



A review of advances in the preparation and application of polyaniline based thermoset blends and composites

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Abstract

For several decades, forming blend and composite of polyaniline (PANI) with insulating polymers has been a widely studied research area because of the potential applications of such blends, which have a unique combination of mechanical properties, the processability of conventional polymers and the electrical property of conducting polymers. The current review paper will emphasize PANI composites or blends with thermosetting polymer matrices. The enhanced electro-mechanical properties of the blends and composites depend on the uniform dispersion of the PANI particle in polymer matrix. Therefore, considerable studies have focused on improving the distribution of PANI particles within the thermoset matrices. In this review paper, all the parameters and conditions that influence the surface morphology and application of PANI thermoset blends and composites will be described systematically. Recent progress on PANI based thermoset system with multifunctional ternary composites research will be highlighted in this paper. Furthermore, encouraging applications of different PANI thermoset composites and blends are discussed, such as flame-retardant materials, lightning damage suppression, metal ion removal, anticorrosive coating, electro-magnetic shielding, conductive adhesives, and sensing materials.

Keywords Thermoset · Composite · Polyaniline

Introduction

Modern technologies require new materials with unique amalgamations of properties. In recent decades, a number of studies have focused on using polymer composites and blending technology to obtain hybrid materials with specific functionality. One such class of material is conducting polymer blends, which is a blend of an insulating polymer with a conducting polymer, and it has shown enhanced optical, electrical and dielectric properties [1–4].

In the electrically conducting polymer family, polyaniline (PANI) is the most popular conducting polymer studied due to its properties, such as ease of synthesis, low cost, stability, wide range of conductivity upon doping and unique protonic doping process [5–8]. However, the processability of PANI has two limitations: the powdered form of the polymer does not dissolve in its doped form in any common organic

solvents and the polymer is degraded at high temperature, which results in poor mechanical strength [9–11].

To overcome the limitations of PANI processability, a number of methods have been studied, and blending and compositing are the two most commonly used techniques [12–15]. In 1990, after the discovery of the solution processability of PANI, research on PANI composites or blends with insulating polymers gained popularity [16, 17]. Over the years, many studies have been performed to find the substitute of conventional inorganic conductive fillers, such as metal particles and conducting carbon black, with conducting PANI fillers [18–20]. A number of research groups have performed extensive work on different synthesis methods and properties of PANI blends and composites with insulating polymer matrices [21–25].

Thermoset is a stronger polymer compared to thermoplastic because its crosslinking is distributed in all three directions [26]. Thus, thermoset polymers are suitable for high-temperature and toxic chemical environment applications because they can maintain their shape and size due to the strong covalent bonds between the polymer chains and cannot be easily broken [27–29]. Thermoset monomers are generally found in either soft solid form or viscous form, and after

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curing, they undergo irreversible changes to form an infusible and insoluble polymer network [30], which is very stable and can't be recycled. Normally, suitable UV radiation or irradiation using electron beam are used to the polymer to initiate the curing process [31–33]. Curing is a very important step of the thermoset composite preparation process. There are number of ways to prepare and cure thermoset composites and blends, such as the reactive combination method, which cures via two-package thermoset systems, curing by atmospheric components, such as oxygen or water vapour, or curing by inhibitors, which are volatile in nature [34–36]. However, for the preparation of all type of PANI thermoset composites, in situ polymerization methods are often used and curing is always the last step. Two methods are primarily used to synthesize PANI composites and blends: the 1st method corresponds to dispersing PANI particles, which are prepared beforehand in the polymer resin; and the 2nd method is the in situ chemical polymerization method, in which aniline is polymerized to polyaniline in the polymer matrix [37–40]. High electrical conductivity and a lower percolation threshold are the most important criteria for the uniform distribution of PANI particles in the polymer matrix. Many research works have been performed using both methods to enhance particle dispersion and rise the affinity between PANI particles and the thermoset resin molecules [41–43]. Lately, thermoset composite using three different components, namely, conducting filler, matrix and an additional filler, has attracted the attention of the researcher due to the additional advantage of the add-on properties [44, 45]. In this process, the organic constituent or inorganic filler are introduced within the polymer matrix to enhance specific properties, such as magnetism [46, 47], thermal sensitivity [48], mechanical properties [49, 50], or barrier properties [51]. In this review paper, we cover the principles for synthesizing binary and ternary PANI thermoset composites.

Principle of polyaniline thermoset blends and composites formation

PANI is infusible and insoluble in conventional organic solvents and degraded at higher temperature [52, 53]. Because of these reasons, PANI is treated as an intractable material. A number of synthetic approaches are used to promote the distribution of PANI particles in the polymer matrix [54]. Therefore, composite formation or blending PANI with any other organic polymer matrix needs special precaution in order to obtain uniform dispersion. The key factors that determine the performance of PANI thermoset blends and composites are uniform dispersion and low percolation, which in turn will decide the electrical conductivity, mechanical properties and processability of the PANI thermoset composites [55]. The formation of successful thermoset blends and composite

depends on extent of interaction between polyaniline and thermoset matrix molecules. Figure 1 shows scanning electron microscope (SEM) images of two different systems showing a coagulated and well-dispersed morphology of PANI on polymer matrix. Introducing of different types of dopants and crosslinking agents during blend and composite formation, can increase dispersion and can change the conducting state with a simultaneous change in colour and electrochemomechanical deformation properties, which are desirable characteristics [55]. Figure 2 shows a scheme of different types of slurries, such as coagulated slurry, slightly coagulated slurry and dispersed slurry. After the curing process is performed using heat or radiation or by mixing with a catalyst, thermoset polymers are also an infusible, insoluble polymer network [56, 57].

Preparation methods of polyaniline thermoset blends and composites

As the fundamental difference between polymer blends and composites is that, blends are single phased system obtain by combining two or more polymers, whereas composites are multiphase system made up of two or more component usually polymeric and a nonpolymeric component [58]. In case of blends, no strong bond or interaction exist between the constituents because mere physical mixing forms it. On the contrary, composites involves different chemical reactions as a result strong chemical and physical bond are evident. In case of PANI- thermoset system, both PANI and thermosets are polymers. Therefore, the preparation methods involve and dispersion determines the nature of the system, whether blend or composite.

Broadly, PANI thermoset blends and composites can be divided into two types based on the number of ingredients used for preparation. Traditionally, the system consists of two main constituents, i.e., the filler (PANI) and the matrix (thermoset), along with other constituents in trace amounts that perform a number of functions, such as catalysis, curing, polymerization, etc. This system is referred to as a binary system. More recently, thermoset blends with ternary systems have been gaining popularity, and they contain an additional constituent along with the filler and matrix to provide specific properties, such as magnetism, thermal sensitivity, low percolation, etc. The following sub sections will elaborate the details of different aspects of both binary and ternary systems. Figure 3, shows a flowchart demonstrating different type of methods used to prepare PANI-thermoset system.

Preparation methods of binary systems

PANI thermoset blends and composites preparation using two ingredients is the most commonly used method. However, the

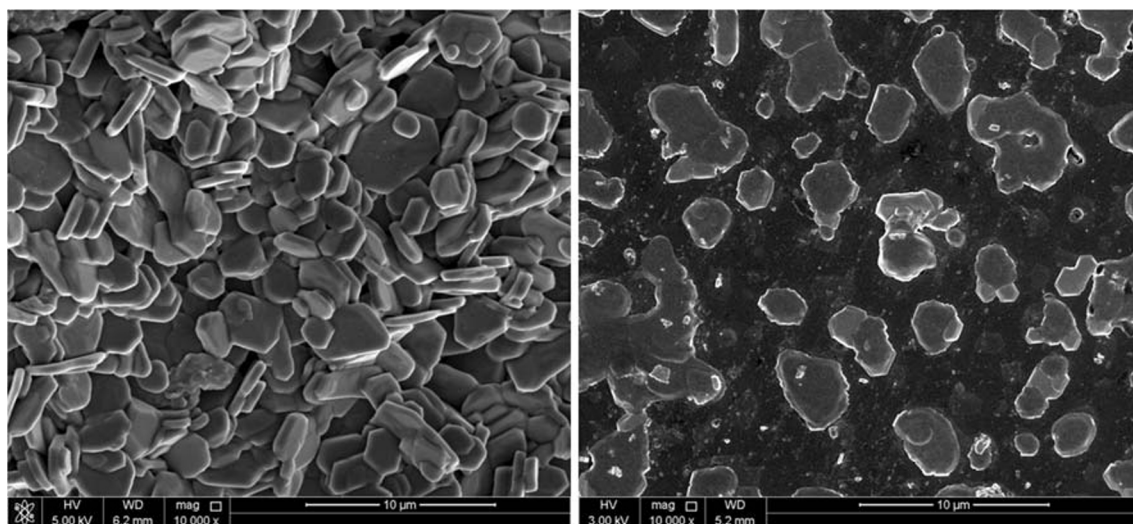


Fig. 1 SEM images showing coagulated PANI particles and dispersed PANI in a polymer matrix resins

binary system has two other approaches: blending using already prepared PANI in the thermoset matrix resin and second approach is converting aniline into polyaniline in the thermoset matrix itself. The systematic explanation of both binary systems of thermoset blend and composite preparation along with the advantages and setbacks will be described in the following subsections.

Solution blending method

The solution blending method is the most classical and simple method to prepare PANI thermoset blends. It is also known as the physical blending method because it involves simply mixing PANI physically with a polymer matrix before curing. Because uniform dispersion of PANI particles in thermoset resin is the most important and first and foremost criteria for the formation of a good blend, scientists have sought to increase the dispersibility of PANI particles by adopting different techniques. One of the most used technique is functionalization of PANI particles using substituents, such as N- or ring substituents, in order to make it more soluble and/or sterically block exchanges with the polymer chain. By

implementing these techniques, the dispersion of PANI can be increased considerably, although at the cost of electrical conductivity. N-substituted PANI, such as poly(N-alkylanilines), is prepared by the chemical oxidation method [57]. Poly(N-alkylanilines) are the electroactive materials with remarkable and flexible electrochromic behaviour but considerable low electrical conductivities in the doped form. The reduction in electrical conductivity compared to the conductivity of unsubstituted PANI is due to overall decreases in contribution of both intrachains and interchains to the whole conductivity. Although poly(N-alkylanilines) are highly processable, their low electrical conductivities restrict their potential applications [59].

