

Preparation/Processing of Polymer–Carbon Composites by Different Techniques



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Abstract In this chapter, the discussion has been made on some important methodologies to prepare polymer/carbon composites. These procedures are solution mixing technique, melt mixing technique, in situ polymerization technique, dry mixing technique, powder mixing technique, and aqueous mixing technique. Solution mixing has been categorized into evaporative casting, vacuum filtration, 3D printing, and wet spinning. In the melt mixing process, the discussion has been focused on melt blending through internal mixer and melt spinning. Some diagrams have been drawn and discussed for better understanding of the composite preparation processes. The advantages and disadvantages associated with the composite preparation processes are mentioned herein where necessary.

Keywords Polymer/carbon composites · Composite processing
Solution mixing · Melt mixing · In situ polymerization · Dry mixing
Powder mixing · Aqueous mixing

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1 Processing of Conducting Composite Materials

Different processing methods have been employed to fabricate various forms of composite materials such as freestanding films, fibers, buckypapers, and printed patterns. Commonly used methods for preparing these composite materials include solution processing, melt mixing, in situ polymerization process, etc. [1–3].

1.1 Composites by Solution Processing

Solution mixing process is an important method for preparing polymer–carbon composite materials in both organic solvents and water [4–6]. In general, this method requires the carbons to be efficiently dispersed in a solvent that can dissolve the polymer. Then both components are mixed by magnetic/mechanical stirring or sonication [2, 3, 7]. Different types of solution processing have been used to produce composite materials including evaporative casting, vacuum filtration, fiber spinning, and printing. These process techniques involve the two important steps: initially dispersing carbons in the polymer matrix and then removal of solvent or dispersant from the mixture (Fig. 1).

1.1.1 Evaporative Casting

In the evaporative casting method, the carbons are dispersed in a solvent with or without dispersants, such as polymers, biopolymers, and surfactants. The dispersion

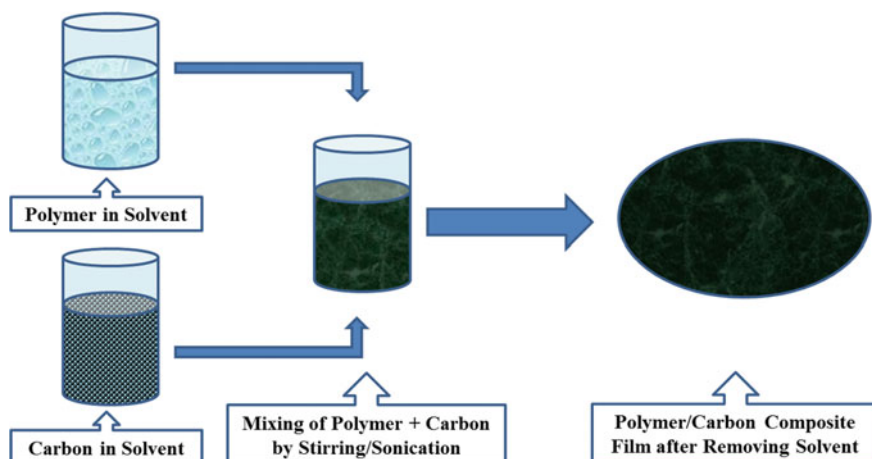


Fig. 1 Flowchart representing the steps of solution processing for preparing polymer–carbon composites

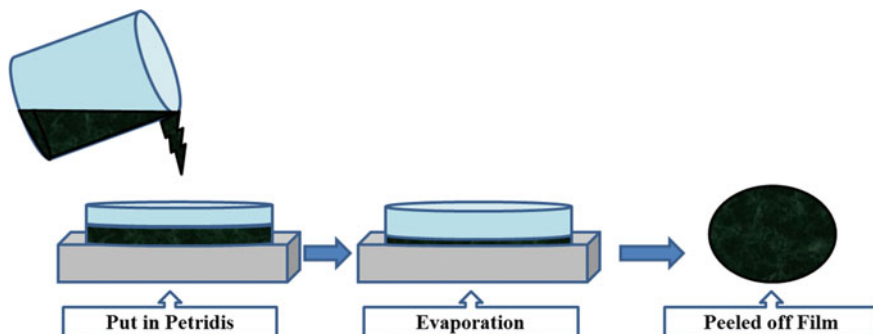


Fig. 2 Schematic of evaporative casting process in order to form freestanding composite film

is then transferred into a mold and the solvent is evaporated in a controlled manner, resulting in the formation of a composite film (Fig. 2) [8, 9]. These films may be either freestanding or attached to the substrate onto which they are cast. A similar well-known film formation method is drop casting [10, 11]. Polymer/carbon composites especially with CNTs have been prepared in the past using this evaporative casting method and discussed their different properties [12, 13]. It has been mentioned herein that the properties like mechanical and electrical are mostly dependent on the polymer and filler ratio that is the increment in filler concentration up to a certain level improve the electrical conductivity and mechanical strength [12].

Styrene butadiene rubber (SBR)/graphene nanocomposites were prepared by solution mixing and evaporative casting method [14]. Initially, graphite intercalated compound (GIC) was subjected to thermal sock at high temperature and then ultrasonicated in tetrahydrofuran (THF) to get graphene nanoplatelets (GNPs). The mixture was added with SBR solution, stirred mechanically at rpm 200, and sonicated for 1 h below 30 °C. The solvent was evaporated at 60 °C, where ethanol was used to precipitate, collect, wash, and dry the composites power. The authors compared their results with the composites prepared by melt mixing technique and reported better dispersion of GNPs within the SBR matrix when prepared by evaporative solution casting method. Graphite oxide (GO)/poly(propylene carbonate) (PPC) composites and poly(methyl methacrylate) (PMMA)/carbon black (CB) composites were prepared by solution mixing followed by evaporative casting technique [15, 16].

1.1.2 Vacuum Filtration

The vacuum filtration method is one of the simplest processes for manufacturing of electrically conductive ultrathin film made of densely packed and homogeneously dispersed carbon networks [17, 18]. These films are called buckypapers in which the carbon networks are entangled and are held together by van der Waals force of attraction at the carbon–carbon interface where it forms a pseudo-two-dimensional

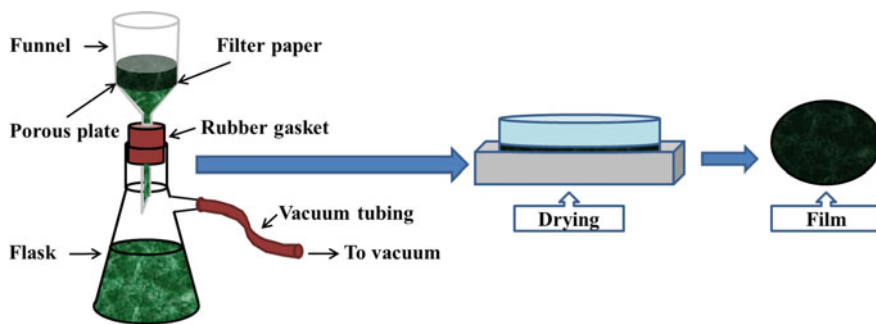


Fig. 3 Schematic for the preparation of composite films using the vacuum filtration method

structure [19]. This technique is having four simple steps: preparation of the carbon dispersions, vacuum filtering of this dispersion through a suitable membrane, washing the product with distilled water and methanol for making composite film, and drying in the oven to easily peel off the films from the filtration membrane [17, 20]. A schematic diagram of vacuum filtration technique is shown in Fig. 3.

