

Characteristics of Polymerization-Filled Polyethylenes ("Norplastics") and Compositions on the Basis of Norplastics

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Synopsis

The peculiarities of a new type of materials—polymerization-filled polymers ("Norplastics")—have been studied. Norplastics were tested as polymer fillers. The structure morphological properties of high-filled polymer composites (HFPC), prepared both with norplastics as fillers and traditional mineral dispersed fillers, have been examined.

INTRODUCTION

Beginning in the 1970s, the addition of fillers to thermoplastics has been on an ever larger scale not only for polymer modification for the purpose of imparting to them some necessary properties, but also for reducing the polymer content of materials in order to economize on the scarce oil and gas raw materials and reduce the cost of plastics.¹ In designing high-filled polymer composites (HFPC), one should try to ensure that their performance will be at least equal to that of unfilled polymer plastics. The method of polymerization filling of thermoplastics seems to be promising in this respect; the concept of the method consists in polymerization of an appropriate monomer on the surface of a mineral filler which has been preactivated with a complex catalyst.²

Each filler particle (designated below as mineral component of norplastics, MCn) is covered with a polymer layer (polymer component of norplastics, PCn or coat). By varying the synthesis conditions one may adjust the molecular mass of PCn to obtain materials with practically any PCn/MCn ratio.

Extensive use of norplastics necessitates a detailed investigation of their physicomechanical and rheological properties, which has been pioneered in a series of studies²⁻⁶ on norplastics of the "PE-perlite" type with molecular mass of PCn $\approx 1 \times 10^6$.

It has been shown that norplastics with high perlite content (80–95% by mass) can be employed as fillers in thermoplastics. The strength of nor-

plastic-based compositions is considerably higher than those of systems obtained by traditional mechanical mixing.²⁻⁶

The melting points of compositions with norplastics are practically the same as those of respective mechanical mixtures, while the mass loss and intensive degradation begin in mechanical mixtures at temperatures 20–30° lower; therefore, the HFPC on the basis of polymerization-filled polyethylene can be processed in a much wider temperature range.⁶

EXPERIMENTAL

Four groups of materials have been investigated: Group I, norplastics synthesized on kaolin, chalk, perlite, and tuffa with different mean particle size (in the range of 8–180 μm), the molecular mass of the polymer component (PCn) being $MM_w \approx 1 \times 10^6$; Group II, composite materials containing norplastics of Group I as fillers and high- or low-density polyethylene matrix; Group III, compositions on the basis of polyethylene and mineral fillers prepared by mechanical mixing. The concentration of components in Groups II and III samples has been identical. This has been achieved by introducing in Group III samples, in addition to the filler, high-molecular linear polyethylene ($MM_w \approx 1 \times 10^6$) in quantities corresponding to the PCn content of the Group II samples; Group IV, mechanical mixtures analogous to those of Group III but without addition of high-molecular linear polyethylene.

Irganox 1010 (an effective thermal stabilizer of polyolefins) has been added to all the HFPC in amounts of 0.5% of total polyethylene.

The compositions were prepared in a laboratory turbomixer and then granulated in a laboratory twin-screw extruder. Rheological properties of the materials (viscosity and high elastic) were investigated over a broad range of stresses, shear rates, and temperatures by the capillary viscometry method with the automatic "Rheograph-2000" flowmeter (Hettfert, W. Germany) at a constant flow rate using capillaries of various diameters and lengths.

Mechanical testing, as well as structural-morphological investigations were performed on samples in the form of blades or bars of standard dimensions prepared from granules on the Kanavets molding machine at injection temperature of 200°C, mold temperature of 50–60°C, and time of exposure to pressure 10–15 s.

The stress-strain behavior of materials was determined by tension on the testing machine Zwick-1464 (FRG); the specific impact strength was determined with the pendulum impact testing machine KM-5T (USSR) (GOST 4647-69).

Thermomechanical testing was performed on the UIP-70 device (USSR) by forcing under a constant load indenter into compacted tablets heated at a rate of 2.5°/min.

Structure-morphological studies were conducted by the methods of analytic electron microscopy. After being coated with a layer of conducting metal (gold) the surface of mineral particles and that of norplastic particles were examined with a help of a scanning electron microscope (SEM-500).

To establish the phase structure of composite materials, the method of etching the surfaces of their cross-sections and low-temperature fracture in

the plasma of high-frequency oxygen charge (oxygen pressure 0.05 Torr, electron energy in the zone of etching, 3 eV, frequency 10 MHz) were used. The etched surfaces were studied either by means of scanning electron microscopy (SEM-500), or with a help of X-ray microanalysis (Edax) as well as single-stage carbon-platinum replicas in transmission electron microscope EM-301.

