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Modification of flax fibres by radiation induced emulsion graft copolymerization of glycidyl methacrylate

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HIGHLIGHTS

- Flax fibers were modified by radiation induced emulsion grafting of GMA.
- Bleaching with 0.7 wt% Na-chlorite was essential for achieving high DOGs.
- Effect of reaction parameters on the degree of grafting were established.
- The incorporation of poly-GMA grafts was proved by SEM, FTIR and XRD.
- The obtained poly-GMA grafted flax fibers have potential for adsorbent making.

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ABSTRACT

Flax fibres were modified by radiation induced graft copolymerization of glycidyl methacrylate (GMA) by pre-irradiation method in an emulsion medium. The effect of reaction parameters on the degree of grafting (DOG) such as concentration of bleaching agent, absorbed dose, monomer concentration, temperature and reaction time were investigated. The DOG was found to be dependent on the investigated parameters. The incorporation of poly(GMA) grafts in the bleached flax fibres was confirmed by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The structural and mechanical changes were evaluated by X-ray diffraction (XRD) and mechanical tester, respectively. The results revealed that reacting bleached flax fibres irradiated with 20 kGy with 5% GMA emulsion containing 0.5% polyoxyethylene-sorbitan monolaurate (Tween 20) surfactant at 40 °C for 1 h led to a maximum DOG of 148%. The grafted fibres showed sufficient mechanical strength and hydrophobicity which make them promising precursors for development of adsorbents after appropriate chemical treatments.

1. Introduction

Natural fibres are receiving a renewed attention because of the fast growing demands for developing of environmental friendly materials in various applications. The merits of the natural fibres are due to their distinct advantages such as combustibility, non-toxicity, low cost, hydrophilic and biodegradable properties (Kalia et al., 2009). Thus, natural fibres found applications not only in textiles but also in green composites, production of agro fine chemicals, medicines and cosmetics as well as nourishment (Mallick, 2007; Cheung et al., 2009; Kozlowski et al., 2010)

To further diversify the utilization of the natural fibres in desired areas, they were grafted with suitable monomers to impart desirable properties. Modification of the natural fibres (flax, jute, kenaf, hemp, etc.) was carried out by graft copolymerization of vinyl or acrylic monomers using chemical (Abdel-Halim et al., 2008), photochemical (Khan, 2004; Zaman et al., 2012), microwave (Kaith and Kalia, 2008), pressure (Singha et al., 2008) and gamma radiation (Khan, 2005; Sharif et al., 2013; Sokker et al., 2004; Seko et al., 2010) grafting methods.

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Among all, radiation induced graft copolymerisation with high-energy radiation (e.g. γ-rays from Co-60 or electron beam, EB) is found to be a versatile method to impart new moieties to the natural fibres originating from the grafted monomers (Nasef and Hegazy, 2004). Notably, this method is capable of introducing the grafted moiety not only to the surface but also to the bulk of the fibres to achieve a homogeneous and tuneable grafting yield to meet specific applications. Moreover, there are no residues from the chemical initiator involved in the reaction left in the matrix of the modified polymers (Ting et al., 2015).

Among natural fibres flax or *Linum usitatissimum* is well known to be one of the first fibres to be extracted and woven into textiles and thus have been used traditionally for making linen fabrics, twines and ropes (Sen and Reddy, 2011), and lately for composites (Yan et al., 2014). Flax fibres are contained in fibre bundles comprising 10–40 fibres in the baste layer. The individual fibres or filaments are composed of cellulose and hemicellulose, which are bonded together by lignin and pectin (Charlet et al., 2007). The flax fibre microstructure is highly complex due to the hierarchical organization at various length scales and the different materials present in variable proportions (Baley, 2002). The flax fibres have high tensile strength resulting from the ability to be highly oriented with the fibre axis and thus they crystallised in the cell walls. Thus, the use of flax fibres to reinforce polymeric matrices for various applications (vehicle, transport, construction etc.) has become a significant area of research in recent years (Zhu et al., 2013).

Modification of flax fibres by grafting of various vinyl monomers mixtures such as methylmethacrylate (MMA)/ethylacrylate (EA), MMA/acrylonitrile (AN) and MMA/acrylic acid (AA) have been reported using microwave radiation (Kaith and Kalia, 2008). Other monomer mixtures such as MMA/vinyl acetate (VA), MMA/acrylamide (AAm), and MMA/styrene were also grafted on flax fibres using microware radiation (Kaith and Kalia, 2008). Earlier MMA was grafted on flax fibres using UV method (Ali et al., 1998). However, there are no reports on modification of flax fibre by radiation induced grafting of glycidylmethacrylate (GMA) with gamma rays or EB. Moreover, there are no reports on using grafted flax fibres as precursor for adsorbent development.