This filtration technique is advantageous because of many reasons: (i) homogeneity as a result of flow dynamics. (ii) Maximum overlap with other nanotubes as they accumulate due to the strong vacuum, which causes the nanotubes to flatten and straighten out. This results in the increase in maximum electrical conductivity and mechanical strength throughout the composite film. (iii) Thickness control of the film by controlling the concentration of nanotubes and volume of the dispersion filtered [17].

It is shown in the literature that the properties of buckypapers composite films are influenced by the condition of preparation method and types of used dispersants [18, 21]. It can be exemplified that the in-plane Poisson's ratio of buckypapers films is tuned by the combination of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [22]. The preparation of buckypapers with the change of MWCNTs length significantly affects the pore diameter present in the final material [18]. It has also been investigated that the sonication time, volume of solvent used, and type of used membrane filter affect the tensile property and surface morphology of SWCNT buckypapers [21]. In addition, it has been reported that the electrical and mechanical properties of buckypapers are shown to decrease with the increase in dispersant's molecular mass [21]. The flexibility and excellent electrical and dielectric properties make the carbon nanotube buckypapers an ideal material for different types of applications such as in solar cell, display system, touch screen, sensor, electronic paper, supercapacitor, and batteries [23–26].

The vacuum filtration technique was used for the fabrication of graphene oxide (GO)/polyvinyl alcohol (PVA) and GO/polymethyl methacrylate (PMMA) composite films with a wide range of filler loading [27]. In this typical process, graphite was pre-oxidized by stirring for 6 h within a mixture of concentrated sulfuric acid (15 mL), potassium persulfate (10 g), and phosphorous pentoxide (10 g). The

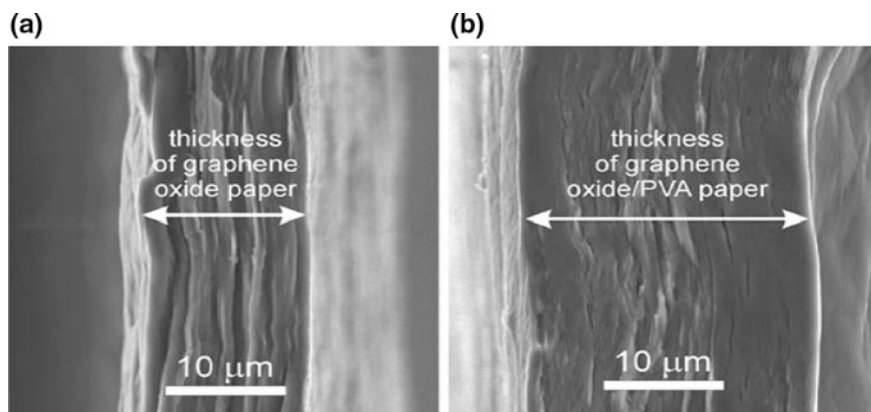


Fig. 4 SEM images of **a** GO paper and **b** GO/PVA composite. Reproduced after permission from Ref. [27]

extracted powder after filtering, washing, and drying was then stirred at 35 °C within the mixture of concentrated sulfuric acid and potassium permanganate to get oxidized graphite. The GO was further exfoliated by ultrasonication in a bath-type sonicator. The GO/PVA composites were obtained by aqueous dispersion of GO within the aqueous solution of PVA, whereas GO/PMMA composites were obtained by dispersing GO within *N,N*-dimethylformamide (DMF) and subsequent mixing with PMMA solution in DMF. The GO film and composite films were obtained by vacuum filtration and later on drying in a Petridis. Scanning electron microscopic images showed the macroscopic paper-like morphology of both GO film and composite film with paper thickness 10–30 μm as shown in Fig. 4.

1.1.3 Fiber Spinning

Spinning is the manufacturing process for preparing composite fibers. This is performed using a spinneret, which is fed by an extrusion process, to eject a thin continuous fiber. Different spinning techniques exist; these include wet spinning, melt spinning, and electrospinning [28, 29].

A common method used to produce composite fibers containing conducting fillers polymers, thermoplastic polymers, and carbons is wet spinning [30–34]. Wet spinning involves injecting of a composite's solution into a liquid bath that contains low molecular weight solution, ensuring that the solvent does not dissolve the composite solution (Fig. 5). Due to the exchange of solvent and non-solvent in the coagulation bath, a solid gel fiber is formed. This solid gel fiber is stretched and dried by passing it over spinning rollers [35]. Previously, it has been shown in the literature that, by adding a small quantity of CNTs, a successful reinforcement of the properties of the polymer fibers was achieved [35]. In another study, biopolymers (gellan gum and chitosan) were used in a wet-spinning technique where one

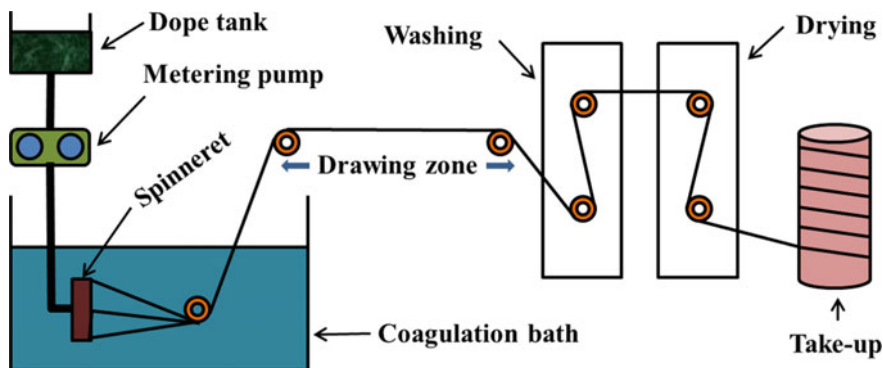


Fig. 5 Schematic illustration of the setup to form fibers using the wet-spinning process

biopolymer was used as CNT dispersant and the other as a coagulant medium for the continuously spun fibers. This was known as polyelectrolytic complexation, as gellan gum and chitosan are oppositely charged biopolymers [32].

