Research Article

Polypropylene-Grafted Poly(hexamethylene guanidine)/Modified Polyethylene Monofilament and Its Antimicrobial Performance

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A polypropylene-grafted poly(hexamethylene guanidine) (PP-g-PHMG)/polyethylene (PE) monofilament was prepared by melt blending and spinning using PE and PP-g-PHMG. The effect of PP-g-PHMG content on the structure, mechanical properties, and antimicrobial properties of PP-g-PHMG/PE alloy monofilaments was studied. Compared with PP/PE without grafting PHMG, Tm of PP-g-PHMG/PE alloy monofilaments increased due to rigidity of PHMG grafted. In the PP-g-PHMG/PE alloy monofilaments, the total degree of crystallinity of alloy monofilaments decreased; hence, the α-relaxation associated with the crystalline region of the polymer matrix becomes weaker as PP-g-PHMG content increases. The breaking strength of PP-g-PHMG/PE alloy monofilaments decreased while the knotting strength increased by increasing PP-g-PHMG content. The antibacterial test showed that the PP-g-PHMG/PE alloy monofilament had obvious inhibitory effect on E. coli and Staphylococcus aureus. Therefore, the PP-g-PHMG/PE alloy monofilament has the potential to make green and highly effective antifouling materials.

1. Introduction

Polyethylene is one of the most commonly used materials in fishery [1, 2]. Because of its good properties, it is widely used in fishing nets and cages [3, 4]. With the development of fishery science, the materials with higher performance are put forward for fishing gear. Conventional polyethylene fiber can no longer meet the special needs of existing fishery specialization as well as requirements on energy conservation and emission reduction in fisheries [5]. After the traditional polyethylene fiber is placed in the sea ocean area for a period of time, it will be covered by marine organisms, which will affect the process of water exchange in the cage, further causing sudden diseases of fish, and cause economic losses to the breeding industry [6, 7]. The antifouling of fishing nets uses physical or chemical methods to prevent the growth of marine organisms on the surface of a net or to remove them from the surface of the net. The existing antifouling methods include manual cleaning, mechanical cleaning, antifouling paint, and metal net antifouling [8, 9]. There are a few concerns about the existing methods, namely, the removal efficiency, the cost, and the pollution to the environment. Therefore, in our current research, we focus on an environment-friendly method that prevents pollution in the long run [10–12]. In order to achieve the goal of antifouling, at present, the most widespread method for antifouling treatment is to apply antifouling paint. Chen et al. [13] proved that preparing waterborne antifouling coatings will take up to 6 months. And there are some other shortcomings of this method; for instance, the effect of prevention to pollution does not last long, it brings pollution to the ocean, it is complicated to carry out, and it is not cost-effective. Wei [14] synthesized dithioamide compounds and their othiazolinone derivatives by experiments and studied their marine antifouling application performance; it was found that these two compounds had obvious inhibitory effect on bacteria and algae. Moreover, it is the most economical and feasible method to process fishing net materials by modification, producing a green and efficient bacteriostatic effect.

Guanidine is a compound containing a guanidine group in its structure. The hydrate of guanidine is a kind of base, a monadic organic base equivalent to sodium hydroxide.
Guandine can be formed by the combination of guanidine ion and acid ion. Polyguanidine salt is most widely used as antibacterial agents [15, 16]. The outer layer of the cell membrane is electronegative, so the guanidine group interacts with the bacterial cell through electrostatic attraction, eventually causing the cell membrane to burst and kill the fineness bacteria [17]. Therefore, guanidine compounds with biological activity are commonly used as antibacterial agents. Nillola et al. [18] modified polyvinyl alcohol with poly(hexamethylen guanidine) hydrochloride (PHMG) and then grafted it onto the polyamide film. The hydrophilicity of E. coli had been improved, the surface roughness had been reduced, and the sterilization effect also had been enhanced. Yang et al. [19] used maleic anhydride and PHMG to graft molten polypropylene wax (PPW-g-PHMG) to obtain polypropylene with long-term antibacterial properties.

In the present study, the PP-g-PHMG/PE alloy monofilaments were prepared using PP-g-PHMG blending with PE during melt spinning [20]. The effect of PP-g-PHMG content on the structure and properties of the PP-g-PHMG/PE alloy monofilament was studied.

2. Experiment

2.1. Materials and the Preparation of the PP-g-PHMG/PE Alloy Monofilament. PE with an MFI of 0.9 g per 10 min and density of 950 kg/m³ was supplied by Sinopec Qilu Petrochemical Co., Ltd., China. PP-g-PHMG with the grafting ratio of PHMG is about 10%, which was supplied by Shanghai Fuyuan Plastic Technology Co., Ltd., China.

PP-g-PHMG and PE were added to premix, and then, the mixture was melted and extruded with a single-screw extruder. The system was treated by melt spinning through a 0.8 mm diameter spinneret. The screw temperature was 240°C-270°C. The single screw aspect ratio was 1:32, and the screw speed was 22 m/min. PP-g-PHMG/PE alloy monofilaments were prepared by three-stage draw production. The water bath temperature was 98°C, and the draw ratio was 8.5, under which the monofilaments were continuously spun. The diameter of the alloy monofilaments was approximately 0.2 mm, and the line density was approximately 35.7-40.3 tex. The weight ratios of PP-g-PHMG to PE were 0 wt%, 10 wt%, 20 wt%, 30 wt%, and 40 wt%. Correspondingly, the PP-g-PHMG/PE alloy monofilaments were named as PE, PP-g-PHMG/PE-10, PP-g-PHMG/PE-20, PP-g-PHMG/PE-30, and PP-g-PHMG/PE-40, respectively. As a controlled group, the PP/PE-10 alloy monofilaments (composition of 90 wt% PE and 10 wt% PP) without grafting PHMG were prepared in the same way.

2.2. Characterization. The microstructures of the monofilaments were examined using a scanning electron microscope (SEM) (6360LA, JEOL Ltd., Japan) operated at an acceleration voltage of 15 kV. The sample is quenched with liquid nitrogen, and the surface of the section is sprayed with gold and fixed with conductive glue.

Dynamic mechanical analysis (DMA) was used in a tensile mode (242C, Netzsch Instruments, Germany) under the frequency of 1 Hz and the amplitude of 30 μm for all samples. The samples were initially cooled from ambient temperature to −180°C and then held at this temperature for 10 min. Then, the samples were heated to 150°C at a heating rate of 3°C/min.

Thus, loss factor, tan δ, is expressed as

\[ \tan \delta = \frac{E'}{E''} \]

where \( E' \) is the storage modulus and \( E'' \) is the loss tangent modulus. \( \tan \delta \) is the most fundamental dynamic property of a viscoelastic material.

Differential scanning calorimetry (DSC) was applied to investigate the melting and crystallization behavior of the monofilaments using the DSC thermal analyzer (204F1, Netzsch Instruments, Germany). The samples were scanned at a heating and cooling rate of 10°C/min in a nitrogen atmosphere. The degree of crystallinity (\( X_c \)) was calculated via the total enthalpy method, according to the following expression:

\[ X_c = \left( \frac{\Delta H_f^{obs}}{\Delta H_f^0} \right) \times 100 \]

where \( \Delta H_f^{obs} \) is the observed heat of fusion values and \( \Delta H_f^0 \) is the specific enthalpy of melting for a 100% crystalline polymer. The \( \Delta H_f^0 \) value of 287 J/g was used for PE, and the \( \Delta H_f^0 \) value of 190 J/g was used for PP [21, 22].

The tensile properties were investigated using the electron tensile tester (4466, Instron Instruments, USA) at a speed of 200 mm/min on a 500 mm long specimen according to SC/T 5005-2014 under ambient conditions. The sample adopts a stretching mode and adopts S-shaped clamp distance. Results are the average of at least 10 specimens.

FTIR spectra were measured using a Nicolet spectrometer (560, Nicolet Instruments, USA). The fiber samples were scanned by using attenuated total reflectance with an additional solid probe system. The samples were applied and scanned 32 times at a resolution of 4 cm⁻¹. Their FTIR spectra were obtained in the range 4000-500 cm⁻¹.