RESULTS AND DISCUSSION

Morphological Properties of Norplastics

Irrespective of the nature of MCn, the norplastics investigated were powders of various grain size. It can be inferred from comparison of the particle size distribution in norplastics with that of the mineral particles burnt out of norplastics, as well as from electron microscope examinations that norplastic particles are basically agglomerates formed by accretion or cohesion of the polymer coats formed on individual particles. The tendency for agglomeration increases with decreasing particle size of the mineral filler. Also, there are fluctuations of the PCn/MCn ratio in different norplastic particles obtained by one and the same synthesis process.

Investigations of structure and morphology by analytical electron microscopy

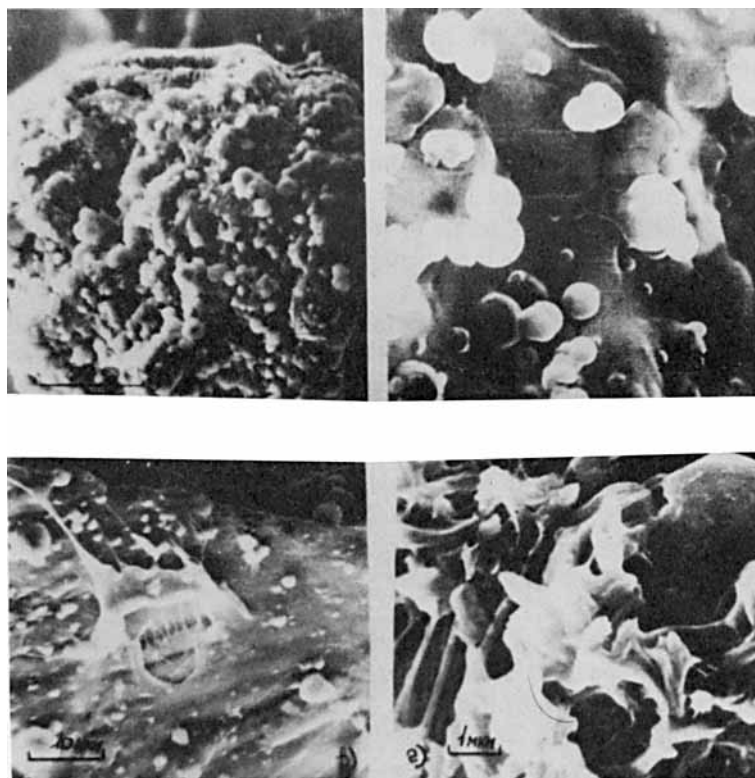


Fig. 1. Morphology of various surface zones of initial norplastic particles (agglomerates) on kaolin.

reveal three types of morphological heterogeneity characteristically observed in the polymer component of norplastics (PCn): First, many particles occur in the form of spheres [Fig. 1(b)] and columns [Fig. 1(d)], their quantity varying from 10^{11} to 10^{14} cm^{-2} depending on the type of filler. Second, spaces between the particles are spanned by a film [Fig. 1(c)], whose thickness is 5–10-fold smaller than the height of the globules. Third, the discontinuities: at small PCn quantities ($\leq 5\%$), discontinuities occur at the surface zones devoid of the “coat”; at high PCn content they are due to fissures formed both at the joints between the globules and films, and in places where the film has come off the surface of the globule as a result of formation and destruction of local contacts during polymerization (probably, during stirring). The relation between these types of defects of the PCn depends on the polymer concentration and nature of the filler. Thus, with perlite, the formation and growth of spherical and, then, of columnar forms is predominant; with kaolin and tuffa small quantities of spherical forms, but chiefly a thin surface film, are formed. Such distribution and growth of the polymer film on the mineral filler surface seems to be related to its structure, since the sorption of complex catalysts occurs chiefly on the filler surface.

From the data obtained by different methods it follows that the individual mineral particle in norplastics is surrounded by a macromolecular layer, which is strongly coupled with the mineral particle surface by chemical or physical bonds. The thickness of this layer is much larger than that of the hardened surface layers (“thin layers”) in common filled polymer systems prepared by conventional mixing. The macromolecules of the next polymer layers surrounding the mineral particle in norplastics may as well not be in a direct contact with the filler but may be mechanically engaged with the strongly coupled surface layer (for instance, the macromolecules of different layers may form parts of one and the same submolecular formation). Thus, the “disturbing” influence of mineral filler particles in norplastics ranges over a significantly larger region than in mechanical mixtures of similar composition.

Investigation of the material deformability under the effect of ball indenter has shown that, at very high filler contents (PCn $\approx 19\%$ by mass), norplastics undergo only elastic deformation, the specimens return to their original state after relief of load. With increasing PCn (“coat”) content up to 60% (by mass) considerable residual deformations appear; the material acquires flowability and can be pressed through viscometer capillaries. Further increase of the PCn content up to 80% (by mass) does not affect fundamentally the behavior of norplastics under viscometry test conditions, but a “stalling” of the flow is to be observed, which will be discussed in more detail below.