1.1.4 Printing

In printing, a material, especially ink is deposited onto a suitable substrate for producing a particular structure. In the previously described processing methods (evaporative casting, vacuum filtration, and fiber spinning) composite materials are prepared in film and fiber forms. Printing methods are mainly classified into two main groups to fabricate composite material in pattern form: inkjet and extrusion printing [36–39].

Inkjet printing is a commonly used industrial printing method due to advantages such as precise and controlled pattern generation, solution saving effects, non-contact injection, high repeatability, and scalability [40, 41]. This method also allows for printing of various materials onto both rigid and flexible substrates [38, 42]. The ink consists of a solute, such as carbons, dispersed in a solvent, such as a polymer, and is jetted from a nozzle by deflection of piezoelectric materials (Fig. 6). This method usually requires low viscous inks and filtration of the ink prior to the jetting to prevent nozzle clogging [43, 44]. It has been demonstrated as a method for printing bio-scaffold and cell [45, 46]. Other applications of inkjet printing include components for drug screening and biosensors [47, 48]. Furthermore, it has a potential use in regenerative medicine and tissue engineering [49–51].

Different conducting materials such as polymers and CNTs were successfully printed using inkjet printing. For example, it has been reported that by inkjet printing SWCNTs and MWCNTs with conductive polymers onto flexible substrates by using a piezoelectric inkjet printer, very low sheet resistance $225 \Omega/\text{sq}$ was reported [36]. Another study showed that inkjet printed patterns of SWNTs

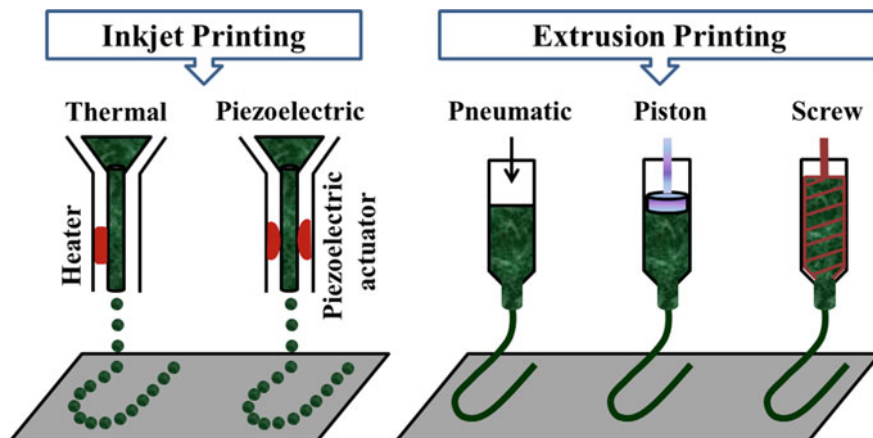


Fig. 6 Schematic illustrations of inkjet and extrusion printing methods

stabilized with poly (2-methoxyaniline-5-sulfonic acid) (PMAS) onto poly(ethylene terephthalate) (PET) sheets displayed a sheet resistance $100 \text{ k}\Omega/\text{sq}$ and optical transparency 85% as well as sensitivity to alcohol vapors under static and flow conditions [52].

Extrusion printing is a process that involves pushing (using constant pressure) the inks through a small nozzle onto a moving substrate [38, 53]. Compared to inkjet printing, extrusion printing creates patterns which can reliably deposit large volumes through cheap and replaceable parts [54]. It has been shown diagrammatically in Fig. 6. This method can also be applied to fabricate three-dimensional structure and to embed material onto substrate [38, 55]. However, extrusion printing is slower and has poorer resolution and scalability compared to the inkjet process. Unlike inkjet printing, extrusion printing allows for the patterning of high-viscosity inks [38]. Very careful control of the flow properties, surface tensions, and wettability of the inks is required in order to successfully produce a high-quality extruded material [56].

In recent studies, it has been shown that both inkjet and extrusion printing methods were used to prepare conducting tracks by depositing a conducting polymer, poly(3,4-ethylenedioxythiophene)/poly(sodium 4-styrenesulfonate), onto a chitosan biopolymer substrate [38]. In that work, a highly viscous paste was used for the syringe extrusion method, and a more aqueous solution was used for inkjet printing. Using extrusion printing, the authors prepared embedded tracks, for potential application as electrodes, by inserting the extruding needle under the surface of the biopolymer solution. The authors reported a higher conductivity for the extruded patterns compared to the inkjet printed ones, due to the greater amount of deposited conducting inks.

Another study found that gellan gums are a good rheological modifier for MWCNT ink [39]. It was found that a single layer of ink printed onto a flexible substrate exhibited resistance value of $7\text{--}8 \text{ k}\Omega/\text{cm}$, which was reduced by

increasing the number of printed layers. Many polymer/carbon composites like ABS/carbon fiber [57], PS/carbon nanofiber and PS/graphite [58], nylon 12/carbon black [59], ABS/graphene and PLA/graphene [60], etc., were prepared by 3D printing technique, where mechanical, electrical, and some important properties were discussed in detailed.

1.2 Composites by Melt Processing

Instead of using a solvent, the polymer substrate can also be melted and then intermixed with carbons using different techniques such as shearing, extrusion, etc. This process is known as melt mixing process [2, 3].

The benefit of melt processing is that it does not use any solvent, simple, and it can be used as an industrial process to impart carbons into thermoplastic polymers such as polypropylene. This method uses elevated temperatures together with applied shear forces to form the polymer–carbon composites and requires equipment such as extruders and injection devices that are designed to withstand these conditions [2, 3]. While this method can also be used to generate composite fibers, the composites prepared through this synthesis route usually have low carbon filler content [6]. However, there are also reports of mixing high content of carbons within the polymer matrices using this methodology [61–65]. A flowchart diagram of this type of mixing process has been depicted in Fig. 7. In this process, polymer, carbon, and other necessary additives/ingredients are fed into mixing mill and processed approximately 20 °C higher than the melting point of the polymer. The mixing is done for a certain time at a specific rotor speed. The molten mass is then taken out and passes through the two-roll mill, and finally, the composite is sheeted out by using any compression mold. The mixing can be done in a batch or continuously, depending on the used mixing machine and our choice.

A previous study reported polycarbonate–CNT composites prepared by melt processing. It was found that by controlling the mixing condition, an electrical percolation threshold of about 1 wt% was obtained [66]. Other studies showed a threefold increase in the modulus and strength for polyamide containing 2 wt% MWNTs compared to the pure matrix [67].



