SYNTHESIS AND CHARACTERIZATION OF LAURYL METHACRYLATE – GRAFT - POLYPROPYLENE FIBER

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Received: 29 August 2015; Accepted for publication: 28 October 2015

ABSTRACT

The graft polymerization of lauryl methacrylate (LMA) onto polypropylene fiber (PP) was investigated by using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The grafting was influenced by AIBN concentration, monomer concentration, the reaction time and reaction temperature. On the basis of a detailed investigation of these factor, the optimal conditions for the grafting of LMA onto PP with the said initiator were as follows: [AIBN] = 0.015 mol/l, [LMA] = 1.25 mol/l, reaction time 240 min, reaction temperature 80 °C, in which the graft yield (%GY) of 15.7 % was obtained. Characterization of the polypropylene fiber-graft-lauryl methacrylate was done by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

Keywords: graft polymerization, polypropylene fiber, lauryl methacrylate.

1. INTRODUCTION

Polypropylene (PP) fibers have been used for valuable purposes in different areas like textile, concrete and some chemical industries [1]. Despite their noticeable properties such as chemical and thermal stability, stiffness, low density, impact resistance and low material cost, however, PP fibers are restricted in their applications because of this polymer has some drawbacks: it does not contain any reactive site, it has extremely poor hygroscopicity, it is difficult to dye, it has low melting and sticking temperatures, it is sensitive to photooxidation, they cannot be used under conditions that require high temperatures [2] and so on. This restricts its use in several technologically important fields. Hence, it needed some modification of its original properties before it could be used for a particular operation.

Among the methods of modification of polymers, grafting is one of the promising methods. In principle, graft polymerization is an attractive method to impart a variety of functional groups
to a polymer. Graft polymerization initiated by chemical treatment, photo-irradiation, high-energy radiation technique, etc. is documented in this review (Several prime controlling factors on grafting are discussed. In the past several years, there has been increased emphasis on applications of grafted polymers). The modified polymers through grafting not only retains most of its original properties but also acquires some additional properties needed for a particular application [3 - 5].

In this work, the graft copolymer of lauryl methacrylate (LMA) onto polypropylene fiber (PP-g-LMA) using AIBN as initiator was synthesized to find out the optimum conditions for the grating. Characterization of the graft copolymer was done by FTIR and SEM.

2. MATERIALS AND METHODS

2.1. Materials

PP fiber were prepared by a melt-blown spinning as follows: tensile strength 350 MPa, specific gravity of 0.91 g/cm³ were used after cutting it to 0.8 – 1.0 cm length were supplied by Thai Polyethylene Co., Ltd (Thailand). All chemical reagents were used as received. Lauryl methacrylate (LMA), 2,2'-azobisisobutyronitrile (AIBN), toluene, absolute ethanol, acetone were of laboratory analytical grade were supplied by HUPC Chemical Co., Ltd (China).

2.2. Graft polymerization

Graft polymerization was carried out under nitrogen atmosphere in a 150 ml three-neck flask equipped with a stirrer and condenser. PP fiber (0.5 g) was immersed in 15 ml of Toluene for 4 hours and a pre-calculated amount of LMA was put into the flask. The flask was placed in the thermostatic water bath at the chosen temperature. A certain quantity of AIBN was slowly added to the reaction mixture and stirred. After the desired reaction period, the product was poured into 100 ml of absolute ethanol to induce precipitation. The graft product was washed several times with absolute ethanol and extracted with acetone to remove the homopolymer of LMA and graft copolymer was then dried under vacuum at 60 °C to constant weight. To confirm the results, each experiment was repeated thrice under the same conditions and the graft yield (GY) values were estimated which were well within the acceptable standard deviation of 0.2 %. The graft yield of PP-g-LMA were determined by the following formula:

\[ \text{GY(\%)} = \frac{m_2 - m_1}{m_1} \times 100 \]

where \( m_2 \) and \( m_1 \) are the weights of PP-g-LMA and PP, respectively.

