Influence of temperature effects on the structure and physico-mechanical properties of filled gels of polyvinyl alcohol

I. Yu. Ukhartseva
V. A. Belyi Institute of Mechanics of Metal–Polymer Systems of the Belarus’ Academy of Sciences, Gomel’, Belarus’

The rapid development of the chemistry of high molecular weight compounds has led to the creation of many new polymeric materials, including polymer composites. Of considerable interest are filled hydrogel systems which are widely used as light- and electrically sensitive materials [1–3], drug and enzyme carriers, membranes [6], magnetic field sources [7, 8], sorbents [9], etc.

Among the synthetic polymers capable of gelation, researchers are paying a great deal of attention to polyvinyl alcohol (PVA) which possesses a number of unique properties [6, 10, 11]. In the formation of PVA gels, a three-dimensional network of polymer macromolecule associates arises in the “PVA–water” liquid system, which deprives the system of flow and gives it elasticity and plasticity.

The presence in PVA of a large number of reactive hydroxyl groups makes it possible to use it as a support for the immobilisation of a whole number of biologically active compounds [6, 12–14]. The introduction into the PVA hydrogel of fillers of different nature leads to the creation of stable systems combining the functional properties of the filler and the unique features of the polymer. In this connection, in the present work a study was made of the influence of the schedules for forming filled PVA gels on their structure and physico-mechanical characteristics.

EXPERIMENTAL

The investigation was carried out on PVA of grade 16/1 (GOST 10779), medical gelatin (GOST 23058), proteolytic enzyme papain (Loba-Chemie, Austria), medical collagen, and sodium salt of carboxymethyl cellulose (Na-CMC). The components were introduced into 8% aqueous solutions of PVA in a quantity of 10 wt.% of the polymer with a pH of the medium in the range 6–7. The PVA solutions were prepared by suspension of calculated quantities of the substance in a known quantity of distilled water with their subsequent swelling for 12 h and heating in a boiling water bath until complete dissolution. To avoid degradation of papain and collagen, calculated amounts of solutions of these components were added to the polymer after it had cooled down to room temperature.

Films were obtained from the composites by casting. The films were formed at a temperature of 293 K and, under low-temperature conditions, at a temperature of 267 K for 24 h. After this time had elapsed, the films were removed from the freezing chamber, thawed out, and dried in air at room temperature. The specimens prepared in this way were used to study physico-mechanical characteristics and determine structural parameters. To produce different products used in medicine and the food and electronics industries, wide use is made of the method of cryomodification, which is accompanied with rupture of the polymer chains and the formation of active cryolysates in the system [15–18].

The physico-mechanical characteristics were determined to GOST 14236 on a 2028R-0.05 tensile machine with a clamp speed of 100 mm/min and a temperature of 293 K.
Swelling of the specimens was carried out in distilled water (pH = 6–7) and in an aqueous solution of nitrofurazone, after they had been dried to constant mass at a temperature of 323 K. The introduction of antiseptic was carried out over a 48 h period.

The swellability of the hydrogels was studied by gravimetry. The degree of swelling was determined by means of the formula

\[ Q = M_s / M_d \]

where \( M_s \) is the mass of the specimen swollen to an equilibrium value, and \( M_d \) is the mass of the initial dry specimen.

The magnitude of the gel fraction \( \sigma \) was calculated as the ratio of the mass of the specimen dried after swelling to the mass taken for swelling of the initial sample \( M_d \) [19]. The result of measurement was the arithmetic mean value obtained by measuring five similar specimens.

The morphology of the films was studied on a JSM-50A electron microscope.

RESULTS AND DISCUSSION

As shown by experiments, different temperatures of forming of the films lead to variation in the structure of the materials. Figure 1 presents micrographs of PVA + Na-CMC films, from analysis of which it is possible to draw a conclusion concerning changes in the supermolecular structure of the polymer under subzero temperatures. Whereas in films obtained at 293 K the structure of the material is homogeneous (Figure 1a), in the case of freezing, the presence of numerous micro- and macropores is observed, formed by ice crystals (Figure 1b). Here, in the former case it is fibrils that are mainly formed in the supermolecular structure, and in the latter case a three-dimensional structure with individual inclusions of the globular type is formed.

Similar changes in structure are observed for the other types of composite investigated and are consistent with data previously obtained [18, 20, 21].

The change in structure of the polymer that occurs during cryomodification and when fillers are added affects the physicomechanical characteristics of the films produced.

It was established experimentally that, when fillers are introduced into PVA, strengthening of the material occurs irrespective of the nature of the filler and the temperature of formation of the specimens. However, films formed at subzero temperature possess lower strength and deformation characteristics (Table 1).