Fig. 7 Flowchart presenting the steps of the melt processing

Rahaman et al. have reported the melt mixing of carbon fiber with ethylene vinyl acetate (EVA) and acrylonitrile butadiene rubber (NBR) and their blend compositions mixed with other ingredients [68]. The mixing process was carried out within Haake Rheocord at temperature of 120 °C for 6 min at shear rate of 60 rpm. The composites were vulcanized by compression molding at 160 °C at 5 MPa pressure at their determined curing time. The polymer, carbon fiber, and other ingredients were added sequentially as follows: polymer → carbon fiber → other ingredients. The mechanical property, electrical conductivity, and electromagnetic interference shielding effectiveness (EMI SE) for these polymer carbon fiber composites were studied. It has been reported that elongation at break and tensile strength have been reduced after the addition of carbon fiber but the tensile modulus within the stress–strain proportionality limit, electrical conductivity, and EMI SE has been increased. More importantly, there is substantial breakage of fiber length within the polymer matrices and the extent of breakage has been increased with the increase in loading of carbon fiber when the authors used this melt mixing technique.

The preparation of polypropylene grafted maleic anhydride (PP-g-MA) and expandable graphite oxide (EGO) composites was carried out by melt mixing technique in Haake kneading mixer [69]. The mixing was conditioned at 200 °C for 30 min at 60 rpm. In this mixing process, PP is nonpolar polymer, and hence MA was used to increase its compatibility with EGO particles. It was reported through XRD analysis that there was not any change in the d-spacing of graphite layers within the PP-g-ME/EGO composites.

Masterbatches of polycaprolactum (PCL)/MWCNT composites were prepared by melt mixing technique using an internal mixer where the mixing was done for 10 min at 65 °C and 60 rpm as reported by Maiti et al. [70]. The masterbatch thus again was melt blended with polycarbonate (PC) at 280 °C at the same time period and rpm. It was investigated through scanning electron microscopic (SEM) and transmission electron microscopic studies that the CNTs were homogeneously dispersed within the polymer matrices at their low loading as shown in Fig. 8. The obtained electrical percolation threshold was 0.14%, which suggested the formation of interconnected continuous conductive networks within the polymer matrices.

The thermoplastic polyurethane (TPU) elastomer was melt blended with high-structure carbon black and carbon nanofiber by a special miniature asymmetric batch mixer [71]. The authors ensured good dispersion of the particles within the polymer matrix. They investigated the thermal, mechanical, electrical, and flammability properties for this composite system.

In another study, the nylon 6/carbon black composite was prepared by masterbatch dilution and melt mixing technique [72]. The effect of carbon black size and their distribution on the mechanical and electrical properties of the composites was investigated. The electrical resistivity of nylon 6 was reduced from 10^{15} to 10^7 Ω cm in case of 1 wt% diluted masterbatch and 6 wt% melt mixed nylon 6/carbon black composites, indicating that composite prepared by masterbatch dilution method gives better property. This is because of the formation of small carbon black clusters when the composite is prepared by masterbatch dilution

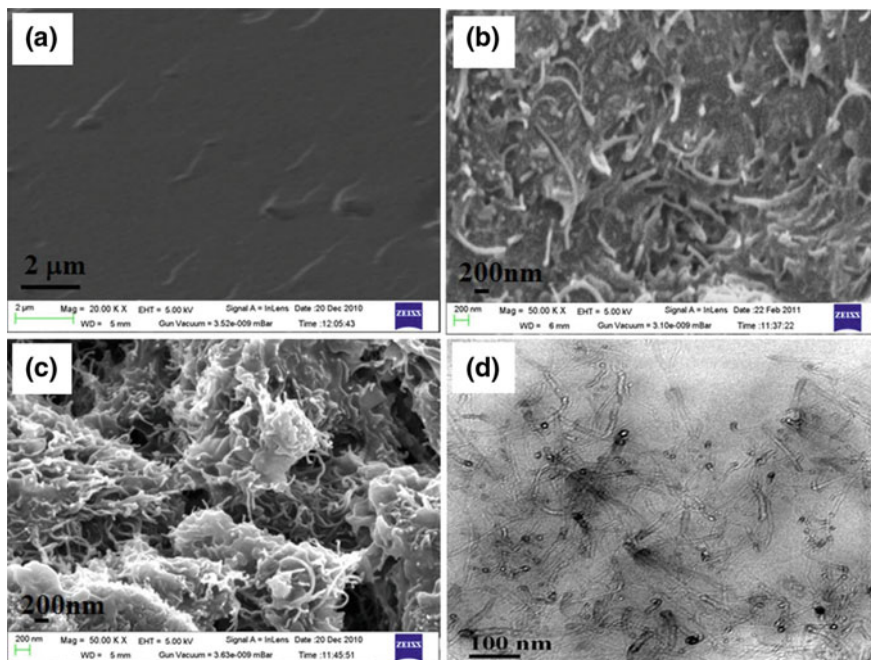


Fig. 8 FESEM image of **a** (90/10 w/w) PC/PCL miscible blend, **b** (90/10/0.35 w/w) PC/PCL/MWCNT composite, **c** (80/20/0.7 w/w) PC/PCL/MWCNT composite, and **d** TEM image of (90/10/0.35 w/w) PC/PCL/MWCNT composite. Reproduced after permission from Ref. [70]

method. The authors also reported that the increment in carbon black content decreases the elongation at break and tensile strength, but increases the tensile modulus. There are also many reports of preparation polymer/carbon black composites by melt mixing technique [73, 74].

Polymer/graphene composites are also prepared by this melt mixing technique. For example, polyvinyl chloride (PVC)/multilayer graphene composite was prepared by conventional melt mixing process for improving the toughness of rigid PVC [75]. Before melt mixing, the powder PVC, graphene, stabilizers, and lubricants were dry mixed at room temperature using a high-speed mixer. The mixture ingredients were then melt mixed using a torque rheometer at temperature of 165 °C for 5 min. The composite blends were then transferred into two-roll mill for further mixing at 170 °C for squeezing into thin sheet. These thin sheets were stacked together and placed into hot-press machine to get flat composite sheets. It was reported that only 0.36 wt% graphene loading into PVC greatly improves the toughness and impact strength of the composites. Besides that, many polymers like poly(lactic acid) (PLA), PP, PU, poly(ethylene terephthalate) (PET), polystyrene (PS), poly(ether ether ketone) (PEEK), styrene–ethylene/butylene–styrene triblock copolymer, etc., were blended with graphene for obtaining the composites by this

method for investigating their mechanical, thermal, and electrical properties along with their morphology [76–82].

