MAJID MAZHAR¹
MAJID ABDOUSS¹
ZAHRA SHARIATINIA¹
MOJDEH ZARGARAN²
¹Department of Chemistry, Amirkabir University of Technology (Polytechnic), Tehran, Iran
²Building and Housing Research Center (BHRC), Tehran, Iran

SCIENTIFIC PAPER
UDC 677.494.742.017:66.095.26-922.3
DOI 10.2298/CICEQ120428104M

GRAFT COPOLYMERIZATION OF METHACRYLIC ACID MONOMERS ONTO POLYPROPYLENE FIBERS

Abstract
In recent years, graft copolymerization has been widely used to insert various functional groups onto polymers. In our study, methacrylic acid monomers are grafted to polypropylene (PP) fibers to make them hydrophilic while maintaining their mechanical properties. Experiments are designed based on Taguchi method and influence of temperature, monomer concentration; crosslinker concentration and time of reaction are investigated. Grafting of methacrylic acid and divinyl benzene is investigated by FTIR spectra and confirmed by SEM micrographs. Tensile strength and toughness of specimens are measured and compared with raw fibers. The effects of grafting on the tensile strength and toughness of fibers are measured and the critical grafting degree to maintain tensile strength and toughness of fibers is defined.

Keywords: mechanical properties, PP fiber, Taguchi method, graft copolymerization, SEM.

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, PP fibers are restricted in their applications because of the lack of chemical functionalities and nonpolarity [2]. For example, they cannot be used under conditions that require high temperatures. These drawbacks can be removed by effecting functionalization of the backbone polymer through grafting [3]. When the interaction with other materials is important, a modification of these polyolefins should be carried out [4]. Modification of different types of polyolefins with polar groups by various methods which includes graft-copolymerization method has been studied almost comprehensively [3,5-8]. The chemistry associated with specific functional groups may change the properties of the graft-modified polymer and potentially improve its usability in applications requiring reactivity, paint-ability, adhesion, stability or impact strength [9]. Graft copolymerization can be performed by various methods such as grafting initiated by chemical means [10,11], grafting initiated by photoradiation [12,13], γ-irradiation [14], thermal [15] and enzymatic grafting [16,17]. Free radical grafting of monomers is one of the most attractive ways for the chemical modification of polymers. It involves the reaction between a polymer and a vinyl-containing monomer, which is able to form grafts onto the polymer backbone in the presence of free radical generating chemicals, such as peroxides [18,19]. As some literature confirms, grafting of the fibers with high grafting degree can weaken their strength in tension [20,21]. But there is not a comprehensive study on the influence of chemical grafting on PP fibers mechanical properties. It is notable that grafting of methacrylic acid onto PP fibers has been performed by the radiation-induced method [22]. In this research, influences of temperature, monomer concentration, crosslinker concentration and reaction time on grafting degree of PP fibers are studied based on the Taguchi method, while effect of grafting on tensile strength and toughness of PP fibers are also investigated. The Taguchi method is a statistical method for experiment designing [23].

Corespondence: M. Abdouss and Z. Shariatinia, Department of Chemistry, Amirkabir University of Technology (Polytechnic), P.O. Box 159163-4311, Tehran, Iran.
E-mail: phdabdouss44@aut.ac.ir (M. Abdouss), shariati@aut.ac.ir (Z. Shariatinia)
Paper received: 28 April, 2012
Paper revised: 12 August, 2012
Paper accepted: 2 November, 2012
MATERIALS AND METHODS

Materials

The PP fiber used was prepared commercially and characterized as follow: tensile strength 350 MPa, 1111 dtex, cross-sectional area of 0.12 mm² and specific gravity of 0.91 g/cm³. Methacrylic acid (MAA) and benzoyl peroxide (BPO) were both purchased from Merck. BPO was recrystallized and then used. MAA was distilled in vacuum at 88 ºC before use. Divinyl benzene (DVB) was utilized as a cross-linker and toluene was used as a solvent (both purchased from Merck).

Scanning electron microscopy (SEM) micrographs were obtained using a Philips XL30 instrument, under vacuum, accelerated at 30 kV. Infrared (FT-IR) spectra were recorded on a Shimadzu spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. The tensile strengths were measured using an Amsler Universal Tension Machine (Germany).