At low temperature, changes occur in the structure of the PVA, leading to degradation of the macromolecules of the polymer, which is accompanied with a reduction in the strength properties of the films. The introduction of fillers leads to an increase in the strength of the material, but to a lesser degree than when the films are formed at a temperature of 293 K. Increase in strength seems to be due to the formation of intermolecular bonds between the PVA molecules and filler.

Table 1. Physicomechanical characteristics and structural parameters of PVA–filler systems

<table>
<thead>
<tr>
<th>Composition of system</th>
<th>Temperature of formation, K</th>
<th>Tensile stress causing failure, MPa</th>
<th>Breaking elongation, %</th>
<th>Degree of swelling, %</th>
<th>Content of gel fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>293</td>
<td>71.8</td>
<td>61</td>
<td>295</td>
<td>–</td>
</tr>
<tr>
<td>PVA + gelatin</td>
<td></td>
<td>88.2</td>
<td>100</td>
<td>264</td>
<td>–</td>
</tr>
<tr>
<td>PVA + papain</td>
<td></td>
<td>80.4</td>
<td>77</td>
<td>244</td>
<td>–</td>
</tr>
<tr>
<td>PVA + collagen</td>
<td></td>
<td>75.3</td>
<td>120</td>
<td>255</td>
<td>–</td>
</tr>
<tr>
<td>PVA + Na-CMC</td>
<td></td>
<td>82.3</td>
<td>40</td>
<td>280</td>
<td>–</td>
</tr>
<tr>
<td>PVA</td>
<td>267</td>
<td>66.8</td>
<td>50</td>
<td>544</td>
<td>70</td>
</tr>
<tr>
<td>PVA + gelatin</td>
<td></td>
<td>80.3</td>
<td>90</td>
<td>694</td>
<td>60</td>
</tr>
<tr>
<td>PVA + papain</td>
<td></td>
<td>75.7</td>
<td>54</td>
<td>694</td>
<td>50</td>
</tr>
<tr>
<td>PVA + collagen</td>
<td></td>
<td>70.4</td>
<td>95</td>
<td>697</td>
<td>55</td>
</tr>
<tr>
<td>PVA + Na-CMC</td>
<td></td>
<td>72.8</td>
<td>35</td>
<td>670</td>
<td>65</td>
</tr>
</tbody>
</table>
Investigation of processes of swelling of PVA films with different fillers showed that, for materials obtained at a temperature of 293 K, the degree of swelling differs little from that for films of pure PVA (Table 1).

At subzero temperature of formation, the degree of swelling of the composites is much greater than for pure PVA. Cryomodification leads to structure formation of the polymer, during which it is transformed from the soluble state to the insoluble state [17]. Here, a three-dimensional network is formed, the density of which is determined by the composition of the composite and the type of filler. The greatest degree of swelling is possessed by specimens containing compounds of protein nature (gelatin, papain, collagen). The introduction of these components increases the degree of swelling of the materials by 20–25% compared with pure PVA. Such an effect, observed at a subzero temperature of formation of films, seems to be due to the emergence in the polymer–filler system of formations that interact both with PVA molecules and with filler molecules. Here, a network of crosslinks is formed, and degradation of the polymer occurs, which leads to an increase in the diffusion rate of water molecules to the low molecular weight part of the PVA and acceleration of its solubility. Fillers that are also high molecular weight compounds are likely also to undergo structural changes at the molecular level during the cryoformation of films. Their partial degradation occurs, intra- and intermolecular bonds are broken, and microcavities are formed, into which solvent molecules penetrate, which leads to an increase in the permeability of the composite as a whole. The data obtained confirm the positions of free volume theory with respect to the unactivated elementary act of diffusion [14], which also holds for composites of PVA with other fillers [17].

Increase in the degree of swelling of the composites compared with the initial PVA is also connected with reduction in the degree of crosslinking of the polymer–filler system. This is indicated, for example, by a reduction in the gel fraction content from 70% for PVA to 50% for the PVA + papain system. Reduction in the degree of crosslinking for all the composites investigated is due to the interaction of filler particles with formations arising in the system at subzero temperature. Such active formations limit the interaction of particles of the polymer with each other. Similar data on the degree of swelling and the gel fraction indices were obtained for specimens placed in a surrounding medium.

Thus, the investigations carried out showed that filled PVA gels formed under different production conditions can be used as the basis for creating materials with controllable properties, making it possible to produce, for example, drug-containing therapeutic systems that are capable of controlled release of the medicine into the surrounding medium.

REFERENCES

15. V. E. Gul’ et al., Effect of cryolysis on structure of rigid-chain polymers. Vys. Soed., 18, No. 1, 1976, pp. 118–121


(No date given)