The polymer/carbon composites fiber is prepared by melt spinning technique, which is very convenient, economical and can be prepared industrially in large scale. In this typical process, the fiber-forming substances that are the mixed polymer and carbon or their prepared master batch are placed in hopper and extruded through spinneret (Fig. 9). The extruded mass is then solidified by cooling. The used polymer should not be volatile in nature or degradable at the processing temperature. Generally, the single-screw or twin-screw extruder is used depending on the nature of polymer and filler particles. The metering pump shown in the diagram, control the flow of molten mass to the spinneret head and filter any unmelted mass before extrusion. The extruded molten fiber mass is cooled by quench air, and then drawn into continuous filament, stretched, and finally take up/wind up in a roll. The strength of the resultant composite fiber depends on the winding speed. The advantage of using this method is that it is cost-effective, can be used for both continuous and staple filaments, no environmental pollution, no requirement of any solvent, nontoxic, and high production rate (1000–2000 m/min). The only disadvantage is that the input of heat is high and the high maintenance cost is needed.

Polycarbonate (PC)/MWCNT (2 wt%) conductive composite was prepared by melt spinning technique using a piston-type apparatus where take-up velocities were up to 800 m/min and draw down ratio 250 [83]. The composite was investigated through TEM, which revealed that the carbon nanotubes were aligned along the fiber axis but its curve shape still existed in the melt spun fibers. At high draw down ratio, the curvature was reduced. It was reported that with the increase in alignment, the electrical conductivity of the fiber was reduced. It was also mentioned that the tensile strength and elongation at break was less at the low take-up compared to neat PC, whereas it was increased at high take-up speed. There are also many reports of preparing polymer/carbon composites by this melt-spinning technique [84–89].

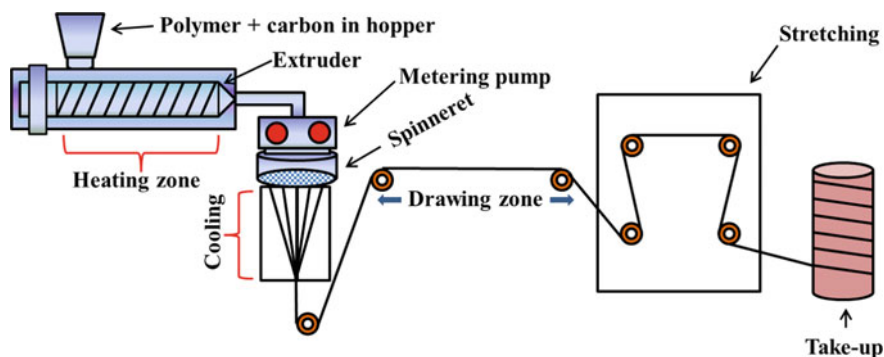


Fig. 9 Schematic illustration of the setup to form fibers using melt-spinning process

1.3 Composites by In Situ Polymerization Process

In situ polymerization is employed in order to uniformly dispersing the conducting filler, while retaining the aspect ratio and improve polymer–filler bonding strength. It is particularly useful for preparing polymers that cannot be produced by solution (insoluble polymer) and melt mixing (thermally unstable polymer) techniques [3].

In this method, the monomer is used as a starting material. It involves polymer and carbons being dispersed in a solvent. This allows for the carbons to act as a template for the polymer's growth. The mixture is then sonicated and stirred to allow for growth. These composite structures are then isolated from the solution by filtering or evaporation to dryness [90]. A general schematic diagram of this type of polymerization process is depicted in Fig. 10.

This method allows the preparation of composite with high carbon weight fraction, which can be diluted by other methods [2]. Composite materials produced by this method are more conductive. This may be because there is an increased interaction between the polymer and the carbons. It may also be due to the fact that the product has a more favorable morphology. Many polymer–CNTs composites were prepared using in situ polymerization, which included polystyrene–MWNT [91] and polyimide–SWNT [92]. In addition, epoxy–CNT [93] and polycarbonate–carbon

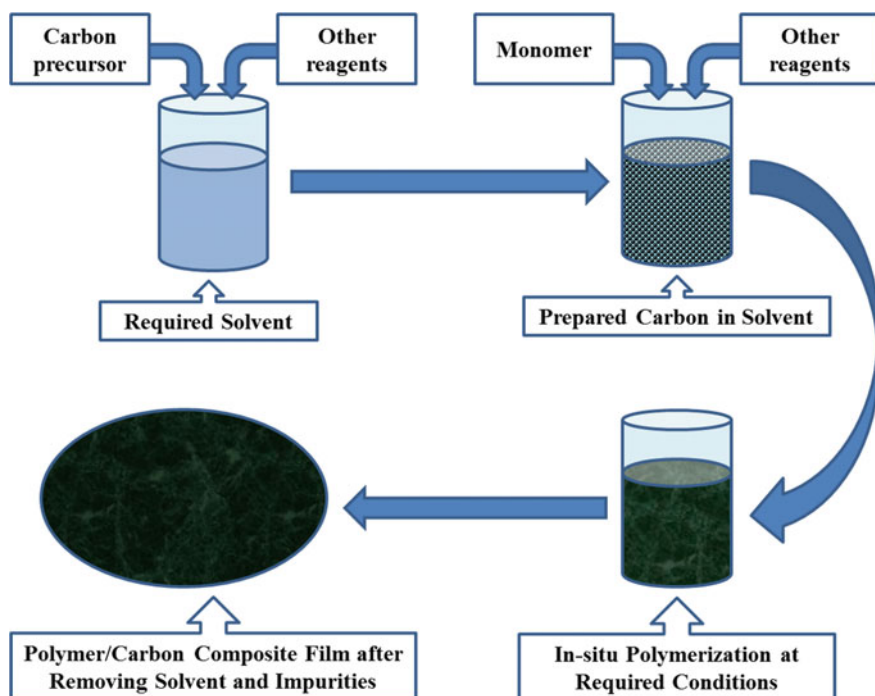


Fig. 10 Flowchart presenting the steps of the in situ polymerization processing

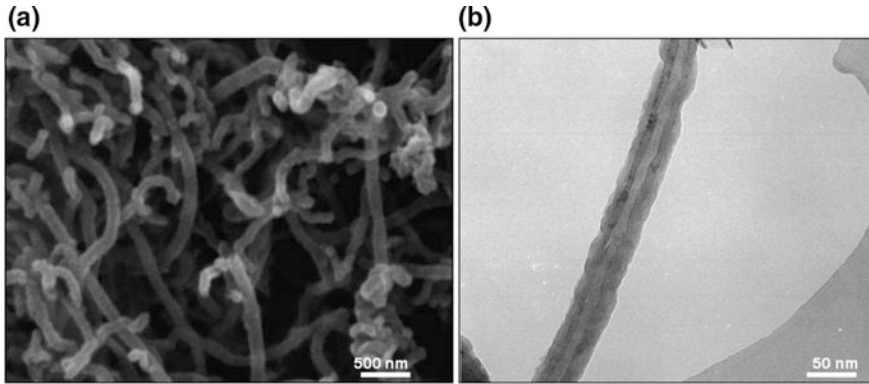


Fig. 11 Scanning (a) and transmission (b) electron microscopy images of polyaniline–MWCNT composites prepared by in situ polymerization processing. Reproduced after permission from Ref. [95]

nanofiber [94] composites have been prepared using this method. Figure 11a, b shows the scanning and transmission electron microscopic image of polyaniline–MWCNT composite made by this in situ polymerization technique [95].