Conversely, the electrical conductivity of poly(N-alkylanilines) salts arefunction of number of carbon atoms present in the alkyl chain. A decrease in the number of carbon atom leads to increases in conductivity value from 1.9×10^{-4} S/m for poly(N-butylaniline) to 5.7×10^{-2} S/m for poly(N-methylaniline) at 21 °C, whereas the conductivity of the base polymers is on the order of 10^{-7} S/m at 21 °C [60]. Poly(aniline-co-phenetidine), which is a ring-substituted PANI, retains the conductivity of the unsubstituted PANI but

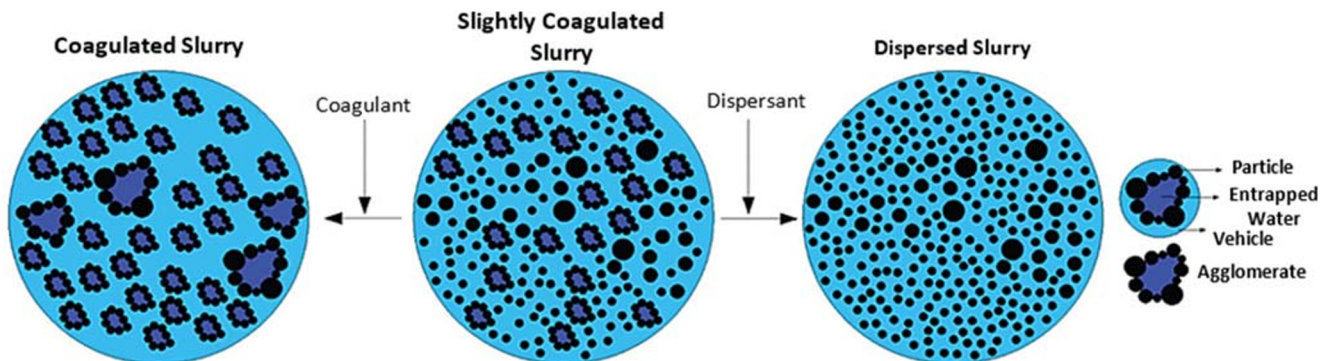
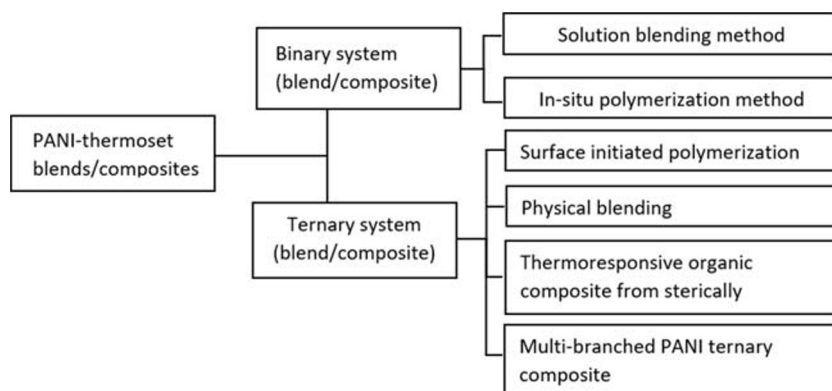


Fig. 2 Scheme illustrating the coagulated slurry, slightly coagulated slurry and dispersed slurry

Fig. 3 Flowchart showing different types of preparation method of PANI-thermoset systems



is compromised in stability towards hydrolysis [1]. Because of these reasons, fewer research publications have focused on the synthesis of N or -ring-substituted PANI thermoset composites. Additional types of substituted PANI are polyaniline-p-toluenesulfonate (PAPTS) and Copoly(o-toluidine/oethylaniline)-p-toluenesulfonate (POTOEPTS), which are blended with poly(urethane-acrylate) resin and cured by the UV light photocuring method [61].

The conductivity of the 1st composite is $9 + 3$ S/cm, and that of 2nd composite is 1×10^{-3} S/cm shown in Fig. 4 reveals that conductivity percolation region for the POTOEPTS blend is missing because POTOEPTS dissolves in dimethylformamide (DMF but not PAPTS). Therefore, the dispersion is uniform and the percolation behaviour is a characteristic of the filler-polymer matrices and not observed when molecules are uniformly dispersed [61].

Another two thermoset epoxy composites prepared by using N-substituted PANI are poly(o-anisidine)-epoxy (PoA-epoxy) and poly(o-anisidine-co-o-phenyldiammine)-epoxy (P(oA-co-oPDA)-epoxy) [62]. These nanocomposites are synthesized using various loadings of PoA (1.0, 1.5 and 2 wt%) and P(oA-co-o-PDA) (1.0, 2.0 and 3.0 wt%) by a solvent casting of epoxy in ethyl methyl ketone [62]. For

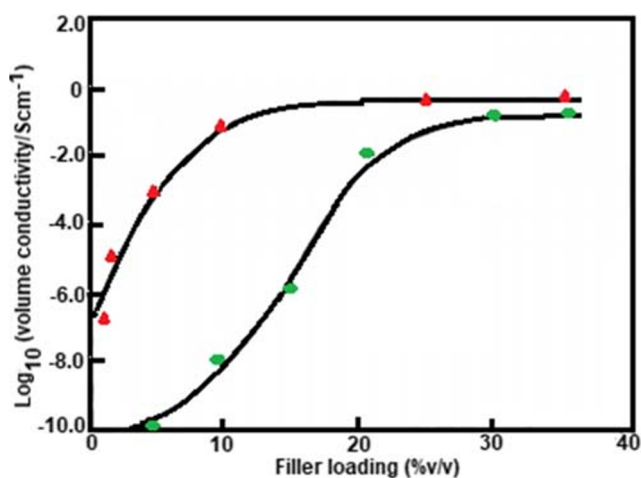


Fig. 4 Volume conductivity vs. filler loading for poly(urethane-acrylate)/▲PAPTS and ▼POTOEPTS nanocomposites [61]

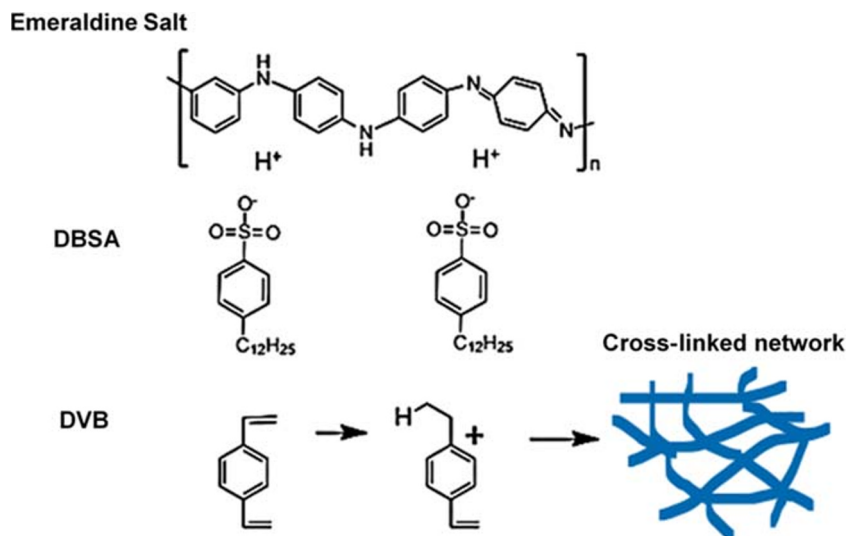
the loading of 3.0 wt% P(oA-co-oPDA) and 1.5 wt% PoA, uniform dispersion is found in the epoxy solution, but a further increase in filler concentration led to agglomeration and phase separation. These nanocomposite coatings showed excellent anti-corrosive properties, and the increase in conducting filler content increased the anti-corrosive performance.

Recently, pure PANI-based thermoset blends have been reported, and they show good conductivity and dispersion by using sulfonic acids as both surfactants and dopants. The long-tailed sulfonic acid dodecylbenzenesulphonic acid (DBSA) is used as a dopant, and divinylbenzene (DVB) is used as a crosslinker to increase the rigidity of PANI-based conductive composites [63].

In the above mentioned system, DBSA acts as dopant to PANI and DVB as a curing agent, therefore, composite doping and curing occur simultaneously. Centrifugal mixing enables the formation of PANI-DBSA micellar mixture via physical mixing as shown in Fig. 5. A constant PANI and DBSA composition of 30:70 wt% and variable DVB content were utilized to make different composite samples. Good dispersion was evident when the DVB content was increased and remarkable electrical properties are achieved for the composites with increasing the PANI content. Flexural modulus and brittleness of the samples were increased as the DVB content is increasing. Finally, surface morphology of the composites revealed that a low concentration of DVB led to poor dispersion or agglomeration of PANI-DBSA within the composite.

Recent observations indicate the popularity of increasing the solubilization of PANI in the thermoset matrix via counterion assisted PANI dispersion technique. The introduction of an anionic surfactant (such as camphorsulfonic acid (CSA), dodecyl sulfonic acid (DSA), DBSA, and toluene sulfonic acid (TSA)) as a dopant during PANI preparation plasticizes the material and increases the bonding between PANI particles and the matrix molecules [63, 64]. The preparation of polyaniline-dodecylbenzenesulfonic acid/epoxy (PANI-DBSA/EP) resin blends has been performed by adopting direct physical mixing method. The blends are obtained by changing the PANI-DBSA concentration within the range of 0 to 10 wt% in the EP matrix with and without using toluene

Fig. 5 Doping and cationic polymerization of DBSA with DVB polymers to form a cross-linked network [63]



as a solvent [65]. Without using toluene, the blend containing 3% of PANI-DBSA particles showed poor conductivity and is insulating in nature (conductivity 10^{-13} S/cm), whereas when toluene used as a solvent for PANI-DBSA system, the percolation threshold is lowered to approximately 2.3 wt%, this is due to creation of fine PANI-DBSA conducting network within the epoxy matrix. In another work, PANI, DBSA and p-Toluenesulfonic acid (PTSA) are mixed in the ratio of 30/62/8 by wt% to form a polyaniline/dodecylbenzenesulfonic acid/ p-Toluenesulfonic acid (PANI/DBSA/PTSA) blend using the three-roll milling process. DVB is later added to the mixture using a centrifugal mixer to form a homogenous suspension. The doping and curing processes of the polyaniline/dodecylbenzenesulfonic acid/ p-Toluenesulfonic acid/divinylbenzene (PANI/DBSA/PTSA/DVB) blends are executed together at 110 °C for 2 h. The electrical conductivity of both the cured PANI/DBSA/PTSA/DVB and PANI/DBSA/DVB samples is measured vs. heating time as shown in Fig. 6.