The different parameters of polymerization is shown in the Table 1.

2.3. Characterization

2.3.1. FTIR spectra

A Nicolet (IMPACT 410, USA) FTIR spectrometer in the range of 4000 - 400 cm⁻¹ was used to record the IR spectra for PP and graft copolymer. The samples were ground with dried KBr powder.
2.3.2. Scanning electron microscopy (SEM)

The scanning electron microscope was used to study the morphology of the surface of PP, graft copolymer. The SEM was of JEOL 6390 model (Japan).

Table 1. The different parameters of polymerization.

| Sr. No. | Time (min) | Temperature (°C) | Catalyst (mol/l) | Monomer (mol/l) |
|---------|------------|------------------|------------------|-----------------|
| 1. Effect of time | 30 | 80 | 0.015 | 1.25 |
| 2 | 60 | 80 | 0.015 | 1.25 |
| 3 | 90 | 80 | 0.015 | 1.25 |
| 4 | 120 | 80 | 0.015 | 1.25 |
| 5 | 150 | 80 | 0.015 | 1.25 |
| 6 | 180 | 80 | 0.015 | 1.25 |
| 7 | 210 | 80 | 0.015 | 1.25 |
| 8 | 240 | 80 | 0.015 | 1.25 |
| 9 | 270 | 80 | 0.015 | 1.25 |
| 2. Effect of temperature | 240 | 65 | 0.015 | 1.25 |
| 2 | 240 | 70 | 0.015 | 1.25 |
| 3 | 240 | 75 | 0.015 | 1.25 |
| 4 | 240 | 80 | 0.015 | 1.25 |
| 5 | 240 | 85 | 0.015 | 1.25 |
| 3. Effect of catalyst concentration | 240 | 80 | 0.01 | 1.25 |
| 2 | 240 | 80 | 0.015 | 1.25 |
| 3 | 240 | 80 | 0.02 | 1.25 |
| 4 | 240 | 80 | 0.025 | 1.25 |
| 5 | 240 | 80 | 0.03 | 1.25 |
| 4. Effect of monomer concentration | 240 | 80 | 0.015 | 0.75 |
| 2 | 240 | 80 | 0.015 | 1.00 |
| 3 | 240 | 80 | 0.015 | 1.25 |
| 4 | 240 | 80 | 0.015 | 1.50 |
| 5 | 240 | 80 | 0.015 | 1.75 |
| 6 | 240 | 80 | 0.015 | 2.00 |

3. RESULTS AND DISCUSSION

3.1. Effect on reaction time

The effect of grafting polymerization time on the %GY is shown in Figure 1. It illustrates the effect of reaction time on the GY. It was observed that the percent grafting increases initially and then remains constant. With an increase in reaction time, the radicals will have more time for reaction, and, as a result, will increase the percent grafting. After some time all initiators are
used up. As a result, no further change in grafting percentage was observed with an increase in reaction time, the optimum reaction time was 240 min.

![Graph showing the effect of reaction time on GY](image1.png)

**Figure 1.** Effect of reaction time on the GY, [LMA] = 1.25 mol/l, AIBN = 0.015 mol/l, reaction temperature: 80 °C.

![Graph showing the effect of temperature on GY](image2.png)

**Figure 2.** Effect of temperature on the GY, [LMA] = 1.25 mol/l, AIBN = 0.015 mol/l, reaction time: 240 min.

3.2. Effect of temperature

The grafting reaction was carried out at different temperatures 65 – 85 °C with the other variables kept constant. The effect of temperature on the %GY is shown in Figure 2. With increasing temperature, %GY increases due to increased decomposition of initiator. Therefore, the number of free radicals as well as their mobility also increases resulting in a higher percent of grafting. Higher mobility also results in mutual termination of free radicals resulting in decreased availability of the free radicals for polymerization.