The synthesis of graphene, graphene oxide (GO), and functionalized graphene oxide (f-GO)—epoxy nanocomposites was carried out by in situ polymerization technique [96]. Initially, the filler, GO/f-GO was dispersed in acetone by means of ultrasonication and then added with epoxy matrix. The mixture was then placed within a vacuum oven at 50 °C. After evaporation of nearly 80% of solvent, *m*-phenylenediamine was added within it and stirred vigorously. It was then poured into a stainless steel mold and heating at 60 °C for removing the residual solvent followed by pre-cure at 80 °C for 2 h in an oven and post-cure at 120 °C for additional 2 h. The prepared composites were then characterized for several studies. It was reported that the better dispersion was achieved for epoxy/graphene and epoxy/f-GO composites compared to epoxy/GO composite.

Fim et al. reported the synthesis of polyethylene (PE)/graphite composites via in situ polymerization technique [97]. Intercalated graphite was prepared from the graphite flake by treating with $\text{H}_2\text{SO}_4/\text{HNO}_3$. It was then heated at 1000 °C in air for 30 s to get expanded graphite (EG), which on ultrasonication in 70% ethanol for 8 h produces graphite nanosheet (GNP). The GNP was surface treated with 15 wt% methylaluminoxane (MAO) by stirring in toluene for 30 min, and then, the solvent was removed under reduced pressure. The ethylene was polymerized using 100 ml PAAR reactor, toluene as solvent, MAO as cocatalyst, bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) as catalyst, at temperature 70 °C, ethylene pressure 2.8 bar, and for time duration 30 min. Different amount of MAO treated GNP was added to the reactor as filler before PE synthesis to get PE/graphite composites. It was mentioned that thermal treatment and ultrasonic agitation had expanded graphite layers along with the reduction of crystal size. The synthesis of

polymer/graphene nanocomposites was also reported in some literature by this in situ polymerization technique [98, 99].

The polymer/carbon composites are also prepared by in situ emulsion polymerization technique. Polystyrene (PS)/carbon black (CB) composites were prepared by this in situ emulsion polymerization technique, where CB was manually mixed with styrene monomer at ambient temperature [100]. The absorption of monomer on the surface of CB made viscous paste, which was reduced by adding a surfactant within it. Azobisisobutyronitrile (AIBN) initiator was added to it for preparing emulsified monomer droplets. The surfactant solution was added to it and ultrasonicated to get well-dispersed system. The dispersion was transferred to the reactor for polymerization conditioned at reaction temperature of 60 °C, mixing speed of 350 rpm, and reaction time of 120 min. It was reported that the particle diameter was 50 nm and high polydispersity index for the polymer. The synthesis of PS/graphene nanocomposites by this in situ emulsion polymerization technique was also mentioned in literatures [101, 102].

1.4 Dry Mixing Technique

This method is most useful for rubbery materials where polymers are soft enough at room temperature. A schematic diagram for the preparation of polymer composites using this type of method is shown in Fig. 12. Initially, the conductive filler along with other ingredients are mixed with rubber in an open mixing mill or internal mixer. Generally, the mixing process starts at room temperature but during mixing the temperature may rise to 60 °C. The mix is then vulcanized at a specific temperature, pressure, and time duration to make the conductive composite.

Liu et al. have prepared styrene butadiene rubber (SBR)/carbon black (CB) composites, where carbon blacks with their different structure were used as conductive filler [103]. The concentration of carbon black within the composite was 50 phr. Other ingredients like aromatic oil (10 phr), zinc oxide (3 phr), stearic acid (2 phr), antioxidant (2 phr), wax (1.5 phr) accelerant DM (1.2 phr), accelerant D

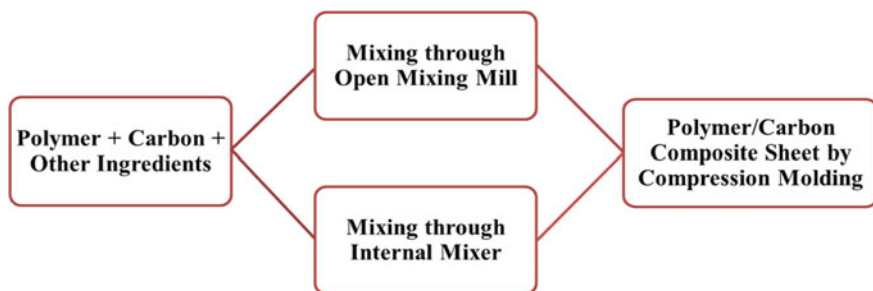


Fig. 12 Flowchart presenting the steps of dry mixing process

(0.6 phr), and sulfur (1.5 phr) were also used. The composites were prepared using two-roll mixing mill at ambient temperature via general compounding method. The composites were vulcanized at temperature of 150 °C and pressure 15 kPa to make sheet thickness of 2 mm. They reported that the mechanical properties of SBR/CB composites increase with the increase in CB loading but the composites loaded with low particle size carbon black exhibits high mechanical properties compared to high particle size ones.

Cardanol-grafted natural rubber (CGNR) and HAF carbon black composites were prepared by simple compounding method using two-roll mixing mill at ambient temperature according to standard ASTM D-3182-07 [104]. The aspect ratio of two-roll mill was length:diameter = 33:15 and friction ratio during mixing was 1:1.2. They reported that during mixing, due to friction, the temperature of two-roll raised up to 80–85 °C. The composites, later on, vulcanized at 150 °C using compression molding machine according to their optimum cure time determined by rheometer. The authors have compared the dispersion of carbon black in CGNR matrix and aromatic oil plasticized NR matrix along with their other mechanical properties. It has been reported that the dispersion of carbon black is better in CGNR matrix compared to the aromatic oil plasticized NR matrix. The mechanical strength of CGNR/CB composites is higher compared to oil plasticized NR/CB composites.