Such PANI based conductive systems with two dopants have significantly higher electrical conductivity (i.e., 1 S/cm) when compared with other conducting nanofiller based polymer composites [66] as well as PANI polymer blends [67]. As heating time increases, conductivity decreased in last two systems due to the fact that though the heat speeds up PANI doping and the curing of DVB, eventually the dedoping of the doped PANI is initiated while curing process of DVB under the influence of uninterrupted heating. Subsequently, after the 2-h curing period the overall conductivity value reduces. In summary, the binary dopant case exhibits a higher conductivity (after the 2-h heating period PANI/DBSA/PTSA/DVB has conductivity value approximately 1.0 S/cm) than the single dopant system (after the 2-h heating period PANI/DBSA/DVB has conductivity value approximately 0.1 S/cm). Through this work, the advantage

of the binary dopant system over the single dopant system is successfully established. Malmonge et al. has published a work on preparing a polyurethane (PU) based on castor oil using the 4,4 -diphenylmethane diisocyanate based prepolymer (F329) and the polyol (21 L) and different concentrations of PANI dissolved in N-methyl-2-pyrrolidone (NMP) [68]. Blending is performed by mixing both the polymer solutions and casting them into a film of 30–100 μ m thick. The obtained films are doped by immersing them in different acid solutions for different doping times. The electrical conductivity of the blend is found to be a function of the doping medium. For instance, as shown in Fig. 7, the electrical

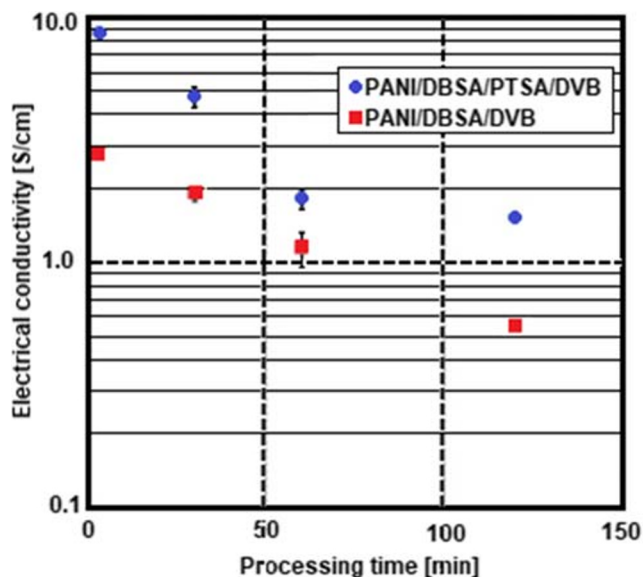


Fig. 6 Electrical conductivity of the PANI-based conductive composites as a function of the processing time at 110 °C [66]

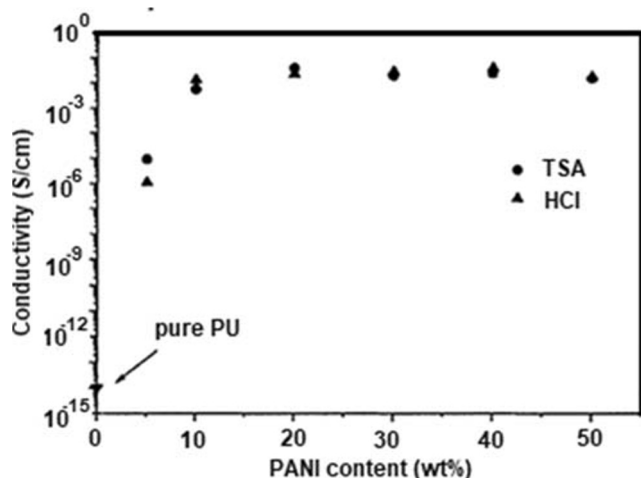


Fig. 7 Conductivity of PU/PANI blends as a function of the PANI content and doped with TSA and HCl in DMF medium [40]

conductivity in the polyurethane /polyaniline (PU/PANI) blends with compositions of 90/10 and 80/20 (wt/wt) are 10^{-9} S/cm and 10^{-4} S/cm for doping using an aqueous solution medium (using either 1 M HCl or 1 M TSA as the dopant), respectively. On the other hand, the conductivity is of the order of 10^{-2} S/cm after doping in DMF solution for both blends, which is correlated to the swelling effect of the polymeric microstructures by DMF, which eases dopant ion diffusion. As PANI content increases, this effect becomes less pronounced.

The solution blending method is one of the most widely adopted method for preparing all types of polymer blends. The advantage of this method is the control of quality and quantity of PANI molecules in the blend and easy preparation method. However, in this technique due to lack of good interaction between the constituents the electrical and mechanical properties are often compromised.

In situ polymerization blending method

Another popular method of preparing PANI thermosetting composites and blends is in situ polymerization. In this method, the conversion of the aniline monomer to a polymer is performed within the thermoset matrix. Therefore, higher uniform dispersion and the miscibility of the PANI particles in the thermosetting polymer matrix are possibility. In-situ polymerization of aniline in the presence of ammonium persulfate (APS) is used to graft PANI onto to radiation cross-linked chitosan films [41]. Figure 8 shows the possible mechanism of PANI-chitosan composite formation. Aniline got polymerized at the active sites at $-OH$ and $-NH_2$ (2 and 5) of chitosan. The percentage of grafting is seen to be directly proportional to the monomer concentration and reversely to crosslinking density.

An aniline-CSA mixture is dispersed in chloroform and epoxy in chloroform and mixed under constant stirring in and ice bath, and then an oxidant is added as an aqueous solution of APS dropwise into the mixture [69]. The resultant suspension is washed thoroughly with distilled water to eliminate the unused CSA and APS and neutralize the system. A dark-green PANI/epoxy mixture is obtained after storing the composite overnight inside the vacuum oven. Both anhydride and alkaline types of hardeners and the imidazole type of catalyst are added to cure the mixtures at $100\text{ }^{\circ}\text{C}$ for 0.5 h and $125\text{ }^{\circ}\text{C}$ for 1 h. The type of hardeners used for curing the PANI/epoxy composites play an important role in determining the electrical and dielectric properties [69]. Figure 9 shows the dielectric constant and dielectric loss as a function of the PANI concentration. Even at high PANI contents, if the alkaline type of hardener is used as a curing agent, the composites show high resistivity and a low dielectric constant because alkaline types of hardener de-dope the PANI salt.

On the other hand, when the composites are prepared by using the anhydride type of hardener and acidic curing agent, they maintained the doping state of the PANI salt, which lead to a low resistivity and much greater dielectric constant. By adopting the process of in situ polymerization, aniline is polymerized and simultaneously deposited on the surface of the polyamide (PI).

electrospin nanofibre membranes, and the deposition time varied from 0 to 24 h [70]. SEM images of PANI-coated electrospin nanofibre membranes are shown in Fig. 10. Subsequently, the PANI-deposited nanofibre membrane surfaces are washed using HCl solution to remove oligomers, unreacted monomers, which are loosely bound with the fibres. Last, the nanofibre membranes are washed with deionized water a number of times and dried at room temperature. The results show that a minimum of 2 h of in situ polymerization is necessary for the PANI-PI membrane to become electrically conductive. As reaction time increases, the electrical conductivity also increased because of the increased quantity of PANI that is deposited on the surface of the PI nanofibers. Passages of electrons through the composite fibre membrane are facilitated with increasing PANI density, which results in a steady growth of electrical conductivity. In another case, PANI is grafted via in situ polymerization of aniline on the surface of crosslinked chitosan films in the presence of the APS oxidant [71]. Aniline polymerization is accomplished in two different acidic media, namely, 1 M HCl and 1 M H_2SO_4 , and these two acids (1 M HCl and 1 M H_2SO_4) doped the polymer film for different durations of time. Further details on the electrical characterization results of all these composite films are illustrated in Table 1 which is adapted from the Sayhi et.al [70]. Electrical conductivity values of chitosan increase as the percentage of grafting increases and decrease with increasing the crosslinking density due to reduced penetration of the aniline monomer inside the polymer matrix.

