of fibers increased, from the investigation the minimum wear rate for collagen reinforced composites of 30% volume loading was observed of 15 N, collagen fibers embedded in epoxies can considerably reduce abrasive wear losses. At a fiber composition of 30% volume fraction, the best wear resistance property was obtained.

In the paper [86], materials based on Multicast polyurethane resin and ISO 2 hardener and copper wires were designed. Based on the results of the experimental tests, in the case of the characteristic curves for the specimens reinforced with three copper wires, an increase in the maximum force can be observed, compared to the unreinforced specimens, by 17.51% and a significant increase in the maximum elongation, by 42.25% compared to of the unreinforced specimens. Glass fiber reinforced polymer (GFRP) laminates, a range of thermosetting resins and an infusible thermoplastic resin were used. SEM showed a transition from matrix-dominated failure in the dry state to failure at the fiber-matrix interface in wet and organic-wet specimens. The overall performance of the infusible thermoplastic was good compared to marine resin systems, however, environmental performance could be improved if the thermoplastic resin is used in conjunction with a fiber size that is tailored for use with acrylic resin systems.

Researchers [87], used vinyl ester (VE) resin for additive manufacturing of high-performance vinyl ester resin by direct writing with UV-thermal dual curing ink. The printed and dual-cured VE nanocomposites achieved a Young's modulus of 3.7 GPa and a tensile strength of about 80 MPa, which exceeds by about 10% conventionally cast pure VE cured with methyl ethyl ketone peroxide (MEKP) and, by also indistinguishable from the tensile properties of cast VE nanocomposites with the same composition. The fracture toughness of dual-imprinted and reinforced VE nanocomposites was 16% higher than MEKP-reinforced neat cast VE.

The influence of resin-based bonding agents loaded with different inorganic filler content, with or without adhesive, on the micro tensile strength, biaxial bending strength and adhesive interface morphology of bonded ceramic specimens were investigated [88]. It was shown that increasing inorganic filler content of experimental resin-based bonding agents strengthened bonded feldspathic ceramics. The bonding agent with high filler content produced significantly higher viscosity and film thickness. In contrast, bond strength was lower and structural reliability decreased if no adhesive was used.

The role of heat diffusion on the occurrence of instabilities during the frontal polymerization of an adiabatic channel of neat DCPD resin and unidirectional carbon/DCPD composites was investigated [89], through a numerical analysis based on a thermo-chemical reaction-diffusion model. Numerical study performed on the neat resin showed how these FP-driven instabilities diminish and the wavelength and amplitude of the thermal peak present at the front decrease as the initial monomer temperature increase, leading to an increasingly the most stable of the front. Although these thermal instabilities can influence the quality of the manufactured polymer component, they do not affect the speed of the polymerization front.

Micro fluidization [90], has been proposed as a very promising method to prepare low MWCNT modified epoxy suspensions with improved thermal properties. Sonication was performed for the same purpose for performance comparison. Micro fluidization was found to have the ability to disperse MWCNTs more homogeneously compared to sonication, thus improving the final thermal properties of the composite. The time to prepare the suspension by micro fluidization was shown to be approximately 9.3 times less than the processing time required to prepare the same suspension by sonication. In short, given the characteristics of the near-spontaneous flow field, micro fluidization can be used to various applications of any nano filled modified thermosetting polymers that require very high-quality requirements in terms of particle size of the dispersed phase, particle size distribution and stability of the resulting suspension.

In [91], fast remote response cross-linked recycled polyurea nanocomposites were synthesized by a two-step method involving in situ photo-induced polymerization and hot compression. The dynamic nanocomposites exhibited excellent and fast photo-induced self-healing abilities and regained their mechanical properties after damage. This aspect can be attributed to the synergistic effect of the dynamic exchange reactions in the CPU matrix and the efficient photo-thermal effect of the filler materials. The nanocomposite prepared using 1% CNT exhibited excellent toughness, high elasticity, high tensile strength, efficient photo-thermal shape, memory effect and good recyclability.

Radiation-synthesized inorganic-organic hybrid nanoparticles of inorganic nanoparticles (Ag and CeO_2) in aqueous dispersions containing radiation-synthesized poly(N-vinylpyrrolidone) (PVP) nanogels (NG) were obtained [92]. The experiments showed that there are strong interactions between the inorganic precursors (Ag^+ and Ce^{3+}) and the nanogel before irradiation. The two hybrid systems (Ag/NG and CeO_2/NG) were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD confirmed the formation of crystalline Ag and CeO_2. TEM proved that the inorganic nanoparticles are uniformly distributed in/on the nanogel. Both XRD and TEM confirmed that the inorganic particle size is controlled by the nanogel.

