THEORY OF THE PREPARATION OF FIBRILLATED POLYPROPYLENE FILM MATERIALS

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The intensive development in manufacture of fibrillated fibrous film materials based on polyolefins, mainly polypropylene (PP), is explained not only by the valuable specific properties of such materials (high strength and low density), but also by the relatively low cost of the starting material and the simplicity of the technological process. As concerns the latter factor, the simplicity of the technology is explained by the ability of polyolefin films to split easily under intensive mechanical stretching into individual relatively thin formations (macrofibrils). On twisting narrow fibrillated films, very diverse articles can be obtained, starting with a high-modulus textile yarn and ending with strong packaging straps and cables. The general technological bases of the preparation of fibrillated film materials from polyolefins have already been set forth in short form [1].

However, the process of preparing such materials has features which are connected with the mechanisms of formation of the starting film and its fibrillation by stretching. This circumstance justifies the need for a more detailed examination of the scientific principles of the formation of fibrillated films. It is advisable to discuss this question in the case of PP as the most frequently used starting polymer for these purposes.

The high breaking strength of oriented polymeric materials (fibres and films) is brought about by the fact that, on very complete orientation of the macromolecules along the direction of action of a load (along the fibre axis), failure of the polymeric material takes place principally due to breakage of the macromolecule chains along the lines of the chemical bonds, and to a very small extent as the result of failure of intermolecular bonds. The energy of the C–C chemical bond is 250–300 kJ/mole, which is many times more than the energy of intermolecular interaction; for nonpolar polymers, particularly polyolefins, this does not exceed 5–10 kJ/mole. Depending on the disorientation angle of the macromolecules, that is, their deviation from the direction of load action, the ratio of the breaking strength of the real material, with an assigned disorientation angle \( \alpha \), to the strength of an ideally oriented polymer \( \alpha = 0 \) can be represented approximately by the following equation [2, p. 283]:

\[
\frac{\sigma_\alpha}{\sigma_0} = \frac{1}{1 + (\beta^2 - 1) \sin^2 \alpha}
\]

where \( \sigma_\alpha \) and \( \sigma_0 \) are strengths; and \( \beta \) is the ratio of the energies of chemical and intermolecular bonds.

According to this equation, as the degree of orientation approaches the limiting degree, the relative strength of the material in the direction of orientation rises rapidly, and the strength in the transverse direction becomes very low. On attainment of the limiting degree of orientation, this ratio can reach 500–3500, if one takes into consideration the values of the chemical bond energy indicated above. Even if one starts from a theoretically estimated PP strength of a few GPa, the transverse strength will be a few MPa. Actually, however, if one considers the defectiveness of real polymeric materials, these strength indices proved to be significantly lower; however, their ratio is basically preserved. By this we also explain the easy "splittability" (fibrillation) of polyolefin films on stretching.

In technology, this fibrillation is usually facilitated by various mechanical devices, particularly with the aid of so-called fibrillators. Splitting of the film can also be stimulated by a special shaping during its formation, which eliminates the need to use needle fibrillators or others. In principle, the fibrillation process can also take place spontaneously, wherein the decisive role is played by natural nonuniformity of the polymeric material itself. This nonuniformity of the material leads to the situation that individual microportions of the polymer, on large orientation stretches, reach the limiting deformation sooner than nearby sections, and the difference in relative rates of deformation confers on the material the structure of alternating lengthwise formations with high and low degrees of order, and, correspondingly, to an alternation of regions which are strong and weak in the transverse direction. A schematic picture of the development of such structural nonuniformity has been previously described [2, p. 71].
Fig. 1. Diffractograms of isotactic PP of the monoclinic (a) and pseudohexagonal (b) modifications.

Fig. 2. Dependence of the strength, $\sigma$, of PP films on the stretch ratio, $\lambda$, under various conditions of cooling after extrusion: 1) in water bath; 2) between cylinders; 3) by air (hose film).

Thus, the high values of absolute strength of oriented film materials are explained by a predominant failure of the polymer due to breakage of macromolecules along the length of chemical bonds, and their easy splitting (macrofibrillation), by a low transverse strength.

However, in this problem it is important to note still another circumstance which is connected with the very high deformability of the film during its orientation stretch, which inherently makes it possible to reach a degree of polymer orientation which is close to the limiting one. The stretch in preparing fibrillated films may exceed tenfold. To explain this, it is necessary to examine the structure and phase state of the starting film obtained after extrusion of the melt through a slot (or annular) spinneret which is subjected, in a later stage of the technological process, to orientation stretching.

Orientation rearrangement of the polymer by uniaxial (or biaxial) stretching is easily attained thanks to the polymorphic phase transformations which take place in the polymer. Just such a phase transformation takes place in the case of isotactic PP due to the fact that it exists in several crystalline modifications. On cooling PP to moderate temperatures (in the range 0-50°C) an imperfect hexagonal crystalline modification arises in it (often called the $\beta$-modification), which is thermodynamically unstable with respect to the equilibrium monoclinic modification (the $\alpha$-modification). In Fig. 1 we give diffractograms of these two modifications. At temperatures above 70°C, the $\beta$-modification goes over into the thermodynamically stable $\alpha$-modification. This fact is also used in preparing fibrillated films.

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After extrusion of the PP melt through the spinneret, the film formed is usually cooled to a temperature of about 20°C. Thereupon, the $\beta$-modification of the polymer is formed. The melting point of this modification, according to the literature [3], is about 150°C. In the orientation stretch stage, the film is heated to a temperature close to this. As a result, a rearrangement of polymer structure begins, wherein, thanks to the relative amount of order in the polymer macromolecules in the original film present in the imperfect $\beta$-modification, orientation stretch is considerably facilitated, as well as rearrangement of the structure in the stable $\alpha$-modification.

Naturally, in the course of cooling the melt, nonuniform temperature conditions are created over the cross section of the film being formed; therefore, together with the formation of the metastable hexagonal modification nuclei of the thermodynamically stable monoclinic modification are formed to some extent. To avoid this, cooling of the film should be carried out under conditions which reduce the temperature gradient over the film thickness.

In particular, this determines the selection of the cooling temperature (the temperature of the cooling liquid or of the surface of the cooling cylinders), wherein both economic considerations in connection with the energy consumption in preparing the cooling agent and the constructional features of the apparatus are taken into account. The latter circumstance dictates, for example, the need to use two-sided cooling, which is effected by passing the film through two cylinders, not one, or by cooling in water.