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Recovery and utilization of graphite and polymer materials from spent lithium-ion batteries for synthesizing polymer–graphite nanocomposite thin films

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ABSTRACT

The present study focuses on the synthesis of polyethylene (PE), polypropylene (PP) and graphite composite thin film (PE/GRx and PP/GRx) using recovered anode (graphite) and separator (polymers) materials of spent Lithium-ion batteries (LIBs). The synthesized PE/GRx and PP/GRx thin films are characterized by X-ray diffraction, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetry and differential scanning calorimetric analysis. The mechanical and electrical properties of the synthesized PP/GRx and PE/GRx composite thin films have been evaluated. The results demonstrated ~10 times increase in tensile strength in composite thin films (PP/$GR_{20\,wt\%}$; 33 MPa; PE/$GR_{20\,wt\%}$; 38 MPa) as compared to neat polymer thin film (PP and PE thin film: 3.4 and 3.0 MPa). Similarly after graphite loading the specific conductance of composite films is increased 5–6 orders compared to the neat polymer thin film. The synthesis of polymer–graphite composite thin film using recovered materials of spent LIBs may effectively be used as an alternative for commercial graphite and polymer. The recovering of waste may decrease the quantity of the solid waste and reduce the potential pollution to the environment.

Introduction

Polymeric composite material occupies ~20–30% of the total volume of solid landfill deposit. Among the polymeric composite materials, polypropylene (PP) and polyethylene (PE) based composites are widely used in packaging due to their unique physical and chemical properties, however their disposal after usage is responsible for increase in the amount of solid waste in landfills [1]. Nevertheless the bio-degradation of polymeric solid waste remains an environmental issue as these composite stays in the soil as semi-permanent residue. Moreover this may be presumably due to the strong resistance of composite polymers against biodegradation, their high hydrophobicity, high molecular weight and lack of an active functional group, respectively. In order to overcome these, utilization of solid wastes such as polymer materials is highly attracted because of the increased demand for environmental protection, resource recycling and economics [2].

Among the solid waste, the disposal of e-waste of used lithium-ion batteries (LIBs) is increasing steadily and causing serious concerns to the environment [3]. Consequently, the global market for LIBs was estimated to $8.6 billion in 2014, especially usage of LIBs in mobile phone and laptop is increasing steadily [4,5] thereby increasing the generation of spent LIBs [3]. Proper disposal of LIBs are important to minimize the hazardous effect and also reutilize the spent LIBs constituents (metal ions, graphite, and polymers) for various applications [6]. The recovered metal ions can substitute a virgin material and reduces mining process. The plethora of pollution control regulations on landfill storage and resource efficiencies are the main reason behind recovery/reuse of LIB contents. The aim of recycling processes is to separate the constituents into different fraction and reintroduced these into