An extrinsic welding method using interfacial covalent bond exchange reactions (CBER) has been investigated to enable strong and repeatable welding of conventional thermosetting composites [93]. Dip treatment and welding time have been shown to significantly affect joint strength. By choosing appropriate immersion and welding conditions, appreciable bond strength has been achieved for epoxy composites. Also, higher resistance could be available for longer welding time.

Researchers [94], made a completely bio-based heat-resistant epoxy network by curing a renewable luteolin-derived epoxy resin (DGELU) with a furan-derived hardener, 5,5′-methylenedifurfurylamine(DFA), anti-flammable and non-toxic for coating applications fire retardant. For comparison, a control sample was prepared by curing commercial petroleum-based epoxydiglycidyl ether of bisphenol A (DGEBA) with a petroleum-based hardener, 4,4′-diaminodiphenylmethane (DDM). The storage modulus at 30 °C and tensile strength of cured DGELU/DFA were 82.5% and 23.2% higher than those of cured DGEBA/DDM. The benzopyrone unit of the luteolin structure led to exceptional carbonization, and the carbon yield for thermal decomposition in nitrogen cured DGELU/DFA was 3.2 times higher than that of cured DGEBA/DDM. The results proved that a bio-derived, anti-flammable, high-strength, and non-toxic heat-resistant epoxy network was successfully developed for highly safe epoxy coating applications.

Polyurea has been used as a reinforcing filler for anti-corrosion and wear-resistant application of epoxy resin [95]. The polyurea nanofiber-reinforced composite layer mainly improved the anti-corrosion performance from three aspects: (a) the polyurea nanofibers were arranged in a staggered arrangement and acted as an excellent barrier for corrosive solutions, the physical barrier effect of the filler was fully applied in coverage; (b) reduction of coating defects resulted in less corrosive environmental infiltration; (c) polyurea nanofibers can evenly distribute the internal stress caused by the expansion of corrosion products and reduce blistering in the coating.

In this paper [96], a new visco-plastic model was developed to predict the rate-dependent nonlinear mechanical behavior of an epoxy resin. The presented model was based on a potential function in which a combination of the second and third invariants of the deviatoric stress tensor as well as the first invariant of the stress tensor was realized. A set of tensile and shear tests at different constant strain rates were performed to investigate the rate dependence of the resin and derive model parameters. Under shear loading, the nonlinearity of the resin stress-strain curve was significantly more evident than that under tensile loading, even at low strain rates. The initial modulus and strength of the resin increased with strain rate under both tensile and shear loads, however this was more significant under shear loading.

A multiscale model was developed and it can simulate the influence of synthetic conditions (such as molar ratio) on the structure and physical properties of thermoset resins (e.g., phenolic resin) by introducing a comprehensive reaction model that includes the addition reaction [97]. The effectiveness of the model was validated by verifying the influence of primary synthetic index, i.e., molar ratio, on the physical and thermal properties (i.e., density and glass transition temperature) of Resol resins. This model can help to develop more efficient and suitable synthetic conditions to obtain products exhibiting the desired material properties.

A new class of high-performance resins based on dicyanoimidazole (DCI) reactive group with flexible structural modification has been developed [98]. This work first introduced a new type of high-performance thermosetting resin with flexible molecular modification capability based on DCI cross-linking groups. Preliminary studies have shown that the synthesized aliphatic-containing DCI model compound (PDBDCI) has higher curing reactivity than phthalonitrile and benzonitrile, and its cured products also exhibit better thermal properties than most thermosetting resins, including phthalonitrile resins containing aliphatic compounds. In conclusion, due to flexible molecular modification, high reactivity, unique aromatic heterocyclic structures, excellent thermal and thermomechanical properties, and easy industrialization, DCI resins present a wide range of application prospects in the field of high-performance thermosetting resins and even functional polymers.