3.3. Effect of initiator concentration

The effect of variation in AIBN concentration on %GY is shown in Figure 3.

AIBN concentration was increased from 0.01 to 0.03 mol/l. As is evident from Figure 3, the %GY increased with increasing initiator concentration but reached a maximum value (15.7 %) at 0.015 mol/l. A further increase in AIBN concentration was accompanied by a decrease in the %GY. The observed increase in %GY, with the AIBN concentration ranging from 0.015 to 0.03, may be due to the fact that in this concentration range, the activation along the backbone took place immediately, followed by the graft polymerization of the monomer onto the backbone. A relatively high concentration of the initiator may have caused a reduction in grafting, due to an increase in the number of backbone radicals terminated. Further, the homopolymer formation at higher concentrations, which competed with the grafting reaction for available monomer, could have led to a decrease in %GY.
3.4. Effect of monomer concentration

The effect of monomer concentration on %GY is shown in Figure 4.

The results shown that the %GY increases initially with an increase in monomer concentration up to 1.25 mol/l and then remains constant. This may be because initially the number of monomer molecules diffusing through the reaction medium and reaching the free radical sites on the polypropylene backbone governs the grafting extent, whereas at higher concentrations of monomer, the %GY remains almost constant as the number of free radical sites available on the polypropylene backbone becomes a limiting factor.

3.5. FTIR spectroscopy

The FTIR spectra of PP and PP-g-LMA have been reported in Figure 5.
Figure 5b. IR spectra of PP-g-LMA.

Figure 5 shows the IR spectra of the original PP and the grafted PP fiber. There were strong bands at 1454 cm$^{-1}$ and 1383 cm$^{-1}$ in grafted PP, corresponding to the bending vibrations of CH$_2$ for both PP and the grafted PP fiber. Compared to the original PP, the appearance of new band at 1731 cm$^{-1}$ in the grafted PP was due to the stretching vibrations of C=O. The characteristic peak indicated that LMA had been grafted onto the PP fibre by grafting polymerization.

3.6. The scanning electron microscopy (SEM)

The surface morphology of PP and PP-g-LMA is shown in Figure 6.

Comparison of SEM micrographs of raw and modified fibers confirms that graft copolymerization has been occurred. The smooth surface of the pristine PP fiber became rough. A heterogeneous grafting layer formed on the surface of the modified fiber.

4. CONCLUSION

In this article, the optimal reaction conditions for the graft polymerization of LMA on to PP fiber were obtained [LMA] = 1.25 mol/l, [AIBN] = 0.015 mol/l, reaction temperature 80 °C.
reaction time 240 min. The graft copolymer with GY of 15.7 % was obtained under optimum conditions. The presence of poly(LMA) chains onto graft copolymer was indicated by FTIR spectroscopy and SEM.

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TỔM TÁT

TỔNG HỢP VÀ ĐẶC TRUNG CỦA LAURYL METACRYLATE – GHẾP – POLYPROPYLEN

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Quá trình tổng hợp ghép lauryl metacrylat (LMA) lên sợi polypropylene (PP) được nghiên cứu, sử dụng chất khởi mao 2,2’– azobisisobutyronitrile (AIBN). Quá trình tổng hợp ghép chịu ảnh hưởng bởi các yếu tố: Nồng độ AIBN, nóng độ LMA, thời gian phản ứng, nhiệt độ phản ứng. Trong cơ sở nghiên cứu chỉ tiệt các yếu tố này, có thể rút ra điều kiện tối ưu cho quá trình tổng hợp ghép như sau: [AIBN] = 0,015 mol/l, [LMA] = 1,25 mol/l, thời gian phản ứng 240 phút, nhiệt độ phản ứng 80 °C. Sợi PP ghép lauryl metacrylat được đạc trung bồi phổ hống ngoại biên đối Fourier (FTIR) và hiển vi điện tử quét (SEM).

Từ khóa: tổng hợp ghép, sợi poly propylene, lauryl metacrylat.