An interesting effect has been found in the studies of the thermal expansion of norplastic specimens. The linear thermal expansion coefficient versus temperature curves of norplastics α ($\alpha = \Delta l/l\Delta t$) (where l is the current specimen height, Δl and Δt are specimen height and temperature increments, respectively) show two extrema. For instance, there are two peaks on the curves of Figure 2 for Group I samples synthesized on expanded perlite: one in the range of 125–135°C, which corresponds to the melting

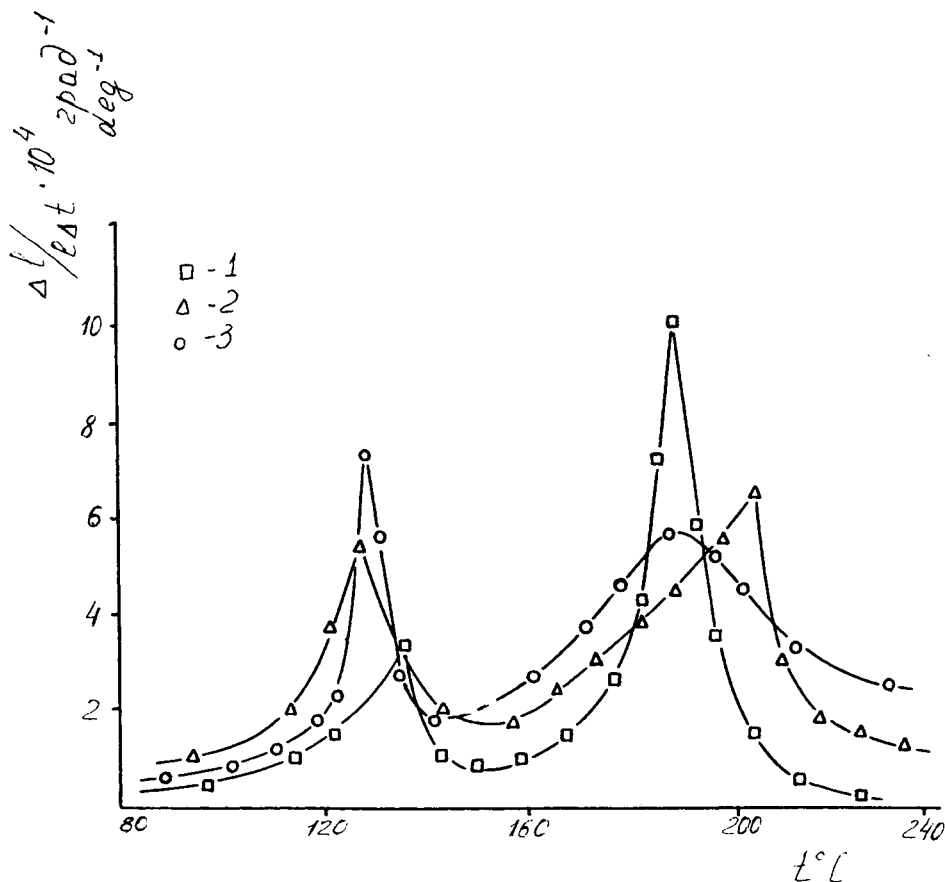


Fig. 2. Temperature effect on the linear expansion indices of pressed norplastic tablets on expanded perlite. PCn content (% by mass) 1 = 8.7; 2 = 15.8; 3 = 19.2.

point of PCn, and the second in the range 180–190°C. At smaller PCn contents the first peak decreases and the second increases. It has been established by microcalorimetric measurements that the first peak corresponds to an endo effect, the second to an exo effect. The nature of the second extremum on the $\alpha(t)$ curves is at present uncertain, however, it can be assumed to be related with the fine structure and morphology of the "coat" polymer.

Experimental investigation of norplastic particles employed as fillers for polyethylenes in HFPC, first of all, the determination of the durability of the "grafted" layer during processing is difficult since the structural characteristics of the "grafted" layer are identical with those of the next layers of the "coat" and the matrix polymer. Considering the present state of the experimental art, estimation of the size of filler particles from the characteristic lines of the respective element by means of the electron-probe microanalysis technique in combination with the morphological determination of the boundary layer size proves to be sufficiently effective. From Figure 3, the size of kaolin particles are much smaller than that of its coat. Com-