The authors [99], of a new flexible binder with improved mechanical properties for bridge deck applications. This research studied the preparation process, microstructural morphology and mechanical properties of a newly developed thermosetting polyurethane (TPUA) modified asphalt binder. The results showed that the viscosity of TPUA was greatly affected by the preparation temperature and the rate of viscosity increases with the increase of the preparation temperature. The curing time was determined by the change in the absorption peak of the infrared spectra of the NCO groups. When the PU modifier content exceeded 30% by mass, the polyurethane resin (PU) formed a continuous polymer network in the asphalt binder, and the PU had relatively good compatibility with the asphalt binder. In general, the mechanical properties of asphalt binder were substantially improved by incorporating PU resin, generating a flexible binder with favourable application prospects, and PU had relatively good compatibility with asphalt binder. TPUA still showed the characteristics of a viscoelastic material at medium and low temperatures.

Waste thermoset unsaturated polyester resins (WTUPR), potassium carbonate, glycol, and polyvinyl alcohol were used to obtain styrene-maleic acid copolymer (SMC) [100]. The hydrophilic carboxylate/hydroxyl groups and the hydrophobic benzene ring structure of SMC endowed the airgel with amphiphilic properties after physical cross-linking with PVA. The concentration of SMC-K has a significant impact on the performance of AAs, and AAs with SMC-K/PVA ratios of 1:1 or 2:1 exhibited hierarchical pore structures, low densities, good mechanical properties, and affinity/high absorption for water and organic liquids. The good comprehensive performance makes AA a candidate for fast and efficient absorbents. This study provides a new route for high value-added reuse of waste thermosetting polymers.

In [101], the rational design of a functionalized silicone polymer for the modification of epoxy-based composites was carried out. The tensile strength of PSOL-(N-TMSPrVaC)/EP composites was improved by 8.9% compared to pure epoxy resin when the content of PSOL-(N-TMSPrVaC) was 0.5 phr. The impact strength of PSOL-(N-TMSPrVaC)/EP composite reaches the highest value with 3.0 phr PSOL-(NTMSPrVaC). It was increased by 18.2% compared to pure epoxy resin. SEM images of the fracture surface of the composites confirmed that the novel silicone polymer PSOL-(N-TMSPrVaC) was uniformly dispersed in the epoxy resin. In addition, the DMA results showed that the thermal stability of the composites was preserved, while the hardness is improved.

Studies have been conducted on composites based on HTV and RTV silicone rubber and carbon nanotubes for sensors and actuators [102]. HTV and RTV silicone rubber were used as rubber matrix and CNT as nanofiller. This study showed that the incorporation of CNT nanofillers significantly improves the mechanical and electrical properties of rubber nanocomposites. TEM investigations showed that the CNTs had 1-D morphology, diameters of 12–15 nm, and aspect ratios of 70-75. The compressive modulus after incorporating CNTs into HTV rubber nanocomposites at 3 phr was improved by 65% and the tensile modulus was improved by 96%. Similarly, the compressive modulus in RTV rubber nanocomposites at 3 phr improved by 110% and the tensile modulus improved by 105%. Addition of 3phr of CNTs in HTV and RTV rubber nanocomposites led to decreases in electrical resistance to 13 kΩ and 0.3 kΩ. Similarly, the actuation displacement was 2.3 mm (a 920% increase) for RTV silicone and 1.55 mm for HTV silicone rubber (a 1025% increase) from 2 to 12 kV. In addition, strain sensors showed a higher measurement factor for RTV silicone rubber than HTV rubber. The flexible piezoresistive strain sensor showed >100% stretch.

Silicone rubber, silica nanoparticles, benzoyl peroxide, and europium nitrate were used to study the effect of fluorescence labelling on the mechanical properties of silica-filled silicone rubber [103]. It has been shown that when the filler loading reaches 30 phr, especially 40 phr, fluorescence labelling rarely affects the mechanical performance of filled silicone rubber. Therefore, the optimal filler loading is 40 phr for investigating the properties of silicone rubber filled by fluorescent labelling of the SiO_2 filler.

An electrically conductive carbon fiber reinforced plastic (CFRP) was developed for lightning protection by infusing the carbon fiber (CF) fabric with a thermoset resin [104]. The new CFRP fabrication method used a liquid dispersion of heat-resistant resin based on styrene derivatives, including micron-sized polyaniline (PANI)/dodecyl benzene sulfonic acid (DBSA) composite particles. The results indicated a non-uniform distribution of PANI-CP particles between the CF fabric layers and the presence of very small particles on the surface of the CFs inside the bundles, which contributed to high electrical conductivity. Non-uniform particle size distribution was found to increase the density of CFs in bundles.

Sprayed polyurea (SPUA) was used to develop a nonlinear visco-hyperelastic tensile constitutive model over the wide strain rate range [105]. The mechanical properties of SPUA were shown to be strain rate sensitive, i.e., the elastic modulus and tensile stress increase with increasing strain rate, while the strain at fracture is linearly negatively correlated with the logarithm of the strain rate. SPUA is a material sensitive to strain rate, dynamic elastic modulus dependencies, tensile stress.

In [106], an effective strategy for improving the interfacial adhesion of immiscible methylvinyl silicone elastomer/thermoplastic polyurethane blends were addressed by developing a hybrid Janus particle with an amphiphilic brush. According to SEM and AFM analyses, the modified Janus particles were stably located and ordered at the polymer blend interface due to the asymmetry structure of the particles and the interaction between the polymer matrix and similar short polymer chains on the particles. Furthermore, the elongation at break, 300% strain and tensile strength of the blends were also significantly increased due to the compatibilizing effect of the modified Janus particles.

Three types of epoxy systems and glass-coated cobalt-based microwires (GCM) were used to predict the interfacial shear strength before use for fiber-reinforced thermosetting composites based on the impedance-stress effect of ferromagnetic microwires [107]. The local interfacial stress induced by the resin microdroplets significantly improved the microwire impedance, but the stress concentration reduces this improvement effect. The increase in impedance has a non-monotonic linear relationship with the total embedded length, and the absolute value of the slope for the descending side shows the same trend as the IFSS of the GCM-3/resin composites. The proposed IFSS prediction method using Co-based microwires can dramatically simplify the testing process and reduce industrial costs, facilitating the performance optimization and application of advanced fiber-reinforced polymer composites.

A novel healing kinetics modeling methodology was established to facilitate matrix formulation [108]. The proposed kinetic curing methodology established an explicit link between material chemistry and material modeling overcoming the traditional limitations of standard curing kinetics phenomenological techniques and reducing experimental effort and development time for resin formulation. The Formulation Ratio Superposition (FRS) approach has been shown to satisfactorily approximate the kinetics of ternary mixtures on a wide variety of amine/epoxide systems. Matrix formulations can be tailored to specific design requirements controlling reaction intensity and reaction time by changing the constituent functional group fraction. Characterization of the curing kinetics of the binary blend and matrix parameterization of the constituent functional groups provided greater design flexibility, as complex matrix formulations can be tailored to improve hardness, damage tolerance, and environmental stability.

This paper [109] is an overview of manufacturing defects in fiber-reinforced resin matrix composites, including: resin defects, fiber defects, interface defects, and processing defects. To characterize the defects of composites, the authors synthesize the non-contact detection of composite defects and prospect the development of composite defects in the future. This article analyses and discusses the generation mechanism, distribution, and optimization methods of manufacturing defects in hot press moulding, resin transfer moulding, and additive manufacturing moulding. The main manifestations of defects produced by the carbon fiber reinforced composites processing process are: delamination; rupture; burrs. Delamination is the most serious machining defect, which results in many engineering application problems such as decreased strength and short lifetime in composite structures.

The static and dynamic compressive and tensile response of highly elastic polyurea was investigated in [110]. Curing of thermoset resin and thermoplastic resin, resin infiltration process in hot pressing, resin transfer moulding and 3D printing were described in this article. The formation mechanism of fiber reinforcement defects such as fiber puckering and curling in composites was introduced, and the influence of these defects on the bending and compression properties of the composites was analysed, and showed that fiber misalignment defects would seriously reduce modulus, strength. and the stability of the supporting structures. The main manifestations were delamination, breakage and burrs, which seriously affected the strength and reliability of the connection between components.

7. Conclusions

As a conclusion, efforts to develop nanostructured polymeric materials have attracted attention due to the increasing importance of these materials in the engineering industry, aerospace industry, food industry or biomedical applications. Also, in this paper, the deepening of some aspects regarding the influence of modifying agents as well as their concentrations on the mechanical behavior of the formed materials intended for the study was sought.

Following the analysis of the obtained experimental results, the following conclusions can be displayed: internal properties of materials such as solubility, polymer-payload interactions, polymer chain flexibility, surface charge, stereochemistry, surface chemistry, molecular weight and crystallization ability, etc. They must be considered for choosing the appropriate preparation method and for the appropriate processing.

From the review, it follows that controlling the nanostructure of polymers and adding nanoparticles has led to improvements in structural and functional properties in a number of polymer systems in response to the continuous demands of advanced industrial sectors.

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