Design of experiments

The experiments are designed by the Taguchi method [23], which is an accepted statistic method for heavily reducing the number of required experiments to investigate the influence of some parameters on the result of a specific reaction. It was selected in this paper to overcome the multiplicity of the required experiments. Without the Taguchi method, it is necessary to perform 4⁴ (256) experiments to fully investigate the influence of 4 factors at 4 levels on the grafting reaction, while just 16 experiments are required to study it in an acceptable way. An L₁₆ array was selected as the appropriate array for this research. This array was modified to four factors at four levels by QUALITEK 4 software [24]. To investigate the influence of four factors (temperature, monomer concentration, cross-linker concentration and time) at four levels (Table 1) on the grafting degree, the experiments were designed as shown in Table 2.

Table 1. Levels of factors

<table>
<thead>
<tr>
<th>No.</th>
<th>Factor</th>
<th>Level</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temperature, ºC</td>
<td></td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>MAA conc., mass%*</td>
<td></td>
<td>25</td>
<td>40</td>
<td>55</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>DVB conc., mass%*</td>
<td></td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Time, h</td>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

*Refers to weight percentage which is calculated as (the component weight) / (total weight of the solution)

Procedure of graft-copolymerization

To remove any chemicals adsorbed on the fiber surface, the fibers were washed with acetone, two times for 3 min and dried in an oven at 30 ºC for 5 h before initial mass was determined. The initiator BPO was dissolved in a small amount of toluene and this solution was mixed with a solution of monomer MAA (0.5 mol%) in 50 ml toluene. The mixture was purged by nitrogen gas for 5 min and then dropped in fibers glass flask under nitrogen atmosphere. Then specified amounts of DVB were added to the mixture.

Table 2. Experimental conditions

<table>
<thead>
<tr>
<th>Trial no.</th>
<th>Temperature, ºC</th>
<th>MAA conc., mass%*</th>
<th>DVB conc., mass%*</th>
<th>Time, h</th>
<th>Degree of grafting, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>25</td>
<td>0</td>
<td>1</td>
<td>2.22</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>40</td>
<td>5</td>
<td>2</td>
<td>5.33</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>55</td>
<td>10</td>
<td>2</td>
<td>11.13</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>70</td>
<td>20</td>
<td>4</td>
<td>12.67</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>25</td>
<td>5</td>
<td>3</td>
<td>7.13</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>40</td>
<td>0</td>
<td>4</td>
<td>8.78</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>55</td>
<td>20</td>
<td>1</td>
<td>8.33</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>70</td>
<td>10</td>
<td>2</td>
<td>9.67</td>
</tr>
<tr>
<td>9</td>
<td>35</td>
<td>25</td>
<td>10</td>
<td>4</td>
<td>9.67</td>
</tr>
<tr>
<td>10</td>
<td>35</td>
<td>40</td>
<td>20</td>
<td>3</td>
<td>11.13</td>
</tr>
<tr>
<td>11</td>
<td>35</td>
<td>55</td>
<td>0</td>
<td>2</td>
<td>8.67</td>
</tr>
<tr>
<td>12</td>
<td>35</td>
<td>70</td>
<td>5</td>
<td>1</td>
<td>8.33</td>
</tr>
<tr>
<td>13</td>
<td>40</td>
<td>25</td>
<td>20</td>
<td>2</td>
<td>10.13</td>
</tr>
<tr>
<td>14</td>
<td>40</td>
<td>40</td>
<td>10</td>
<td>1</td>
<td>9.78</td>
</tr>
<tr>
<td>15</td>
<td>40</td>
<td>55</td>
<td>5</td>
<td>4</td>
<td>15.33</td>
</tr>
<tr>
<td>16</td>
<td>40</td>
<td>70</td>
<td>0</td>
<td>3</td>
<td>14.67</td>
</tr>
</tbody>
</table>

*Refers to weight percentage which is calculated as (the component weight) / (total weight of the solution)
The flask was placed in an oil bath at various temperatures and was shaken for specified times with a shaking speed of 150 rpm. MAA-grafted PP fibers were removed from the reaction flask and washed with a solution of 5% NaOH in water/ethanol (50:50, v/v) and extracted using methanol as the solvent with a soxhlet extractor for 24 h to remove any residual monomer and homo polymers. The fibers were then washed with large amounts of water, dried and weighed. Degrees of grafting \( D_g \) were determined using the equation \( D_g (\%) = \left( \frac{W_1 - W_0}{W_0} \right) \times 100 \), in which \( W_1 \) is the weight of grafted fibers and \( W_0 \) is the initial weight.

RESULTS AND DISCUSSION

Grafting results

Experiments were performed according to the above procedure and conditions were controlled as mentioned in Table 2. The results (Table 2) were interpreted by Qualitek 4 software. Influences of four different factors on the grafting reaction are presented in the following sections.

Temperature effect

Interpreting the experimental results by Qualitek 4 software revealed the effects of factors on the grafting reaction. For temperature efficacy (Figure 1), it can be concluded that high temperatures lead to an increment in grafting degrees. Also, the slope of the curve is increased by raising temperature. This behavior indicates that to achieve high grafting degrees, it is essential to use higher temperatures. Raising temperature increases the number of free radicals generated by the thermo-decomposition of the initiator, which results in more active sites on the fiber surface. Another effect is that high temperatures enhance the diffusion of the monomer to the active site for polymerization. This procedure certainly has a limitation and increasing temperature partly can increase the grafting degree, because higher temperatures cause the initiator to decompose rapidly and increase the number of generated radicals, leading to the formation of homopolymers, which surely will decrease expected amount of copolymer and grafting degree. The maximum effect of temperature on grafting degree in the studied interval was achieved at 40 °C (level 4 for temperature).

Monomer concentration effect

Interpretation of grafting results by the software revealed the monomer concentration effect on the graft copolymerization as shown in Figure 2. Raising the monomer concentration increases the grafting degree but the slope of curve logically decreases in high monomer concentrations. High monomer concentration results in high viscosity of solution because the gel effect might be generated in homogenous reaction systems. Thus, the diffusion of monomers from bulk solution to fiber surface is prevented by high viscosity, which results in a decrease of the curve slope and could even decrease the grafting yield. The optimum effect of monomer concentration is achieved with 70% w/w monomer concentration.

Figure 1. Effect of temperature levels on grafting degrees.
Cross-linker concentration effect

As mentioned, DVB was used as a cross-linker in this work. Interpretation of the grafting results by the software revealed the DVB concentration effect on the graft copolymerization as shown in Figure 3. DVB has a slight influence on grafting yield, but raising its concentration relatively increases the grafting degree. The presence of DVB in the reaction environment branches side-chains, which results in more grafting of monomers. DVB has two vinyl groups and can participate in the reaction with both of these groups. When doing so, it makes the side-chains to generate and branch. If produced branches reach to other side-chains, DVB acts as cross-linker and if not, it acts to branch the side chains. In the latter case, because of multiplicity of growing branches, more monomers can attach to the growing chain, as Figure 4 demonstrates.

Reaction time effect

Using the grafting results, Qualitek 4 software interpreted the effect of reaction time on grafting degree (Figure 5). The reaction time has a remark-
able effect on grafting yield. With raising the reaction time, amounts of monomers that are grafted to the fibers are increased. The slope of the curve tends to decrease by raising the time of reaction. Graft copolymerization is a relatively slow reaction. Whenever required amounts of the substances are added to the reaction environment, they need time to react with each other. Therefore, having more time for the reaction results in more attachment of monomers to the growing side and more grafting yield. Obviously, after elapsing appropriate time and consuming reactants, the rate of grafting decreases and the grafting reaction tends to stop and be completed. The appropriate time to achieve higher grafting degrees in the studied interval was determined as 4 h.

**Optimum condition**

The software determined the main effects of levels of each factors on grafting degrees (Table 3). Main effect of each level represents contribution of that level to the grafting degree. Greater main effects

![Figure 4. Structure of synthesized copolymer including DVB branching mechanism and vibrational modes of some important bonds in FTIR spectroscopy.](image)

![Figure 5. Effect of the reaction time levels on grafting degrees.](image)

Table 3. Main effects (contributions) of levels of the factors to the grafting degree

<table>
<thead>
<tr>
<th>No.</th>
<th>Factor</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
<th>Level 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temperature, °C</td>
<td>7.837</td>
<td>8.477</td>
<td>9.449</td>
<td>12.477</td>
</tr>
<tr>
<td>2</td>
<td>MAA conc., mass%</td>
<td>7.287</td>
<td>8.755</td>
<td>10.864</td>
<td>11.335</td>
</tr>
<tr>
<td>3</td>
<td>DVB conc., mass%</td>
<td>8.585</td>
<td>9.03</td>
<td>10.062</td>
<td>10.565</td>
</tr>
<tr>
<td>4</td>
<td>Time, h</td>
<td>7.164</td>
<td>8.449</td>
<td>11.014</td>
<td>11.612</td>
</tr>
</tbody>
</table>

*Refers to weight percentage which is calculated as \((\text{component weight}) / (\text{total weight of the solution})\)
result in greater grafting degrees. From this table, it can be inferred that the level four of each factor has more effect in increasing the grafting yield. Furthermore, if the optimum condition refers to the highest amount of grafting, these levels could be recommended. The expected grafting degree at optimum condition was estimated by the software as 17.305%. It should be considered that the reaction was optimized with 16 experiments based on the Taguchi method instead of 256 required experiments by varying each of the parameters. The reported maximum degree of grafting is for the conditions studied in this research. In fact, achieving high grafting yield was not our purpose in this work, because high grafting yields result in decrement of mechanical properties of the fibers. Accordingly, moderate conditions were selected here. Obviously, if greater amounts were selected for the factors, grafting degrees became higher than those achieved.

**Verification of graft copolymerization**

To confirm that grafting is performed, FT-IR spectra of three specimens were investigated. Figures 6-8 are related to the raw PP fiber, specimen (16) grafted by methacrylic acid monomers without crosslinker (DVB) and specimen (13) grafted by methacrylic acid with contribution of DVB as cross-linker, respectively. The peak at 1716 cm\(^{-1}\) in Figure 7 refers to the stretching of the C=O group in MAA grafted to PP fiber. Due to the stretching of the O-H bond, a distinct peak is seen at about 3400 cm\(^{-1}\) in Figure 7. There is a peak at 1255 cm\(^{-1}\) and two peaks around 950-990 cm\(^{-1}\) that can be attributed to the stretching of the C-O bond and out of plane vibration of the O-H bond in MAA grafted to the PP fiber. These peaks verify DVB contribution in the graft copolymerization. Some important vibrational modes are demonstrated in Figures 7 and 8.

Comparison of SEM micrographs of raw and modified fibers confirms that graft copolymerization
Figure 7. FTIR Spectrum of MAA-g-PP.

Figure 8. FTIR Spectrum of MAA and DVB grafted to PP fiber.
has been occurred. The SEM micrographs of the modified fibers exhibit varying degrees of grafting (Figure 9). White solids on the fibers are increasing by raising grafting degrees which can verify occurrence of grafting reaction.

**Mechanical properties of fibers**

As mentioned before, grafting affects the mechanical properties of fibers. To investigate this effect, tensile strength and toughness of raw and modified fibers were examined. Tensile strength tests were repeated five times for each specimen and the average of maximum points of load-displacement curves per fibers cross-sectional area were considered as their average ultimate tensile strength. To realize grafting effect on the tensile strengths of fibers, average ultimate tensile strengths of the fibers were plotted against grafting degrees in Figure 10. Tensile strength values of the fibers grafted under 5.33% are very close to the value of raw fibers. It shows that grafting below 5.33% does not affect significantly the fibers mechanical properties. Consequently, 5.33% in a strict conclusion can be defined as critical point to graft PP fibers with methacrylic acid monomers in the mentioned conditions with maintaining their tensile strength. On the other hand, in the interval of 5-9%, the decrease in tensile strength is negligible too. Thus, to achieve high grafted fibers, little decrement in their mechanical properties in some utilizations can be acceptable. With this attitude, about 9% grafting can be suggested as the critical point. This behavior demonstrates that grafting of PP fibers more than 9% results in significant loss in tensile strength of them and makes them inappropriate for applications such as FRC’s which need fibers with high tensile strengths.