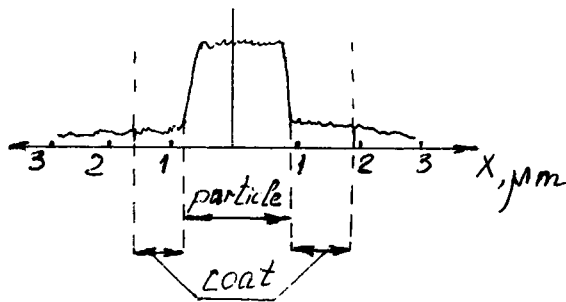
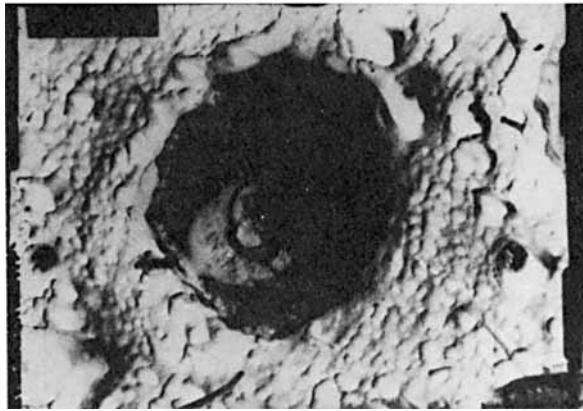
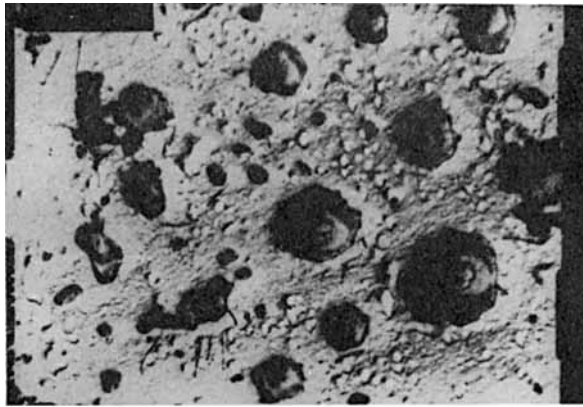


Fig. 3. Structure of polyethylene filled with norplastic on kaolin (a). Norplastic particle (b). Distribution of X-radiation intensity $K\alpha Si$ along the scanning direction indicated by arrow (c).

parison of the layer thickness determined by the above technique with the dimensions of the film initially synthesized on the kaolin particle surface shows the layer in the matrix to be somewhat thicker. This is probably due to the effect of the "coat" on the ambient of low-density polyethylene (LDPE) matrix.

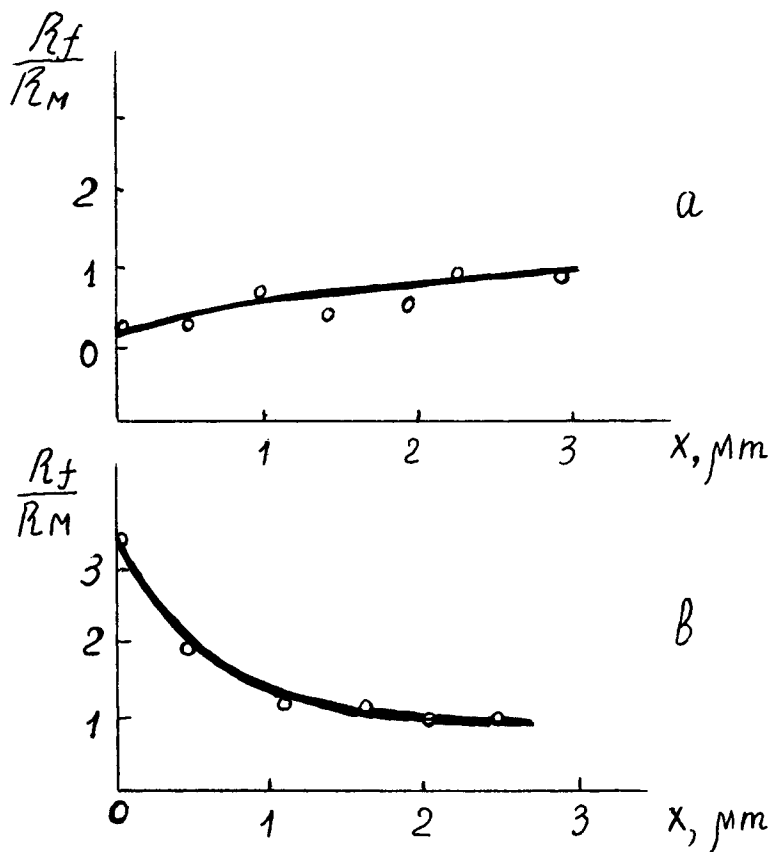


Fig. 4. Change in polyethylene crystallite size in compositions filled with kaolin (a) and norplastics on kaolin (b) with increasing distance from the filler particle surface (in case (b), from the grafted norplastic layer).

An attempt has been made to estimate the dimensions of transition layers near the filler and norplastic particles in individual systems. The approach was morphological, involving (as is shown in Figure 4) the determination of average dimensions of crystallites in matrix (R_m) and by radius (x) at a different distance from the particles of the dispersed phase (R_p). The results of microphoto processing are given in Figure 4. It can be seen that the disturbance range is comparable with the effective particle radius in compositions with pure fillers, and with the dimensions of the grafted layer in compositions with norplastics. Note that similar effects can be achieved by treating the surfaces of common fillers with finishing agents.

