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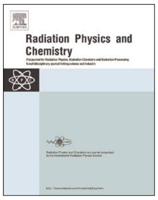

Modification of nylon-6 fibres by radiation-induced graft polymerisation of vinylbenzyl chloride

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HIGHLIGHTS

- Modification of nylon-6 fibres by radiation induced grafting of VBC in methanol.
- Establishment of relations between DG and reaction parameters.
- Evidence of VBC grafting was provided by FTIR, SEM, XRD, DSC and TGA.
- The properties of VBC-grafted nylon-6 fibres depend on DG.
- Amendable VBC-grafted nylon-6 fibres retain favourable properties.

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ABSTRACT

Modification of nylon-6 fibres by radiation-induced graft copolymerisation (RIGP) of vinylbenzyl chloride (VBC) using the preirradiation method was investigated. A number of grafting parameters such as type of solvent, total dose, monomer concentrations, reaction temperature and reaction time were studied to obtain desired degree of grafting (DG). The DG was found to be a function of reaction parameters and achieved a maximum value of 130 wt% at 20 vol% VBC concentration in methanol, 300 kGy dose, 30 °C temperature and 3 h reaction time. Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed to evaluate the chemical, morphological and structural changes that occurred in the grafted fibres, respectively. Thermogravimetric analysis (TGA) was also applied to determine the thermal stability, whereas differential scanning calorimeter (DSC) and universal mechanical tester were used to analyse respective thermal and mechanical properties of the grafted fibres. The results of these analyses provide strong evidence for successful grafting of VBC onto nylon-6, and the variation in the properties of the grafted fibres depends on DG.

1. Introduction

Radiation-induced graft polymerisation (RIGP) using high-energy radiation provides an effective and convenient method to incorporate new moiety that originated from monomers into polymer substrates to modify their properties towards meeting requirements of a variety of applications (Nasef and Hegazy, 2004). In particular, RIGP is capable of introducing polymers in a bulk quantity with a homogeneous grafting yield to various types of polymer substrates of different forms such as fibres, fabrics, films and powders. The distinct advantages of RIGP is in its ability to easily control the grafting yield to meet specific applications while the modified (grafted) polymers have high purity as there is no residues from the chemical initiator involved in the reaction left in the matrix of modified polymers.

RIGP of vinyl and acrylic monomers onto various fibres has received considerable interest in recent years. This yields polymers having grafted moieties distributed over a large surface area. In particular, RIGP was used to modify a large number of natural (e.g., flax, jute, ramie and pine needle) (Khan and Ahmad, 2006; Wojnárovits et al., 2010) and synthetic (e.g. polypropylene, polyethylene, polyacrylonitrile and nylon) fibres (Ikeda et al., 2011; Nasef and Hegazy, 2004). However, natural polymers in their raw forms have weak chemical and thermal properties compared with

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synthetic polymers; therefore, they become unstable in harsh chemical environments (Albano et al., 2002; O'Connell et al., 2008).

Among synthetic fibril polymers, nylon fibres occupy a special position because of their excellent characteristics of textural properties, mechanical strength, toughness and chemical and thermal stability (Liu et al., 2007) in addition to low cost and abundance. Such advantages have made nylon attractive for various applications including the development of functional/ionic polymers (Ikeda et al. 2011; Miyazawa et al. 2009). For example, monomers such as glycidyl methacrylate (GMA) (Ikeda et al., 2011), vinyl benzyltrimethylammonium chloride, and sodium styrene sulphonate (Miyazawa et al., 2009) were grafted onto nylon-6 fibres to produce precursors of ion exchange adsorbents.

Improving nylon properties by RIGP was also reported in several occasions. The dyability of polyamide-6,6-nylon was improved by the grafting of 2-hydroxyethyl methacrylate (Kaur et al., 2000). Grafting of a mixture of vinylbenzyl trimethyl ammonium chloride and 2-hydroxyethyl methacrylate by a simultaneous irradiation method was also used to impart the flame retardant property to nylon-6 fabric (Kolhe and Kumar, 2007). Antidripping property was introduced to nylon-6 (in the forms of fabric and granules) by RIGP of acrylic acid, methacrylic acid and acrylamide. Earlier, RIGP of acrylic acid (Zahran et al., 1985) and a mixture of acrylonitrile with 4-vinyl pyridine (Kaur et al., 1996) on nylon fabric under various grafting parameters was also studied. Despite the advantages of nylon fibres, the number of studies on using them as polymer substrates for RIGP is comparatively smaller than those on using polyethylene and propylene fibres. Moreover, reports on RIGP of vinylbenzyl chloride (VBC) onto nylon-6 cannot be found in literature.