Sethi and his co-workers have reported the preparation of polychloroprene (CR) rubber and carbon black composites by this dry mixing technique [105]. The mixing was performed using two-roll mixing mill at ambient temperature by maintaining the friction ratio 1:1.1. All the mixing was done at the identical condition and the same sequence of adding the ingredients. Later on, the composites were cured at 150 °C under compression molding at hydraulic pressure 5 MPa according to optimum cure time determined from the rheometric curves. The authors investigated the effect of different mechanical deformation and temperature on electrical and dynamic mechanical properties of CR/CB composites. The electrical conductivity and dynamic mechanical properties dropped when both the number of bending cycles and compression flex cycles of deformation was increased. Figure 13 shows that the electrical conductivity of different carbon filled CR composite has reduced after bend flexing of the composites. The increase in temperature also resulted in the variation in electrical conductivity of the composites.

MWCNT based NR nanocomposites were also prepared by this dry mixing technique using an open two-roll mixing mill at the friction ratio 1:1.1, nip gap 1 mm, mixing time 19 min at room temperature [106]. In this study, MWCNT was surface functionalized with silane, 3-aminopropyltriethoxysilane and investigated its effect on the rheological and mechanical properties of NR vulcanizates. It was reported that the modulus and strength were increased due to the interaction between silane functionalized MWCNT and NR vulcanizates. There are also many reports of preparation of polymer/carbon composites by dry mixing technique in the past [107–110].

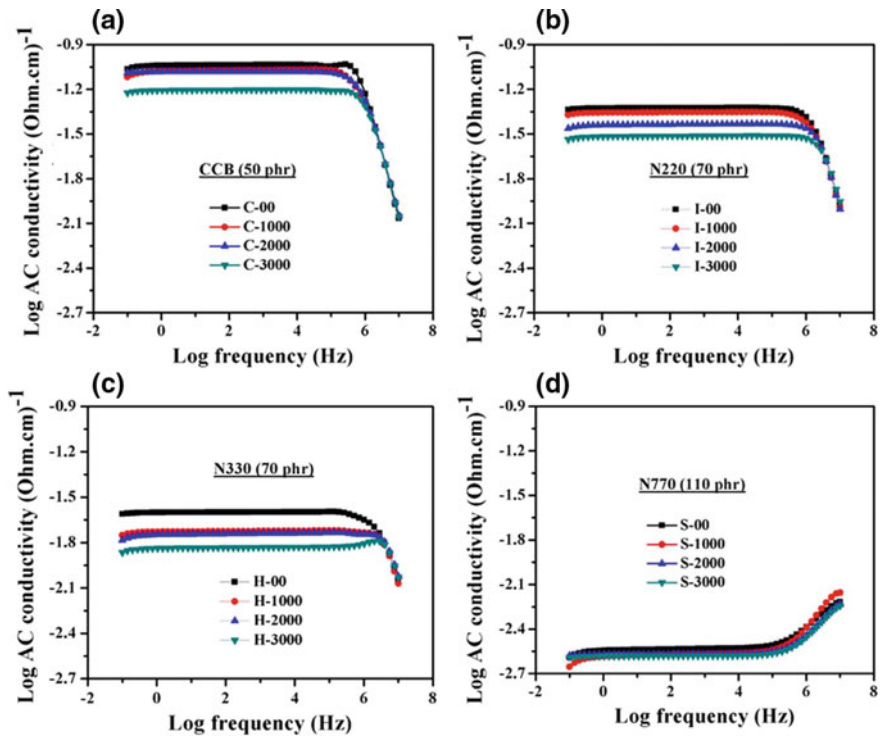


Fig. 13 AC conductivity of CR/CB composites measured before and after bend flexing at the highest loading of different CB **a** CCB, **b** N220, **c** N330, and **d** N770. Reproduced after permission from Ref. [105]

1.5 Powder Mixing Technique

Powder mixing is a very important technique that is widely used in many domestic areas and industrial fields. This is a type of dry mixing technique. In domestic areas, it is used in food making and gardening, whereas in industrial fields, it is used in the manufacturing process of pharmaceuticals, ceramics, plastics, fertilizers, detergents, cement, food production, powder metallurgy, animal feed, etc. [111–113]. In short, one can say that this technique is practiced when particulate materials are processed [111]. This technique can also be effectively used for both thermoplastic and thermosetting resins. A general diagram of this type of mixing processes is shown in Fig. 14. In this method, powdered polymer or oligomer is mixed with carbon filler along with other ingredients. The mixing is done using a blender normally at ambient temperature. The resultant mixture is then processed in batch-wise or continuously depending upon the nature of final product. The powdered polymer, in this case, is considered as continuous phase and the carbon particles as dispersed phase. In a batch-type process, the mixture is molded in either in hot or cold

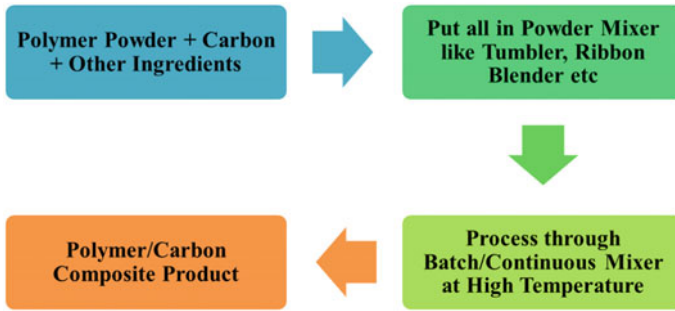


Fig. 14 Diagram representing powder mixing technique

condition to get polymer/carbon composite. The continuous mixing process is adopted for making any composite fiber or long tube/sheets, where the continuous removal of mixture is important.

Polyamide 11 (PA11)/graphene nanoplatelets (GNP) nanocomposites were prepared by this powder mixing technique aiming to be used as electrostatic discharge material [114]. They used Resodyn™ Resonant Acoustic and Thinky™ mixers for this powder–powder mixing and the mixture powder was pressed to make thin film for characterization. The SEM, TGA, Raman spectroscopy, and electrical conductivity were studied. It was revealed that the addition of GNP reduced the thermal stability of composites because of its poor dispersion. The electrical conductivity for all composites was within the electrostatic dissipation range.

Islam et al. have prepared the polyvinyl chloride (PVC)/carbon black (CB) composites in a blender, where both ingredients were in dry and powdered form [115]. The mixing was done for 1 min at 1000 rpm. Then, the mixture was compression molded at temperature of 185 °C, pressure of 200–250 kN, and mixing time for 10 min. An additional pressure of 50 kN was applied to make void-free specimen. All the molding was done at the identical condition. The compression-molded samples were taken out from the mold. The dimension of samples was 14 cm in diameter and 4 mm in thickness. Carbon content within the composites ranges from 5 to 30 wt%. The composites were tested for their electrical and mechanical properties. Electrical conductivity was increased with the addition of CB but the mechanical properties were improved only up to 15 wt% of CB and thereafter decreased. Microstructural analysis showed good dispersion of CB within the PVC matrix.

