ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА КОМПОЗИТНЫХ МАТЕРИАЛОВ НА ОСНОВЕ МЕДИ И ПОЛИОЛЕФИНОВ

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В работе приводятся результаты исследования влияния концентрации меди на физико-механические свойства композитов на основе полиэтилена высокой плотности и полиэтилена низкой плотности. Изучались такие свойства металлонаполненных композитов, как разрушающее напряжение, относительное удлинение, модуль упругости на изгиб, показатель текучести расплава и теплостойкость. Введение меди в состав полиэтилена низкой плотности способствует монотонному возрастанию разрушающего напряжения и модуля упругости на изгиб. При увеличении меди в состав полиэтилена высокой плотности наблюдается закономерное снижение разрушающего напряжения и относительного удлинения композитов. Показано, что при использовании компатibilизатора, представляющего собой модифицированный малеиновым ангидридом полиэтилен, наблюдается значительное повышение величины разрушающего напряжения композитов на основе полиэтилена высокой и низкой плотности. Приводится схематическое изображение структуры композитов с интерпретацией вероятного механизма упрочнения материала в присутствии компатibilизатора.

Ключевые слова: медь, малеиновый ангидрид, разрушающее напряжение, компатibilизатор, относительное удлинение, полиэтилен низкой плотности, полиэтилен высокой плотности

PHYSICOMECHANICAL PROPERTIES OF COMPOSITE MATERIALS ON BASIS OF COPPER AND POLYOLEFINS

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The paper presents the results of a study of the effect of copper concentration on the physicomechanical properties of composites based on high density polyethylene and low density polyethylene. The properties of metal-filled composites, such as ultimate tensile stress, elongation at break, elastic module, melt flow rate, and heat resistance, were studied. Loading of copper into the composition of low density polyethylene contributes to a monotonic increase in the ultimate
tensile stress and the elastic module. When copper is loading into the composition of high density polyethylene, on the contrary, a natural decrease in the ultimate tensile stress and elongation at break of the composites is observed. It is shown that when using a compatibilizer, which is polyethylene modified with maleic anhydride, a significant increase in the ultimate tensile stress of high and low density polyethylene composites is observed. A schematic representation of the structure of composites with an interpretation of the probable mechanism of hardening of the material in the presence of a compatibilizer is given. It is shown that the crystallinity of the initial polyethylene has a significant effect on the hardening effect of composites. It is assumed that polyethylene of high density macrochains free of maleic anhydride are involved in the formation of crystalline formations, and small sections of macrosegments containing polar groups are concentrated mainly in amorphous regions and in defects in crystalline structures in the form of passage chains. The concentration of copolymer of polyethylene with maleic anhydride macrosegments in the narrow amorphous space of polyethylene of high density favorably affects the increase in the adhesive forces of interaction on the surface of copper particles, which affects the preservation of the ultimate tensile stress at a relatively high level over a wide range of copper concentrations.

Key words: copper, maleic anhydride, ultimate tensile stress, compatibilizer, elongation at break, low-density polyethylene, high-density polyethylene

EXPERIMENTAL PART

As polyolefins, low density polyethylene (LDPE) and high density polyethylene (HDPE) were used.

HDPE – ultimate tensile stress – 31.3 MPa, elastic module – 753 MPa, elongation at break – 435%, density 946 kg/m³, melt flow index (MFI) 5.6 g/10 min, heat resistance -119 °C, melting point – 131 °C, crystallinity 80%.

LDPE – ultimate tensile stress – 11.2 MPa, elastic module – 196 MPa, density – 927 kg/m³, elongation at break – 720%, heat resistance -85 °C, melting point – 101 °C, MFI = 1.9 g/10 min, crystallinity 57%.

The compatibilizer is high density polyethylene functionalized with 5.7 wt % of maleic anhydride – PEMA.

Fine copper particles (Cu) with a particle size of 1.0-1.5 μm were used as a metal filler.

The size of the nanoparticles of the composites was determined on a STA PT1600 Linseiz Germany model instrument.

Mixtures based on LDPE, copper and PEMA were prepared on hot rollers at a temperature of 140 °C by loading a filler into the polymer melt for 10 min. First, PEMA was loading into the composition of LDPE, and then filler.

Mixtures based on HDPE, copper and PEMA were prepared on hot rollers at a temperature of 160 °C by loading a filler into the polymer melt for 8-10 min. And in this case, first PEMA was loaded into the composition of HDPE, and then filler.
Derivatographic analysis was performed on a Paulik, Paulik, and Erdei brand instrument.

Heat resistance was determined by the Wick method.

Ultimate tensile stress and elongation at break of polyethylene and their nanocomposites were determined in accordance with GOST 11262-80, elastic modulus according to GOST 9550-81.

MFI of polymeric materials were determined on a MELT FLOW TESTER, CEAST MF50 capillary rheometer (INSTRON, Italy) at a temperature of 190 °C and a load of 5 kg.

RESULTS AND DISCUSSION

To improve the compatibility of the polyolefin with finely dispersed copper particles, maleinized polyethylene (PEMA) was used as a compatibilizer. The objective of the study was to select the optimal concentration of compatibilizer at which the maximum compatibility of the neutral polyolefin with polar copper is achieved. By maximum compatibility should be understood the best strength characteristics of composites. According to the results of experimental studies, it was found that for composites with a copper content in the range of 0.5-5.0 wt % the most optimal is the content of the compatibilizer in an amount of 1.0 wt %, for composites with 10-30 wt % copper content – 2.0 wt %. The optimum content of the compatibilizer is fixed by the maximum value of the ultimate tensile stress and elastic modulus. These data are listed in Table 1 and Table 2. Table 1 shows the results of a study of the effect of the concentration of copper and compatibilizer on the basic physicomechanical properties of LDPE-based composites. From a comparative analysis of the data in this table, we found that with an increase in the concentration of copper in the composition of the composite, there is a general tendency to increase the ultimate tensile stress, elastic module, while reducing the elongation at break and MFI of the composites. In the pattern of changes in the ultimate tensile stress, some disturbances are observed in the linearity of its growth depending on the concentration of copper. So, for example, if the initial LDPE had a ultimate tensile stress of 11.2 MPa, then for composites with 0.5 wt % copper content of the ultimate tensile stress increases to 12.4 MPa. Then at 1.0 wt % content of copper, the ultimate tensile stress drops and only at 5.0 wt % again there is a slight increase in the value of this parameter. It is characteristic that, as the concentration of copper increases, a decrease in the elongation at break is predominantly observed.

Table 1

<table>
<thead>
<tr>
<th>№</th>
<th>Composite composition</th>
<th>Ultimate tensile stress, MPa</th>
<th>Elongation at break, %</th>
<th>Elastic module, MPa</th>
<th>MFI, g/10min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LDPE + 0.5% Cu</td>
<td>12.4</td>
<td>350</td>
<td>201</td>
<td>2.12</td>
</tr>
<tr>
<td>2</td>
<td>LDPE + 1.0% Cu</td>
<td>10.9</td>
<td>470</td>
<td>222</td>
<td>1.92</td>
</tr>
<tr>
<td>3</td>
<td>LDPE + 5.0% Cu</td>
<td>11.2</td>
<td>155</td>
<td>240</td>
<td>1.61</td>
</tr>
<tr>
<td>4</td>
<td>LDPE + 10% Cu</td>
<td>12.2</td>
<td>140</td>
<td>270</td>
<td>1.41</td>
</tr>
<tr>
<td>5</td>
<td>LDPE + 20% Cu</td>
<td>13.3</td>
<td>100</td>
<td>292</td>
<td>1.13</td>
</tr>
<tr>
<td>6</td>
<td>LDPE + 30% Cu</td>
<td>14.4</td>
<td>55</td>
<td>307</td>
<td>0.92</td>
</tr>
<tr>
<td>7</td>
<td>LDPE + 0.5% Cu + 1.0% PEMA</td>
<td>10.1</td>
<td>265</td>
<td>232</td>
<td>1.85</td>
</tr>
<tr>
<td>8</td>
<td>LDPE + 1.0% Cu + 1.0% PEMA</td>
<td>10.6</td>
<td>145</td>
<td>255</td>
<td>1.68</td>
</tr>
<tr>
<td>9</td>
<td>LDPE + 5.0% Cu + 1.0% PEMA</td>
<td>11.8</td>
<td>100</td>
<td>280</td>
<td>1.29</td>
</tr>
<tr>
<td>10</td>
<td>LDPE + 10% Cu + 2.0% PEMA</td>
<td>12.1</td>
<td>65</td>
<td>304</td>
<td>1.12</td>
</tr>
<tr>
<td>11</td>
<td>LDPE + 20% Cu + 2.0% PEMA</td>
<td>13.2</td>
<td>60</td>
<td>336</td>
<td>0.83</td>
</tr>
<tr>
<td>12</td>
<td>LDPE + 30% Cu + 2.0% PEMA</td>
<td>13.8</td>
<td>35</td>
<td>349</td>
<td>0.59</td>
</tr>
</tbody>
</table>

If we compare with the data of composites (7-12) modified with PEMA, we can, firstly, find a regular increase in the ultimate tensile stress of the composites with an increase in copper concentration, and, secondly, a uniform decrease in the elongation at break and MFI of the samples. Moreover, the elongation at break of the samples (LDPE + Cu + PEMA) has slightly lower values in comparison with composites based on LDPE + Cu (1-6).

A decrease in the MFI of composites can be associated with an increase in the melt viscosity, due to the formation of a kind of “transitional monolayer” on the surface of copper particles, which is enhanced in the presence of PEMA [11-13]. This increase is due to the fact that PEMA enhances the adhesion of macrochains on the surface of copper particles. The results of the studies showed that with increasing copper concentration in the composition of LDPE from 0.5 to 30 wt % an increase in the melting temperature of composites from 101 to 104 °C is observed, and the heat resistance of composites increases from 86 to 95 °C. In LDPE + Cu composites con-
taining PEMA, the heat resistance varies from 88 to 98 °C, respectively. The data obtained confirm our assumption about an increase in the adhesive strength of the PEMA bond on the surface of copper particles.

Composites based on HDPE and copper were also investigated, the analysis results of which are shown in Table 2. From a comparative analysis of the data given in Tables 1 and 2, it was found that, in contrast to LDPE-based composites, the pattern of change in the ultimate tensile stress in HDPE-based composites differs significantly from samples obtained on the basis of LDPE. As can be seen from Table 2, in an unmodified composite (HDPE + Cu), an increase in the filler concentration contributes to a uniform decrease in the ultimate tensile stress. However, after the loading of PEMA into the composition of the composite, an increase in the copper concentration significantly affects the nature of this dependence. As can be seen from this table, with an increase in the concentration of copper in samples 1-6 from 0.5 to 30 wt %, a decrease in the ultimate tensile stress by 17% was established. In samples 7-12 modified with PEMA, the maximum strength is manifested in a sample with a 5% copper content. The value of this parameter in the considered concentration range of copper varies within 8.5%. From a comparative analysis of the data presented in Table 2, it can be argued that in a polymer matrix with a relatively high degree of crystallinity (HDPE), the mechanism of crystallization and the formation of a supramolecular structure in the presence of copper and PEMA particles differs to a certain extent from composites based on LDPE + Cu + PEMA. There is reason to believe that the main reason for such noticeable differences in the properties of composites is due, first of all, to differences in the degree of crystallinity of the initial polymer matrix.

If we analyze the experimental data in Table 2, we can establish that with an increase in copper concentration from 0.5 to 30 wt %, a constant increase in the elastic module and a decrease in elongation at break are observed. Polyolefins are characterized by a decrease in elongation at break with the loading of solid particles of the filler [14, 15].

Table 2
Effect of copper concentration on the properties of composites based on HDPE + Cu and HDPE + Cu + PEMA

<table>
<thead>
<tr>
<th>№</th>
<th>Composite composition</th>
<th>Ultimate tensile stress, MPa</th>
<th>Elongation at break, %</th>
<th>Elastic module, MPa</th>
<th>MFI, g/10min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HDPE + 0.5% Cu</td>
<td>32.4</td>
<td>130</td>
<td>770</td>
<td>5.71</td>
</tr>
<tr>
<td>2</td>
<td>HDPE + 1.0% Cu</td>
<td>30.6</td>
<td>400</td>
<td>792</td>
<td>5.85</td>
</tr>
<tr>
<td>3</td>
<td>HDPE + 5.0% Cu</td>
<td>30.7</td>
<td>340</td>
<td>812</td>
<td>4.62</td>
</tr>
<tr>
<td>4</td>
<td>HDPE + 10% Cu</td>
<td>28.6</td>
<td>50</td>
<td>825</td>
<td>2.83</td>
</tr>
<tr>
<td>5</td>
<td>HDPE + 20% Cu</td>
<td>27.7</td>
<td>40</td>
<td>834</td>
<td>2.39</td>
</tr>
<tr>
<td>6</td>
<td>HDPE + 30% Cu</td>
<td>26.8</td>
<td>30</td>
<td>851</td>
<td>1.71</td>
</tr>
<tr>
<td>7</td>
<td>HDPE + 0.5% Cu +1.0% PEMA</td>
<td>32.6</td>
<td>50</td>
<td>777</td>
<td>5.48</td>
</tr>
<tr>
<td>8</td>
<td>HDPE + 1.0% Cu +1.0% PEMA</td>
<td>33.2</td>
<td>75</td>
<td>809</td>
<td>4.66</td>
</tr>
<tr>
<td>9</td>
<td>HDPE + 5.0% Cu + 1.0% PEMA</td>
<td>33.5</td>
<td>50</td>
<td>838</td>
<td>3.42</td>
</tr>
<tr>
<td>10</td>
<td>HDPE + 10% Cu + 2.0% PEMA</td>
<td>34.1</td>
<td>40</td>
<td>852</td>
<td>2.38</td>
</tr>
<tr>
<td>11</td>
<td>HDPE + 20% Cu + 2.0% PEMA</td>
<td>35.6</td>
<td>30</td>
<td>873</td>
<td>1.64</td>
</tr>
<tr>
<td>12</td>
<td>HDPE + 30% Cu + 2.0% PEMA</td>
<td>35.1</td>
<td>30</td>
<td>897</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Figure shows a schematic representation of the mechanism of “interstructural filling” and the formation of a supramolecular structure in a polyethylene-metal-PEMA system. According to the schematic image in Fig. a, it can be noted that the loading of PEMA into the composition of the composite based on HDPE is accompanied by the redistribution of copper solid particles mainly in the volume of PEMA. This circumstance is interpreted by the fact that during the growth of crystalline formations, the polar groups and copper particles are displaced into the interspherolite amorphous space [16]. And with the further growth of crystals, PEMA and copper particles are forcedly redistributed in a narrow inter-spherulitic space. The crystallinity of the initial HDPE is 80%. That is why copper particles are predominantly distributed in the volume of PEMA. PEMA sandwiched in the interspherolite space creates a narrow polar interphase interlayer that combines well with polar copper particles.

In all likelihood, in the LDPE-based composites, the formation of the crystalline and amorphous phases will proceed in a slightly different way. As can be seen from the schematic image in Fig. b, copper particles are distributed in the volume of the LDPE-based composite mainly in the inter-spherulite space and partially in the volume of PEMA. To explain this assumption, it is enough to note that about LDPE has...
a relatively low degree of crystallinity, about 57%. In this case, copper and PEMA particles are expected to be distributed in a rather large amorphous LDPE space. Such a mechanism of structural organization formation in LDPE composites suggests a relatively low probability of interaction of copper particles with PEMA. Based on the foregoing, with an equal content of the mixture components in the composite, the concentration of copper and PEMA particles in the narrow interfacerolithic amorphous space of HDPE will always be higher than in the relatively large amorphous space of LDPE. Apparently, the loading of PEMA in the composition of composites based on HDPE promotes its uniform redistribution at the phase boundary and the creation of a monolayer of the melt with reduced mobility. Moreover, we believe that the formation of a monolayer on the surface of copper particles will lead to a decrease in the probability of their agglomeration, which will result in an increase in the total surface area of the contact with the polymer matrix. It is this approach to the interpretation of the mechanism of the formation of the supramolecular structure in the composites under consideration that explains the positive effect of PEMA on the effect of hardening of their structure [17, 18].

Fig. Schematic representation of the process of structure formation in the interfacerolithic space of composites based on HDPE + copper + PEMA (a) and LDPE + copper + PEMA (b): 1- monolayer of PEMA; 2- crystalline phase; 3- copper particles in the interfacerolithic space and inside the monolayer

The mechanism of the process of interstructural filling can be interpreted in more detail, based on the assumption that the amorphous region is polarized in the presence of PEMA. According to existing ideas, the mechanism of crystallization of polyolefins is based on the ordering of HDPE macrochains with the subsequent formation of long-range crystalline formations in the supramolecular structure [9, 19-21]. It is quite obvious that in the case of PEMA, only chains or segments free of maleic anhydride are included in the crystallization process. According to this mechanism of the formation of crystalline structures, all segments of macrochains containing maleic anhydride or side hydrocarbon branches present in the LDPE, HDPE and PEMA macrochains will be pushed into the interfacerolithic amorphous space, forming “passage chains”. Passing chains saturated with polar groups will increase the overall polarity of the amorphous region. As shown above, copper particles will also be displaced into the same region during crystal growth. The polarization of the interfacerolithic region will positively affect the increase in the adhesion forces of the contact of the passage chains on the surface of copper particles. Based on the general theory of polymer adhesion on a metal surface, PEMA macrochains containing maleic anhydride in composites based on HDPE and LDPE should be considered as “adhesive” and copper particles as “substrate” [9]. At the same time, we should not exclude from consideration the fact that the effect of the PEMA polar groups on the adhesive strength of the adhesive-substrate bond can be characterized by a “cohesive” type of failure, i.e. by weight of the polymer base. This approach to the interpretation of the polymer-copper adhesion contact mechanism is in good agreement with the data in Table 2, according to which the ultimate tensile stress of the HDPE + copper + PEMA composites is almost independent of the filler concentration (samples 7-12).

CONCLUSION

Based on the foregoing, we can conclude that metal-filled composites based on LDPE, HDPE, copper and PEMA have a significant impact on the basic physical-mechanical properties of composites based on them.

It was found that the loading of PEMA in the composition of the HDPE + copper and LDPE + copper composite leads to a noticeable increase in the ultimate tensile stress, which is interpreted as an improvement in the process of orientation of the macrochains of the polymer matrix and PEMA on the surface of copper particles and an increase in the adhesive interaction between them.

A schematic representation of the proposed mechanism for the formation of the interfacerolithic layer in composites based on HDPE and LDPE is presented. It is shown that the loading of a PEMA compatibilizer into the composition of composites is characterized by the formation of a monolayer on the surface of copper particles.

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