Synthesis and Characterization of Polypyrrole and Graphene/Polypyrrole/Epoxy Composites

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Abstract Conducting polypyrrole (PPy) nanoparticles were synthesized via four different radical polymerization systems changing the time and other parameters. The characterization of PPy nanoparticles was done by Fourier transform infrared spectrometer. Graphene was synthesized from intercalated graphite by exfoliation at 1000°C for 30 s in tube furnace, and particle size was assessed using scanning electron microscope. Polypyrrole/graphene nano-composites were prepared by mixing PPy with graphene. Prior to this, graphene was coated with silane to enhance the bonding between PPy and graphene. The PPy-coated graphene composite was mixed in epoxy resin and cured using curing agent. The amount of PPy in nano-composites varied in the range of 1–20 % by weight. The effect of PPy/graphene nanoparticles on mechanical and electrical properties and thermal stability of epoxy nano-composites was investigated. Thermal gravimetric analysis has shown that incorporation of PPy nanoparticles has improved the thermal stability of the epoxy nano-composites. Two probe electrical conductivity measurements have shown that increasing amount of graphene in PPy/epoxy nano-composites increases the conductivity of PPy significantly. In order to improve the dispersion of graphene in PPy, mechanical disperser was employed. Composites prepared with disperser have exhibited improvement in mechanical and thermal properties.

Keywords Conducting polymers · Polypyrrole · Graphene · Epoxy · Nano-composite

1 Introduction

Macromolecular science covers an interesting field of research focusing on the conception and the understanding of materials that are designed out of very high molecular weight molecules. Such compounds are required for a broad variety of various important applications. These high molecular weight compounds which are termed as macromolecules or polymers are made up of very long linear chains. One of the main features of the polymers is reciprocated entanglement of the chain molecules making them to have excellent mechanical properties when applied in films or fibers. These materials can be processed due to their thermoplasticity for suitable processing of polymers into manifold commodity products via extrusion or injection molding, and orientation of the chain molecules in fibers and textiles which leads to extraordinary tensile strengths [1].

An oxidation or reduction process is usually escorted with adding or withdrawing of electrons, proposing that an electron can be removed from a material through oxidation or introduced into a material through reduction process. This impression indicates that a polymer might be electrically conductive by withdrawing electron through oxidation (i.e., hole) or by adding electron through reduction; this process was later described by as ‘doping’. This concept was realized by three awarders of Chemistry Nobel Prize in 2000, who were Hideki Shirakawa (University of Pennsylvania, Philadelphia, USA), Alan G. MacDiarmid (University of Pennsylvania, Philadelphia, USA) and Hideki Shirakawa (University of Tsukuba, Japan). In 1977, Alan J. Heeger (University of California at Santa Barbara, USA) and these three publicized that...
insulating \(\pi\)-conjugated polyacetylene could become conductor having conductivity of \(10^3\) S/cm because of iodine doping. This unpredicted discovery not only broke a traditional concept, which organic polymers were only regarded as the insulators, but also established a new field of conducting polymers, which are also termed as ‘synthetic metals’ [2].

Polymer composites are basically the advancement of the organic polymers which modified by the incorporation of different type of additives with some exception of multi-phase systems that have all the particles off additives enclosed by the polymer matrix. The subsequent mixtures are then analyzed by various methods. These additives have different geometries like fibers, flakes, spheres and particulates mainly. Thus, they consist of multi-phase constituents. The additives for composites can be continuous like fibers or ribbons, and these are implanted in the polymer in a certain geometrical arrangements that lengthen all over the dimensions of the product. When these additives are dispersed at nanoscale in the polymer matrix, then these types of composites are called as nano-composites. This is the main reason due to which nano-composites gain much more importance all over the world. That is why they can be characterized on the basis of origin of either matrix or filler [3].

The nanoparticles incorporated into polymer matrix are mainly responsible for the properties of the resultant nano-composite [4].

Nano-composite has very old history but this is the recent advancement of the research by which we control all the parameters of nano-composites which leads to the new inventions in the area of material science [5].

Geim A et al. were awarded Nobel Prize in the field of nano-science because of their unique work on two-dimensional material of graphene. They extracted graphene sheets from graphite via micromechanical cleavage method [6].

This invention of graphene leads it to open the new doors of research due to having tremendously unique physical chemical and mechanical properties [7–11].

Graphene shows excellent electrical mechanical and chemical stability similar to as CNTs that are used in different energy devices with various specific capacitances and recently achieved by using an ionic liquids [12, 13].

A variety of conducting polymers are synthesized by using different methods. The preferred mechanism for the synthesis of conducting polymer is in situ polymerization that involves the oxidation of monomer in the presence of filler [14].

Many conventional fillers like carbon black metallic particles are replaced by CNTs and carbon nano-fibers to achieve the conductivity of the same level. The reason behind is that the GNPs are synthesized by using affordable and copious natural graphite which in comparison is inexpensive and cost-effective substitute [15].

Liu Y et al. focused to work on the nano-composite tubes and fiber that were carbon-based nano-composites. This work was elaborated by B. Arsh et al. who investigated that they show good mechanical and elastic properties of carbon nanotubes/polymer composites. While another scientist Chi Hao investigated that polyaniline/graphene-based nano-composites exhibit anti corrosive properties [16–18].

This work is based on the synthesis of hybrid composites with the boosted electrical properties by the addition of graphene nano-platelets. PPy gains much more importance in the class of conjugated polymers due to its high electrical thermal and environmental stability not only this but also by the ease of synthesis it’s all the parameters can be controlled easily. PPy was synthesized by four different methods in the current projects; the reason behind this is to get the maximum properties as well as yield as one of the four projects gives us very good and improved results which were further selected for the research. Graphene nanoparticles were dispersed in PPy matrix which was coated with 3-aminopropyltriethoxysilane, and the purpose is to enhance the adhesive forces. This composite is then dispersed in epoxy matrix to produce hybrid composite and characterized by FTIR, electrical conductivity, thermal analysis, mechanical properties, optical microscopy, SEM and AFM.

2 Experimental

2.1 Synthesis of Graphene

Graphene nano-platelets were synthesized from intercalated graphite oxide which was produced by electrochemical oxidation of graphite (3–4 mm size) at 6 V for 6 h. The graphite powder was placed in a perforated platinum crucible which was anode and cathode was graphite rod. The intercalated graphite/graphite oxide was thermally exfoliated in a tube furnace at 1000 °C for 30–60 s under flow of nitrogen gas (100 ml/min). The exfoliated graphene obtained was ultrasonicated in ethanol for 8 h to produce graphene nano-sheets.

2.2 Synthesis of Polypyrrole

The PPy was synthesized via four different methods. In these methods, different oxidants (ammonium persulfate, sodium dodecyl sulfate) were used and the effect of time of polymerization on the PPy quality and yield was studied. 8.645 ml pyrrole monomer was added into distilled water, and mixing was carried out for 10 min using magnetic stirrer. Then, 2.5 M FeCl₃ was added dropwise as an oxidant. The polymerization was allowed to continue for 24 h at room temperature. After this, the mixture was filtered and washed with a mixture of water and ethanol several times to remove any traces of FeCl₃ from polymer.