

Some aspects of chemistry and physics of plastic flow

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Abstract - The paper deals with the behaviour and transformations of polymeric materials under the simultaneous action of high pressure (up to tens of kbar) and shear deformation. The physical mechanism of pulverization under the above-mentioned conditions has been established. The point is that, under shear deformation, the elastic energy accumulated in the polymer is spent on the endothermal process of a new surface formation. It has been shown that under these conditions "coefficients" of diffusion or mass transfer increase by several orders of magnitude. Machines have been designed which allow to pulverize different synthetical and raw materials (thermoplastics and reactoplastics, rubbers, vulcanized rubbers, wood, cellulose-containing materials, etc.) with considerably smaller energy consumptions per unit weight of superfine powder compared with traditional methods.

Numerous studies on the behaviour of organic and inorganic substances under the simultaneous action of pressure and shear deformation led to the discovery of a number of so far unknown phenomena which cannot be explained by traditional concepts of the plastic flow process. Moreover, it turned out that substances subjected to the action of high pressures and shear deformation acquired new properties which were not characteristic of the initial substance. After the removal of loading, some of the new properties remained while others immediately disappeared.

New phenomena which follow the deformation and new properties remaining after the deformation are most pronounced in composites and heterogeneous systems. That is why when studying the properties of composite materials under the action of different loadings and predicting their durability, one should also take into account the special features mentioned above.

It was shown that at relatively small pressures (10-15 kbar) at the moment of shear, reactions of polymerization, polyaddition and polycondensation accompanied by the formation of high-molecular-weight compounds took place in solid monomers. Such monomers as methyl methacrylate, styrene, vinyl chloride, etc. which are also readily polymerized under usual conditions (melt, solution and gas), are polymerized and copolymerized under the above conditions. These monomers form either a homopolymer or a statistical copolymer. Monomers such as maleic anhydride, stilbene, etc., which under usual conditions form only copolymers, under high pressure and shear deformation in the solid phase form homopolymers. Moreover, such substances as benzene, naphthalene, anthracene, etc., are polymerized with ring opening. As has been unambiguously shown, the reaction proceeds only at the moment of plastic flow (post-effect is not observed).

Figure 1 shows the devices used in our experiments, which all are able to induce the required pressures and shear deformation. Bridgeman anvils and a mixer of a "Banbery" type operate in a periodic mode, while the device for solid-phase extrusion and extruders operate continuously.

A typical kinetic curve is given in Fig. 2. This is not a common kinetic curve, since it is not time dependent, but a certain characteristic α (a rotation angle on the Bridgeman anvils) (non-linearly) proportional to time plotted as abscissa. The special feature of these processes lies in the fact that the reaction conversion depends only on the value of shear deformation. It is independent of such factors as temperature (activation

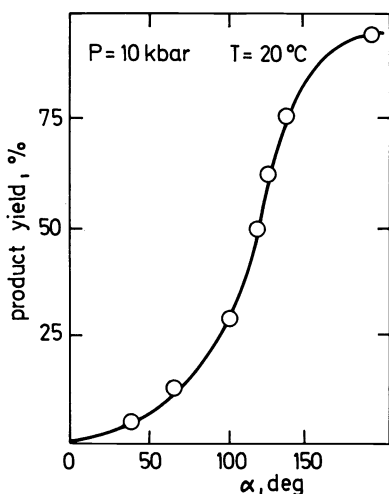
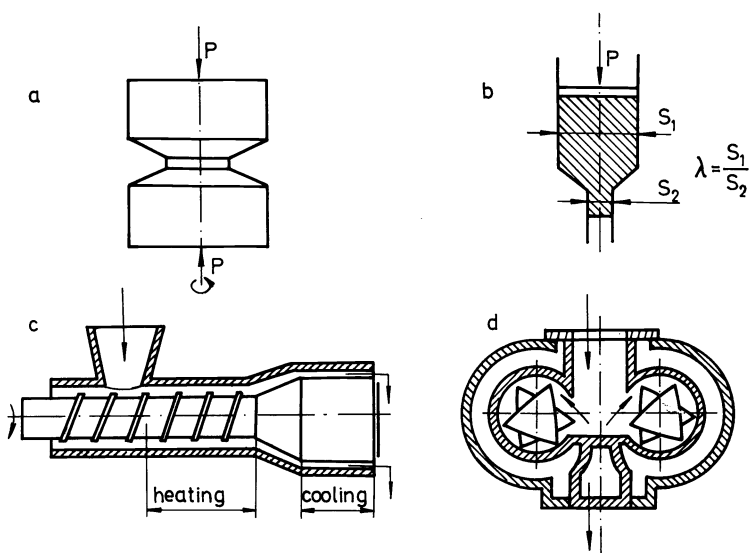


Fig. 2. Polymer yield vs rotation angle α (deg).

energy about 1 to 1.5 kcal/mol), pressure ($\Delta V \sim 3\text{--}5 \text{ cm}^3/\text{mol}$), rate of plastic flow (rate of α changing from 0.5 to 25 deg/s), direction and periodicity in the change of deformation direction, etc.

The rates of chemical reactions under the given conditions are extremely large, not only compared with usual solid-phase reactions, where the limiting stage of the process is the diffusion of reactants, but also with the rates of these reactions in the liquid phase. Qualitative calculations showed that under plastic flow conditions the "rate constant" of active center addition to monomer was by three to eight orders of magnitude larger than that in the liquid phase (like methyl methacrylate, styrene, acrylamide, etc.).

These special features of solid-phase reactions under plastic flow conditions were used for the development of new highly-efficient technologies for industrial large-scale production.

When studying chemical processes under the simultaneous action of high pressure and plastic flow, we found another very important phenomenon. Under solid-phase reaction conditions, chemical reactions do not usually proceed in the directions expected from laws of the classical organic chemistry (liquid phase and solutions). They choose some new directions characteristic only of solid-phase reactions. For instance, benzene, being a classical inert solvent, in the solid phase under high pressure and shear deformation can be polymerized with ring-opening. Acrylamide, fumaric and maleic acids are not polymerized by double bonds, but by the formation of polyacrylamides and polyesters, respectively. There are many examples of such (non-classical) routes of chemical processes in the solid phase. Moreover, it turned out that

classical routes of a chemical process and known rearrangements of chemical compounds were not observed, but the formation of substances of quite different composition took place. This is due to the fact that our knowledge of the classical organic chemistry is based on the experience acquired by the mankind during the last 200-300 years. Since in the solid phase reactions proceeded very slowly due to diffusion hindrance, we did not know the basic laws characteristic of the solid phase. Using the laws of these new solid-phase reactions, we managed to synthesize a number of new organometallic compounds and composites.

The most important is the phenomenon of an unusually high "mobility" of molecules and atoms, observed in the solid phase under high pressure and shear deformation. This fact is confirmed by numerous phenomena found during the study of the behaviour of organic and inorganic substances under high pressure and shear deformation.

1. Mixtures of powders of two solid monomers (methyl methacrylate and styrene) form a statistical copolymer, but not a block copolymer, as could be expected.
2. In the processes of polyaddition and polycondensation, in which in order to form an oligomer with the polymerization degree n an oligomer with the polymerization degree $n-j$ should react with an oligomer with the polymerization degree j (j varies from 1 to $n-1$), we really obtain high-molecular weight compounds of regular composition.
3. Macroscopic particles of metals (tin, iron, etc.) react with porphyrins, graphite and other compounds with double bonds and form the metal complexes in a very short time.
4. Under high pressure and shear deformation conditions, macroscopic powders of two metals form solid solutions (iron-nickel, iron-copper, etc.). All the processes last several seconds or several tens of seconds. The most demonstrative in this respect is the fact of rapid mixing of two polymer macromolecules (hydrogen polyethylene and fully deuterated polyethylene; polyethylene and polypropylene; synthetical polypropylene-ethylene rubber and polypropylene, etc.). These experimental data unambiguously show that under high pressure and shear deformation conditions the processes of "diffusion" or mass transfer proceed very rapidly. Qualitative calculations indicate that the "coefficient" of diffusion in the solid body at plastic flow differs from the usual diffusion "coefficient" by 10 to 15 orders of magnitude.

It is known that two homopolymers are thermodynamically incompatible because of a small value of the free energy of mixing. This is due to the fact that the enthalpy of the interaction of two polymers is rather small and it cannot be compensated by the entropy of mixing, since the number of interacting molecules in a unit volume is small because of rather high molecular weights. This is why mixtures of two polymers are heterogeneous systems.

However, under solid-phase plastic flow conditions mixtures of two polymers are homogenized at large rates, and the systems in the solid phase are not heterogeneous. If we melt such a homogeneous system, each polymer in the melt passes into its phase and the system becomes heterogeneous again. This unambiguously indicates that the homogenization of two polymers in the solid phase is a purely kinetic process independent of the thermodynamics of mixing. We used this phenomenon for obtaining new polymeric materials on the basis of two different polymers (low-density polyethylene and high-density polyethylene, cellulose and polyethylene, cellulose and polyvinyl chloride, etc.). These new materials are characterized by unique properties which are not typical either of each of them or of their mixtures obtained in the liquid phase.

To explain the new phenomena just mentioned (high reactivity, new directions of chemical reactions, homogenization, etc.) one should assume that together with chemical processes, the formation of new surfaces takes place under high pressures and shear deformation. The physics of the phenomenon is the following: the elastic energy accumulated in a solid body under high pressure and shear deformation is mainly spent on the formation of a new surface (endothermal process). We used this physical phenomenon for the development of a new principle of pulverization. It is known that numerous disintegration machines (ball mills, vibratory mills, jet mills, etc.) are mostly based on two physical principles: fragile fracture (crystalline materials, glasses,

etc.) and cutting (soft materials). The establishment of this new physical law allowed us to develop machines of different design (single screw and double screw extruders, rollers, etc.), in which a substance is exposed to a certain pressure, thus accumulating elastic energy. Shear deformation which follows leads to the formation of a new surface, i.e. the formation of powders. In this way we managed to pulverize thermoplastics and reactoplastics, rubbers, vulcanized rubbers, rubberized-fabric and sandwich materials, wood, cellulose-containing materials, composites, etc.

The elastic-deformation method is characterized by rather small energy consumption per unit weight of the pulverized product (2-3 times less compared with traditional methods).

The study of the pulverization process showed that the process was avalanche-like and all the particles were formed simultaneously, but not successively. The physical mechanism of the process is the following: during the formation of an initial new surface, one can observe the release of energy spent on the formation of the next surface which in turn leads to the formation of the next surface. In this way the avalanche-like fracture of the initial substance is brought about, i.e. the process has a branched chain character. In this case, particles are formed with the size distribution function close to the most probable one (Gaussian distribution).

We obtained two rigorous proofs in favour of the branched character of the fracture process. The first proof was obtained by measurements of the average molecular weights of macromolecules as a function of the particle size. If the mechanism of powder formation is successive, i.e. each particle with a size i is formed from particles with a size j ($j > i$), then, the smaller the particle size, the larger the action of mechanical fields on this particle during its formation.

On the other hand, the calculations show that, even if a macromolecule is seen as a rigid rod (which is wrong, since usually the macromolecule has a coil conformation and its average size ℓ is much smaller than the size L of a stretched rod), the molecular weights of macromolecules will not practically decrease in the process of pulverization, since the sizes of the forming particles are considerably larger than ℓ . This is why the decrease ratio is ℓ/R . The observed decrease in the molecular weight of polymers during their fragile fracture (e.g. in ball mills) is due to the fact that macromolecule rupture takes place inside the particle itself because of deformation. Thus, in the case of a successive formation of particles (i.e. smaller particles are formed from the larger ones), one can expect that the smaller the particle size, the less the molecular weight, since these particles were exposed to a greater action of mechanical fields. In the case of the avalanche-like mechanism of particle formation (elastic-deformation method of pulverization) the average molecular weight does not depend on the size of particles since the particles are formed simultaneously. Our experiments showed (Fig. 3) that the molecular weight decreased only slightly with the decrease in the size of the particles obtained. Therefore, the formation of these particles is avalanche-like.

The second proof consists in the fact that, while measuring the mechanical moment of force necessary for pulverization as a function of time, we obtained a curve (Fig. 4) which is concave downward, but not vice versa, which would correspond to the successive mechanism of particle formation.

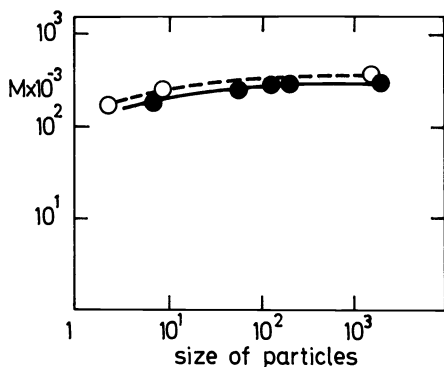


Fig. 3. Average molecular weight of the polymer vs particle size (block polystyrene).

