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Abstract

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INVESTIGATION OF THE PRODUCTS OF THE INTERACTION OF POLYPROPYLENE WITH ALKALINE SULFATE LIGNIN

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At present polypropylene is attracting increasing attention from chemists because of a number of advantages in comparison, for example, with polyethylene.

Despite the complex of valuable properties inherent in polypropylene, it has a very substantial drawback: owing to its crystallinity it possesses a comparatively high brittle temperature, which significantly limits the areas of its application.

Methods are known for increasing the frost resistance of polymeric materials; one of the most widespread is the introduction of a plasticizer into the polymer ([1]). However, as was shown by V. A. Kargin, T. I. Sogolova, and G. Sh. Talipov ([2]), the introduction of plasticizers into crystalline polymers promotes crystallization of the latter, which has an adverse effect on the frost resistance of materials obtained from such polymers. Therefore, an increase in the frost resistance of isotactic polypropylene cannot be achieved solely by introducing a plasticizer. The introduction of alkaline sulfate lignin into isotactic polypropylene leads to amorphization of the crystalline product, as evidenced by a certain increase in the narrow component of the NMR lines in polypropylene containing 5% lignin as compared with the initial polypropylene.

In addition, the introduction of lignin apparently leads to crosslinking of the linear molecules of polypropylene, which is a positive factor in plasticization.

In the present study we set ourselves the task of obtaining a frost-resistant material based on polypropylene without any substantial change in its strength; for this purpose, under processing conditions, alkaline sulfate lignin was introduced into polypropylene simultaneously with a plasticizer, as a crosslinking agent.

M. B. Neiman and co-workers ([3]) showed that the process of thermo-oxidative degradation of isotactic polypropylene in the temperature range 120–150° is described by the equation of a bimolecular reaction:

$$\mathrm{ROOH} + \mathrm{RH} = \mathrm{RO}^{\cdot} + \mathrm{H_2O} + \mathrm{R}^{\cdot}. \tag{1}$$

chemical structural scheme: radical (a) and isomeric/tautomeric forms (b), (c), (c′)

Figure 1: chemical structural scheme: radical (a) and isomeric/tautomeric forms (b), (c), (c′)

chemical structural scheme: dimerization of forms (b) and (c′) to form a secondary structural unit of lignin

Figure 2: chemical structural scheme: dimerization of forms (b) and (c′) to form a secondary structural unit of lignin

At T = 120-150°, the hydroperoxide radical of polypropylene of the following structure is formed:

$$R_1{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle O^{\cdot}}{C}}{-}CH_2{-}R_2 \qquad (2)$$

This radical, in our view, is the source of interaction with alkaline sulfate lignin with the formation of a spatial structure. According to Freudenberg ([4]), lignin formation occurs as a result of dehydrogenation of coniferyl alcohol, which is ···

···structural unit of the lignin macromolecule. The radical formed (a) can be represented in several isomeric and tautomeric forms (b), (c), (c′):

As a result of spontaneous dimerization, these forms of the mesomeric radical are stabilized, forming dimeric quinonemethide radicals and intermediate products —secondary structural units of lignin—which, by dehydration and, chiefly, by further addition reactions, form the branched macromolecule of lignin:

The presence of a five-membered strained ring in the lignin macromolecule apparently makes the lignin molecule reactive under processing conditions in an extruder at $T = 220°$.

We assume that, under these conditions, rupture of the five-membered ring becomes possible with the formation of two reactive sites in the product formed, through which cross-linking of polypropylene macromolecules occurs.

The following facts indicate cross-linking of polypropylene macromolecules during its heating with lignin under processing conditions:

1) A change in the swelling kinetics of cross-linked polypropylene depending on the concentration of the introduced alkali sulfate lignin in decalin at $T = 110°$, and of the original polypropylene in decalin at $T = 110°$ (Fig. 1).

It is evident from Fig. 1 that the original polypropylene dissolves under these conditions in 2.5 hours, whereas cross-linked polypropylene only swells to a

Fig. 1

Figure 3: Fig. 1

Fig. 2

Figure 4: Fig. 2

limited extent; moreover, the degree of swelling of the cross-linked polypropylene increases with increasing lignin concentration, since, with an increase in the degree of cross-linking, the number of polypropylene macromolecules capable of passing into solution decreases.