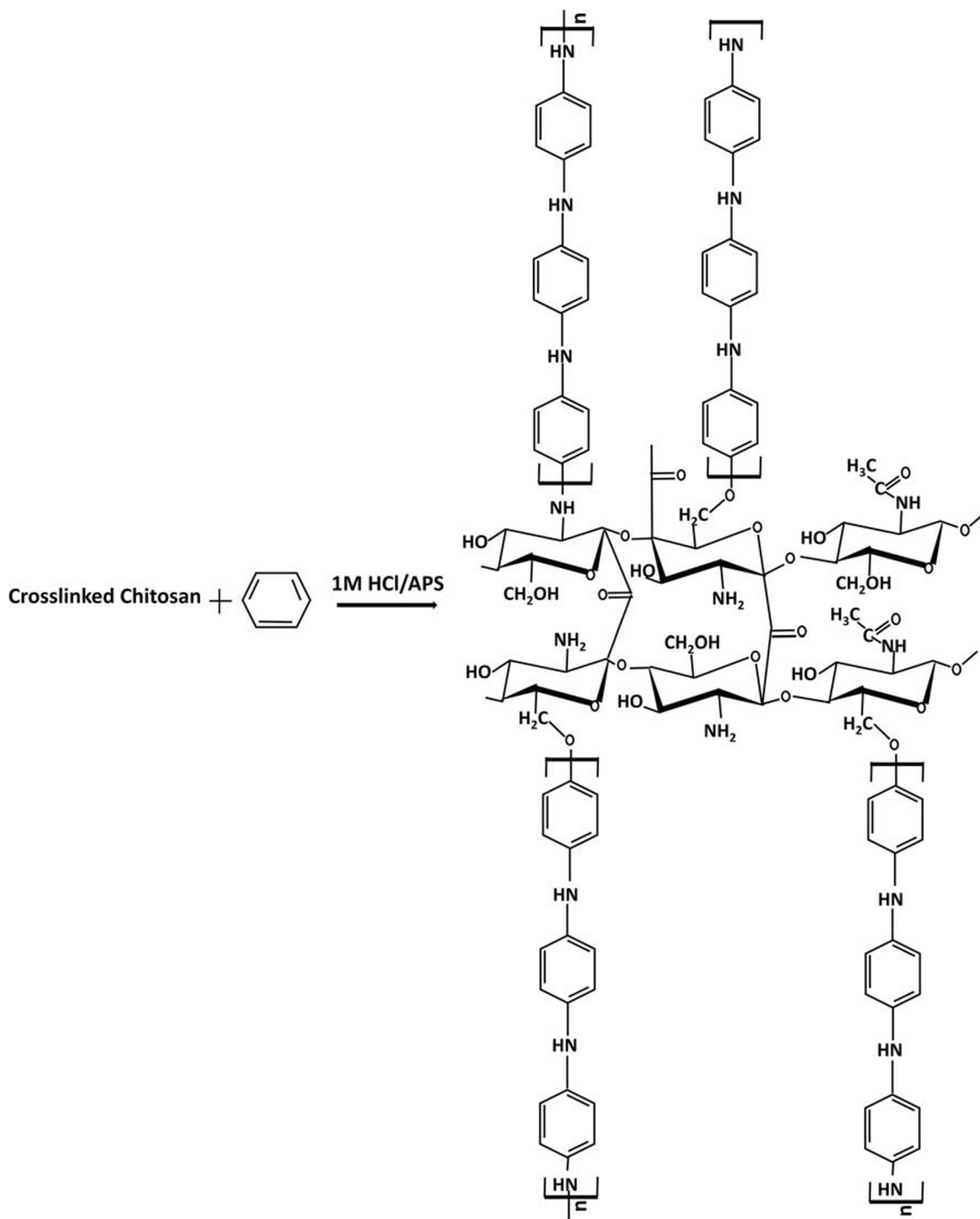
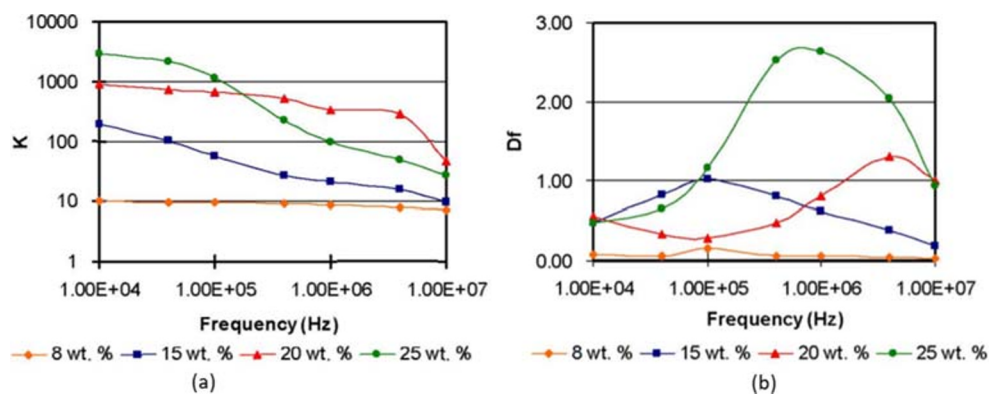


Fig. 8 Mechanism of grafting of PANI with crosslinked chitosan [41]

Between both widely used preparation methods for thermosetting blends, namely, solution casting and in situ polymerization, the latter one leads to higher conductivity with the same quantity of conducting filler. Soares et al. performed a systematic study on both solution casting or physical mixing and in situ polymerization preparation methods to synthesize epoxy resin/polyaniline- 4-dodecylbenzenesulfonic acid (ER/PANI-DBSA) blends [72]. The strategy adopted for the

physical mixing process is the physical mixing of a variable amount of PANI-DBSA powder and then dispersal in epoxy resin (ER) using a mortar and pestle. For the in situ polymerization method, fixed concentrations of ER are dissolved in chloroform, and different amounts of aniline (between 0.87 and 18.7 g) and DBSA are used. The percolation curve shown in Fig. 11 depicts the effect of the polyaniline- 4-dodecylbenzenesulfonic acid (PANI-DBSA) content on the

Fig. 9 Frequency dependence of the (a) dielectric constant (K) and (b) dielectric loss (Df) of in situ PANI/epoxy blends with various contents of PAN [69]



electrical conductivity of the ER/PANI-DBSA networks prepared by both preparation methods. From this plot, it is clearly seen that a sharp insulator–conductor transition ensued in the percolation of blends prepared by the in situ polymerization method at a very low PANI content.

However, the percolation curve for the blend synthesized by the physical mixing method has a gradual percolation region that is approximately 30% PANI. The electrical conductivity value reached using the ISP system is approximately $5.15 \times 10^{-2} \text{ Scm}^{-1}$ whereas by PM method highest conductivity value achieved is approximately $8.85 \times 10^{-4} \text{ Scm}^{-1}$. The conductivity parameters are also significantly higher than that of the ER-PANI system synthesized by the in situ

polymerization method and doped with CSA [39]. From these results, it can be concluded that DBSA-doped PANI blends could lead to higher conductivity compared with CSA-doped PANI blends. From the percolation curve, the threshold points of PANI concentration are found to be 10 wt% and 2 wt% for the ER/PANI-DBSA blends synthesized by physical mixing and in situ polymerization methods, respectively. The low percolation threshold value found for the ER/PANI-DBSA blend synthesized by the in situ polymerization method is attributed to the formation of more orientated networks chains, which led to an effective conducting pathway with less conducting filler. Figure 12 describes the SEM micrograph

Fig. 10 SEM micrograph of (a) highly aligned electrospun PI nanofibre membrane, (b) surface-treated PI nanofibre membrane, (c) PANI deposited on the aligned PI nanofibre membranes prepared by FeCl_3 oxidization polymerization for 12 h and (d) the as prepared neat PANI powder [70]

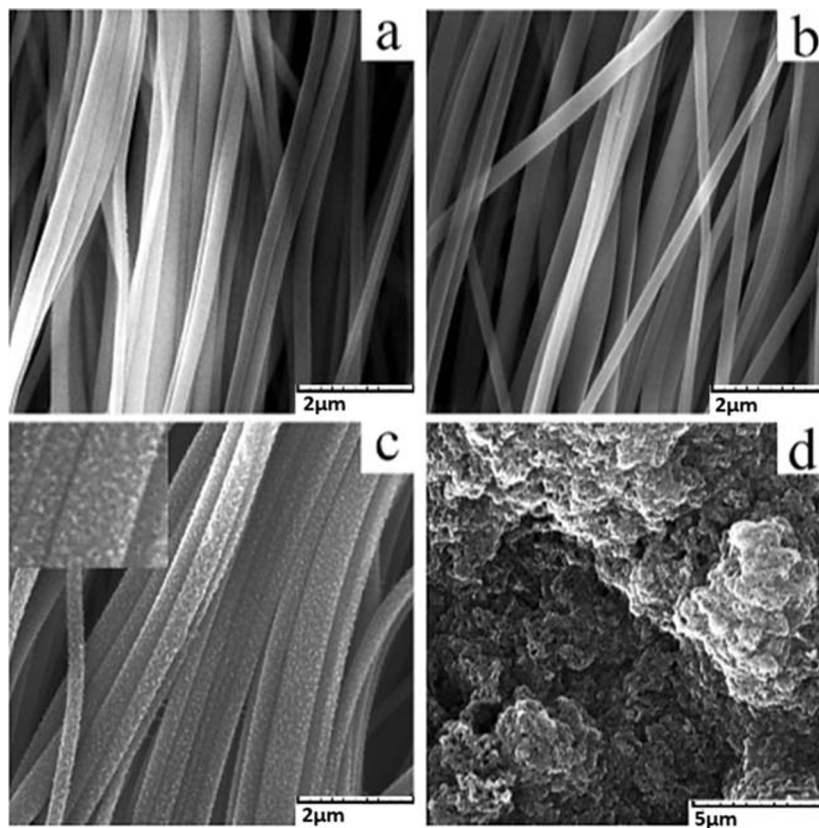


Table 1 Surface conductivity of graft polymer doped with 1 M HCl for different time intervals [71]

Sample code	Surface conductivity(S/cm ²)									
	HCL medium					H ₂ SO ₄				
	0 h	2 h	4 h	6 h	24 h	0 h	2 h	4 h	6 h	24 h
C ₂₅ P _{0.1}	4.86 × 10 ⁻¹¹	5.05 × 10 ⁻³	6.57 × 10 ⁻³	7.92 × 10 ⁻¹	8.69 × 10 ⁻³	3.17 × 10 ⁻¹¹	4.63 × 10 ⁻⁴	5.51 × 10 ⁻⁴	6.31 × 10 ⁻⁴	7.17 × 10 ⁻⁴
C ₂₅ P _{0.25}	2.5 × 10 ⁻¹¹	8.79 × 10 ⁻³	9.57 × 10 ⁻³	1.28 × 10 ⁻²	1.49 × 10 ⁻²	2.56 × 10 ⁻¹¹	1.18 × 10 ⁻³	1.20 × 10 ⁻³	6.82 × 10 ⁻⁴	2.05 × 10 ⁻³
C ₂₅ P _{0.5}	1.72 × 10 ⁻¹¹	1.06 × 10 ⁻²	2.38 × 10 ⁻²	2.85 × 10 ⁻²	3.53 × 10 ⁻²	1.79 × 10 ⁻¹¹	3.10 × 10 ⁻⁴	5.65 × 10 ⁻³	7.08 × 10 ⁻³	9.69 × 10 ⁻³
C ₅₀ P _{0.1}	2.74 × 10 ⁻¹¹	1.13 × 10 ⁻³	1.53 × 10 ⁻³	4.45 × 10 ⁻³	–	2.24 × 10 ⁻¹¹	4.65 × 10 ⁻⁴	6.11 × 10 ⁻⁴	6.62 × 10 ⁻⁴	8.95 × 10 ⁻⁴
C ₅₀ P _{0.25}	3.03 × 10 ⁻¹¹	1.05 × 10 ⁻³	9.87 × 10 ⁻³	1.14 × 10 ⁻²	–	3.33 × 10 ⁻¹¹	5.07 × 10 ⁻⁴	7.47 × 10 ⁻⁴	9.12 × 10 ⁻⁴	1.12 × 10 ⁻³
C ₅₀ P _{0.5}	2.04 × 10 ⁻¹¹	4.55 × 10 ⁻³	6.71 × 10 ⁻³	7.90 × 10 ⁻³	–	2.14 × 10 ⁻¹¹	8.81 × 10 ⁻⁴	1.22 × 10 ⁻³	5.07 × 10 ⁻⁴	7.83 × 10 ⁻³
C ₇₀ P _{0.1}	1.68 × 10 ⁻¹¹	–	–	–	–	1.73 × 10 ⁻¹¹	–	4.81 × 10 ⁻⁴	5.49 × 10 ⁻⁴	7.05 × 10 ⁻⁴

*Subscript C stands for dose, and subscript P stands for aniline concentration

of both the physical method and in situ method for the ER/PANI-DBSA blends.

