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Melting grafting polypropylene with hydrophilic monomers for improving hemocompatibility

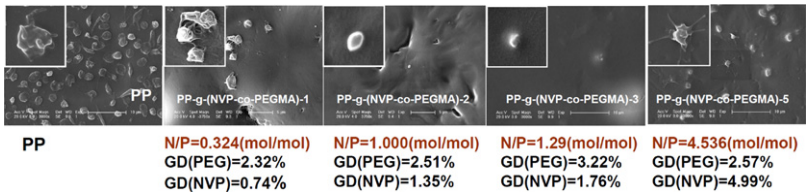
Jing Jin[a,b], Chang Zhang[a,b], Wei Jiang[a,*], Shifang Luan[a], Huawei Yang[a,b], Jinghua Yin[a,*], Paola Stagnaro[c]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] Istituto per Io Studio delle Macromolecole, Consiglio Nazionale delle Ricerche, Via de Marini 6, 16149 Genova, Italy

HIGHLIGHTS

- We fabricated PP-g-(NVP-co-PEGMA) with NVP as a co-grafted monomer of PEGMA.
- Solvent inducement was introduced to increase the hydrophilicity of the modified film.
- The balance of PEGMA grafting degree and NVP crosslinking was significant to hemocompatibility.

GRAPHICAL ABSTRACT



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ABSTRACT

Polypropylene was successfully grafted with poly (ethylene glycol) methacrylate (PEGMA) using N-vinyl pyrrolidone (NVP) as a co-grafted monomer through melting reactive grafting modification. The grafting degree of PEGMA could be obviously enhanced by the introduction of NVP at the NVP/PEGMA molar feeding ratio of 1.3. To improve the surface hydrophilicity further, hydrophilic monomers were enriched onto the surface by solvent inducement. The water contact angle of the copolymers decreased obviously and X-ray photoelectron spectroscopy (XPS) showed that the surface energy and the polar component of the modified films depended on the PEGMA grafting degree. The hemocompatibility of copolymers films were improved by increasing the PEGMA grafting degree and deteriorated by augmenting the NVP grafting degree. It was found that the balance of PEGMA grafting degree and NVP crosslinking was significant to the blood compatibility of the modified films. The biomaterial PP-g-(NVP-co-PEGMA) with the largest PEGMA grafting degree (up to 3.22 wt.%) and moderate NVP grafting degree (1.76 wt.%) could effectively resist to protein adsorption and suppress platelet adhesion.

1. Introduction

Polypropylene (PP) is one of the widely used materials in medical apparatus and instruments, owing to its non-toxic and excellent mechanical properties [1,2]. Many studies have been devoted to improve its biocompatibility with hydrophilic monomers via bulking [3] and surface grafting [4], or polymer blending [5]. The surface grafted modifications have some limits in industry because it requires relatively expensive equipment and probably lead to significant surface aging of the base material [6]. Thus, the bulk grafting modification for improving the hydrophilicity and hemocompatibility of PP is imperative for preparing PP-based biomaterials. Previous studies show that the hemocompatibility of polyolefin materials can be improved by bulk modification using melting [7,8] and solution grafting [9]. Tethering of functional monomers such as polyethylene glycol (PEG), glycidyl methacrylate (GMA), or N-vinyl pyrrolidone (NVP) is an effective means to improve hemocompatibility to polyolefin. Unlike surface modification, during the melting grafting process, most of hydrophilic grafted chains are embedded in polymer bulk. There are two problems need to be considered for improvement the hemocompatibility of PP. One is that the graft efficiency of hydrophilic monomers on the PP main chains is confined by steric hindrance of monomers. The other is that the surface hydrophilicity does not

* Corresponding authors. Tel.: +86 431 85262151; fax: +86 431 85262126.
E-mail addresses: wjiang@ciac.jl.cn (W. Jiang), yinjh@ciac.jl.cn (J. Yin).

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always increase with increasing the grafting degree of hydrophilic monomers in bulking modification. Therefore, solvent inducement is generally used to enrichment the hydrophilic monomer on the surface for enhancing the hemocompatibility [8].

Immobilized PEG molecules on a surface can result in a dramatic reduction in the protein adsorption and platelets adhesion [10,11]. The high protein resistant of PEG has been explained in terms of steric stabilization, chain mobility and hydration [12]. The theoretical analysis shows that the osmotic repulsion is a main reason for the resistance to adsorption [13], which uses a simplified model of polymer chains and protein molecules. NVP is a hydrophilic and non-ionic monomer, the homopolymer of NVP, poly (N-vinyl pyrrolidone) (PNVP) has a great potential application in different biomedicine owing to its strong hydrophilicity and excellent hemocompatibility [14–16]. NVP also is employed as a co-grafted monomer with glycidyl methacrylate (GMA) [7], maleic anhyride (MA) [17], acrylamide (AAm) [18] and 2-hydroxyethyl methacrylate (HEMA) [19] to be graft on polymer surface for enhancing grafting degree and improving hemocompatibility. Georgiev et al. reported that there was a minimum value of MA concentration in the NVP/MA comonomers mixture, up to which an alternating copolymer was obtained [20]. It is found that a known charge–transfer-complex (CTC) mechanism can be explained this electron donor–acceptor interaction. However, the crosslinking in the binary monomers system can influence the hydrophilicity and hemocompatibility of the surfaces. Because the mobility of hydrophilic molecular chains can be restricted by a large increase of crosslinking, which give rise to reducing the excluded volume of flexible polymer chains in an aqueous medium and deteriorating the hemocompatibility of modified films [21]. Thus, NVP was used as a co-grafted monomer of PEGMA with a proper ratio to enhance the biocompatibility of polypropylene.