DEFORMABILITY AND STRENGTH OF HIGH-FILLED POLYMER COMPOSITES

The preparation of HFPC from low-molecular thermoplastics with norplastics (with 80–90% by mass of MCn) as fillers may prove in certain cases

to be more attractive technologically than the direct synthesis of polymerization-filled material with a given amount of filler. The main problem—whether such compositions have any advantage over traditional mechanical mixtures, primarily as regards mechanical characteristics—has been solved positively in our studies.²⁻⁷ From the data obtained recently, as well as from previous experience, the following generalizations can be made:

1. Whatever the nature of MCn and matrix polyethylene in systems with norplastics, the dependence of strength (ultimate tensile stress) on the norplastic content has a peak (Fig. 5).

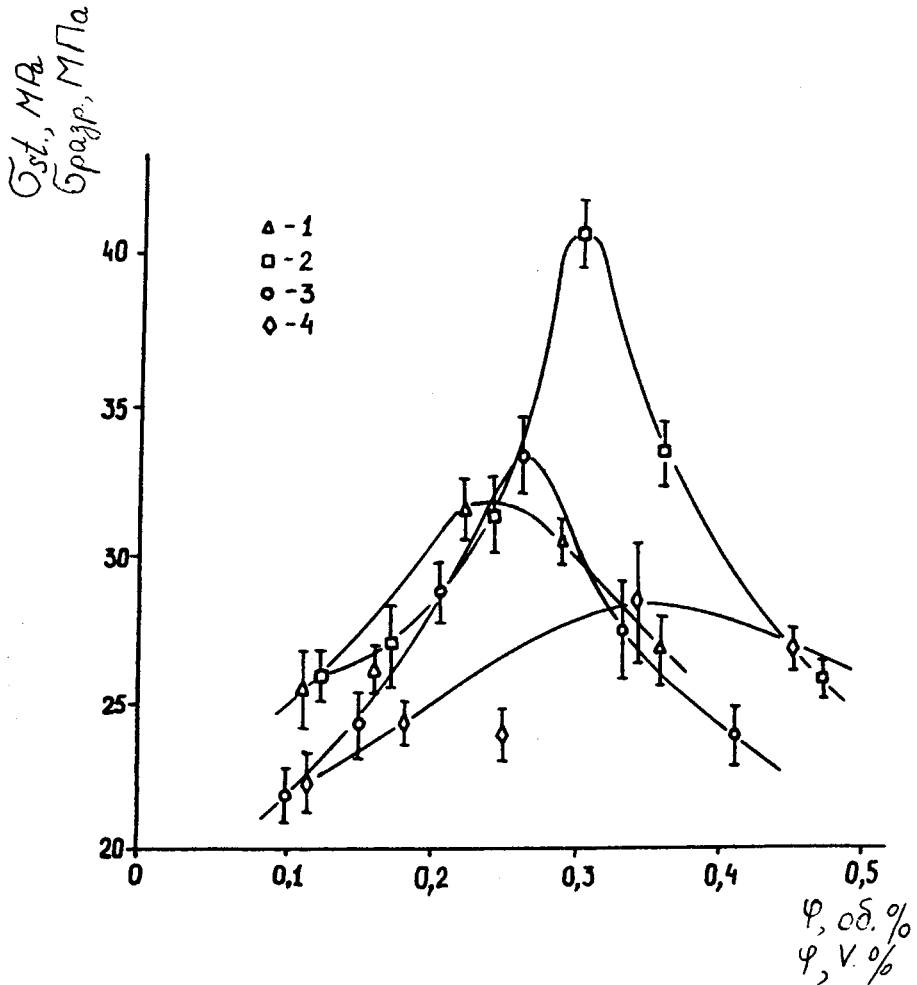


Fig. 5. Effect of the volume fraction of HDPE (4) and the mineral filler added with the norplastics (1-3) on the strength of LDPE-based compositions. The fillers are: 1 = norplastics on expanded perlite; 2 = norplastics on tuffa, 3 = norplastics on calcium carbonate. PCn content (% by mass): 1 = 10.6; 2 = 12.5; 3 = 17.

2. The strength of samples with norplastics is equal or higher than that of the matrix polyethylene. This holds practically in the entire investigated range of mineral filler concentrations (30–70% by mass).

3. Strength and specific impact strength decrease in the series of Groups II-III-IV; this has been shown with tuffa compositions (Fig. 6).

4. The elongation at rupture for high-filled specimens of Group II is similar to that of the matrix polymer at flow limit point, being usually somewhat lower for Groups III and IV.

5. With the mineral filler content in compositions constant the strength characteristics increase symbatically with the "coat" polymer content in norplastics.

6. In compositions with norplastics on expanded fillers (for examples, expanded perlite) the strength characteristics increase with the initial size of the mineral particles for a constant norplastic and PCn content; an opposite tendency has been observed for the other mineral fillers studied.