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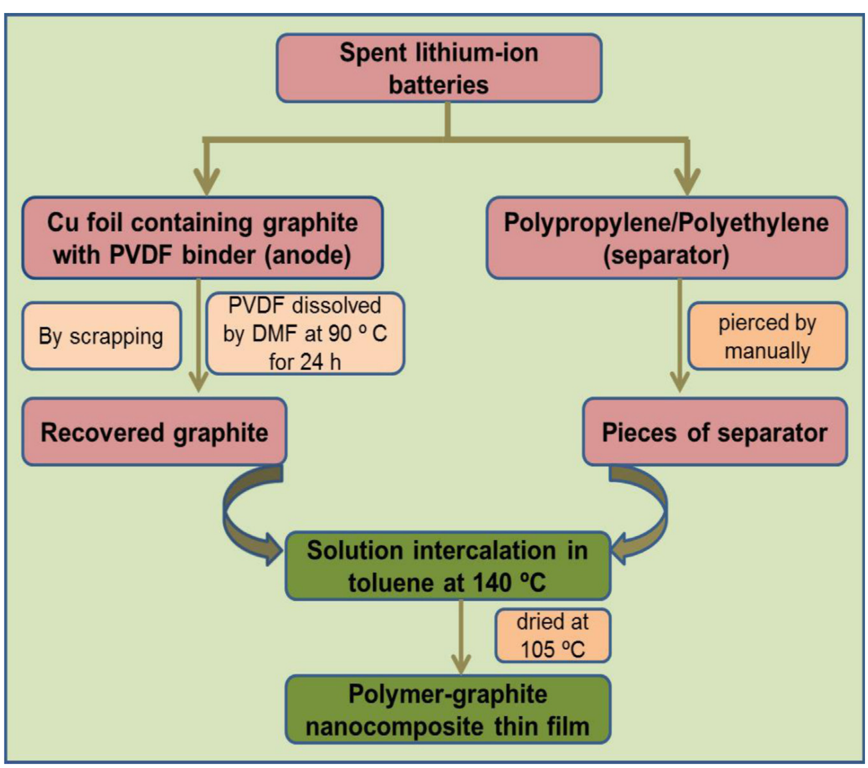
production. Literature review shows that so far, LIB cathode was explored due to its economic importance of valuable metal ions (Al foil containing mixed metal oxides) and less attention has been paid in the reusability of anode (Cu foil containing graphite) and separator materials (PP, PE) [7]. Mostly, after dismantled both plastics and steel cases, anode and separator are separated manually from the cathode of spent LIBs. The processes for recycling of spent LIBs are pyro-metallurgy, hydrometallurgy and bio-metallurgy [8,9]. Hydrometallurgy is a well-established process for the separation of metal ions from spent LIBs. In this process, acids and solvents are used to separate the metal oxide and graphite from their respective foils [10,11]. The anode and separator materials have not been investigated about their reuse possibility [7]. Graphite is a key material in LIB anode (80–85%); and separator is a microporous polyolefin membrane made of polypropylene or polyethylene or their blends. The preparation of polymer composite materials with carbon (graphite) material having specific physical and chemical properties is highly attracted [12]. The polymer materials have limited concentration of free charge carriers and are nonconductive in nature. To overcome this, filler material (graphite) is used in the polymer matrix which possesses exceptional properties, such as extremely high Young's modulus, thermal stability and electrical conductivity etc. [13]. Subsequently, the interfacial bonding between the filler and polymer influences the efficiency of polymer nanocomposite (PNC) and also exhibits better mechanical, dimensional and thermal stability [14]. Successively commercial polymer (polypropylene, polyethylene) and graphite materials have been widely used to synthesize nanocomposites; and used in various applications such as gas barrier, package and thermal applications [15]. Herein the synthesis of polymer-graphite composite thin films using recovered LIBs anode (graphite) and separator materials (polypropylene (PP), polyethylene (PE)) blend is investigated.

Generally PP/graphite, PE/graphite composites are synthesized by direct mixing, melt compounding, solution intercalation, in situ polymerization and thermo kinetic mixing etc. [16,17]. Among these solution intercalation process is an easy way to produce the polymer–graphite composite and has unique advantages over other processes. In the present study, the spent LIBs are collected to recover the cathode, anode and separator materials respectively. Subsequently the recovered anode (graphite) and separator (polymers) materials were used to prepare the different percentage of graphite loaded polymer–graphite (PP/GRx and PE/GRx) composite film by solution intercalation method. The prepared composite was characterized by various physicochemical techniques and its properties like mechanical, thermal, electrical properties has been evaluated. To our knowledge this is the first report detailing the utilization of anode and separator material for reuse purpose.

Experimental

Removal of graphite and polymers from spent LIBs

The spent LIBs were collected from local market of Bhavnagar, Gujarat, India. The LIBs mainly consists of cathode, anode and separator in which the cathode is made up of various metal oxides coated on the aluminium foil; the anode contains graphite and separator (polymer) materials. The graphite was scrapped from copper foil and dispersed in dimethyl formamide (DMF, Fisher Scientific, 99% purity) under heating (90 °C) for 24 h to remove the binder (polyvinylidene fluoride, PVDF) used for graphite coating on the copper foil. Subsequently the graphite was filtered and dried at 150 °C for 12 h (Scheme 1). Polymers (PP and PE) were washed with acetone (to remove the surface impurities) and cut into small pieces and used for preparation of polymer–graphite thin film nanocomposites.



Scheme 1. Flowchart for the preparation of polymer–graphite nanocomposite thin film.