Grafting of selective functional group on a polymer substrate is an interesting approach to prepare polymer adsorbent (Nasef and Güven, 2012). To design such adsorbent materials with high surface area and fast kinetics, cheap fibrous substrates are proposed (Awual et al., 2011; Seko et al., 2004, 2005). The selection of appropriate functional groups and the control of their level on the grafted chains allow imparting higher selectivity and more efficient adsorption properties to the adsorbent materials. These properties can be adjusted by variation of the degree of grafting which is a function of reaction parameters (Nasef and Hegazy, 2004). Therefore, it is highly important to understand the effects of reaction parameters on the degree of grafting to optimise them in a way allowing the achievement of efficient and reproducible degree of grafting to obtain specially designed selective adsorbents for specific applications.

In this study, we report the modification of nylon-6 by RIGP of VBC with electron beam (EB) to obtain grafted fibres with amendable moiety suitable for hosting functional groups after post-grafting treatment without compromising the favourable chemical, thermal and mechanical properties of nylon-6. This approach is expected to yield a selective fibrous adsorbent for environmental applications with high chemical stability and better regeneration properties. The use of VBC as a grafting monomer with its aromatic structure is likely to impart higher chemical stability to the final absorbent than previously grafted aliphatic monomers such as GMA, acrylic acid, methacrylic acid and acrylamide. The relations between the degree of grafting (DG) and various grafting parameters were established. The obtained fibres were characterised using various material research aspects such as FTIR, SEM, XRD, TGA, DSC and universal mechanical tester.

2. Experimental

2.1. Materials

VBC (mixture of 3- and 4-isomers, 97% contains 700–1100 ppm nitromethane as an inhibitor, 50–100 ppm *tert*-butylcatechol as an inhibitor) was purchased from Sigma-Aldrich. The monomer was used as received without any treatment. Nylon-6 fibre of 15 μm in diameter was supplied by Reliance Sdn. Bhd. (Malaysia).

Methanol, ethanol and propanol were supplied by Merck. Butanol and pentanol were obtained from Sigma-Aldrich. All solvents were reagent grade and used as received without any purification.

2.2. Grafting of VBC onto nylon-6

Nylon-6 fibre was irradiated using an EB accelerator (EPS 3000). The accelerating voltage used was 1.0 MeV with a beam current in the range of 5–10 mA. A transport system using a conveyor with various speeds was used to obtain a total absorbed dose ranging from 25 to 500 kGy at a 10 kGy/pass. Nylon-6 fibres were cut into pieces and weighed prior to use. The samples were placed in PE bags with zipped lips and purged using purified N_2 gas to remove air prior to irradiation on a dry ice placed on the top of the tray. The irradiated samples were stored in subambient temperature before their use for grafting experiments. The grafting solution with desired VBC concentration and solvent was deaerated using purified N_2 gas for 1 h. The oxygen-free VBC was transferred to the irradiated fibres kept in an evacuated ampoule using a vacuum stopcock adapter, and the ampoule was sealed and placed in a thermostatic bath in the range of 5–70 °C for a specific period of reaction time. At the end of the reaction, the grafted fibres were extracted and washed a few times using methanol then dried under vacuum (40 °C for 20 h), and the process is redone until a constant weight was achieved. This is to remove homopolymer and unreacted monomer that remained on the grafted fibres. The DG was obtained from the following equation:

$$DG(\%) = \frac{W_f - W_i}{W_i} \times 100 \quad (1)$$

where W_i and W_f are the weights of the initial original and finally grafted nylon-6 fibres, respectively.

2.3. Fourier transform infrared (FTIR)

FTIR analysis was carried out on a Perkin-Elmer Spectrum One FTIR spectrometer. Samples were scanned in a transmission mode at a frequency range of 500–4000 cm^{-1}. The scan resolution was 4 cm^{-1}.

2.4. Scanning electron microscopy (SEM)

SEM images of the fibres were obtained using a FEI Quanta 4000, scanning electron microscope. All fibre samples were sputter-coated with gold layer before imaging. All images were captured at applied voltage of 20.0 kV and working distance of 10 mm.

2.5. Differential scanning calorimetry (DSC)

DSC analysis of the fibre samples was analysed using a Mettler-Toledo, DSC 822e calorimeter. The measurement was carried out in the range of 30–300 °C with a heating rate of 10 °C/min in an N_2 atmosphere. Percentage of crystallinity (X_c) in pristine fibres is calculated from the area under DSC melting peaks using the following equation: