The study concerns composite materials based on polymer mixtures of a styrene-acrylic polymer, glycidyl ether, and a 3-aminopropyltriethoxysilane (APTES) compatibilizer. The use of a silane-type compatibilizer improves the compatibility of the components and has been shown to significantly increase the degree of crosslinking of the composition components. In this work, the structural parameters of the polymer network of the composition components depending on the compatibilizer concentration were researched by the method of equilibrium swelling. The optimal concentration of the compatibilizer was found to maximize the degree of crosslinking with a minimal number of active chains. This fact proves that the crosslinking in the composition is complete and the molecule does not contain active sites that have not reacted with the compatibilizer. The swelling kinetics of the polymer composite films proves that with an increase in the degree of crosslinking, the swelling of the polymer films decreases. Polymer films with a low proportion of active chains practically do not swell after the crosslinking process.

The article describes a possible mechanism of compatibilization involving 3-aminopropyltriethoxysilane as well as styrene-acrylic and glycidyl ether polymers. The 3-aminopropyltriethoxysilane compatibilizer has active functional groups that are located on opposite sides of the molecule; these are three active hydroxyl groups and one active amino group. Due to the presence of various functional groups, this compatibilizer can bind the polymers and thereby form strong polymer films.

This gives grounds to assert that the control of the compatibilizer concentration and the degree of crosslinking of the composition components provide prospects for the creation of polymer films with high physical and mechanical characteristics due to the high interfacial adhesion of the components in the composition.

Keywords: composite polymer films, compatibilizer, 3-aminopropyltriethoxysilane, physical and mechanical characteristics, degree of crosslinking of components

1. Introduction

When studying the properties of polymer composite materials, research to assess the impact of each component of a mixture on its structural features and deformation-strength characteristics is of paramount importance. It is known that as a result of mechanical mixing of dissimilar polymers it is possible to obtain composite materials with completely new properties [1].

The use of simply random mixtures of polymers consisting of components with certain properties is not enough to obtain high-quality materials. This feature can be ex-
plained by the lack of compatibility of most polymer pairs due to the low entropy of their mixing and poor adhesion in the interfacial area. The latter circumstance is one of the main causes of phase separation and deterioration of the physical and mechanical characteristics of composite materials.

A significant improvement in the interoperability of polymers can be achieved by selecting polymer pairs that would result in a strong intermolecular interaction between them. In a study of chemical reactions between the components of the mixture, it was found that this leads to the so-called interpolymer [2].

At the present stage, it is important to select methods for regulating the properties of mixtures of polymers using interfacial additives such as compatibilizers – graft copolymers containing active functional groups. Such compounds are reactive and form strong bonds with polar polymers, and their use helps to get closer to the problem of improving the quality characteristics of immiscible components of the mixture and finished materials made of polymer compositions [3].

2. Literature review and problem statement

It is known that the introduction of compatibilizers having functional groups leads to an increase in the specific intermolecular interaction between the chains in the system. The use of highly effective modifiers and compatibilizers for incompatible polymer mixtures is one of the main and priority areas of research to improve the technology of obtaining composite materials of high quality.

In the process of conducting a set of studies to improve the compatibility of different pairs of individual polymers by selecting the appropriate compatibilizers, scientists have got as close as possible to the possibility of their uniform mutual dispersion during mixing. The problem of polymer compatibility at the interface has been solved, and it has been determined that this area accounts for the formation of a set of physical and mechanical properties of composite materials [4]. Adjusting the content of the compatibilizer in polymeric materials helps to obtain compositions with different combinations of performance properties. For example, the introduction of only 0.5–1.0 % of the compatibilizer increases the toughness by 1.3–1.5 times and the strength by 1.2–1.35 times. Despite the practical significance of such results, the main structural parameters of the newly created polymer compositions were not presented in [4]. Accordingly, it is difficult to analyse exactly how the application of the compatibilizer affected the degree of crosslinking of the components.

In [5] it was found that the introduction of an ABS-based compatibilizer enhances the bond strength at the interface due to the formation of additional “bridges” and prevents delamination. At the same time there is an increase in the elasticity of the finished products. Thus, the elongation at break increases by approximately 2.0 to 2.5 times with the introduction of 2 % of the compatibilizer based on ABS and 0.8 % of methacrylic acid.

However, the article did not describe the process of chemical bonding between the polymer and the compatibilizer, which significantly limits the understanding of the mechanism of compatibilization.

The most common compatibilizers are silane compounds (RSiX3) [6]. In [7] it was shown that the organic radical interacts with the polymer matrix and SiX3 forms O-Si type bonds on the polymer surface. It was established in [8] that silane compounds play the role of an agent in combining two dissimilar phases. As a result of [9], a correlation was established between the bond strength of the phases, depending on the chemical nature of the components of the polymer composition although with no characteristics of the main physical and mechanical parameters of the polymer composition. Besides, the study did not establish the dependence between the structure and deformation characteristics of a finished product either.

Based on analysing advanced research, it was found that to determine the properties of polymer compositions formed by a mixture of polymers, it is important to analyse the structural parameters of the components and the mechanism of bonding. A thorough study can establish preconditions for formation of products with high physical and mechanical characteristics.

3. The aim and objectives of the study

The aim of the study is to analyse the physical and mechanical characteristics of polymer films based on a mixture of polymers and a 3-aminopropyltriethoxysilane (APTES) compatibilizer. This will make it possible to create new composite materials with high values of tensile load and elongation, which will later be widely used as multifunctional polymer composite films.

To achieve this aim, the following tasks were set and done:
- to determine the effect of the concentration of the 3-aminopropyltriethoxysilane compatibilizer on the structural parameters of the polymer composite film and to study the swelling kinetics of polymer films by establishing the relationship between the degree of crosslinking and swelling;
- to establish the peculiarities of the formation of chemical bonds and to determine the influence of the degree of crosslinking of the polymer components of the composition on the main physical and mechanical characteristics of polymer films, namely tensile strength, elongation, and internal stress.

4. Materials and methods of research on physical and mechanical properties of composite films

4.1. Materials used to develop polymer compositions

Aqueous dispersion of a copolymer of butyl acrylate and styrene – Acronal S 790 (brand BASF). Triglycidyl ether of polyoxypropylenetriol – Laproxide 603 (LLC Macromer, Vladimir, Russia). Compatibilizer – 3-aminopropyltriethoxysilane (APTES) (Sigma-Aldrich brand).

The formation of polymer films from the mixture of the polymers and the compatibilizer took place on a glass surface, followed by drying at 80 °C to constant weight for 30 minutes.

4.2. Sol-gel analysis of composite polymer films

Sol-gel analysis of polymer films was performed according to standard methods on the Soxhlet apparatus for ex-
traction by acetone for 18 hours and by benzene for 16 hours. The mass of the swollen sample was dried at 60 °C, and the dry residue was weighed [10].

The value of the sol fraction (in %) was determined by the formula
\[ S = \frac{m_a - m_b}{m_a} \times 100, \]  
where \( m_a \) is the mass of the sample after the acetone extraction; \( m_b \) is the mass of the sample after the benzene extraction.

The degree of crosslinking of the polymer (in %) was determined by the experimentally obtained value of the sol fraction \( S \) by the formula
\[ j = \frac{1}{S + \sqrt{\frac{S}{1-S}}} \times 100, \]  
(2)

The proportion of active chains was calculated by the formula
\[ V_c = (1-S)^2(1-2S)(1+jS), \]  
(3)

where \( S \) is the value of the sol fraction; \( j \) is the degree of crosslinking.

4.3. Methods for determining the physical and mechanical characteristics of composite polymer films

Evaluation of the physical and mechanical characteristics of polymer films was carried out according to the following indicators: elongation at break and tensile strength. The physicomechanical characteristics were evaluated on a rupture machine PM-30-1 at a lower capture rate of 300 mm/min.

Tensile strength (in MPa) of the sample was determined by the formula
\[ \sigma_l = \frac{P_0}{w_0 \cdot d_0}, \]  
(4)

where \( P_0 \) is the force that causes the rupture of the sample; \( H \); \( w_0 \) is the width of the sample before the test, mm; and \( d_0 \) is the average value of the sample thickness, mm.

The elongation at break of the film samples (in %) was determined as follows:
\[ \varepsilon = \frac{l_0 - l}{l_0} \times 100, \]  
(5)

where \( l_0 \) is the distance between the marks at the time of rupture of the film samples, mm; \( l \) is the distance between the samples’ labels before the tests, mm.

The internal stress in the polymer film (in MPa) was determined by the formula
\[ \sigma_h = \frac{E(h_0 - h_1)}{h_0}, \]  
(6)

where \( h_0 \) is the initial thickness of the wet film, \( \mu m \); \( h_1 \) is the thickness of the film after glazing, \( \mu m \); and \( E \) is Young’s modulus.

5. The results of studying the effect of the compatibilizer on the main characteristics of composite polymer films

5.1. Research on the effect of the 3-aminopropyltriethoxysilane concentration on the degree of crosslinking of the components in the composite film

Table 1 shows the effect of the compatibilizer’s concentration on the compatibility of the composition components and the properties of the finished polymer films.

<table>
<thead>
<tr>
<th>Composition of the polymer composite film</th>
<th>Degree of crosslinking, ( j, % )</th>
<th>Number of active chains, ( V_c )</th>
<th>Equilibrium degree of swelling, ( a, % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acronal S 790–90 % Laproxide 603–10 %</td>
<td>6.06</td>
<td>142.5</td>
<td>55</td>
</tr>
<tr>
<td>Acronal S 790–88 % Laproxide 603–10 % APTES – 2 %</td>
<td>2.01</td>
<td>2,433.9</td>
<td>63</td>
</tr>
<tr>
<td>Acronal S 790–85 % Laproxide 603–10 % APTES – 5 %</td>
<td>15.54</td>
<td>6.6</td>
<td>17</td>
</tr>
<tr>
<td>Acronal S 790–80 % Laproxide 603–10 % APTES – 10 %</td>
<td>3.16</td>
<td>803.9</td>
<td>23</td>
</tr>
<tr>
<td>Acronal S 790–75 % Laproxide 603–10 % APTES –15 %</td>
<td>3.81</td>
<td>499.1</td>
<td>34</td>
</tr>
</tbody>
</table>

It is determined that the highest degree of crosslinking is possible with the introduction of 5 % of the APTES compatibilizer to a polymer composition based on a copolymer of butyl acrylate and styrene and glycidyl ether (Fig. 1). In this case, the degree of crosslinking is 15.54 % and the number of active chains is 6.6 units. That is, the use of this concentration of the compatibilizer contributes to the crosslinking of more active chains in the polymer composition.

![Fig. 1. The effect of the 3-aminopropyltriethoxysilane compatibilizer concentration (C, %) on the degree of crosslinking (j, %) and the number of active chains \( V_c \) in the polymer composite films: – Crosslinking degree, \( j, \% \); – Active chains, \( V_c \).](image.png)
Further increase in the concentration of the APTES compatibilizer does not increase the degree of crosslinking in the polymer composition, and the proportion of active chains remaining after the crosslinking reaction is quite high.

From the presented data characterizing swelling of polymeric films, it is obvious (Table 1) that all films are exposed to hydrolytic destruction, but to a different extent. The highest rate of 55 % is of the film without the compatibilizer. Significantly lower degrees of swelling of the films with a compatibilizer concentration of 5 and 10 % are 17 and 23 %, respectively.

5. 2. Research on the influence of the compatibilizer concentration on the physical and mechanical characteristics of composite polymer films

The physicomechanical properties of the studied composite films were evaluated in terms of tensile strength, elongation at break, and internal stress. The results of these tests are presented in Table 2.

The compatibilizer concentration effect on the physical and mechanical characteristics of the composite polymer films

<table>
<thead>
<tr>
<th>TOC concentration, %</th>
<th>Tensile strength, MPa</th>
<th>Relative elongation at break, %</th>
<th>Internal stress, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.0</td>
<td>110</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
<td>520</td>
<td>0.35</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>700</td>
<td>0.25</td>
</tr>
<tr>
<td>10</td>
<td>6.0</td>
<td>400</td>
<td>0.40</td>
</tr>
<tr>
<td>15</td>
<td>4.2</td>
<td>350</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The obtained data show that higher content of the compatibilizer in the composition significantly increases the tensile strength (Fig. 2, Table 2). This is due to the reduction in the number of chains of macromolecules per unit volume of swollen polymer that counteract the destruction.

At an APTES concentration of 5 % there is a significant increase in elongation at break to 700 %. In the case of tensile forces, longer segments of chains between the crosslinking nodes are able to straighten to a greater extent than short ones, which increases the relative elongation.

Fig. 2 shows the dependence of tensile strength and elongation of the material on the concentration of APTES. As the concentration of the compatibilizer increases, the tensile strength increases, too (Fig. 2). However, at concentrations greater than 10 wt. %, on the contrary, the strength decreases again. The drop in strength of the polymer composite films with 15 wt. % APTES content can be explained by the fact that at high concentrations the compatibilizer of this nature breaks the order in the location of the monomolecular layer and, instead, forms a relatively thick interfacial layer. The latter acts as an independent phase, ultimately contributing to the deterioration of the bond strength at the interface.

6. Discussion of the results of studying the effect of the compatibilizer on the physical and mechanical characteristics of composite polymer films

In the study of composite materials, an important point is the effect of the compatibilizer's concentration on the compatibility of the components and the properties of the formed polymer films. Fig. 1 shows the dependence of the change in the degree of crosslinking on the concentration of the compatibilizer, and Fig. 2 shows the dependence of the tensile strength of the studied polymer films on the different content of APTES. Upon analysing the obtained data, a conclusion can be made that with increasing the degree of crosslinking, the physical and mechanical characteristics of the material are also improved. The optimal amount of the compatibilizer to achieve the maximum degree of crosslinking of the components is 5 %. Further increases in the concentration of the compatibilizer do not increase the degree of crosslinking. We can assume that at a high concentration of the compatibilizer, of 15 %, the thickness of the interfacial layer increases so much that it forms an independent phase and the effect of compatibilization is lost. As a result, it is not possible to achieve an improvement in the physical and mechanical characteristics of the polymer films. At the optimum concentration of the compatibilizer, which is 5 %, there is a significant increase in the strength of the polymer composite film from 3.0 to 7.5 MPa. The formed films are characterized by significant elasticity, and the relative elongation is 700 %.

The correlation between the degree of crosslinking and the physical and mechanical characteristics of the polymer films shows that the optimal concentration of the compatibilizer helps to form elastic polymer films with high elongation and high tensile strength.

The obtained data completely coincide with the previous studies [4, 5]. However, in contrast to the known research results [6–9], the structural parameters of polymer films with different concentrations of the compatibilizer have been analysed. Based on these data, the mechanism of bonding between the compatibilizer and the polymers is predicted.

Due to the active functional groups, the APTES compatibilizer forms strong bonds with the polymers that also have active functional groups, which prevents delamination of the material. The possible mechanism of this reaction is presented in Fig. 3.

We assume that the Si–OR group in APTES as a result of hydrolysis is converted to Si-OH, which is more reactive. Thus, the styrene-acrylic polymer in the interaction of terminal carboxyl groups forms a strong bond with Si-OH by the esterification reaction. Epoxy groups of glycidyl ether are able to react with the amino group of the compatibilizer, also forming strong bonds. Further research will focus on
the relationship between the components of the composition using infrared spectroscopy in combination with scanning electron microscopy.

This study has shown that the degree of crosslinking of the components of the polymer composition can have different effects on the physical and mechanical properties of the finished products. This creates certain restrictions for the use of this method. It is known that each component of the polymer composition subsequently affects the degree of crosslinking and the number of active chains. Accordingly, to predict the physical and mechanical properties, the composition of the mixture should be monitored in detail and the active groups that are able to form chemical bonds with each other should be analysed, which significantly limits the use of different components.

Despite a number of fundamental works in the direction of obtaining polymer mixtures [4–9], the processes of formation of interfacial areas with the participation of compatibilizers have not been fully studied yet. In the future, it is also necessary to take into account the ratio of those components in the mixture with which the phases become inverted.

7. Conclusion

1. It has been experimentally established that the best parameters of the polymer network are achieved by introducing 5 wt. % compatibilizer content into the composition. A further increase in the content leads to a thickening of the adhesive layer, which reduces the effect of compatibility and the degree of crosslinking of the polymer components from 15.5 % to 3 %. Polymer films with the compatibilizer swell less; the degree of swelling is 17 % compared to films without the compatibilizer, in which case the degree of swelling is 55 %.

This indicates that films with the compatibilizer are characterized by a greater degree of crosslinking and, accordingly, a denser spatial network, so the solvent molecules cannot get into the deep parts of the phase.

2. The peculiarities of interaction between glycidyl groups of the polymer and amino groups of the compatibilizer, as well as the esterification reaction resulting in a bond between the compatibilizer and the polymer, establish preconditions for creating polymer composite films with a high degree of crosslinking. It has been determined that polymer films with a degree of crosslinking of 15.5 % are characterized by the best physical and mechanical properties such as tensile strength of 7.5 MPa, elongation of 700 %, and internal stress of 0.25 MPa.

Acknowledgments

Funding: This research was supported by the Visegrad Scholarship Program of the Visegrad Fund (application number ID # 52010736).

References

1. Introduction

The effect of hydrodynamic cavitation – the formation and subsequent collapse of liquid bubbles – is widely used in chemical technology to selectively supply energy to the reaction zone. Each bubble can be regarded as a separate reactor in which a change in the cavitation mode can control the temperature and pressure, increasing them locally by tens of cycles of cavitation treatment at a pressure at the outlet from the nozzle of 9.0 MPa. A reduction of 0