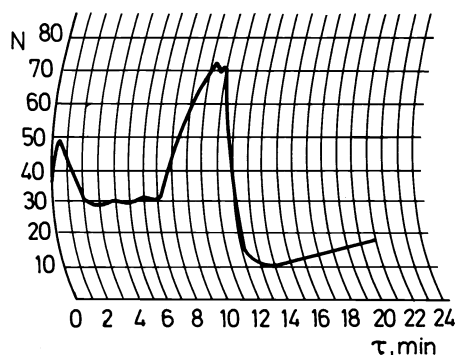


Fig. 4. Mechanical moment of shaft rotation vs time.

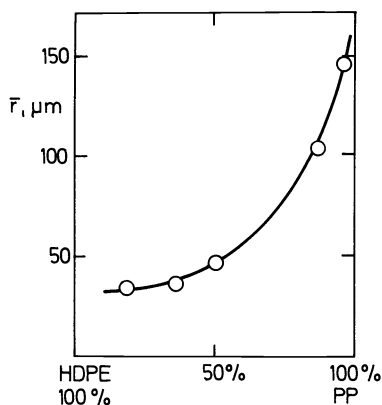


Fig. 5. Average particle size vs pulverized mixture composition.

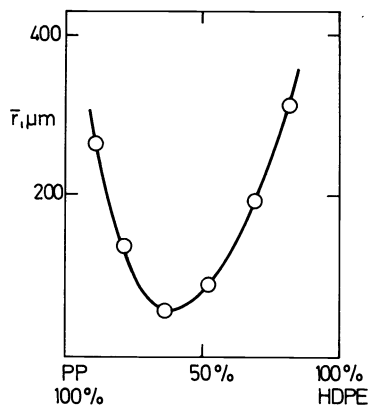


Fig. 6. Average particle size vs pulverized mixture composition.

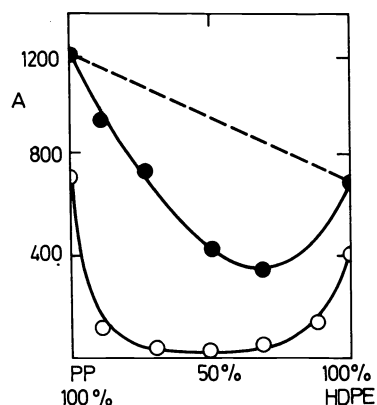


Fig. 7. Specific power consumption per unit of the forming surface and particle size vs the pulverized polymer mixture;
 ○ slow cooling,
 ● quenching.

Thus, all the data obtained unambiguously testify to the fact that during pulverization the elastic energy accumulated in the substance according to some unknown physical mechanism is released as the formation of a new surface takes place, and immediately spent on the formation of a new larger surface.

The process of avalanche-like pulverization of organic solid substances under the action of elastic energy is usually followed by a number of new phenomena which can be explained with the help of the physical mechanism of the pulverization process.

Four most important phenomena should be mentioned:

1. The process of elastic-deformation pulverization of polymeric materials depends on many factors, such as temperature, pressure, rate, dimensions of deformation, etc. It turned out that under the given conditions some polymers are readily pulverized, while others are not pulverized at all. However, if the polymer is not pulverized under the given conditions, a small addition (3-5 %) of some other polymer pulverizable under these conditions makes the mixture of these polymers pulverizable (Fig. 5).
2. If under the given conditions two polymers alone are not pulverized, their mixture is readily pulverized with the formation of superfine powder (Fig. 6).
3. The study of energy consumption per unit weight of the pulverized substance and the average size of the powder obtained as a function of the composition of two polymers, which are not pulverizable by themselves, showed that in spite of the expected additivity, there was a distinct synergism (Fig. 7).
4. During the combined pulverization of a mixture of a polymer and metal foil (copper, aluminium, iron, etc., foil thickness $\sim 60 \mu\text{m}$), superfine metal powder is formed. If the mixture of a polymer and foil is passed through the disintegrating machine when the polymer is in the molten state, the foil is not pulverized. However, if the temperature is lower than the melting temperature of the polymer, the polymer is pulverized; under such conditions the pulverization of foil is possible up to rather small sizes (80 % of particles $< 2 \mu\text{m}$).

The variety of the phenomena observed cannot be explained by using traditional concepts of the effect of mechanical fields on a polymeric substance. Apparently, to understand the problem completely, one should take into account electric fields formed due to the effect of mechanical fields on dielectrics, and the interaction of dielectrics with metal.