It is also specially applied for the modification of electrical conductivity of polytetrafluoroethylene (PTFE). Suh et al. have reported the electrical property and morphology of PTFE/FLG (few-layer graphene) composites prepared by this solid-state powder mixing technique and subsequent hot pressing [116]. Planetary milling process was used for the preparation of composites at 50 rpm for 10 min using stainless steel balls with diameter 10 mm and 4.5 g in weight. The weight

ratio of ball to powder was 10:1. The mixture powder was compacted at ambient temperature within steel compaction die under pressure 15 MPa. The mixture powder within the compacted die was further hot pressed for 30 min at pressure 15 MPa and temperature 300 °C. A significant increase in electrical conductivity was observed by this technique using a small amount of conducting filler. It was shown that FLG was compacted on the surface of composite and overlapped without making any gaps in between them. The preparation of polymer/carbon composites was also reported using this powder mixing technique in literature [117–119].

1.6 Aqueous Mixing Technique

Biopolymer composites and conductive coatings can be prepared by this technique [13, 120, 121]. A schematic diagram of this process is shown in Fig. 15. In this process, the polymer in granules/powder form is dissolved in an aqueous medium either at room temperature or by heating in a hot plate with the help of a mechanical or magnetic stirring during a certain time period. Thereafter, carbon particle is added to this aqueous solution of polymer and disperse by mechanical stirring or sonication over a certain time period. The mixture is then evaporated by solvent casting method or vacuum filtrated to form a film of polymer/carbon composite. This methodology is same as solution mixing technique: the difference arises in the use of solvent only. In solution mixing technique, one can use any suitable solvent for dissolving the polymers, whereas in this case, only aqueous medium can be used. Hence, the composites based on only water-soluble polymer can be prepared by this technique. For the preparation of conductive coatings, the very small powdered particles of conductive fillers are added in an aqueous emulsion of polymers. The emulsion can be coagulated or used directly for the purposes.

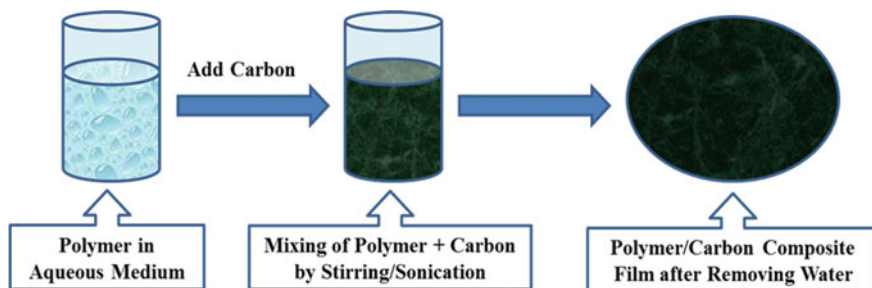


Fig. 15 Flowchart representing the steps of aqueous mixing technique

Zhao et al. have reported the preparation of poly(vinyl alcohol) (PVA)/graphene composites via facial aqueous solution mixing technique [122]. Initially, they prepared PVA/graphene oxide (GO) composites and then reduced GO to exfoliated graphene nanosheet. GO was first dispersed in aqueous solution using sonicator and stabilized by adding 0.5 wt% sodium dodecylbenzenesulfonate (SDBS). The GO was reduced to graphene using hydrazine and ammonia. The resultant mixture was then cast in a clean glass plate using a doctor blade and dried in an oven for film formation. They have shown that there was 150% increment in tensile strength and 10 times increment in tensile modulus for 1.8 vol.% PVA/graphene composite compared to neat PVA.

Preparation of chitosan/MWCNT nanocomposites was performed by simple solution mixing and evaporative casting method in aqueous medium [123]. In this typical procedure, the MWCNTs were first swelled in the required amount of distilled water (100 ml) and homogenized for 60 min in an ultrasonic bath. Acetic acid (1 ml) and chitosan (1 g) were then added with this already made MWCNT suspension and shaken for 1 h for dissolving chitosan. The solution mixture was stirred mechanically at 18,000 rpm for 30 min and then sonicated for 20 min for removing any bubble present in the system. The composite solution was poured in a plastic Petridis and heated at 50 °C for evaporating water. The obtained film has an average thickness of 0.08 mm. The authors investigated the morphology of the composite system through SEM, TEM, optical microscopy, XRD, and mechanical properties like tensile and nanoindentation. Their results showed that the CNTs were homogeneously dispersed within the chitosan matrix. Moreover, 93 and 99% improvement in tensile modulus and strength, respectively, were reported for 0.8 wt % MWCNT loaded composite.

Our research group has investigated the electrical, dielectric, and impedance spectra behavior of PVA/starch (70/30) blend graphene nanocomposites prepared by solution aqueous mixing and evaporative casting technique [124]. In this procedure, 4.2 g of PVA was separately dissolved in 50 ml of deionized water in a beaker. In another beaker, starch (1.8 g) mixed with glycerol (3 g) was dispersed in 50 ml of deionized water. Different amounts of graphene were dispersed in deionized water by ultrasonication for 2 min at amplitude of 30%. Subsequently, the starch and graphene dispersions were added to the already dissolved PVA solution and continuously stirred for 4 h at 400 rpm. The mixture was degassed, decanted into flat glass plate, and evaporated overnight at 50 °C to get composite film. The polymer/carbon composites were also prepared by several authors in the past by this aqueous mixing technique [125–130]. This method is advantageous in the sense that it is economical and less hazardous because of the use of aqueous medium in the processing of composites.

1.7 Conclusions

The preparation of polymer/carbon composites by different techniques has been discussed in this chapter. Solution mixing method is suitable for the polymers that are soluble in some common solvents. Moreover, in some cases, solution mixing process gives a better dispersion of carbons within polymer matrices. However, for making buckypaper, vacuum filtration is a favorable process. Melt mixing technique is important because of its industrial viability and for those polymers, which are insoluble in common solvents. Wastage of solvent gives more cost to the solution mixing, whereas in melt mixing, energy loss due to heating produces more cost to the process. For making composite fiber, one has to follow either wet or melt spinning technique depending on the nature of polymer and carbons. Dry mixing is favorable for those polymers which are quite soft at ambient temperature and the other ingredients are in soft, liquid, or powder form. Rubbery materials are generally processed through this technique. Powder polymers are processed through the powder mixing technique when the other ingredients are either in powder or liquid form. Biopolymer composites are generally prepared through aqueous mixing technique as they are water-soluble in nature.

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