Effect of Matrix Graft Modification Using Acrylic Acid on the PP/Mg(OH)$_2$ Composites and Its Possible Mechanism

Wen-Yen Chiang* and Chia-Hao Hu

Department of Chemical Engineering, Tatung University, 40, Chungshan N. Rd., 3rd Sec., Taipei 104, Taiwan, R. O. C.

Received October 15, 1999; revised December 21, 1999; accepted January 27, 2000

Abstract: The matrix graft modification using an acrylic acid (AAc) was employed on the polypropylene/Mg(OH)$_2$ flame-retardant composite. The graft modification of PP matrix was carried out via an in-situ reactive extrusion by a twin-screw extruder. The tensile strength of the composites was analyzed using an equation developed by Pukanszky from which both matrix tensile strength $\sigma_0$ and interfacial adhesion strength were found to be increased. The enhancement of $\sigma_0$ is due to the intermolecular crosslinking of PP by AAc grafting. This crosslinking causes increases of tensile strength, Young's modulus, impact resistance, and thermal resistance, but decreases the elongation at break of the composites.

Keywords: Polypropylene, Acrylic acid, Matrix graft modification, Magnesium hydroxide, Flame retardant.

Introduction

Magnesium hydroxide, Mg(OH)$_2$, is one of the popular inorganic flame-retardant additives [1]. The most important advantage of these inorganic flame retardants is free of toxic gaseous products and low smoke generation during burning [2]. The characteristic of Mg(OH)$_2$ filled polymer has a high thermal resistance. On the other side, a heavy loading of Mg(OH)$_2$ is necessary to achieve the optimum flame retardancy. Consequently, the poor impact strength of the composite is usually the main defect of these materials. The situation is worse as the inorganic flame retardants are employed in a polyolefin matrix such as polyethylene (PE) or polypropylene (PP) because of their low polarity. A usual solution for the above problem is employing an approach of matrix graft modification.

Matrix graft modification is an effective technique to improve the interfacial adhesion of composites [3-8]. Functional groups, such as acrylic acid (AAc) [9,10], styrene (St) [11], methyl methacrylate (MMA) [12], and maleic anhydride (MAH) [13], are usually applied to graft onto matrix polymers, either in solutions or by reactive melt extruding processing for specific purposes [14-17]. Other monomers such as fumaric acid, dimethyl maleinate, methyl nadic anhydride, and tetrahydrophthalic anhydride can also be used for the graft modification [18]. The graft reaction is usually proceeded by using UV-irradiation, photo-initiation, or a peroxide initiator [19,20].

In this study, acrylic acid (AAc) was chosen to graft onto PP for the matrix modification. The AAc grafted PP (PP-g-AAc) with different grafting ratios were utilized in preparing PP/Mg(OH)$_2$ composites. The particulate Mg(OH)$_2$ powder has no enforcing effect on the matrix strength in the composites. Moreover, the loading of filler decreases the area fraction of the continuous matrix on cross section. However, the situation changes after the application of PP-g-AAc. The mechanical properties of the composites are closely related to the volume fraction of Mg(OH)$_2$ powder in composites. The tensile strength of the composites will be discussed and fitted as functions of volume fraction $\phi$, and through that operation, two parameters, $\sigma_0$ and $B$, are obtained to describe the variations of matrix strength and adhesion strength.

*To whom all correspondence should be addressed.
Tel: 886-2-2592-5252 ext 3488; Fax: 886-2-2586-1939
E-mail: chiang@ttu.edu.tw

J. Polym. Res. is covered in ISI (CD, D, MS, Q, RC, S), CA, EI, and Polymer Contents.
Experimental

1. Materials

Isotactic polypropylene (PP) used in this study was the commercial product of the Taiwan Polypropylene Co. Ltd., Taiwan, designated as profax PC-366. The reagent grade acrylic acid (AAc) was purchased from Wako Pure Chemical Industries Ltd., Japan. Benzyl peroxide (BPO), reagent first grade, made by Kokusan Chemical Works, Ltd., Japan, was employed as an initiator for the AAc grafting reactions. The inorganic flame-retardant filler, magnesium hydroxide, Mg(OH)$_2$, with specific gravity of 2.36 and average particle size of 11.5 μm, was acquired from Konoshima Chemical Co. Ltd., Japan.