The objective of articles is to report radiation induced emulsion grafting of GMA onto preirradiated flax fibres with EB for preparation of precursor for selective adsorbent for removal of some pollutants from water and waste water. The use of the emulsion grafting in this study is more environmental friendly than solvent grafting and is likely to lead to a reduction in the monomer consumption and absorbed dose (Nasef and Güven, 2012). The selection of GMA containing an epoxy ring that can be opened under mild reaction conditions offers the possibility for hosting a variety of ionic moieties targeting specific pollutants such as heavy metals ions and days (Eckert et al., 2000; Saito et al., 2002; Hoshina et al., 2007). The effects of reaction parameters such as monomer concentration, absorbed dose, temperature and reaction time on the degree of grafting (DOG) were investigated to control the level of modification. The incorporation of poly(GMA) and its impacts on the fibres properties with respect to chemical, morphological and mechanical changes were investigated using materials research aspects.

2. Experimental

2.1. Materials

Flax fibres were supplied by Tanta Flax Ltd. Co. (Egypt). GMA (purity 97% containing 100 ppm monomethyl ether hydroquinone as inhibitor), polyoxyethylenesorbitan monolaurate (Tween-20) and isopropanol, were purchased from Sigma Aldrich and used without further purification. 97% Sodium hydroxide, 80% Sodium chlorite and $\geq$65% nitric acid (Sigma Aldrich) were used to prepare respective solutions with desired concentrations using double distilled water.

2.2. Pre-treatment of flax fibres

2.2.1. Mercerization

Flax fibres were pre-treated with 18% sodium hydroxide solution for 6 h under a constant stirring at 60 °C. The flax fibres were drained and washed repeatedly with distilled water and dried in an oven at 60 °C for 12 h.

2.2.2. Bleaching

The dried flax fibres were treated with sodium chlorite solution after adjusting its pH to 4 using 1 M nitric acid solution. The flax fibres were kept in sodium chlorite solution of desired concentration at 70 °C for 6 h with a continuous stirring. Later, the flax fibres were drained and washed repeatedly with distilled water and dried in an oven at 60 °C for 12 h.

2.2.3. Determination of lignin and cellulose contents

The lignin content in the flax fibres was determined according to TAPPI T222 om-02 method [APPI T222 om-02. Acid insoluble lignin in wood and pulp (2002)]. In this method lignin is defined as constituent fibres insoluble in 72% sulfuric acid. The content of cellulose is determined with an anthrone reagent (Ververis et al., 2004), in which fibres were boiled at 100 °C in a mixture of nitric/acetic acid (1:8, v/v) for 1 h to remove the lignin and hemicelluloses. The fibres is subsequently extracted with centrifugation and treated with 67% sulfuric acid solution. The amount of cellulose was determined using UV–vis/NIR, Perkin Elmer UV–vis/NIR spectrometer at 620 nm using cold anthrone.

2.3. Grafting of GMA onto raw and pre-treated flax fibres

Raw and bleached flax fibres of desired length with known weight were packed into polyethylene bags, which were deaerated by flushing with pure N_2 gas, and thermally sealed. The flax fibres were irradiated on a dry ice using an EB accelerator (EPS 3000, Nissin High Voltage, Japan) operated at an accelerating voltage of 1.0 MeV with a beam current of 10 mA. The total absorbed dose was varied from 10 to 50 kGy at a 10 kGy/pass by means of a conveyer system. The doses were verified using cellulose triacetate (CTA) dosimeter film based on ASTM E 1650–97 and JAERI-Memo 6948 (Tanaka et al., 1984). The irradiated flax fibres were kept in a dry ice temperature prior to use.

The GMA emulsion with desired concentration (1–9 wt%) was prepared by adding distilled water to GMA followed by 0.5 wt% of Tween 20 (Tw-20) and the mixture was homogenized for 60 min at room temperature. The obtained milky looking emulsion was found to be stable for 48 h. The GMA emulsion was bubbled with pure N_2 gas for 30 min before it was sucked into an evacuated glass ampoule connected to vacuum line and containing the EB-irradiated flax fibres and finally the ampoule was sealed. The grafting reaction was carried out by keeping the glass ampoule in an oven having turbo fan at 40 °C for time intervals ranging from 1 to 4 h. After completion of the reaction, the poly(GMA) grafted flax fibres were removed, washed with methanol several times to remove residual monomers and occluded homopolymer and were eventually dried. The amount of poly(GMA) grafted onto flax fibres represented by the degree of grafting (DOG) which was calculated using the following equation.