Table 2 summarizes the results for the mechanical and electrical properties prepared by both methods [39]. For both methods, an increase in the PANI-DBSA content decreases the load required to break and the elongation at the break because PANI-DBSA introduces some faults in the bulk polymer network as predicted. However, because the in situ polymerization method leads to a more homogeneous distribution of PANI within the matrix, the shearing strength is increased, whereas the physical method causes PANI agglomeration, and thus, causes a failure during fracture.

Preparation methods of ternary systems

In recent decades, research interest on ternary PANI thermoset composites has dramatically increased. A large number of scientific reports on incorporating both organic and inorganic particles with excellent physical or chemical properties in PANI-thermoset blends has been published. Ternary blend preparation methods can be categorized into four different types: physical blending, surface initiated polymerization

(SIP), thermoresponsive organic composite from sterically stabilized PANI dispersion and lastly multi-branched PANI ternary composite. A brief description of these preparation methods is provided below. Physical blending is the simplest approach [10]. In this methodology, the composites are prepared by directly mixing all three ingredients. To improve the mixing, a solvent is generally used, which is followed by ultrasonic agitation to assist in the dispersion of all components. The epoxy/PANI blend is prepared by incorporating short carbon fibres (SCFs), and the resultant blend has enhanced electrical and (Fig. 13).

The surface initiated polymerization (SIP) technique is used to synthesize epoxy nanocomposites reinforced using magnetic nanoparticle (magnetite (f-Fe₃O₄) nanoparticles (NPs)) functionalized with PANI [73]. The formation of polymer nanocomposite is initiated by the amine functional group available in the (polyaniline- magnetite) PANI-f-Fe₃O₄ NPs, which undergo a copolymerization process within epoxy resin matrix as illustrated in Fig. 14.

Dynamic mechanical analysis (DMA) characterization results for polymer nanocomposites indicated an increase in the stiffness of the polymer chains. The DMA also showed a shift of T_g by 7 °C after adding the functionalized Fe₃O₄ NPs compared to that of the cured pure epoxy resin. A number of works have used the SIP method to enhance the mechanical properties (tensile strength) of polyaniline-epoxy (PANI-epoxy) and polyaniline- polyurethane/epoxy (PANI-PU/epoxy) graft interpenetrating polymer network (IPN) [74].

Nanocomposites have been loaded with functionalized silica, carbonyl iron, zinc oxide and barium ferrite [2, 73–75] nanoparticles, and Jlassi et al. recently prepared a clay/PANI-epoxy nanocomposite using the SIP method [76].

The clay materials used are bentonite-DPA/polyaniline (B-DPA/PANI) synthesized using ISP method with aniline in the presence of 4-diphenylamine diazonium (DPA)-modified bentonite (B-DPA), which produces a highly exfoliated clay as shown in Fig. 15. The contribution of the NH- group to the

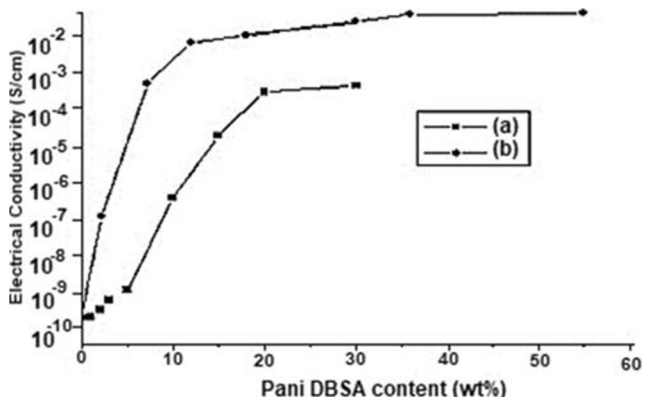


Fig. 11 Comparison of the effect of the PANI-DBSA content on the electrical conductivity of the ER/PANI-DBSA networks prepared by the two different methods [39]

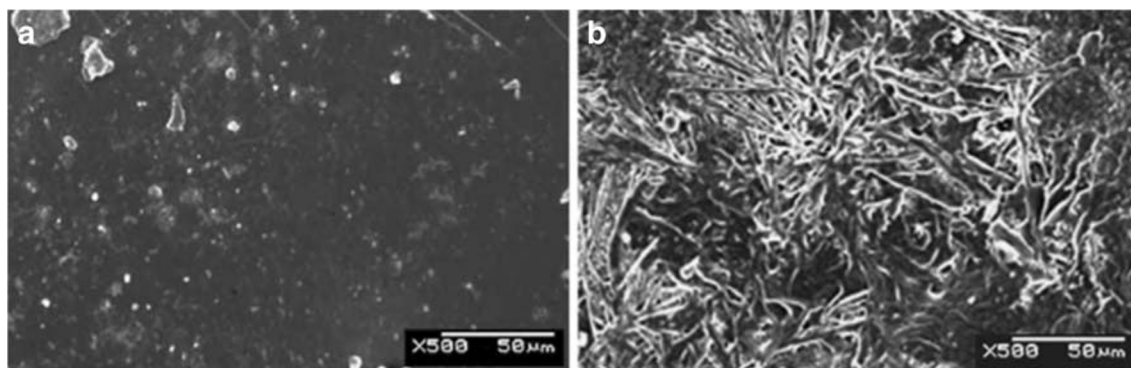


Fig. 12 SEM micrograph of the ER/PANI-DBSA blends obtained by (a) physical mixing method (b) in situ polymerization method [39]

exfoliated clay comes from either DPA or PANI, which form a covalent bond to attach with the epoxy by the ring opening process. Incorporating only a small quantity (0.1 and 0.5 wt%) of B-DPA/PANI nanofiller leads to a more than 200% enhancement in fracture toughness and approximately 100% increase in the dielectric conductivity from 10^{-8} S/cm to 10^{-3} S/cm. Few reports on the electrical properties of the ternary thermosetting composites have been found in the literature, which is likely related to the relatively low electrical conductivity associated with the use of the amine curing agent for crosslinking the epoxy resin. Recently, Kalasad et al. reported the synthesis of a 3D hierarchical multiscale structure using polyaniline-cellulose nano whiskers/natural rubber (NR) (PANI-CNs/NR) nanocomposites [75]. In this work, the surface of the CNs is used as a biotemplate to polymerize aniline by the ISP method to form polyaniline-cellulose nano whiskers (PANI-CNs) nanohybrids with a uniform dispersion (Fig. 16).

Finally, NR latex is introduced in the PANI-CNs suspension followed by curing process. In addition, through the coagulation process of the system, the interstitial space between the microspheres of NR latex is selectively filled with the PANI-CNs nanohybrid, this leads to the formation of 3D hierarchical multiscale conductive assembly. Electrical property study indicates that the PANI-CNs/NR nanocomposites exhibits lower percolation threshold (3.8 phr, 3.6 vol%) in electrical conductivity as compared to the polyaniline/natural

rubber PANI/NR composites (8.8 phr, 8.0 vol%). Additionally, a large difference is observed in the value of conductivity with the same loading % for the two systems. The difference in electrical conductivity is 11 orders of magnitude for the same loading fractions of conducting fillers. The reason behind this enhancement of conductivity has been associated with the biotemplate effect. Where, CNs acts as biotemplate for the formation of 3D hierarchical multiscale conductive assembly in the NR matrix [75]. Gao et al. has reported that anticorrosive activity can be increased considerably by using thermoresponsive PANI/NPs as additives to PANI-epoxy composites [5]. By adopting the oxidative polymerization process, aniline is polymerized in aqueous medium containing thermoresponsive poly(vinyl alcohol) conjugated with 2-isobutyramidepropanoate moieties (PVA-AI). In this system PVA-AI is used as the dispersing agent to produce a stable dispersion of PANI/NPs in the epoxy matrix. Anticorrosion efficiency of the film made of polyaniline nanoparticles-poly(vinyl alcohol)-2-isobutyramidepropanoate moieties (PANI/NPs-PVA-AI) epoxy composite in aggressive NaCl solution is superior to that of the polyaniline nanoparticles-poly(vinyl alcohol) (PANI/NPs-PVA) epoxy films. The reason behind such improved behaviour of PANI/NPs-PVA-AI is the presence thermoresponsive characteristics of PVA-AI. When the temperature is below the cloud point the hybrid additives are hydrophilic in nature; however, they are hydrophobic when the temperature is above the cloud point or when

Table 2 Adhesive strength of the epoxy cured with anhydride as a function of the PANI-DBSA content and the blend preparation procedure [39]

Adhesive	Preparation procedure	Load required to break (N)	Deformation (%)	Conductivity(S/cm)
ER		1300 ± 72	7.2 ± 0.2	$(2.7 \pm 0.2) \times 10^{-10}$
ER/PAni.DBSA(7%)	Physical mixing	900 ± 40	6.0 ± 0.1	$(2.7 \pm 0.2) \times 10^{-8}$
ER/PAni.DBSA(7%)	In situ polymerization	1000 ± 60	6.9 ± 0.5	$(6.1 \pm 0.6) \times 10^{-4}$
ER/PAni.DBSA(18%)	Physical mixing	780 ± 25	6.2 ± 0.2	$(7.0 \pm 0.2) \times 10^{-5}$
ER/PAni.DBSA(18%)	In situ polymerization	930 ± 18	5.4 ± 0.2	$(1.2 \pm 0.2) \times 10^{-2}$

*The adhesive strength measurements are performed in steel plates of 120 mm × 25 mm and a thickness of 1.8 mm

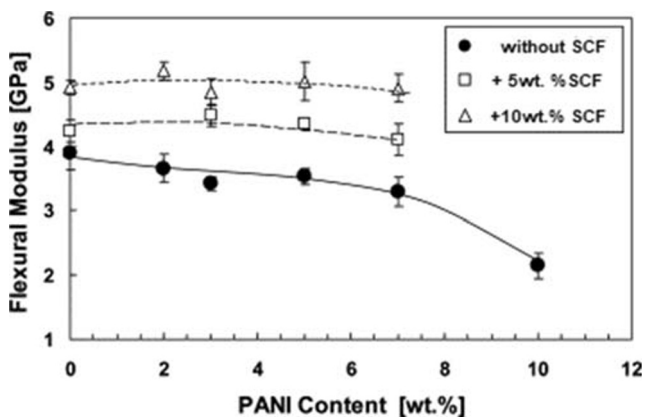


Fig. 13 Influence of SCF on the flexural properties of the EP/PANI-SCF blend. [10]

the presence of inorganic salt, like NaCl, causes dehydration of water that surrounds PVA-Al molecules. Such hydrophobic effect which is triggered by salt will limit the accessibility of water molecules from the PVA-Al metal interface and ultimately enhance the anticorrosion ability. Another ternary composite is synthesized by using multi-branched PANI (MSiPA), multi-walled carbon nanotube (MWCNT) and epoxy in three successive steps [9]. In the first step, synthesis of the multi-branched polyaniline is carried out in another three substeps, they are firstly synthesis of substituted PANI, secondly ring-open reaction between PANI and (3-glycidioxypropyl)trimethoxysilane, and lastly controlled hydrolysis of PANI that contain silane PA-K to give MSiPA. Lastly followed by the final step of mixing the two components, namely, PANI and MWCNT, by the blending method.