2. Matrix graft modification

The AAc grafted PP (PP-g-AAc) with 2 and 4 wt% of AAc was prepared by a free radical initiated grafting reaction in a twin-screw extruder [21]. For 400 g of PP powder, 8 g of AAc for 2 wt% and 16 g of AAc for 4 wt% were dissolved in 400 mL of acetone together with 1.0 g of BPO, respectively. After that, the PP powder was completely immersed into the acetone solution with proper stirring. Then the sludge mixtures were placed in a hood overnight, where the acetone was volatilized naturally. Further evaporation was carried out in a vacuum oven. After the acetone had been completely evaporated, AAc and BPO were coated on the surface of the powdered PP. The pretreated PP powder was then extruded through a W&P ZSK-30 twin-screw extruder at 200 °C, with a screw rate of 150 rpm. The extruded PP-g-AAc was cut into grains and collected.

3. Compounding and molding of FR-PP

The flame retardant PP/Mg(OH)$_2$ blends (Table 1) were compounded by a W&P twin-screw extruder with the temperature profile of 190, 195, 200, 215, and 220 °C. The rotating rate of screw is 120 rpm. 0.5 Phr of Irganox 1076 was used as an antioxidant, and 1 phr of magnesium stearate was added as a lubricant. The samples were molded via an injection molding with the temperature profile of 180, 190, 195, and 200 °C, respectively.

<table>
<thead>
<tr>
<th>ϕ($)</th>
<th>Mg(OH)$_2$</th>
<th>vol%</th>
<th>wt%</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.05</td>
<td>5</td>
<td>12.1</td>
<td>13.76</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>10</td>
<td>22.6</td>
<td>29.20</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>15</td>
<td>31.6</td>
<td>46.20</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>20</td>
<td>39.9</td>
<td>66.06</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>25</td>
<td>46.6</td>
<td>87.27</td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>30</td>
<td>52.9</td>
<td>112.31</td>
<td></td>
</tr>
</tbody>
</table>

(a) The volume fraction of Mg(OH)$_2$ in PP/Mg(OH)$_2$ composites.

Table 1. The contrast between volume fraction, weight percentage, and phr of PP/Mg(OH)$_2$ composites.

tive load bearing cross section (1 − ϕ), which is the matrix area in the cross section perpendicular to the tensile stress load direction:

\[
\sigma_{xc} = (1 - \Psi)\sigma_{ym}
\]

where \(\sigma_{ym}\) is the yield strength of the matrix. Pukanszky have chosen a simple hyperbolic function, going through \(\phi = \Psi = 0\) and \(\phi = \Psi = 1\) to describe the change of the effective cross section as a function of filler volume fraction [22]:

\[
(1 - \Psi) = \frac{1 - \Phi}{1 + 2.5\Phi}
\]

\[
\sigma_{xc} = \frac{1 - \Phi}{1 + 2.5\Phi} \sigma_{ym}
\]

The dependence of \(\sigma_{ym}\) on \(\phi\) was found to be an exponential function, so Eq.(3) can be expressed as the following formula:

\[
\sigma_{xc} = \frac{1 - \Phi}{1 + 2.5\Phi} \sigma_{y0} \exp(B\Phi)
\]

where the parameter \(\sigma_{y0}\) equals to the yield strength of unfilled polymer within the experimental error. The parameter B has no direct physical meaning itself, but is obviously related to the interfacial properties of a given system.

Results and Discussion

It is well known that the heavy loading of inorganic additives will cause a serious decrease in mechanical strength of polymer materials. The influences of fillers on the mechanical properties of filled polymers are often discussed in terms of the length fraction, area fraction, or volume fraction of fillers [22]. Figure 1 shows that the yield strength...