The mechanism of the reinforcing effect of fillers in materials of Group II in comparison with Groups III and IV has not been fully elucidated. At present, only a few possible reasons for such a behavior of compositions with norplastics can be assumed, viz. a more uniform distribution of the mineral filler particles in the polymer; a closer adhesion between the "coat" and the mineral filler and the "coat" and the matrix polyethylene than between the matrix and the mineral filler in composition of Groups III and IV; PCn acts as a damper, preventing crack formation and propagation in samples.

Since the investigation of physical and mechanical properties of compositions has been performed with molded samples, important factors such as different degrees of macromolecular orientation, the possibility of special orientations of the filler in various types of compositions should also be taken into account.

RHEOLOGICAL PROPERTIES OF HFPC

Specimen viscosities were determined from the relationships between the effective viscosity of melts (η) and the shear stress (τ), η being found, as usual, from the relationship $\eta = \tau/\dot{\gamma}$ ($\dot{\gamma}$ is the mean shear rate across the channel, i.e., the normalized flow rate defined by $\dot{\gamma} = 4Q/\pi R^3$, where Q is the flow through a round channel with radius R). The value of τ has been determined as the apparent shear stress on the channel wall (without correction for pressure loss in the inlet section), i.e., $\tau = \Delta PR/2L$ (ΔP is the pressure drop in a capillary of length L).

With the mineral filler content being constant, the viscosity of polyethylene systems with norplastic fillers has been found to increase with increasing PCn content. At the same time, the relative viscosity of compositions ($\eta_{\text{rel}} = \eta_{\text{comp}}/\eta_{\text{mat}}$) under a constant shear stress τ (or shear rate $\dot{\gamma}$) has been found, in studies with expanded perlite,^{4,5} to be a unique function of the volume content of norplastics. Subsequent investigations showed that this is true for all the norplastics studied. From this follows an important property of norplastics of the examined type (as fillers of thermoplastics):

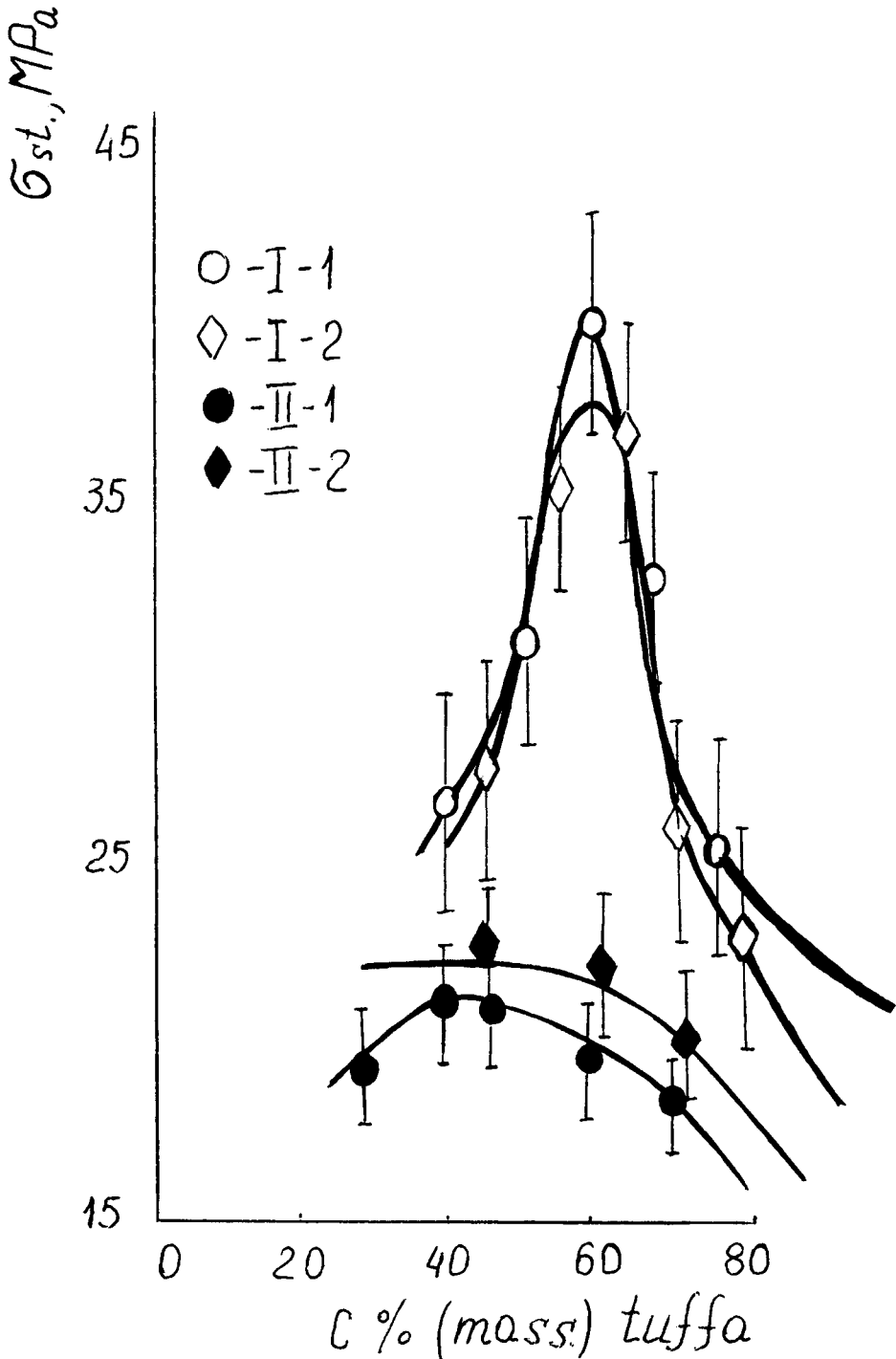


Fig. 6. Relationship between tuffa content and the ultimate tensile stress of compositions on the basis of LDPE. I = compositions with norplastics; II = model systems. Mean size of initial tuffa particles (μm): I-1 and II-1 = 12.5; I-2 and II-2 = 80. PCn content (% by mass) I-1 = 12.5; I-2 = 17.2.

the effect of norplastics on matrix polymer viscosity is practically independent from the nature and grain size of the MCn, but only depends on the fineness of the norplastic particles. The effect of norplastics on the matrix polymer viscosity is identical with that of superhigh-molecular polyethylene particles when other conditions are the same.

Channel blocking has often occurred when the high-filled polymer compositions with uncoated mineral particles were pressed through test channels due to filler clogs formed in the capillary inlet, which sometimes stops the flow altogether.^{3,4} Such a phenomenon has not been noted with compositions containing norplastics, which is another important characteristic of norplastics as fillers.

Filling of linear polymers has been found to cause flow "stalling"^{3,4} even where it has not been observed in the matrix polymer. At higher filler contents in compositions, smaller capillary lengths and volumes of the material of the pressure-head versus flow-rate curves have been observed to change from those with a characteristic hysteresis loop to curves with a break (Fig. 7).

The effective shear stress initiating the flow stall decreases with increasing filler content; however, the effect of the filler content is insignificant and the value of τ_{cr} can be taken as 2.5×10^5 Pa for technical calculations.

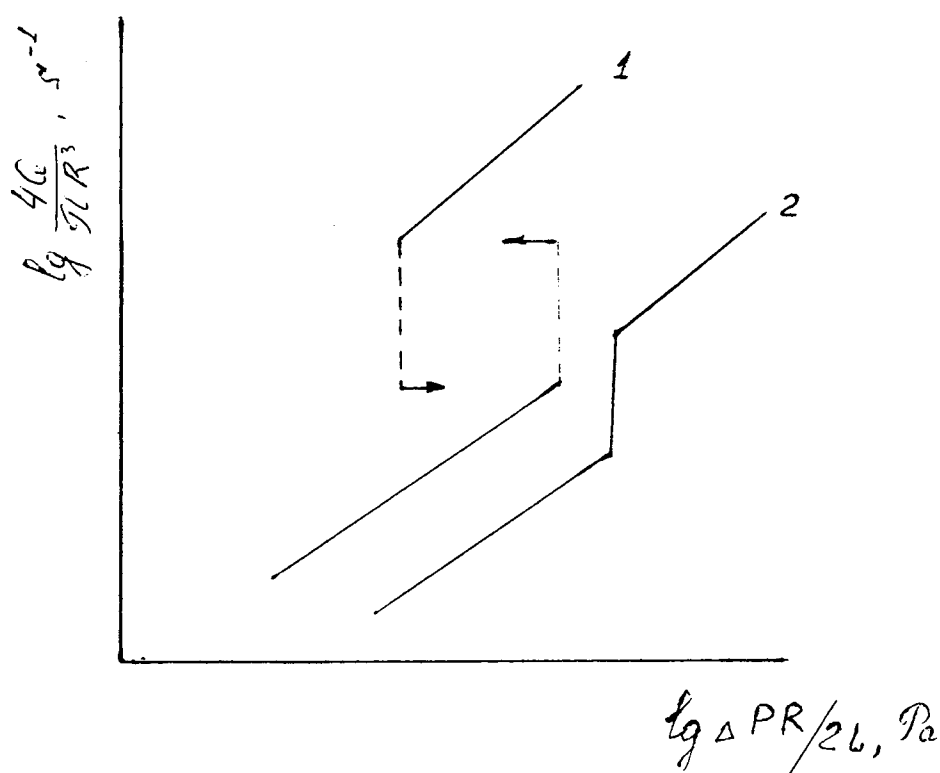


Fig. 7. Scheme of flow-rate characteristics of composite material, illustrating the change from flow-rate curves with a hysteresis loop (1) to those with a break (2).