Fig. 14 Scheme of the polymer nanocomposite formation mechanism [2]

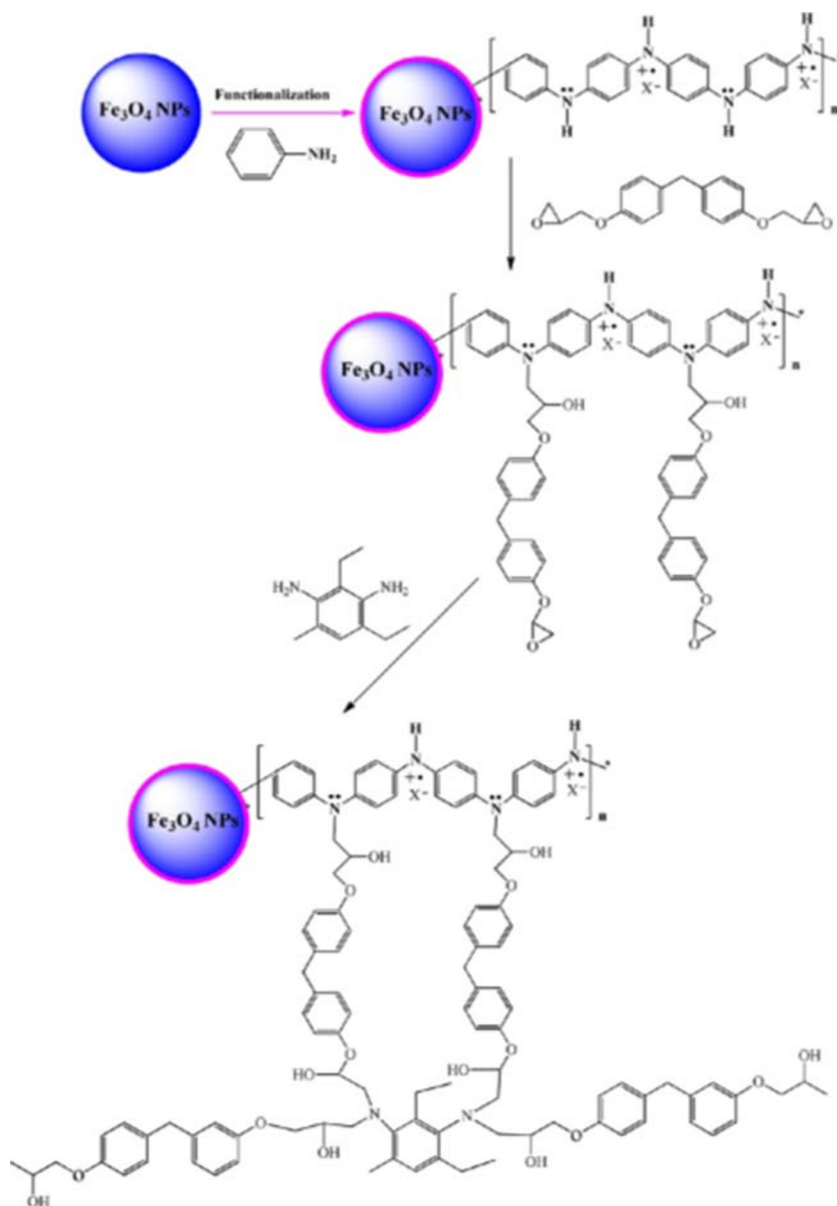
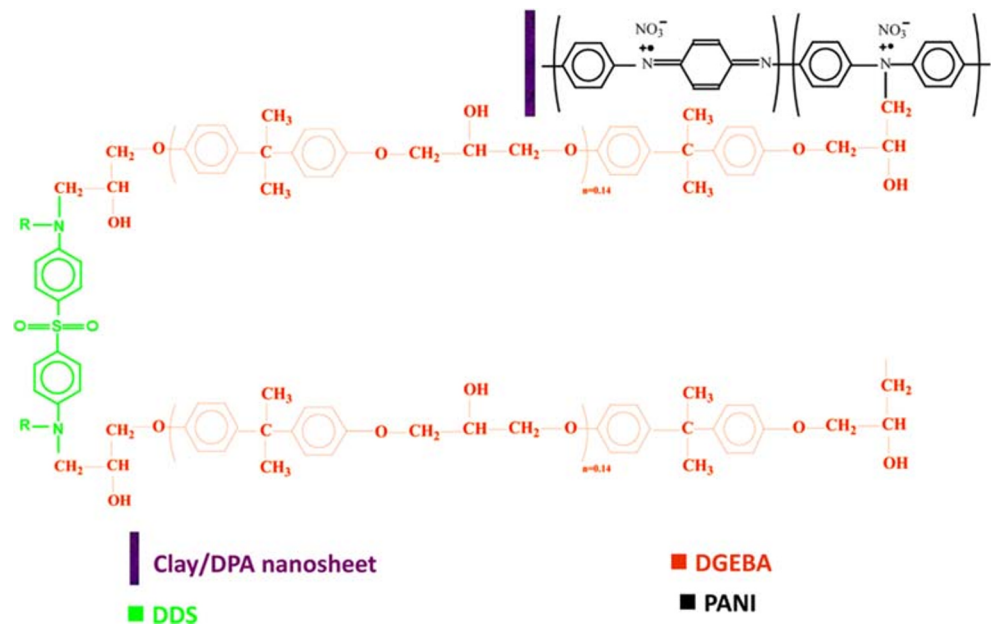


Fig. 15 Scheme illustrating the molecular interaction between epoxy and bentonite- DPA/ polyaniline [12]



The ternary composite is finally achieved by physical blending the polyaniline-multi-walled carbon nanotube (PANI-MWCNT) with the epoxy resin.

The solution blending method is one of the most widely adopted method for preparing all types of polymer blends. The advantage of this method is the control of quality and quantity of PANI molecules in the blend and easy preparation method. However, in this technique due to lack of good interaction between the constituents the electrical and mechanical

properties are often compromised. Whereas, insitu method involves many complicated steps and techniques. Moreover, it is difficult to know yield of PANI content after polymerization within the blend and composite. At the same time unreacted monomers, oligomers and other chemical cannot be removed from the system. The advantage of this method is that because of presence of good crosslinking between all the components of the system electrical and mechanical properties resultant material are generally more pronounced.

CNs supported PANI

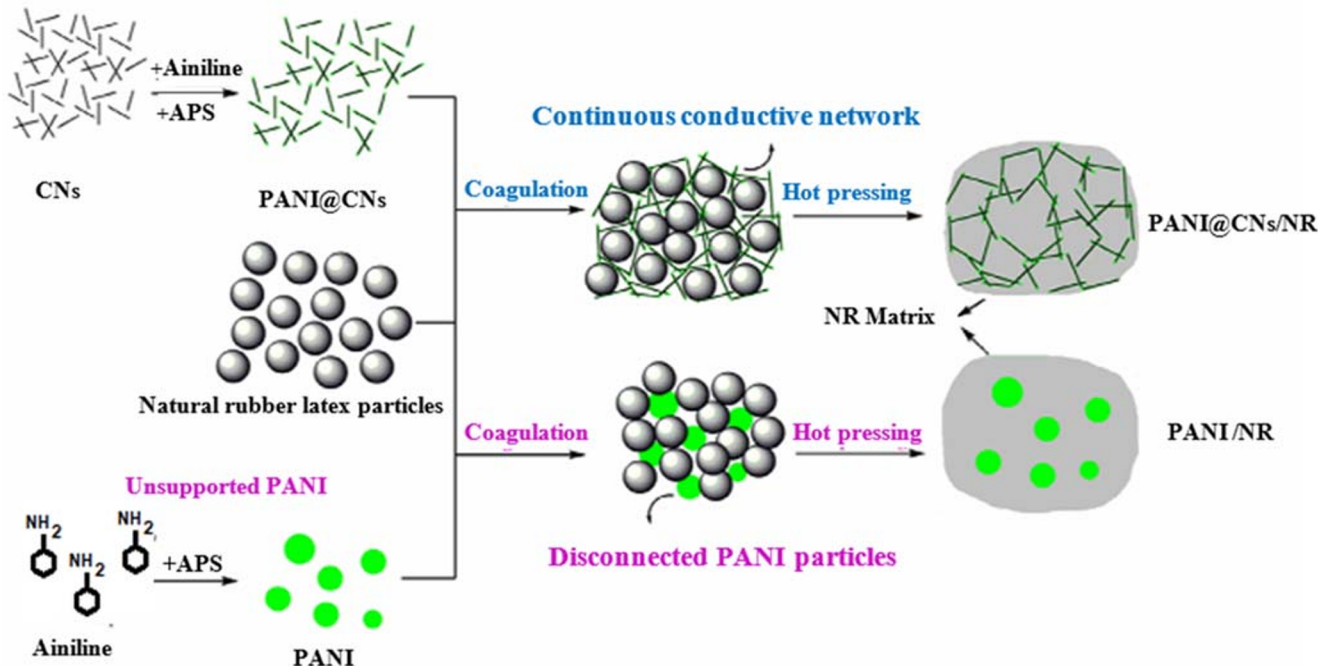


Fig. 16 Schematic illustration for the preparation of PANI-CNs/NR nanocomposites with a 3D hierarchical multiscale structure [6]

Table 3 Examples of some binary and ternary system

Type of system	Polymer matrix	Additive/dopant	Preparation method	Conductivity S/cm	Reference
Binary system	Epoxy resin	HCL	Physical mixing	10^{-14} – 10^{-4}	[62]
	polyurethane	H ₂ SO ₄	Physical mixing	10^{-12} – 10^{-7}	[72]
	chitosan	HCl and 1 M H ₂ SO ₄	Insitu polymerization	10^{-10} – 10^{-2}	[41]
	Epoxy resin	CSA	Insitu polymerization	10^{-7} – 10^{-6}	[38]
Ternary system	Epoxy resin	Fe ₃ O ₄ / PTSA	Insitu polymerization	–	[2]
	Bisphenol F epoxy resin	Short carbon fibers /DBSA	Physical mixing	10^{-14} – 10^{-4}	[10]
	Polyamide	N,N -Bis(4 -aminophenyl)-1,4-quinonenediimine	Surface initiated polymerization	–	[53]
	Poly(vinyl alcohol)	2-isobutyramidepropanoate moieties/ HCl	Thermoresponsive organic composite from sterically stabilized PANI dispersion	–	[6]
	Epoxy	MWCNT/ <i>o</i> -Toluidine, <i>m</i> -aminobenzenesulfonic	Multi-branched PANI ternary composite	10^{-8} – 10^{-3}	[9]

Table 3 summarizes some examples of material development and methods of binary and ternary system.

Application of PANI-thermoset blend and composites

Lightning damage suppression

For lightning damage suppression application carbon fibre-reinforced polymer (CFRP) based composites are mostly utilized. CFRP broadly utilized in huge constructions, for instance aircraft structures, automobiles and wind turbine blades, to increase fuel efficiency and diminish weight, emissions and maintenance expenses due to their eminent mechanical and corrosion/fatigue resistance properties [76, 77]. A comparative study on effectiveness of shielding between carbon fiber/polyaniline (CF/PANI) and carbon fiber/epoxy (CF/Epoxy) is summarized in Fig. 17 [78]. Generally, CFRP is composed of insulating polymers and carbon fibres, with

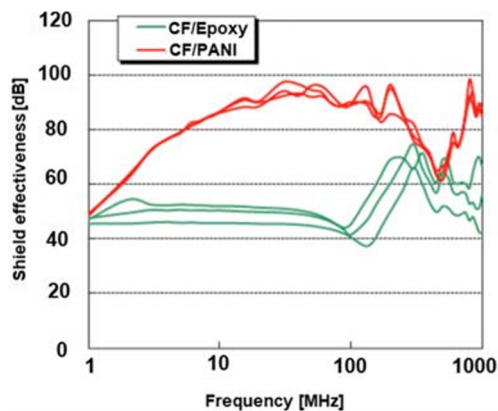
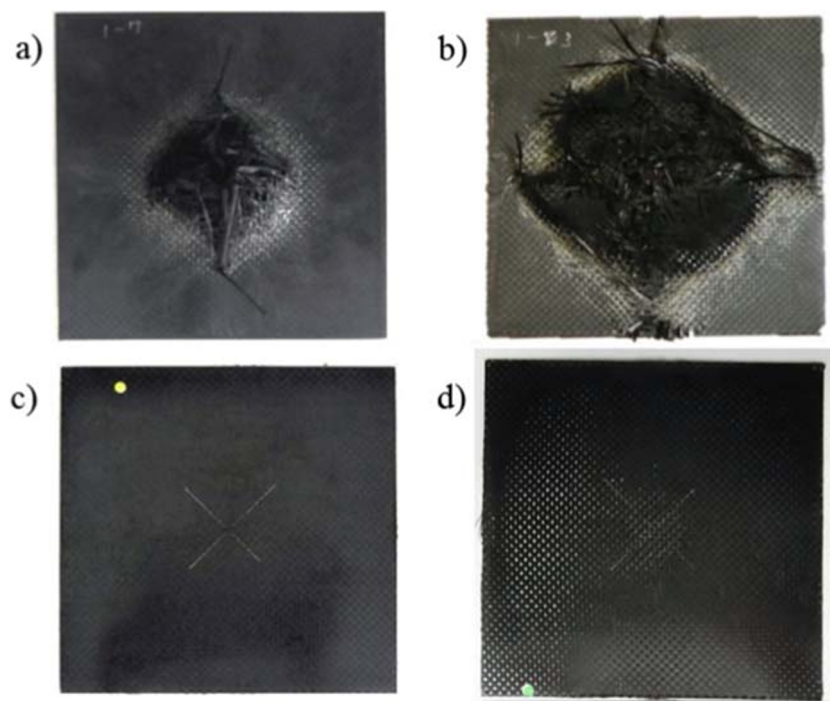


Fig. 17 Comparison of the electromagnetic shielding effectiveness between CF/PANI and CF/Epoxy [78]

essential characteristics, that includes low electrical conductivity, nonuniform and anisotropic electrical properties when it is compared to the classical metallic type of materials, which require a consideration of the risk of lightning striking the composite structure.

Lightning initiates serious harm to CFRP from complex electrical currents, acoustic shock and thermal decay of the polymer [77, 79–83]. The typical damage incurred by applying a simulated lightning current is shown in Fig. 18. The CF/epoxy laminate tested both at –40 kA and at –100 kA shows damage that consists of broken fibres. However, in the case of the CF/PANI laminate, the specimens tested at both –40 and –100 kA barely show any damage. Therefore, to satisfy safety conditions, it is important to utilize a lightning strike protection (LSP) system (e.g., metallic cross sections) on the composite structure to allow both electromagnetic interference (EMI) and currents to move over the inclusive structure safely [74]. However, one disadvantage of the LSP system is that it increases manufacturing costs as well as the total structural weight; moreover, lightning strike damage cannot be entirely eliminated [74]. Therefore, to provide sufficient lightning damage resistance and ameliorate the electrical conductivity of CFRP, an alternative approach to LSP is applied by substituting the insulating matrix resin with a conductive polymer [84–88]. The CFRP is prepared by mixing a carbon fibre with an extremely conductive thermosetting composite system that included PANI as a conductive polymer filler, divinylbenzene (DVB) as a crosslinking polymer and dodecyl-benzenesulfonic acid (DBSA) as a dopant [89, 90]. The anticipated polymer system shows ideal properties as a matrix in a CFRP to improve electrical properties and manufacturability [74]. Recently, polyaniline (PANI) and its derivatives have become one of the most-frequently studied classes of conductive polymers [74] because of their high conductivity, low-cost manufacturing processes, easy synthesis and good environmental stability.

Fig. 18 Specimen damage after simulated lightning current tests: a) CF/epoxy -40 kA (E-1), b) CF/epoxy -100 kA (E-3), c) CF/PANI -40 kA (P-1), and d) CF/PANI -100 kA (P-3) [74]



Conductive adhesives

Generally, an electrically conductive adhesive system (ECA) is prepared by dispersing metallic fillers (e.g., carbon black) within a polymeric matrix. Therefore, it is commonly utilized in several application fields, such as the medical electronics, optical, aerospace and automotive industries [27]. Although to obtain ECA system with high conductivity level a large quantity of metallic filler (60–90 wt%) with good electrical conductivity is required [27], because the majority of these fillers are protected by an insulating oxide layer coating, which reduces the effective conductivity [51]. At the same time thermal cycling, carbon black-based adhesives system undergo insufficient stability of its electrical conductivity. Therefore, to prepare ECA system with good and stable mechanical and electrical characteristics, PANI-thermoset based composites are trending to compete with the above overall approaches [27, 39]. Recently, an interesting approach in which polyaniline is blended with epoxy resin can provide conductive coatings with high conductivity values and decent adhesive properties, which is partially associated with PANI's ability to be converted reversibly into an insulating or conducting form over a simple deprotonation-protonation of the polymer. In this approach in situ polymerization method is used to prepare the blend. The authors claimed that, it has superior adhesion property and higher electrical conductivity for the epoxy/PANI system when compared to the physical mixing technique [39].

Anticorrosion

Electrically conductive polymers have been shown to be capable materials for anti-corrosion purposes, and their practical applications have improved the processability of conductive polymers [51]. Polyaniline (PANI) has been found to be very efficient at protecting metals from corrosion, including steel, aluminium, magnesium and their alloys [91]. Furthermore, it has been confirmed with both standard corrosion testing and surface analytical methods along with electrochemical methods [91] that PANI coatings have corrosion resistance ability; therefore, it can spread to scratched areas where the bare steel surface is exposed to an aggressive environment [51]. Additionally, solutions of undoped PANI are utilized to solve problems in coating development due to the use of conducting emeraldine salt with poor solubility [92]. Recently, electrically conductive epoxy coatings based on conductive PANI (< 2.0 w/w%) are produced for anti-corrosion applications [91]. Therefore, to improve the environmental stability of coatings, the effective polyaniline containing primer has been top coated with polyurethane or epoxy [91]. Generally, corrosion protection mechanisms are interpreted as a shift of the electrochemical interface, anodic and barrier protection, and physical adsorption. However, the exact mechanism underlying the corrosion protection provided by polyaniline (PANI) is controversial the mechanism is dependent on many experimental conditions, e.g., type of coating, test methods, emeraldine