A sound velocity orientation test was measured with the sonic velocity orientation tester (SCY-III, School of Materials, Donghua University, China). With the velocity value (C), the velocity orientation factor \( f \) of the sample is calculated by the following formula:

\[ f = \left( 1 - \frac{C_m}{C} \right) \times 100 \]

where \( C_m \) is the sound velocity value of polyethylene with random orientation (1.65 km/s) and \( C \) is the sound velocity of the sample (km/s).

The antibacterial test of PP-g-PHMG/PE alloy monofilaments with different contents was measured by using the inhibition zone method. Escherichia coli was selected as the representative of Gram-negative bacteria and Staphylococcus aureus as the representative of Gram-positive bacteria. The bacterial solution was gradient diluted with 0.9%
physiological saline, and 100 μL was evenly coated on a brain heart infusion (BHI) solid agar plate.

Then, the steps below were followed:

(i) Use sterile forceps to take the cut sample
(ii) Place the sample on the surface of the solid plate that has been coated with bacterial solution
(iii) Place the sample in a 30°C incubator and incubate it for 24 hours
(iv) When the inhibition zone is more obvious, take photos and record the results

3. Results and Discussion

3.1. Microstructure. The dispersion of PP-g-PHMG in a matrix is evaluated visually by SEM images, as shown in Figure 1. PE exhibits a homogeneous phase (Figure 1(a)). However, PP-g-PHMG/PE alloy monofilaments show obvious phase separation (Figures 1(b) and 1(c)). It also can be seen that the PP exists in a granular form in the PP-g-PHMG/PE alloy monofilament matrix. Compared to PE, PP has higher viscosity under the same temperature which results in a diffuse PP domain. This is similar to the results of isotactic polypropylene/high-density polyethylene blends reported by Jose et al. [23], and it was found that the domain size of the dispersed phase depends on the viscosity difference between the two phases. From Figure 1, one can estimate that the PP particles show a diameter range of 1-10 μm, consistent with the quantitative measurement results using the SEM images and Nano Measurer software.

The FT-IR spectra of PE and PP-g-PHMG/PE alloy monofilaments are shown in Figure 2. For PP-g-PHMG, the observed significant peak at 1640 cm⁻¹ is attributed to the guanidine groups of PHMG [24]. Another obvious peak is near 1463 and 721 cm⁻¹, which corresponds to the

![Figure 1: SEM image of (a) PE, (b) PP-g-PHMG/PE-30, and (c) PP-g-PHMG/PE-40.](image)

![Figure 2: FT-IR spectra of PE and PP-g-PHMG/PE alloy monofilaments.](image)

![Figure 3: Velocity orientation factor of PP-g-PHMG/PE monofilaments with different PP-g-PHMG contents.](image)
The stretching vibration of -CH₂ and -(CH₂)ₙ - of PE. And the observed significant peak is at 1378 cm⁻¹, which corresponds to the stretching vibration of -CH₃ of PP. Strong absorption peaks are observed near 2916 cm⁻¹ and 2848 cm⁻¹, which could be assigned to the symmetrical stretching vibration of C-H bonds of PE. Moreover, the growing PP-g-PHMG molecular chain results in a decrease of 2916 cm⁻¹ and 2848 cm⁻¹. After PP-g-PHMG blending with PE, the peaks

![DSC curves](image1.png)

**Figure 4:** (a) DSC curves of PP/PE monofilaments without grafting PHMG and PP-g-PHMG/PE alloy monofilaments, (b) DSC curves of PP/PE monofilaments with different PP-g-PHMG contents, (c) the dependence of crystallinity for PE and PP, and (d) the dependence of total crystallinity on PP-g-PHMG content.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tₘ of PE (°C)</th>
<th>ΔHᵣobs of PE (J/g)</th>
<th>Tₘ of PP (°C)</th>
<th>ΔHᵣobs of PP (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>139.3</td>
<td>218</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP-g-PHMG/PE-10</td>
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<td>162.2</td>
<td>163</td>
<td>5.2</td>
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<tr>
<td>PP-g-PHMG/PE-20</td>
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<td>163.8</td>
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<tr>
<td>PP-g-PHMG/PE-30</td>
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<td>165</td>
<td>15.9</td>
</tr>
<tr>
<td>PP-g-PHMG/PE-40</td>
<td>140.4</td>
<td>134.6</td>
<td>165.3</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 1: Melting and crystallization behavior of PP-g-PHMG/PE alloy monofilaments.
of PE and PP-g-PHMG all appear, and this result is the same as that of Wei et al.’s research [24].