In this study, we fabricate PP-g-(NVP-co-PEGMA) with NVP as a co-grafted monomer of PEGMA. Solvent inducement is introduced to increase the hydrophilicity of the modified film surface. The hemocompatibility of copolymers films are improved by increasing PEGMA grafting degree and deteriorated by augmenting NVP grafting degree. Melting modification combined with solvent inducement is an effective method to improve the hemocompatibility and has wide perspective and practicability.

2. Experimental

2.1. Materials

Polypropylene powder with melt flow rate (MFR) of 13 g/10 min (2.16 kg, 230 °C) used in this study was purchased from Jilin Petrochemical Company of China. Poly (ethylene glycol) methacrylate (PEGMA, M_n = 360), and N-vinyl pyrrolidone (NVP) was purchased from Aldrich Company. Dicumyl peroxide (DCP), xylene, acetone and ethanol were all purchased from Beijing Chemical Factory of China. DCP was recrystallized from a chloroform/methanol mixture before use. Bovine serum albumin (BSA; pI = 4.8, M_w = 66,000) was obtained from Sigma chemical Co. Phosphate-buffered saline (PBS 0.9% NaCl, 0.01 M phosphate buffer, pH 7.4) used for protein adsorption and platelet adhesion experiment was prepared freshly. The amount of protein adsorption was determined using Micro BCA™ protein assay reagent kit (AR1110, Boster Biological Technology, Co., Ltd. Wuhan, China). Other reagents were AR grade and used without further purification.

2.2. Grafting reactions

The PP powder, initiator (DCP), and monomers were premixed, and then were charged into a Brabender (Shanghai, China) mixer at 180 °C. The grafting reaction time was 5 min and the speed of rotors was set at 80 rpm. Modified PP (3 g) was dissolved in 100 ml xylene and refluxed under stirring until a clear solution was obtained. The solution was precipitated in 300 ml acetone/ethanol to remove unreacted monomers, washed with excessive acetone/ethanol, vacuum filtered, and then dried in vacuum oven at 80 °C for 24 h. Acetone was used as precipitator for grafting reaction of PP-g-PEGMA, whereas ethanol was used for PP-g-(NVP-co-PEGMA). In order to clarify the effect of NVP in the co-grafting of PEGMA in the system of PP-g-(NVP-co-PEGMA), different molar feeding ratios (NVP/PEGMA) range from 0 to 6.480 were been studied.

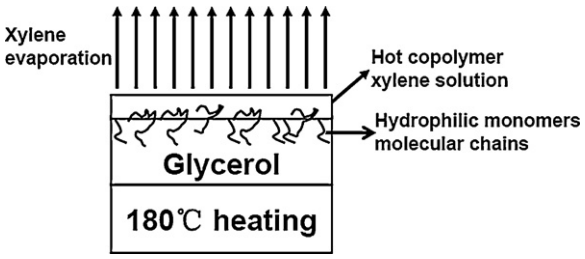

Fig. 1. The schematic diagram of solvent inducement enrichment of hydrophilic monomers molecular chains onto the surface of modified PP.

2.3. Solvent inducement enrichment of hydrophilic monomers chains onto the surface of modified PP.

Modified PP was dissolved in xylene (5.0 wt.%) at 130 °C with 2 h until forming homogeneous solution, then a drop of hot grafted copolymer xylene solution with 1.0 ml was dipped onto the surface of hot glycerol with a heating device keeping the temperature at 180 °C. After gradual evaporation of xylene at 180 °C, a thin layer of PP film was formed on the interface between glycerol and xylene, as shown in Fig. 1. The composition of modified film surface was determined by XPS after cooling and removing all the solvents.

2.4. Characterization of the graft copolymers

The calibration curve with the additional absorption of carbonyl group (C=O, A_{1723}) was used to determine the PEGMA concentration in the grafting copolymers. PP and PEGMA were dissolved in xylene to form homogenous phase solution at 130 °C and dried in vacuum oven at 60 °C for 24 h to completely evaporate the solvent, and then compression-molded into films at 180 °C for the FTIR test [22]. The ratio of the absorbance of the methyl group (A_{1450}) in PP main chain to the addition of the absorbance of C=O (A_{1723}) in PEGMA was selected as an abscissa, and PEGMA concentration in the blend samples was set as an ordinate. The films were characterized using a Bruker Vertex 70 FTIR spectrometer operating from 4000 to 500 cm^{-1} at a resolution of 2 cm^{-1} for 32 scans. The thickness of the film was 50–100 μm. Fig. 2 shows calibration curve for the quantitative measurement of the grafting degree and FTIR result. The grafting degree was calculated from the ratio of the IR absorbance of PEGMA (1723 cm^{-1}) to that of 1450 cm^{-1}, where the absorption at 1723 cm^{-1} was assigned to the C=O stretching vibration of the carbonyl and that at 1450 cm^{-1} to the CH_2 rocking vibration of PP main chains. The grafting degree was calculated by the following equation:

$$\mathrm{GD(wt.\%)} = \frac{33.86A_{1723}}{A_{1450}} \quad (1)$$

The determination of NVP grafting degree was the same as the PEGMA, while the IR absorbance of NVP was 1680 cm^{-1}.

Rheological measurements were carried out with a PHYSICA MCR 300 instrument (Stuttgart, Germany). Frequency sweeps for