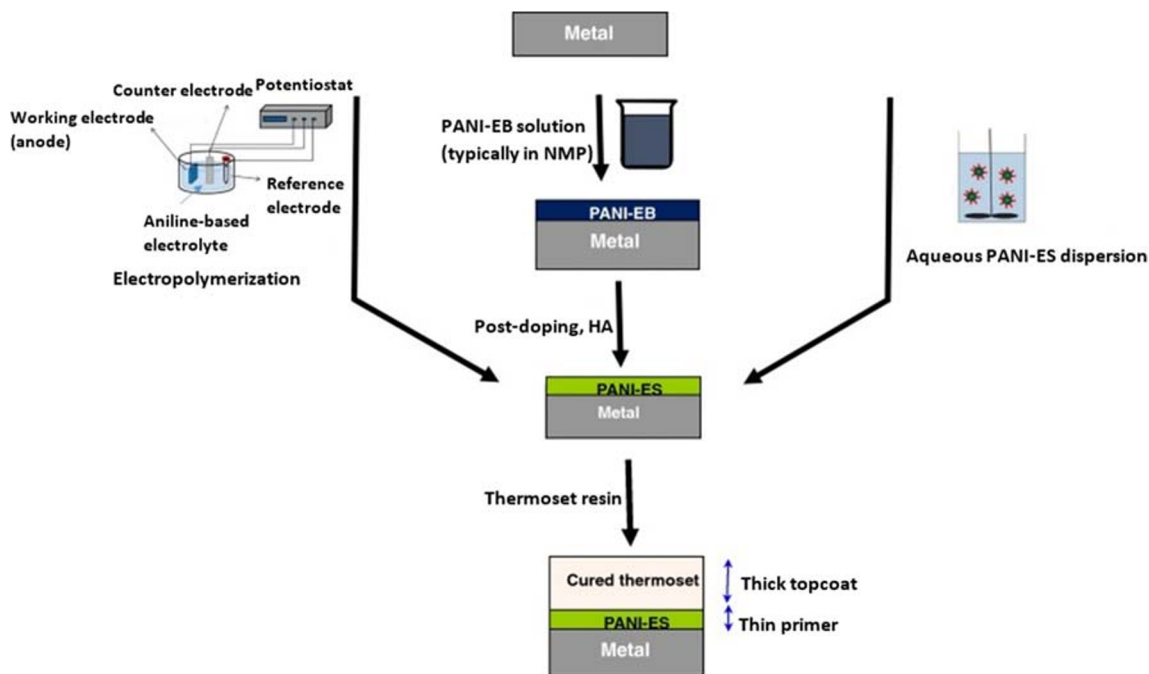


Fig. 19 Preparation of PANI/thermoset assemblies with anticorrosion properties

environment, etc. [93]. The first method for the preparation of anticorrosion coatings is proposed by Zhang et al., in which a coating of PANI nanofibres mixed with the self-healing epoxy microcapsules is included as an additive to the epoxy/polyamide composite. This system shows very high efficient protective anticorrosive coating when applied on mild steel [94]. In the second approach towards protective coatings application, a layer PANI is applied as a primer in the surface of PANI-thermoset stratified assembly. Figure 19 presents this second method and summarizes the core methods for processing PANI/thermoset stratified coatings with anticorrosion properties. Therefore, a layer of polyaniline-emeraldine salt (PANI-ES) as a primer is obtained either by electrochemical polymerization method or by deposition using solution casting technique in which, undoped polyaniline-emeraldine base (PANI-EB) coated and followed by doping process using an appropriate dopant [95]. Between the two methods, the PANI primer obtained by depositing PANI dispersed in water is an interesting environmentally friendly alternate method. Lately, long-chain alkyl phosphonic acid-stabilized colloidal polyaniline dispersive system are synthesized and coated on the steel substrate as a primer. In this system alkyl phosphonic acid (n-decylphosphonic acid, DPA) are seen to act both as a surfactant and as a corrosion-inhibitive dopant [96].

Metal ion removal

In previous decades, contamination of water via heavy metal ions has negatively impacted the environment. Rapid industrialization leads to production of different types of chemical and physical pollutants such as heavy metal, that are finally drained to nearby water bodies. Polluted water highly

Table 4 Langmuir and Freundlich isotherm parameters for cadmium and lead onto PANI grafted crosslinked chitosan at different temperature [97]

Mental ions	Isotherm model	Parameters	25 °C	35 °C	45 °C
Cadmium	Langmuir	Q _m (mg/g)	98.4	115	145
		b (l/mg)	0.02	0.05	0.07
		R ²	0.995	0.987	0.999
	Freundlich	n	2	3.2	3.4
		KF (mg/g)	2.3	3.9	4.6
		R ²	0.854	0.966	0.911
Lead	Langmuir	Q _m (mg/g)	92.9	103.5	114
		b (l/mg)	0.02	0.08	0.15
		R ²	0.999	0.986	0.993
	Freundlich	n	1	1.7	2.3
		KF (mg/g)	5.4	12.8	15.2
		R ²	0.885	0.926	0.942

concentrated with metals ions when disposed in water causes a health threat to the living organism because they are not biodegradable [97]. For instance, cadmium is produced via the mining, smelting, metal plating, battery and phosphate industries and causes health hazards, such as renal damage, tai-tai, hypertension, emphysema and testicular atrophy [98, 99]. In contrast, lead is used in the paint, battery, exhaust, insecticide, plastic, water pipe, food, and beverage industries and causes health hazards, essentially kidney and liver threat, abnormalities in pregnancy, anaemia, brain damage and infertility [100, 101]. Recently, PANI-grafted crosslinked chitosan are used in order to remove cadmium and lead ions from polluted water [97]. Table 4 summarizes the cadmium and lead adsorption mechanism using Langmuir and Freundlich isotherm parameters onto PANI-grafted crosslinked chitosan at different temperature. Amidst numerous adsorptive materials chitosan based materials has recognised to be an effective adsorbent because of its unique features, like non-toxicity, biocompatibility, antimicrobial activity, and low cost [97]. Furthermore, the efficiency of chitosan can remove metal ions at concentrations close to zero [102]. Chitosan is a derivative of N-deacetylation from chitin obtained from a naturally occurring polysaccharide in crustaceans, i.e., shrimp and crab, and fungal biomass [103]. In addition, the existence of amine and hydroxyl groups in the polymer backbone of chitosan gives it high binding capacity during adsorption processes. Firstly, during the preparation process crosslinking of chitosan beads are done by treating it with glutaraldehyde. The process is then, followed by grafting of crosslinked chitosan beads with PANI chains by the method of in situ polymerization. Generally, during metal-ion removal application using PANI-Chitosan system, the major contribution as a adsorption sites for metal ion comes from amine groups of chitosan, and on the other hand the function of the grafted PANI chains on the adsorption mechanism is not well understood [104].

Flame retardant conductive composites

Among different types of common flame retardant materials used, nitrogen based flame retardants are in abundant. There are two main ways by which nitrogen-based flame retardants works. Firstly by undergoing endothermic reactions that emits ammonia gases at high temperature and this dilutes the concentration of oxygen and other combustible gas content present and secondly by supporting the formation of carbonaceous char. Epoxy resins filled with PANI nanofillers has both these factors therefore it can be one of the good options as a flame retardant material. In case of PANI-epoxy composite, the presence of PANI can significantly reduce the heat release rate of epoxy resin and rise the char residue [63]. In epoxy PANI composite, PANI even acts as a curing agent for epoxy resin depending on the covalent bond formation between the amine groups of PANI and the epoxy resin [105].

Furthermore, the heat release rate is also found to be the function of PANI particle shape. The observation concludes that heat release rate of PANI nanospheres is higher than PANI nanofibres as shown in Fig. 20. This higher heat release rate is due to the bigger surface area of the nanofibres as compared to the nanospheres, this is because of the fact that higher number of amine groups present in PANI nanofibres can react with the epoxy resin. On the other hand, the heat release rate peak of epoxy resin reinforced with PANI-stabilized silica nanoparticles is seen to decrease intensely with increasing silica loadings. This indicate the fact that flame-retardant efficiency is also depend on the phosphoric-acid doped PANI [13].

Conclusions

This review paper provides an overview of studies on the synthesis and applications of PANI thermoset blends and composites. This analysis showed that a number of studies have been performed to improve the homogenous dispersion of conducting fillers in thermoset polymer matrix resin. However, both the blending mechanism and blending process of PANI with thermoset polymer are complex because a large number of factors influence and play important role in the morphology and intrinsic properties of PANI thermoset composites. Moreover, small changes in a processing parameter may affect the composite properties. The paper summarized several of these parameters and some of the specific approaches that greatly enhance the dispersion of the conducting form of PANI and improved the electrical and mechanical properties off the composite. The structure and surface morphology of the conducting fillers and the type of dopant, curing process and processing method are among the factors that played a pivotal role in blend formation. The dispersion of

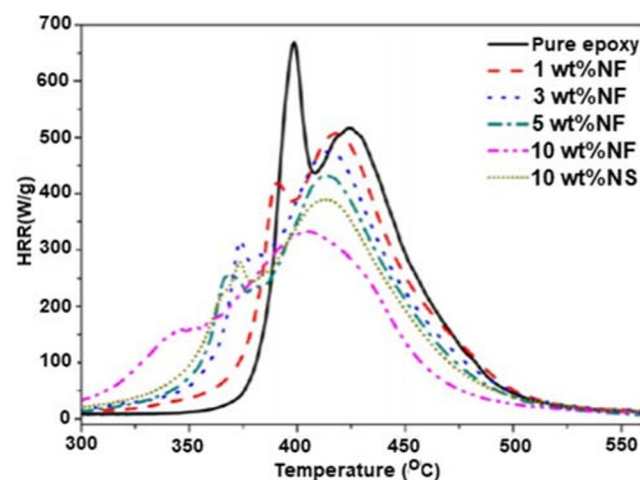


Fig. 20 Peak heat release rate (HRR) – temperature curves of the cured pure epoxy and its PNCs with PANI nanofibres and nanospheres [63]

substituted PANIs or short-chain PANI has superior solubility compared with PANI and higher molecular weight PANI. Another approach to increasing dispersibility is the use of dopants that could increase solubilization by inducing counter ions or through the use of a reactive dopant. The main rule of thumb for the curing condition is to choose the correct ratio of curing agent to thermoset resin and in some cases using PANI itself as a co-curing agent. Another approach is to use an active solvent, such as specific amine hardeners, as a solvent for the epoxy thermoset, or by conducting an absorption transferring process. Furthermore, PANI EB composite films undergo post-doping and curing in an acidic medium that produce to highly conducting polymer composite films. Although a number of advancements have been achieved in the field of PANI thermoset blends and composites, much more elaborate work must be performed to identify all the factors that determine the nature and properties of thermoset composites. Furthermore, recently emerging PANI-based ternary composites could represent promising multifunctional advanced materials for a broad range of potential applications in different electronics fields. Among the various approaches for preparing ternary blends, surface initiated polymerization (SIP) is considered to be the most convenient methodology. By adopting the SIP method, aniline is polymerized within nanofillers, such as clay, MWCNT, and graphene, as a template. The result is a highly conductive polymer composite with a significantly low percolation threshold. Such composites have superior mechanical properties due to the low PANI content.

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