The results of the sonic velocity orientation test reflect the orientation of the molecular chain in the sample. Figure 3 shows the results of the sound velocity orientation test of PP-g-PHMG/PE monofilaments with different PP-g-PHMG contents. It can be found that all the f of PP-g-PHMG/PE monofilaments is higher than that of PE monofilaments. This is because the entanglement degree of the PE molecular chain falls down by introducing PP-g-PHMG, which makes it easier to conduct orientation along the stretching direction in the stretching process [25].

3.2. Crystallization. The DSC heating curves of alloy monofilaments are shown in Figures 4(a) and 4(b), and the dependence of PP-g-PHMG content on calculated $X_c$ and calculated total $X_c$ is plotted in Figures 4(c) and 4(d). The results are depicted in Table 1. It can be seen that the blending monofilaments show two melting endotherms reflecting two crystalline phases. The melting point ($T_m$) of PE and PP is 138°C and 164°C, respectively. Compared with PP/PE-10 without PHMG, the $T_m$ of PE for PP-g-PHMG/PE monofilaments increases by 5.3°C due to the introduction of the polar group PHMG in the main chain of the molecule which reduces the flexibility of the PE chain. Hence, the melting entropy decreases and the $T_m$ turns to high temperature. Furthermore, the $T_m$ value of the PP peak has little change. In the alloy monofilaments, both of the $T_m$ for PE and PP increased and the melting peak became narrow with the increasing PP-g-PHMG content. The PHMG increases steric
hindrance of internal rotation, and the rigidity of the molecular chain also went up with an increase in PHMG content, thereby reducing the melting entropy and increasing the \( T_m \) value [26]. However, Jose et al. reported that the blending has no effect on the \( T_m \) of PP and HDPE and showed that the two polymers are highly immiscible and the blends are incompatible [23].

With the increase in PP-g-PHMG content, the crystallinity of PE for alloy monofilaments decreases while the crystallinity of PP for alloy monofilaments increases. When the PP-g-PHMG content is 40 wt\%, the crystallinity of PE for alloy monofilaments decreases by 29.06\%, compared with that of PE monofilaments. The crystallinity of PP increases due to the increasing content of PP, which is consistent with the research results of Li et al.’s research [27].

The total degree of crystallinity includes both phases. \( X_{c,total} \) is calculated as the sum of degrees of crystallinity of the pure components: \( X_{c,total} = X_{c,PE} W_{PE} + X_{c,PP}(1 - W_{PE}) \), where \( X_{c,PE} \) and \( X_{c,PP} \) are the degrees of crystallinity of PE and PP, respectively, and \( W_{PE} \) is the weight fraction of PE [28]. Furthermore, the total crystallinity of the PP-g-PHMG/PE alloy monofilament shows a downward trend with increasing PP-g-PHMG content. This may be because the molecular chain became more irregular after introducing PHMG, resulting in a decrease in the total crystallinity.

3.3. Viscoelastic Properties. The viscoelastic properties of PP-g-PHMG/PE alloy monofilaments are studied by dynamic mechanical analysis. Figure 5(a) shows the temperature dependence of the dynamic mechanical properties of the PP-g-PHMG/PE alloy monofilament. The addition of PP-g-PHMG reduces the \( E' \) of the PP-g-PHMG/PE alloy monofilament, which reflects the lower elastic modulus of the PP-g-PHMG/PE alloy monofilament.

As shown in Figures 5(b) and 5(c), two relaxation processes are observed in the testing temperature range for the PE and PP-g-PHMG/PE alloy monofilaments. The relaxation transition at low temperature is called \( \gamma \)-relaxation, which is associated with the amorphous phase of PE [29]. After the introduction of PHMG, the \( T_\gamma \) of the PP-g-PHMG/PE alloy monofilament moves to higher temperature compared with that of PP/PE-10, from -134.8°C to -128.2°C. This is because the flexibility of the molecular chain is decreasing and the energy required for random chain movement becomes higher. The relaxation transition at a positive temperature is called \( \alpha \)-relaxation, which corresponds to the motion of restricted chain segments near the crystalline region [30, 31]. The result of DSC shows that the crystallinity of PE decreases after adding PHMG, which indicates that the number of molecular motions in the crystal region is decreasing, resulting in a decrease in the height of \( \alpha \) peak. In addition, the PP-g-PHMG/PE alloy monofilament has a higher \( \alpha \)-transition temperature (80°C) than PE did, which results in its good mechanical properties in the low temperature range (0–50°C). The \( \alpha \)-transition temperature of alloy monofilaments is significantly different from the working temperature, and the temperature dependence on the mechanical properties is relatively low; these findings have been proven in our previous study. With the increase in PHMG content, the value of \( tan \delta \) for \( \alpha \) peak significantly decreased (Figure 5(c)). The high PP-g-PHMG content results in the small fraction of the crystalline region in the nanocomposites, as observed previously by DSC. With the decreasing fractions of the crystalline region, \( tan \delta \) also decreased.

3.4. Mechanical Properties. The mechanical properties of PP-g-PHMG/PE alloy monofilaments are shown in Figure 6. It seems to show a downward trend for the breaking strength of the PP-g-PHMG/PE alloy monofilament by increasing PP-g-PHMG content. This is consistent with DMA results. However, the knotting strength increased with the growing PP-g-PHMG content. Taking PP-g-PHMG/PE-40 as an example, the knotting strength increases by 42\%, compared with that of PE. Crystallinity and orientation are two important factors that affect the mechanical properties. Although the degree of orientation has increased slightly, the grafted PHMG reduces the total crystallinity of the PP-g-PHMG/PE alloy monofilament significantly, which leads to a decrease in the regularity of the molecular chain and weakens the intermolecular force; this is the result of the combined effect of the two factors. As discussed above, PP-g-PHMG segments are homogeneously distributed throughout the continuous PE phase; the addition of PP-g-PHMG decreases the spherulite size by occupying the interspherulite region [23] and thereby leads to the enhanced toughness.

Cao and Qiao [32] studied the effects of different contents of HDPE into PP on the mechanical properties of the blend alloy and found that the mechanical properties of the blend system were slightly better than that of a single material. Therefore, adding an appropriate amount of PP-g-PHMG to PE can improve its knotting strength.

3.5. Antibacterial Test. PP-g-PHMG exhibits excellent antimicrobial properties. In the previous work, it is found that...
PP-g-PHMG has high antimicrobial activities against both Gram-positive and Gram-negative bacteria [33, 34]. In this study, as shown in Figure 7, we chose E. coli and Staphylococcus aureus as the testing bacteria to investigate the antimicrobial properties of the PP-g-PHMG/PE alloy monofilament. The results show that different concentrations of PP-g-PHMG have different inhibitory degrees on Staphylococcus aureus and Escherichia coli. There is no obvious bacteriostatic zone in PE and PP-g-PHMG/PE-10 monofilaments; however, an obvious bacteriostatic zone in 20 wt%, 30 wt%, and 40 wt% is observed, and the scope of the bacteriostatic zone is gradually expanded. The reason may be that the 10 wt% content of PP-g-PHMG is too low and the antibacterial effect is not significant. In contrast, the pure PE material has no obvious bacteriostatic circle. These results indicate that PP-g-PHMG/PE alloy monofilaments (the content of PP-g-PHMG > 20 wt%) have excellent antibacterial activity. In addition, we find that the PP-g-PHMG/PE alloy monofilaments are typically more active against Staphylococcus aureus than against E. coli. This phenomenon is attributed to their different cell structures. As we know, the Staphylococcus aureus has only a loose cell wall, while the E. coli has an outer membrane structure in the cell wall. The outer membrane is able to act as an additional barrier to prevent invasion of PHMG [35, 36].

In addition, the PP-g-PHMG/PE alloy monofilament (the content of PP-g-PHMG > 20%) exhibits excellent antibacterial activity. And we found that the PP-g-PHMG/PE alloy monofilament is typically more active against Staphylococcus aureus than against E. coli.

**Data Availability**

The data used to support the findings of this study are included within the article.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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