Finally, for all high-filled polymers, irrespective of the nature of the matrix and filler, a strong increase of pressure losses, as determined by Bagly's method at the inlet has been observed under deformations in a certain range of temperatures and rates. It is typical of norplastics that the increase in pressure losses at the inlet begins under lower ejection rates, while the filler content remains the same [Fig. 8(a)]. In this case the experiments were performed with LDPE filled with 30 v% of perlite, norplastics on perlite (PCn = 19.2% by mass) and superhigh molecular liner polyethylene. It is characteristic that a sharp change in pressure losses for the latter two systems occurs under shear stresses sufficient to cause flow stall of the liner polymer [Fig. 8(b)].

The investigations have shown that the use of norplastics in compositions with a given set of properties appears to be promising not only in that it

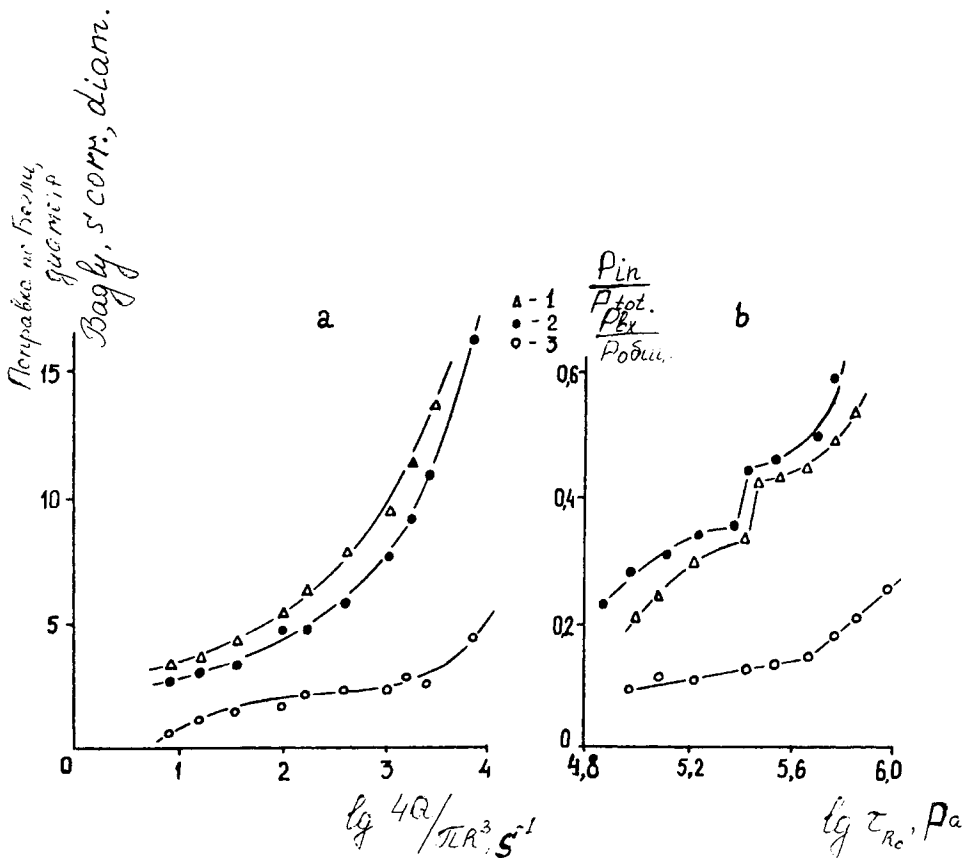


Fig. 8. Dependence of the Bagly's correction on the normalized flow rate by volume (a); dependence of pressure loss at inlet (in relation to the total pressure drop) on the value of the corrected shear stress (b) in compositions on the basis of LDPE: 1 = with norplastics on expanded perlite, PCn content by mass = 19.2%; 2 = with HDPE; 3 = with expanded perlite. Filler content in all the compositions was 30% by volume (for norplastics the filler content was determined as the sum of PCn and MCn).

improves the strength of materials, but also reduces the wear of the processing equipment.

Further studies should involve both investigations of structure-morphological features of norplastic-based composite materials and determination of their long-term strength characteristics.

CONCLUSIONS

From the conducted studies one can make the following main conclusions:

1. Whatever the nature of the mineral component of norplastics (MCn) and matrix polyethylene in systems with norplastics, the dependence of strength on the norplastic content has a peak.

2. With the mineral filler content in compositions' constant, the strength characteristics and the viscosity of systems increase with the polymer component (coat) in norplastics.

3. The effect of norplastics on matrix polymer viscosity is practically independent from the nature and grain size of MCn, but only depends on the fineness of the norplastic particles.

4. From the point of view of physicomechanical and rheological properties compositions with norplastics are more prospective compared with those containing mineral-dispersed fillers.

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