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Physical and Physicochemical Effects on the Rheological Properties of Polymers during Processing

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New principles and processes for the treatment of polymers and polymer-based composites are discussed. The controlled effects of physical and mechanical fields on the rheological properties of polymers are analysed as a promising method of developing new component forming techniques. The following topics are discussed: solid-phase extrusion and hydro-extrusion, the cyclic deformation of melts in shear, the interaction of transverse and longitudinal ultrasonic vibrations, and the preparation of ultra-strong films and fibres.
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I. INTRODUCTION

Developments in the chemical technology of plastics during the past 25 years have included some important advances in the application of physicochemical principles in the synthesis of polymers. For example, the method of synthesis of isotactic polypropylene (PP) has suggested possible ways of obtaining other stereoregular polymers; ultra-high molecular weight polymers with a molecular mass (MM) greater than 10^6 have been produced; the polyamide industry can now offer polydodecaneamide (PA-12); new chlorinated thermoplastics have been developed. Lastly, in the Soviet Union the scientific basis of a new production technology for composite materials has been developed: it consists in chemical filling by polymerisation, giving highly filled polymeric composite materials (HPCM) by direct synthesis. These HPCM are called Norplasts (see Refs.1–3 and the review by D'yachkovskii and Novokshonova on p. of this issue).

The conversion of polymers into articles has been carried out by traditional methods (mainly extrusion, injection moulding and pressing). Developments in manufacturing technology have been in scale rather than in kind: larger-diameter extruders have been produced, and the maximum injection volume and speed of rotation of the feed screw in automated thermoplastic production units have been increased. Equipment now available can produce sheet material in widths of 24 m or more, it can mould articles weighing 10 or even 20 kg, it can draw oriented films 2–5 μm thick now and < 1 μm when current developments have been completed, and it can extrude sheets and slabs more than 20 mm thick. However, these achievements have brought the traditional methods close to their ultimate capabilities, and it is evident that a further increase in the size (and hence in power and raw material consumption) of conventional polymer plant cannot be cost-effective.

Further progress in polymer production is likely to result from intensive rather than extensive developments, relying on new methods of forming the wanted articles with much better productivity and product quality and a saving in raw materials and power consumption. The successful realisation of these aims requires the application of the latest advances in the physical chemistry and mechanics of polymers, in the rheology of continuous media, gas-containing media, and dispersed system, and in mathematical modelling and process optimisation methods. We believe that only this approach can offer the substantial improvements in plastics processing techniques which have for many years been the aim of the large teams of specialists working on these important and complex problems in scientific and industrial laboratories.

This paper reviews the scientific basis of some of the new methods of polymer treatment developed under the general direction of N.S.Enikolopov and in many cases from his personal work and ideas.

II. CONTROLLED INTERACTION OF PHYSICAL (MECHANICAL) FIELDS WITH POLYMERS AS A POSSIBLE WAY OF DEVELOPING NEW PROCESSING METHODS

The processing of polymers usually consists in converting the material into a state capable of viscous flow, giving it the required shape, and fixing this shape by cooling (or hardening) of the melt. The production processes include many physical and chemical transformations of the material, such as degradation and cross-linking of polymers, melting, crystallisation, visco-elastic flow, etc. The analysis and control of the process are further complicated by the simultaneous occurrence of most of these changes, with "overlapping" and mutual interaction, so that the individual effects are very difficult to separate and to study.

The properties of polymeric materials and of the articles prepared from them by traditional methods are controlled by two basic and well understood methods: the addition of a plasticiser, and varying the temperature and formation rate regime. Each of these methods has a number of weaknesses. For example, the control of the rheological and technological properties of the basic material by introducing a plasticiser is limited to a relatively small range of polymers by the loss of strength and increase in cost of the finished article: no satisfactory plasticiser has yet been found for the most important of all thermoplastics (polyolefins). Raising the temperature and formation rate can be considered only if the material is stable towards thermal and mechanical degradation, and the danger of loss of quality of the finished article is ever present. The development of new polymers and the ever-growing range of HPCM have created additional problems, arising from the poor thermal stability and very high viscosity of some of the melts, which limit and often preclude the use of standard methods of component production.

Recent work has shown that an effective method of controlling the properties of the polymer during the production process and of optimising the yield of high-quality articles can be based on the controlled action of physical (mechanical) fields on the material, leading to changes in the parameters of the micro- and macro-stresses in the state of the system[4-8]. By controlling the properties of polymers and of composite materials with an appropriate mechanical stress field at the formation stage we can organise the manufacturing processes in an entirely new way and produce articles with a set of properties not accessible by the conventional technology. There are many new methods of forming, but all are based on the same physical principle: the application of controlled mechanical actions on polymers during the formation process. Under these conditions an additional shear stress contributes to the basic flow of the polymer, and the material develops a complicated stress pattern. This deformation scheme can be applied to both solid and liquid substances.

1. Solid-phase Extrusion and Hydro-extrusion

The extrusion of polymers in the solid state by the simultaneous application of high pressure and shear stresses is being intensively studied[9-11] as a method of producing highly oriented materials. Its advantages over alternative methods of producing such materials include the production of articles with a cross-section of unusual shape and a high rigidity and strength from standard industrial polymers. Thus Enikolopov and co-workers[12] have prepared fibres having a strength and stiffness close to the theoretical maximum by extrusion and drawing of PE and PP polymer mixtures. However, because of the wide molecular mass distribution (MMD) of the initial polymers of technical grade a wide range of strength and stiffness parameters was obtained. A more selective specification of initial polymers, with optimum values of the MM, yielded fibres with mechanical properties almost indistinguishable from the theoretical values.

Solid-phase extrusion followed by drawing has been used[13] with a mixture of two high-density polyethylenes: ultra-high molecular weight (MM = 2×10^6) and ordinary (MM = 6.7×10^4). Fibres with a tensile elastic modulus of $E = 222$ GPa were obtained, equivalent to ~ 92% of the E value for the crystalline polyethylene lattice[14].

The structure and properties of the resulting articles are strongly influenced by the basic parameters of the extrusion process (pressure, temperature, etc.). Therefore one of the most essential contributions to this new method is a detailed study and description of the dynamics of the process in the two basic operating regimes: at constant feed rate and at constant pressure. In the first case the extrusion of solid polymers can be likened to the bulk pressing of metals. However, attempts to apply the theory of metal pressing[15,16] to polymer extrusion proved fruitless, because the model does not allow for the special features of plastic flow and orientation strengthening in polymeric materials.

We have recently proposed[9] a model of the extrusion of amorphous–crystalline polymers which assumes a power law for the increase in strength of the material. The following relationship between the extrusion pressure (p_{ext}) and the maximum elongation of the polymer (λ_{max}) was obtained:

$$p_{ext} = \sigma_0 \frac{1 + k \cot \psi}{m + k \cot \psi} (\lambda_{max}^{m+k \cot \psi} - 1) \qquad (1)$$

where σ_0 is the fluidity limit of the polymer before hardening, k is the coefficient of friction at the metal–polymer interface, 2ψ is the feed angle, i.e. the angle at the apex of the conical draw plate, and m is the hardening coefficient of the polymer.

Eqn.(1) satisfactorily describes the experimental results. We note that the extrusion pressure is strongly dependent on the friction at the metal–polymer boundary. Thus very low pressures are needed in the extrusion of Teflon (a polymer with a very small value of k).

Several ways of lowering the boundary friction (and hence the energy consumption) in solid-phase extrusion can be suggested. Firstly, the inner surface of the forming device can be coated with a layer of fluorinated polymer[17]. Secondly, the hydro-extrusion principle is applicable in principle to solid-phase extrusion. The provision of an intermediate hydro-layer lowers the friction between the forming channel and the polymer being processed. However, the practical use of hydro-extrusion is complicated by the tendency of the liquid (especially at high pressures) to diffuse in the surface layer of the polymer where it can cause undesirable changes in properties[11]. Two other approaches to this problem have been suggested in recent years: the application of high-frequency vibrations to the forming device and the provision of a stratified (two-layer) flow of polymer. We know[18,19] that the coefficient of friction can be markedly decreased by applying vibrations of high enough frequency to one of the contacting surfaces of a friction couple. The application of low-amplitude shear vibrations at ultrasonic frequencies (~ 2×10^4 Hz) to the forming device lowers the dry friction almost to zero[19]. This effect offers a substantial improvement in the quality and speed of solid-phase extrusion, giving high-grade products.

The stratified flow of polymers is the basis of the co-extrusion of two-layer and multi-layer sheets, films, filaments, and fibres. The theoretical foundations of co-extrusion were developed in Refs.8 and 20–23. A new way of exploiting two-layer flow[8,24] has been used successfully to accelerate the formation of highly viscous polymer systems (for example, PE with a MM $\geq 10^6$, and HPCM such as Norplasts). Two-layer or pseudo-two-layer flow is created in the forming device, with the layer of low-viscosity component (~ 200–300 μm thick) in contact with the channel wall while the high-viscosity core constitutes the main material. This flow geometry can be achieved by different methods, for example by injecting a low-molecular-weight polymer into the "dead" zones of the input side of the forming device (the "dead zone supply" method), or by adding a low-molecular-weight component to the polymer composition and pressing the low-viscosity component towards the wall of the forming channel (see Fig.1). As a result, the hydrodynamic resistance of the forming device (apparent, or effective viscosity of the system) is greatly reduced, but the properties of the resulting articles are determined by the main material. The formation process in this case can be treated as a special type of hydro-extrusion in which the liquid is replaced by a melt of low-molecular-weight polymer, by a liquid oligomer, or other low-viscosity substances.

An example of pseudo-two-layer flow is given by the production technology of HPCM based on Norplasts. As often reported[25-27], the low-molecular polyethylene into which the Norplast is injected as a filler concentrate is effectively pressed towards the wall of the forming channel, so that the finished articles consist of a "core" of Norplast and an outer "skin" with a low concentration of filler.

The two-layer and pseudo-two-layer flow method could also usefully be applied to solid-phase extrusion to increase the speed of the process and lower its energy consumption. However, experimental tests are needed to identify possible side effects and to characterise the rheologically important changes in flow patterns.

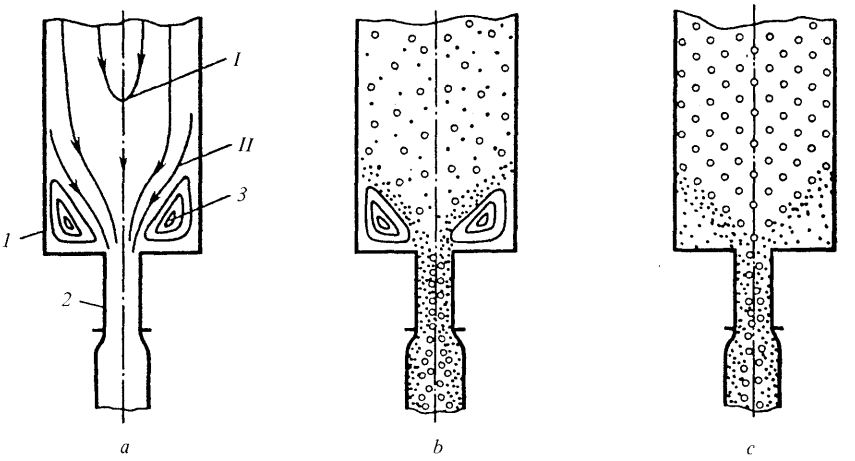


Figure 1. Generation of a two-layer flow in the forming of thermoplastics: (*a*) "dead" zones in the corners of the viscometer cup, (*b*) creation of two-layer flow by introducing a low-viscosity component into the "dead" zone, (*c*) formation of pseudo-two-layer flow by expressing the low-viscosity component from the mixture; *1*) reservoir (or "bomb"), *2*) capillary, *3*) "dead" zone; *I*) line of maximum tensile stress, *II*) line of maximum shear stress[8].

Further developments in solid-phase extrusion should also be aimed at increasing the formation pressure and lowering the formation temperature. These changes should yield materials with improved mechanical properties.

2. Cyclic Shear Deformation of Polymer Melts

Recent work has shown[4-7,28,29] that the complex stress patterns produced in melts by the imposition of additional shear on the basic flow can lower the viscosity of polymeric and dispersed systems. Complex shear can be produced in melts by rotation or by vibration (longitudinal or transverse with respect to the extrusion axis) of the elements of the forming device.

The simplest example of imposed shear is the screw (helical) flow created by forcing the substance through an annular orifice under a constant pressure drop while rotating the cylinders at constant speed (or one of the cylinders, for example the nozzle or the shaft of the extrusion head). An analysis[5,8,30] of helical flow based on the theory of viscous flow[31] has yielded the basic equations for the rheological characteristics of abnormally viscous liquids in terms of the flow conditions and of the geometry of the flow device. The influence of the elasticity of the polymer melts on the extrusion parameters under cyclic shear deformation conditions has been calculated[8,25,30]. The construction and application of extrusion systems with an imposed shear generated by reciprocating rotations of the elements of the forming head (i.e. by low-frequency vibrations of relatively large amplitude) have been discussed in detail[30,31].

Whatever the chosen method of applying the additional shear (rotation of the shaft, reciprocating large-amplitude rotational vibrations, with the moving element located in the pre-inlet chamber or in the forming head itself, and with the vibrations normal to the main flow or coaxial with it) very similar rheological and technological effects are obtained: for a constant drop in pressure in the channels and a constant temperature the viscosity of the polymer and its post-extrusion swelling decrease, and the consumption of liquid and the critical parameters for the onset of unstable flow increase very markedly. For example, in the extrusion of PP reciprocating rotational vibrations of the forming device with an angular amplitude of 22.3° and a frequency of 25 Hz increase the throughput of the extrusion head by a factor of 1.3–1.4,[29] increase the critical flow parameters by 2–5, and lower the swelling coefficient by 1.3–1.5.

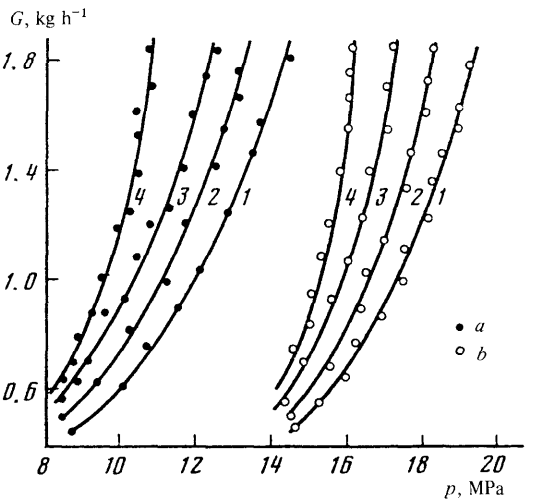


Figure 2. Operating characteristics of the apparatus (plots of the throughput G against the pressure drop in the extrusion head p) for the processing of PP filled with 10 wt.% of chalk (*a*) and 20 wt.% of asbestos (*b*) at 210 °C and different shaft vibration amplitudes: *1*) 0°, *2*) 4.8°, *3*) 11.5°, and *4*) 22.3°[32].

The use of imposed shear is even more effective in high-viscosity systems (for example, filled thermoplastics). Thus in filled polyolefins (30–40 wt.% chalk, carbon black, or asbestos) a 40–80% increase in productivity can be achieved, or if the throughput is kept constant the pressure in the extrusion head can be decreased by at least 20–30% (see Fig.2). Longitudinal vibrations in these melts enhance the orientation effects and produce a slight hardening of the article in the extrusion direction. Reciprocating vibrations of the shaft give a product with isotropic properties, but because of the better homogenisation of the melt the mechanical properties are slightly better (in both directions) than those of the conventionally extruded articles.

We should stress that in spite of the expenditure of power in creating the additional shear by rotation or vibration of the forming elements the overall power consumption of the polymer processing plant is lower (at the highest forming rates) than the power needed to rotate the worm screw in the extrusion through a head (draw plate) with a fixed shaft. Thus forming in the presence of imposed shear may even cause a saving in specific energy consumption[8,29,30]. This effect is most marked in highly filled thermoplastics (for example, asbestos-filled PP[29,32]).

3. Effect of Ultrasonic Shear Vibrations on Polymer Melts

In polymer melts strong vibrational effects can be induced relatively easily by applying high-frequency (ultrasonic, US) vibrations from rod or disk emitters mounted in place of the normal elements of the extrusion head. High-frequency techniques are recommended because the rheological properties of visco-elastic materials are affected by vibrations only above a critical amplitude of the rate of deformation $\varepsilon'_0 = \varepsilon_0\omega$ (where ε_0 is the amplitude of the deformation and ω is the angular frequency), so that at high frequencies we can expect a substantial decrease in effective viscosity[33]. Therefore by using high frequencies we can obtain the desired effect from small-amplitude periodic deformations.

The effect of shear US vibrations has been discussed repeatedly[34–36]. It was shown[37] that the decrease in the largest Newtonian viscosity coefficient of thermoplastic melts produced by US vibrations can be described by the formulae

$$\eta_0 = \eta_{0,0}\exp(-\varepsilon_0/k_1)$$

$$\eta_0 = \eta_{0,0}\exp(-\varepsilon_0'/k_2)$$

Here $\eta_{0,0}$ and η_0 are the largest values of the Newtonian viscosity coefficients in the absence of vibrations (i.e. for $\varepsilon_0 = 0$ and $\varepsilon'_0 = 0$) and in the presence of ultrasound respectively (at a frequency of ~ 20 kHz); k_1 and k_2 are effectiveness coefficients whose value is approximately $k_1 = 1.1 \times 10^{-2}$ and $k_2 = 1100\ s^{-1}$ for a large group of industrial thermoplastics (PVC, PS, PE, and PP).

Using the criterion for the onset of elastic turbulence $(\gamma'_{cr} \cdot \theta_r) = \text{const}$ (where γ'_{cr} is the critical shear rate and θ_r is the characteristic relaxation time) we can reduce the role of the vibrations to a lowering of the parameter η_0, and hence of θ_r, which allows the parameter γ'_{cr} to rise. Data obtained for polyolefins[8,32,38] confirm that $1/\eta_0$ and γ'_{cr} vary with ε'_0 in the same sense (Fig.3): this conclusion is consistent with the explanation of the effect of vibrations on the rheological properties of melts in terms of a controlled change in the relaxation characteristics, and it also confirms the validity of the assumption that unstable flow is due to a relaxation transition in the polymer.

The use of shear US vibrations in polymer processing technology has been described in detail[8,37,38], and it was pointed out that the new processing method is especially useful in the production of thin sleeve films (up to 10 μm thick) by stabilising the process and giving a product of uniform thickness.

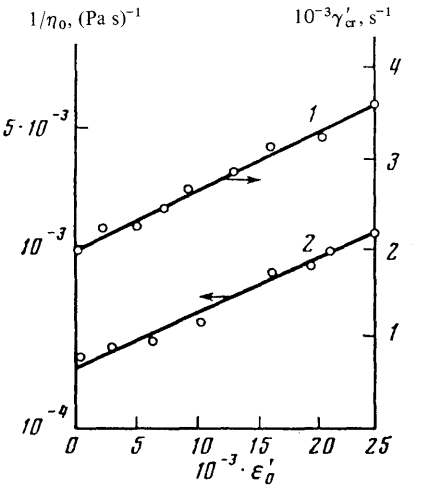


Figure 3. Dependence of the lowest fluidity $1/\eta_0$ and of the critical shear rate γ'_{cr} on the rate of deformation ε'_0 for polyethylene[37].

4. Acoustic Cavitation Phenomena in Fluid Polymers and Compositions Based on Them

The acoustic cavitation (AC) phenomenon is well known in low-molecular liquids, especially in water. However, it has been studied also in solutions of polymers[39–41], and mechanical degradation of the polymer molecules and other secondary effects have been reported for cavitation in low-viscosity solutions. As the viscosity of the liquid increases, we observe a decrease in the mean size and in the rate of growth and collapse of the cavitation bubbles, and the strong secondary effects of cavitation disappear. It was shown both theoretically and experimentally that when the viscosity of the liquid is higher than 1.5–2.0 Pa s the secondary effects of the acoustic cavitation are no longer detectable, i.e. the cavitation is fully suppressed[42,43]. For this reason the acoustic cavitation of polymer melts was not discussed in published papers until recently.

Work carried out between 1978 and 1983 has shown[44–48] that acoustic cavitation can be produced and studied in detail in melts of both model and industrial polymers. It was pointed out that in order to induce cavitation in a melt of a high-molecular polymer the sound pressure level should exceed the bulk strength of the material. Since the strength of a polymer is a minimum in a triaxially stressed state it was reasonable to expect that acoustic cavitation can be excited only by volume US vibrations (as opposed to the shear vibrations considered in the previous Section). For example, in a polymer such as polybutadiene (with a narrow molecular weight distribution and a viscosity coefficient of 10^6 Pa s) the bulk tensile strength is less than 1 MPa,[49] i.e. of the same order as the static bulk strength of ordinary low-viscosity liquids such as water[39], in which AC is relatively easily induced.

By using a special viscometer (with provisions for the application of ultrasound to polymer melts) acoustic cavitation has been detected and its properties have been studied systematically, noting that because of the marked viscoelastic properties of the melts the conditions of formation and the growth and collapse dynamics of the cavitation bubbles are not the same as those in low-molecular low-viscosity liquids.

The AC phenomenon has been observed not only in melts of model polymers (monodispersed polybutadienes) but also in high-pressure and low-pressure PE, PS and PP, and also in HPCM (polyethylene filled with kaolin, chalk, perlite, or glass spheres of average diameter 50 μm[44–48]). Visual observation in ordinary (non-polarised) light and high-speed photography have revealed the formation and growth in an acoustic field of cavitation bubbles which disappear when the source of ultrasound is switched off.

An important experiment was carried out with fluid high-molecular polymers. A small sound pressure detector was embedded in a sample of rubber and connected to an ultrasonic frequency spectrum analyser. It was found that the spectrum of the signal contained, in addition to the fundamental frequency of 17.8 kHz, higher harmonic and subharmonic multiples of this frequency. This phenomenon has been observed many times in ordinary low-viscosity liquids[43], and is typical of AC. It is consistent with the formation in the polymeric liquid of bubbles of resonant size, which suffer strong deformation by the acoustic field and nonlinear changes in the fundamental vibration frequency.

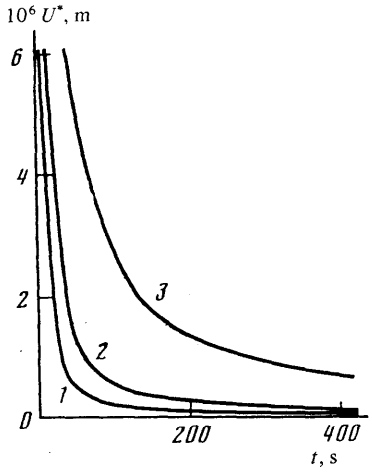


Figure 4. Threshold amplitude of the acoustic vibrations U^* against processing time t of monodispersed polybutadienes of molecular mass MM = 1.6×10^5 (*1*), 3.5×10^5 (*2*), and 5.3×10^5 (*3*)[47].

The following properties and secondary effects of acoustic cavitation in polymer melts have been identified[44–48]. Firstly, the AC is a threshold phenomenon, i.e. each polymer has a characteristic amplitude of acoustic vibrations (U^*) at which cavitation sets in. The parameter U^* depends on time t (see Fig.4), and it is analogous to a long-term strength (durability) function for the polymer[49]. Increasing the MM of the polymer increases its stability towards the formation of AC. The dependence of U^* on t (Fig.4) is described satisfactorily by a power law at low amplitudes of the bulk US vibrations and by an exponential function at relatively large amplitudes:

$$t = A_1 (U^*)^{B_1}$$
$$t = A_2 \exp(B_2 U^*)$$

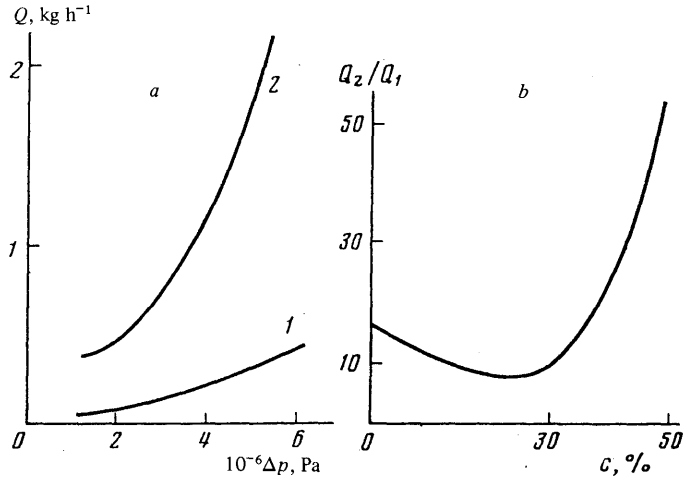


Figure 5. Pressure–flow characteristics of high-density polyethylene (HDPE) melts: (*a*) unfilled HDPE at 264° and acoustic vibration amplitude 0 μm (*1*) and 8 μm (*2*); Q is the flow, Δp is the pressure drop; (*b*) relative flow Q_2/Q_1 (where Q_2 is for the presence and Q_1 for the absence of acoustic vibrations) in HDPE filled with perlite as a function of filler concentration c (temperature 240 °C, amplitude of acoustic vibrations 8 μm)[47].

Secondly, by inducing AC in melts of industrial polymers we can lower the effective viscosity of melts of thermoplastics and HPCM based on them (Fig.5). Depending on the nature of the polymer, on the U^* value, and on other factors, the viscosity can be lowered 5–100-fold, giving a sharp, irreversible increase in the fluidity of the material exposed to the acoustic field. However, this explanation applies only to a part of the increased fluidity (i.e. to the increased throughput). There is a change in the nature (and therefore also in the mechanism) of the flow: the flow collapse phenomenon in the extrusion of the material before exposure to ultrasound is replaced by bubble flow.

Thirdly, in addition to mechanical degradation and changes in the nature of the flow, both of which produce a large decrease in the viscosity of the melt, AC also produces marked changes in the structure of the extruded articles: a decrease in the average characteristic length of the structure elements and a narrower size distribution[48,50], and in the case of filled systems the filler particles become smaller and more uniformly dispersed in the polymer matrix[46,47].

We should stress that the combined effect of these favourable aspects and of the unfavourable mechanical degradation of the polymer matrix caused by the acoustic cavitation is a slight improvement (by 10–20%) in the tensile strength and

in the elongation at break of the extruded articles in comparison to similar articles produced under ordinary conditions[47].

Further studies are needed on the technological aspects of this new phenomenon, which has important consequences in the physics, mechanics, and processing technology of polymers.

5. Production of Ultra-strong, High-modulus, and Ultra-thin Films and Fibres

The preparation of thin and ultra-thin films with the highest possible strength and elasticity from flexible-chain polymers is currently of interest[51]. The main problem is to straighten out the macromolecular chains as far as possible, because this configuration should give an elastic modulus close to the theoretical maximum, though the strength may fall well short of the maximum owing to defects in the structure. Various approaches are possible: multistage film drawing to give an oriented array of chains with the optimum structure, directional crystallisation, setting up a liquid-crystal state in thermoplastics, etc.[51,52].

By developing the concept of orientation by deformation and by applying it in practical systems Enikolopov and coworkers prepared PP films 30–40 μm thick with values of the tensional elastic modulus close to the theoretical maximum[53]: for example, for $\lambda = 28–30$ the mechanical parameters of the films were $\sigma_r = 1.3–1.5$ GPa and $E = 36–43$ GPa.

These results were confirmed by measurements of the velocity of ultrasound (v_{us}) in polypropylene films prepared with different values of λ.[64] Thus, for $\lambda = 33.7$ and a temperature of 93 K, v_{us} was 8700 m s^{-1}, a value not previously achieved in oriented flexible-chain polymers. For comparison we note that the v_{us} value of steel lies between 5 and 6 × 10^3 m s^{-1}, i.e. well below the value for highly oriented polypropylene. The specific elastic modulus E/ρ (where ρ is the density of the polymer) was three times greater for these films than for steel.

These abnormally high mechanical parameters in highly oriented PP can be explained in several ways: the high degree of orientation of the macromolecular chains, the difference in structure between crystalline and amorphous regions (the through chains being more numerous in the latter as well as having a different conformational spectrum), etc.

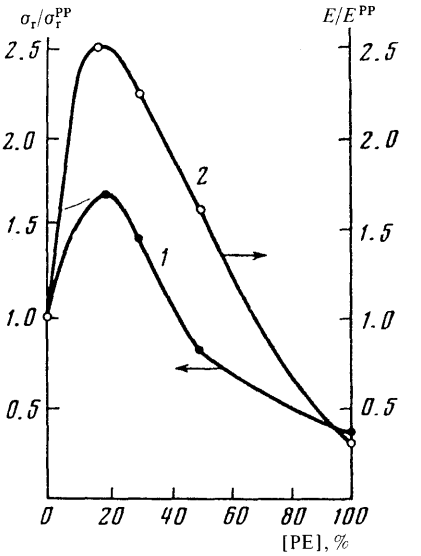


Figure 7. Tensile strength σ_r (*1*) and elastic modulus E (*2*) against composition of PP–HDPE samples for an elongation $\lambda = 15$; temperature of elongation 120–130 °C, σ_r^{PP} and E^{PP} are the tensile strength and the elastic modulus of PP.

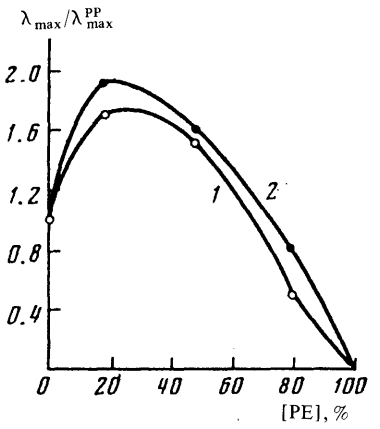


Figure 6. Effect of the composition of PP–HDPE samples on the maximum elongation λ_{max} at different temperatures: *1*) 125, *2*) 145 °C; λ_{max}^{PP} is the maximum elongation of PP.

Polymer–polymer composite materials (PPCM) are another class of potentially useful materials for preparing high-strength, high-modulus thin films. In these films the dependence of the maximum elongation λ_{max} on the composition of the PPCM goes through a maximum (Fig.6). For example, in PP–PE compositions the highest value of λ_{max} is obtained for a PE content of 20–30%. Since the elastic modulus E and to some extent the tensile strength σ_r of the material are monotonic functions of the degree of elongation λ (see, for example, Fig.7) we can expect films with higher values of E and σ_r from PPCM than from single-phase systems.

III. PHYSICOCHEMICAL METHODS OF CONTROLLING THE PREPARATION AND PROPERTIES OF COMPONENTS MADE FROM POLYMERS

Almost any technological process applied to polymer materials is accompanied by a complex set of physical and physicochemical phenomena. This is specially the case when we are concerned not merely with the formation of articles but with developing materials with new and prescribed properties. The approach developed by Enikolopov and his coworkers involves stimulating chemical and physicochemical

changes in the materials by new (non-traditional) methods and studying these changes in polymers and in composite materials under extreme processing conditions.

1. Modification of the Properties of Polymers by High Pressure and Shear Deformation

The processes accompanying plastic flow in polymers under high pressure and shear deformation have been studied extensively in recent years (see the review by Zharov on p.140 of this issue).

One of the most important aspects of this essentially new area in the physical chemistry and mechanics of the solid state is polymer modification. Traditional methods of polymer modification have been reviewed in detail[54,55]. However, the processing of mixtures of polymers and reactive monomers under the combined influence of high pressure and shear deformation offers new possibilities of producing composite materials and articles having specified properties by grafting growing macromolecules onto the polymer matrix. The method can be used, for example, to prepare graft copolymers not available by conventional methods. Thus a conversion of the monomer of ~ 75% has been obtained in studies of the polymerisation kinetics of *N,p*-tolylmaleic imide in a PP matrix, with up to 90% of the resulting polymer grafted to the matrix. As a result of the modification ~ 40% of the composite material was found to be insoluble in boiling tetralin.

It was also shown that forming polymers under these conditions is accompanied by various structural changes (for example, amorphisation and changes in the crystallinity of the lattice[56]), as well as by a large decrease in the molecular weight of the polymer produced by mechano-chemical degradation[57].

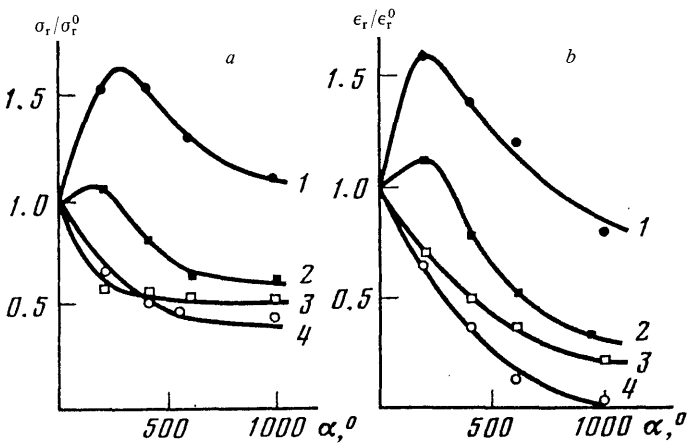


Figure 8. Relative changes in tensile strength (*a*) and in elongation at break (*b*) of samples from PP–SKEP (*1*) and PP–HDPE mixtures (*2*), HDPE (*3*), and PP (*4*), deformed at 10 kbar pressure, as a function of the angle of rotation of the anvil α [58].

The kinetics of these processes are reasonably well described by the relationships usually applied to mechanical degradation processes[41]. We should note, however, that marked differences exist between different polymers: thus in PE mechanical degradation is observed only at pressures above 10 kbar, whereas in PP it sets in at 5 kbar. Lowering the MM of the polymers produces a sharp decrease in fluidity (σ_t), tensile strength (σ_r), and relative elongation at break (ε_r), which converts the fracture from a necking process to a brittle fracture[58].

A very interesting result was obtained in the study of the plastic flow of a mixture of polymers under combined pressure and shear: mixtures of thermodynamically incompatible polymers were found to form a homogeneous system in the amorphous phase under these conditions[59]. As a result the changes in the mechanical properties of the material are not the same as for the homopolymers (Fig.8). We note from curves *1* and *2* of Fig.8 that σ_r and ε_r go through a well defined maximum as a function of the shear deformation in these mixtures for rotation angles of the anvils of 200–300°. The height of the maxima is different in the different polymer systems: for example, in PP–SKEP mixtures the increase in the parameters near the maximum is 60%, but in a PP–PE mixture it is much smaller. We may assume that this marked improvement in the physico-mechanical properties of the mixtures of polymers (as compared with the homo-polymers) is the result of the formation of much smaller and more uniformly distributed heterogeneous phase regions.

The improved understanding of the plastic flow of polymer mixtures under pressure led to the production of high-strength and high-modulus fibres (see above).

To conclude this Section we note that from many points of view (mechanical degradation, decrease in size of the structure elements, amorphisation of the polymers, increased structural uniformity and homogeneity) the effect of combined pressure and shear on polymeric materials is similar to the effect of vibrations, especially the effect of ultrasound in the acoustic cavitation regime. This is consistent with the general principle of using strong physical (mechanical) fields for processing polymers and composite materials.

2. Physico-mechanical and Rheological Properties, and Processing of Polymerisation-filled Plastics (Norplasts)

The principle of polymerisation (or chemical) filling consists in polymerising the appropriate monomer on the surface of a filler (which can be of almost any type: dispersed or filamentary, mineral or organic) after activating its surface with a complex catalyst. This method can be used to produce materials with any desired ratio of polymeric component to filler[1,2].

The wide practical application of these materials (Norplasts) must be preceded by a detailed study of their physico-mechanical, rheological, and technological properties: a series of investigations under the direction of N.S.Enikolopov[25–27,60–63] marks the beginning of this area of research. Because of the multiplicity of the types of material in this new class, of the complexity of their structure, and of their unique properties, extensive and sustained studies are still needed, but some important aspects of the structure and properties of Norplasts have already been established, and the following recommendations for the processing of Norplasts can be formulated.

Whatever the nature of the mineral component, Norplasts are obtained as powders of different particle size. The particles are agglomerates produced by the growing together (or interlinking) of the polymeric coating formed on the

separate particles of the filler. In the Norplasts, therefore, the mineral particles are surrounded by a layer of macromolecules firmly bound to the filler surface by chemical or physical forces. The thickness of this layer is much greater than the thickness of the strengthened surface layers in ordinary filled systems prepared by mechanical mixing of the components followed by granulation on the extruder. The region affected by the presence of the particle of mineral filler is much more extensive in Norplasts than in mixed composites of a similar composition.

At very high filler contents (> 80 wt.%) the Norplasts with a polymeric component of MM $\cong 10^6$ show only elastic deformation. The material develops a tendency to flow only if the amount of "coat" is increased to 40–60% (depending on the MM of the polymer), but a further increase in the amount of polymer (to 80%) does not affect the viscosimetric and extrusion behaviour of Norplasts.

Some interesting effects were observed in studies of the thermal expansion of Norplasts. The temperature dependence of the linear expansion coefficient $\alpha = \Delta l/(l\Delta T)$ (where l is the length of the sample, Δl and ΔT are the increments in length and temperature respectively) includes two maxima: the first at 125–135 °C, corresponding to T_m for the polymeric material, and the second at 180–190 °C. The height of the first peak decreases when the amount of polymer in the Norplast is decreased, and the height of the second peak increases; furthermore, the first peak corresponds to an endo-effect, and the second to an exo-effect. The nature of the second maximum in the $\alpha(T)$ curves is still not fully understood, but we may assume it to be related to the detailed structural features and morphology of the polymeric "coat"[27].

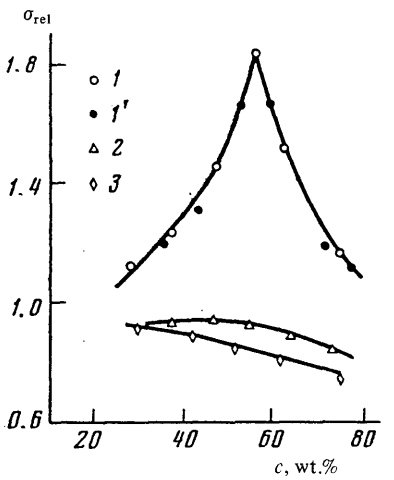


Figure 9. Relative strength ($\sigma_{rel} = \sigma_c/\sigma_m$) of materials as a function of the content of tuff c; compositions with Norplasts containing 12.5 wt.% PE and tuff of average particle size 8 μm (*1*) and 17.2 wt.% PE and tuff of average particle size 80 μm (*1'*); *2*) are model compositions prepared by mixing PE, filler, and ultra-high-molecular-weight PE, 3) are ordinary mechanical mixtures[27].

Structural and morphological studies of the intermediate layers near the filler particles and near the particles of Norplast introduced into a matrix of polyethylene by mechanical mixing have revealed the changes in the number and size of the crystals as a function of distance from the particle surface. In composition containing the pure filler the size of the perturbed region was comparable to the effective radius of the particle, whereas for Norplast it was comparable with the size of the bonded polymer layer. We note that similar effects are observed when the surface of ordinary fillers is treated with dressing compounds. In this sense the Norplast can be described as a filler dressed with a high-molecular-weight polymer of the same nature as the matrix of the main polymer. Since the wear of the equipment is not decreased but is actually made worse by ordinary dressing compounds this method of "dressing" by polymerisation is to be preferred in polymer processing.

The use of Norplasts containing 80–90 wt.% of mineral component as fillers for thermoplastics in the production of HPCM may be technologically preferable to the direct synthesis of the material with the required filler content.

Data obtained so far justify the following conclusions[27]:

a) irrespective of the nature of the mineral filler and of the PE matrix, in Norplast compositions the strength (maximum tensile stress) goes through a maximum as a function of filler content (Fig.9);

b) the strength of the Norplast composites is equal to or greater than the strength of the basic PE over practically the whole range of filler concentration in the material (30–70 wt.%);

c) the relative elongation at break of a HPCM containing Norplasts is close to that of the basic polymer at the fluidity limit, whereas it is lower in ordinary mixed compositions;

d) for a fixed content of the mineral component in composites the strength characteristics increase with the amount of polymeric component (i.e. with the thickness of the "coat") in the Norplasts;

e) the specific shock viscosity of materials filled with Norplasts is higher than for ordinary mixtures of the same composition;

f) the wear of the parts of the processing plant is much lower for HPCM containing Norplasts than for mechanical mixtures with conventional fillers.

A systematic study of the rheological (viscous, and viscoelastic) properties of these new materials[25,27,60–62] has shown that for a fixed shear stress (τ) the relative viscosity of the compositions $\eta_{rel} = \eta_c/\eta_m$ (where η_c and η_m refer to the composition and the matrix polymer respectively) is uniquely determined by the content by volume of Norplast in the mixture, and that for a fixed filler content the viscosity of the system increases with the amount of polymeric component in the Norplast used as a filler concentrate.

We note that undesirable "blocking" effects (with formation of a "stopper" of filler at the mouth of the forming channel) do not take place during the extrusion of Norplasts, though they are common in the pressing of ordinary HPCM mixtures.

The addition of fillers to linear polymers produces flow collapse (Fig.10) even if the effect is absent in the base material[26,27,60]. Increasing the concentration of filler or decreasing the length of the channel and the volume of material in front of the channel tends to convert the pressure–flow curves from characteristic hysteresis loop curves into flow curves with a break. The effective value of the stress τ_{cr} or of the flow Q_{cr} corresponding to the onset of collapse decreases as the concentration of filler in the system increases, but the effect is slight and for practical calculations the parameter τ_{cr} can be assumed to have the constant value 2.5×10^5 Pa.

Lastly, in all HPCM (whatever the nature of the matrix and of the filler) a sharp increase in the pressure drop at the inlet is observed over a well defined range of temperature and strain rate (the Bagley correction). In the case of the Norplasts the increased loss of inlet pressure for a given concentration of mineral filler sets in at lower extrusion rates, as shown in Fig.11. Typically, the sudden step in the loss of inlet pressure occurs at τ values corresponding to the flow collapse in linear PE.

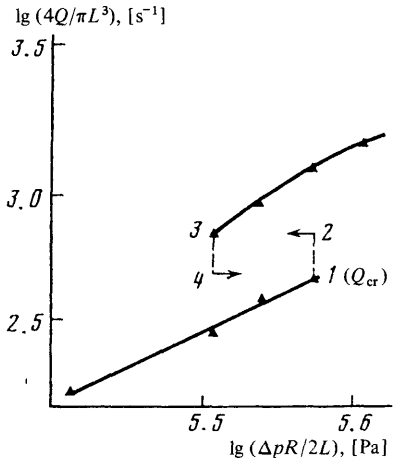


Figure 10. Flow curve for a PE composition containing 30 wt.% of perlite introduced as a Norplast; capillary size 1 mm × 30 mm, temperature 200 K. Point *1* (Q_{cr}) corresponds to the onset of pressure self-oscillations of amplitude equal to the distance between lines *1–2* and *3–4*; the arrows denote the onset of flow collapse (Q is the flow, Δp is the pressure drop, R is the channel radius, and L is the channel length)[27].

The addition of Norplasts to compositions lowers the swelling of the extruded product very considerably, thus assisting the production of shaped articles with improved dimensional tolerances.

Equations and procedures for predicting the viscosity properties of composites filled with Norplasts have been proposed[25–27,61].

Thus recent work has demonstrated the value of Norplasts as components of HPCM offering a prescribed set of properties. This allows us not only to improve the strength characteristics but also to decrease the wear on the extrusion devices (as compared with similar compositions prepared from mechanical mixtures by the traditional technology). The processing of these materials should be carried out in equipment with forced feed (single-screw extruders with a channelled sleeve in the load region, or double-screw extruders) with an attachment for degassing the melt. As in the processing of mixed compositions, the extrusion machinery must have a high-power drive as compared to the extruders for pure polymers.

Further work on these materials should be aimed at the structural and morphological properties of composites containing Norplasts and at determining their long-term stability. We can hope that new materials with a high long-term stability (durability) will emerge from current work on polymerisation filling.

There is little doubt that important advances in the industrial treatment of plastics can be expected from the more general application of mechanical and acoustic fields to polymers in the viscous liquid or the solid state.

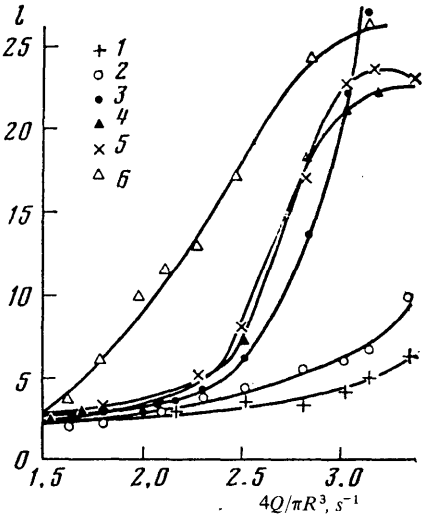


Figure 11. Dependence of the inlet effect (length of the inlet region l) on the normalised volume flow for PE–Norplast (perlite) compositions with different concentrations of filler: *1*) 0, *2*) 10, *3*) 20, *4*) 25, *5*) 30, *6*) 40 wt.%; temperature 180 °C[27].

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