The toughness of fibers, like their tensile strength, can be affected by grafting. Toughness is the ability of a material to absorb energy and plastically deform without fracturing. The area under the stress-strain
curve of fibers represents their toughness. To realize the effect of grafting on toughness of fibers, their average toughness is plotted versus grafting degrees (Figure 11). Toughness of the fibers obviously decreases by increasing the grafting degrees. This reduction is more significant after 9% grafting. This procedure reveals that to protect fibers from remarkable decrement in toughness, it is essential to keep degree of grafting below 9%.

Considering the tensile strength and toughness of the fibers demonstrates that 9% grafting of fibers can be a critical point. In other words, in this research, 9% grafting by hydrophilic monomers can be defined as a critical point to improve PP fibers hydrophilicity with protecting their tensile strength and toughness, approximately. Justifications to decrement in mechanical properties of modified fibers needs more researches to be decisive but possibly, it can occur because of attacks of radicals generated from peroxides to PP chains, which results in rupturing of the chains and decreasing tensile strengths and toughness of fibers. In addition, another possibility comes from electrostatic and steric repulsions between side chains, which results in creation of tensile residual stresses on PP chains and therefore, decreases the tensile strength of the fiber. Moreover, a combination of both supposed pathways could occur and affect the mechanical properties of the fibers. The mechanical properties data can be almost a confirmation for the latter assumption because the most loss in mechanical properties occurs in grafting degrees greater than 9%, which lead to high concentration of radicals and repulsion between side chains due to high grafting degree that causes tensile residual stresses to be significant in these fibers. However, as mentioned, further investigation is needed to comprehend this behavior.

CONCLUSIONS

In this work, the effects of temperature, monomer concentration, cross-linker concentration and reaction time on graft copolymerization of MAA in moderate conditions were studied and the optimum conditions to achieve maximum grafting degree were determined. The effects of grafting on the mechanical properties of PP fibers were also investigated and it was concluded that grafting decreases tensile strength and toughness of fibers. This decrement is remarkably higher after 9% of grafting and this point can be approximately defined as a critical point to make PP fibers hydrophilic with maintaining their mechanical properties.

Acknowledgements

The financial support of this work by the Research Councils of Amirkabir University of Technology (Polytechnic) and Building and Housing Research Center (BHRC) is gratefully acknowledged.

REFERENCES

MAJID MAZHAR1
MAJID ABDOUSS1
ZAHRA SHARIATINIA1
MOJDEH ZARGARAN2

1Department of Chemistry, Amirkabir University of Technology (Polytechnic), Tehran, Iran
2Building and Housing Research Center (BHRC), Tehran, Iran

NAUČNI RAD

GRAFT KOPOLIMERIZACIJA MONOMERA METAKRILNE KISELINE NA POLIPROPILENSKA VLAKNA

U posljednjih nekoliko godina, graft kopolimerizacija se uveliko koristi za umetanje različitih funkcionalnih grupa na polimere. U ovom radu, monomeri metakrilne kiseline su kalemljeni na polipropilenska (PP) vlakna, čime ih hidrofilnim i zadržavajući njihove mehaničke osobine. Ekspерimenti su izvedeni na osnovu Taguchi metode, pri čemu je proučavan uticaj temperature, koncentracije monomera, koncentracije umrživača i vremena reakcije. Kalemljenje metakrilne kiseline i divinilbenzena je praćeno pomoću FTIR spektroskopije i potvrđeno SEM mikrografijom. Zatezna čvrstoća i žilavost uzoraka su mereni i uporedni sa sirovim vlaknima. Uticaj kalemljenja na zateznu čvrstoću i žilavost vlakana su takođe izmereni, a određen je i kritični stepen kalemljenja pri kome su zatezna čvrstoća i žilavost vlakana definisani.

Ključne reči: mehaničke osobine, PP vlakna, Taguchi metoda, graft kopolimerizacija, SEM.