2) A change in the ratio of reversible to irreversible deformation. This ratio was determined for samples of cross-linked and uncross-linked polypropylene, previously stretched to a relative elongation of 500%, during heating at $T = 130°$. From Fig. 2 it is evident that···

the ratio $\varepsilon_{\text{rev}}/\varepsilon_{\text{irrev}}$ for the original polypropylene is 9, while for polypropylene containing 1.0% lignin it is about 16. The increase in the ratio $\varepsilon_{\text{rev}}/\varepsilon_{\text{irrev}}$ in the case of cross-linked polypropylene, as compared with the original, is explained by a loss of mobility of the macromolecules as a whole, occurring as a result of transverse cross-linking.

Fig. 1. Dependence of the degree of swelling of modified polypropylene on time (in decalin at $T = 110°$).
1 –original polypropylene, 2 –polypropylene + 2% lignin, 3 –polypropylene + 5% lignin, 4 –polypropylene + 10% lignin, 5 –polypropylene + 15% lignin

Fig. 2. Dependence of deformation on heating time at $T = 130°$.
1 –original polypropylene, 2 –polypropylene + 1.0% lignin, ε_{tot} –total deformation before heating, ε_{rev} –reversible deformation, ε_{res} –residual deformation

If a plasticizer is additionally introduced into cross-linked polypropylene, its frost resistance increases to $-60 \div -70°$. The polypropylene modified in this way is not inferior in strength to the original polypropylene, as is evident from Fig. 3.

Fig. 3. *a* –dependence of tensile strength on lignin concentration in modified polypropylene; *b* –change in T_{fr} as a function of lignin concentration in modified polypropylene:
I –original polypropylene, II –polypropylene + 7% DOS, III –polypropylene + 15% DOS

Figure 3a shows the dependence of the strength of polypropylene plasticized

Fig. 3

Figure 5: Fig. 3

with dioctyl sebacate (DOS) on the concentration of lignin, which is the cross-linking agent (CA). From this figure it is evident that the optimum content of lignin introduced into polypropylene, at a DOS content of 15%, is 4–5%. When the DOS content is decreased, the optimum shifts toward lower degrees of cross-linking, i.e., the greater the plasticizer content, beginning with 7%, the more lignin should be introduced into polypropylene so that the strength of the material does not decrease in comparison with the original polypropylene.

Curve II lies in the region of higher strengths than curve I. This is associated with strengthening of the material upon the introduction of small amounts of plasticizer as a result of an increase in the degree of orientation before rupture. On curve III, the sharp increase in strength is replaced by its monotonic decrease, which is due to the predominance of weakening of the intermolecular interaction of the polypropylene molecules and to a decrease in the effectiveness of the process of chain orientation ([6]). As for the frost resistance of the material obtained, it is evident from Fig. 3b that with increasing plasticizer concentration the frost resistance increases. At a content

With the addition of 15% DOS and 4% lignin, the strength of the material increases from 215 (for the original polypropylene) to 250 kg/cm^2, while the frost resistance (determined by the method of M. D. Frenkel et al.) (5) increases correspondingly from $-18°$ to $-65°$.

It should be noted that the "cross-linked polypropylene—plasticizer" system (poprolin) is stable, as is shown by testing films of polypropylene with 1% lignin and 7% DOS and polypropylene with 3% lignin and 15% DOS on a "Falzer" -type apparatus. The tests showed that a film subjected for a long time to repeated deformations (more than 20,000 double bends) undergoes no changes and no exudation of the plasticizer occurs. At the same time, in a film made from the original polypropylene some exudation of the plasticizer is observed.

Experiments carried out on the aging of polypropylene and poprolin showed that the original polypropylene is destroyed after 46 hours, whereas poprolin withstands more than 150 hours under the same conditions.

The aging tests were carried out in an "Atlas"-type artificial-weather apparatus with two arc electric lamps, with an irradiation intensity of 0.5 ± 0.005 cal/cm^2; the temperature on the surface of the specimen was $+70°$, GOST 10226-62. The aging experiments on polypropylene and poprolin were conducted at NIIPM in laboratory No. 17 under the supervision of N. N. Pavlov.

The determination of NMR spectra was carried out at NIIPM in laboratory No. 42 under the supervision of I. Ya. Slonim.

As a result of the investigation performed, it has been shown experimentally that, upon introducing lignin into polypropylene as a cross-linking agent and dioctyl sebacate as a plasticizer under processing conditions at $T = 220°$, a new frost-resistant modification of polypropylene—poprolin—is formed, whose strength does not change substantially in comparison with the strength of the original polypropylene.

It has been shown that the frost resistance of polypropylene increases from −18 to −65° when 15% dioctyl sebacate and 4% lignin are introduced into it, with a slight increase in strength.

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Note: Figure translations are in progress. See original paper for figures.