Modification of polypropylene. Part 1. Effect of nucleating agents

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INTRODUCTION

One method for modifying the crystal structure of polymers is to introduce artificial nucleating agents [1, 2]. In the present work an investigation was made of the effect on the properties of polypropylene of nucleators belonging to different classes of chemical compounds. The concentration dependences of the effect of nucleators on the properties of polypropylene were obtained.

MATERIALS INVESTIGATED

The base polymer used was polypropylene of grade Lipol A7. The nucleating agents employed were talc, sodium benzoate (NaOBz), dibenzylidene sorbitol (DBS), di-p-methylidibenzylidene sorbitol (MDBS), sodium 2,2’-methylene-bis{(4,6-diterbutylphenyl) phosphate (NA-1), and hydroxyaluminium bis{2,2’-methylene-bis(4,6-diterbutylphenyl) phosphate (NA-2).}

METHODS OF INVESTIGATION

Regimes for Compounding of Composites and Injection Moulding of Standard Specimens

Mixtures were produced on a Baker–Perkins twin-screw vacuum extruder, L/D = 25:
- The temperature regime of extrusion for the various zones from the charging zone to the head was 190–235°C.
- The screw rotational speed was 200 rpm.
- The throughput was 6 kg/h.
- The moment was 65–70%.
- Standard injection moulded specimens were obtained on an Allrounder 370 CMD automatic thermoplastics injection moulding machine (Arburg Maschinenfabrik Hehl & Sohne).
- Injection moulding conditions: $T_{\text{injection\,cylinder}} = 200–250°C$; $T_{\text{mould}} = 40–75°C$; $P = 30/55$ MPa.

Differential Scanning Calorimetry

The melting and crystallisation temperatures were determined, and also the heat effects, on a Perkin Elmer Pyris6 DSC; the heating and cooling rate was 20 K/min, and the medium was nitrogen.

The samples weighed 8.0–9.0 mg.

Physicomechanical Tests

By standard procedures, the following parameters of the materials were determined:
1. Elongation to GOST 11262–80. Tensile strength, yield point in elongation, breaking elongation, and yield point were monitored. Testing was conducted on an Instron 1185 tensile testing machine. Standard type-2 dumb-bell testpieces were used. The speed of the crosspiece was 25 mm/min.
2. Static bending to GOST 4648–71. The bending stress under prescribed load and the bending stress under a deflection of 1.5 times the thickness of the specimen were monitored. The tests were conducted on an Instron 1185 instrument. Standard specimens were
used for the tests – 80 × 4 × 10 bars. The loading rate was 25 mm/min.

3. Determination of the Charpy impact strength to GOST 4647–80. The impact strength was determined on 80 × 10 × 4 bars, unnotched and with a V-notch. Tests were conducted on a CEAST 6545/000 pendulum impact device.

4. Determination of light transmission was conducted in accordance with GOST 15875–80 on standard specimens (50 × 2 mm discs). The method consists in a direct comparison of the light flux passing through the testpiece with the light flux falling on the photoelement when there is no specimen there. Tests were conducted on a “Pulsar” colorimeter with light source according to GOST 7721–76.

RESULTS AND DISCUSSION

For the study of the crystallisation behaviour of polymer melts and assessment of the effectiveness of artificial nucleating agents, use is most often made of methods of thermal analysis [differential thermal analysis (DTA) and differential scanning calorimetry (DSC)] [3]. Observation of melt crystallisation is carried out during its cooling at a constant rate, and here the temperature at which the heat effect reaches a maximum, which corresponds to the maximum crystallisation rate, is recorded. With increase in the density of nuclei, i.e. increase in the activity of the structure-forming agent, this temperature increases.

As can be seen from the dependence of the crystallisation temperature of polypropylene on the content of nucleating agent (Figure 1), finely dispersed talc and sodium benzoate, even though they are structure-forming agents, exhibit fairly low effectiveness, which is entirely consistent with published data [4]. When DBS was introduced, a considerable shift in the crystallisation temperature of the polymer into the high-temperature region was observed: thus, the crystallisation temperature amounted to 122°C at a concentration of 0.3%DBS, which is 14 K higher than the crystallisation temperature of the initial polymer. The greatest effectiveness was found when organophosphates NA-1 and NA-2 were introduced, and also MDBS. Even a small amount of these nucleating agents (~0.05%) shifts the crystallisation considerably (10–12 K) into the high-temperature region. The conducted investigations made it possible to select the most effective nucleators.

A fundamental question is assessment of the effect of nucleating agents on the service characteristics (physicomechanical and optical properties) of polypropylene. An investigation was made of the effect of the following nucleating agents: NA-1, NA-2, and MDBS in the concentration range 0.1–0.3%.

![Figure 1. Dependence of $T_c$ of polypropylene on nucleator concentration](image)

![Figure 2. Dependence of tensile strength and tensile elastic modulus on nucleator concentration](image)
When the investigated nucleators were introduced into polypropylene, the following changes in physicomechanical characteristics were observed: there was a considerable increase in the Young’s modulus in bend and the tensile elastic modulus, an increase in tensile strength and yield point in elongation (Figure 2), and here there is a reduction in elasticity. The materials become more rigid. Similar effects were also observed by Fujiyama and Wakino [5].

The impact and strength characteristics (besides the elastic modulus) remain roughly at the same level. With the introduction of organophosphates NA-1 and NA-2, the composites are characterised by higher physicomechanical properties. Similar relationships can be observed on the dependence of the crystallisation temperature on the nucleator concentration – composites containing organophosphates are crystallised at a slightly greater temperature, which indicates higher crystallisation rates, even by comparison with MDBS.

On the other hand, composites with the addition of MDBS have far greater optical properties than organophosphates NA-1 and NA-2. Figure 3 presents the dependences of the coefficient of light transmission on the nucleator concentration. It is also worth mentioning that there exists a limiting concentration of additive, beyond which the optical properties cease to improve. In some cases it is even possible to speak of a deterioration in optical properties. This seems to be due to the fact that, at a high concentration, the nucleator is unable to be evenly distributed in the polymer.

It must be pointed out, in particular, that the nucleating agents investigated have different effects on the physicomechanical and optical properties. Composites containing nucleators – organophosphates NA-1 and NA-2 – are characterised by higher physicomechanical properties (elastic modulus in particular). These additives are best used in those cases where there is no need to achieve high optical characteristics but it is necessary to increase the productivity of the process of manufacturing products by shortening the injection moulding cycle (productivity increases by 15–30% as a function of the types of product and the moulding method). Here, the effects of increase in elastic modulus and reduction in shrinkage are achieved. PP composites containing MDBS, on the other hand, possess better transparency but inferior physicomechanical characteristics by comparison with PP composites containing organophosphates.

REFERENCES


(No date given)