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Effect of a Solid Surface on Relaxation and Structure-formation Processes in Polymer Layers Adjoining the Walls

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Data on the characteristic properties, in particular crystallisation properties, of low-molecular substances in layers adjoining the walls are briefly discussed. The methods for and the results of the determinations of the thickness of wall layers of solutions and melts of many polymers are quoted. Data on the effect of a solid surface on the rate of relaxation processes and the properties of the polymers due to them are reviewed.
The effect of artificial nucleating agents on the structure (and properties) pf polymers, the suppression of structure formation in thin layers in certain systems, and epitaxy are discussed.
The experimental data presented are treated from the standpoint of the hypothesis of the packet structure of polymers and the effect of the interaction between the solid surface and the polymer on the enthalpy and entropy of the system.
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1. INTRODUCTION

The specific features of thin layers of polymers (1 – 20 μm thick) in contact with a solid surface have increasingly attracted the attention of investigators in recent years. The physicochemical foundations of recipes for and the technology of the processing and applications of filled polymeric materials, adhesives, and paint and varnish coatings would be impossible without an understanding of the structural characteristics of such layers and their behaviour under conditions of use.

As early as 1935–1936, Rebinder related the effectiveness of the filler to the fraction of the polymer, which, as a result of adsorption interaction with the filler surface, passes into a "special film state" with enhanced mechanical properties[1,2].

In recent years, particularly in the last decade, numerous observations have accumulated, showing that surface layers of the polymer (or layers adjoining the walls), arising when it comes into contact with another (particularly solid) phase, differ in structure and properties from the polymer at a fairly large distance from the phase boundary, and have a thickness, which sometimes reaches many micrometres.

A chemically inert solid surface acts on the surface layers of polymers (and low-molecular substances) via intermolecular attraction and repulsion forces; these forces are responsible for adsorption interaction between the system components and for the purely geometrical restriction on the space available for migration by the kinetic units of the substance in the wall layer.

The unusual properties of the structure of surface layers are a consequence not only of the interaction between the atoms and molecules of the solid and the polymer layer located directly on its surface but also on the transmission of this interaction (more precisely its results) from the layers nearest to the surface to more remote layers. The effect of one phase on another via an interface theoretically extends throughout the entire bulk of the phase and on moving away from the phase boundary, the value of a property of the phase approaches asymptotically the value characteristic of the phase in the absence of such influence[3]. Therefore, the thickness of the wall layers determined in any experiment is only an effective thickness characterising the behaviour of the system under the conditions of the given experiment; the effective thickness varies with the property investigated and the sensitivity of the method employed. The gigantic size of polymer molecules and the presence of supermolecular formations results in a much greater thickness of wall layers in polymers than in low-molecular substances. This fact is of great practical importance in the study of wall layers of polymer systems.

In the vast majority of investigations which have been made, the surface layers of polymers were examined not by direct study of the layers themselves but by studying the properties of complex systems in which the behaviour of certain polymer layers plays a significant role. Quantitative relations governing the effect of an extraneous surface on the structure and properties of a polymer wall layer are not as yet available and qualitative generalisations have been made only concerning certain aspects. The results obtained by different investigators are sometimes contradictory and the reasons for such contradictions are not always clear.

In the present paper an attempt is made to describe the available literature data on the principal properties of polymer wall layers from the standpoints of the energy and geometrical effects of the solid surface on a structured (in packets or crystallites) polymer.

2. PROPERTIES OF WALL LAYERS OF LOW-MOLECULAR SUBSTANCES

In a series of investigations Deryagin and coworkers showed that the wall layers of a number of low-molecular liquids under the influence of the surface forces of the solid acquire properties different from those of the bulk-phase liquid. Thus it was found[4] that the elasticity of

water in a layer adjoining a glass surface becomes equal to that of the bulk-phase water only at a distance of about 0.07 μm and the shear elasticities of wall layers of water, acetone, hexanol, and octanol on quartz are about a factor of ten higher than the bulk-phase values[5]. In the thin pores (diameter about 0.01 μm) of amorphous silica water does not exhibit the anomalous thermal expansion (in the range 0–36°C) [6]; similar results were obtained in studies on the behaviour of water in glass capiliaries[7,8] and in carbon pores[9]. The heat capacity of nitrobenzene mixed with a glass powder (activated by treatment in a glow discharge), where the average thickness of nitrobenzene layers was 0.2–0.3 μm, was lower than the bulk-phase value approximately by 10%†.

Purified mineral oils in a gap between steel surfaces begin to exhibit boundary mechanical properties when the gap thickness is less than 0.3 μm and in gaps 0.1 μm thick, the layer begins to show elastic properties[11].

The unusual properties of liquids in wall layers are caused not only by direct interaction with the surface of another phase but, at least in the majority of cases, by the orientation of molecules in this layer. One may refer, as examples, to the orientation, demonstrated by electron diffraction, in thin films of certain straight-chain hydrocarbons on copper, rock salt, and glass[12] and of lubricating oil (mixtures of saturated and unsaturated hydrocarbons) on a number of metals and alloys[13]; the electron diffraction patterns of the surface layer of the mercury meniscus (at the boundary with air) also show a distinct texture[14].

The effect of the solid surface on the structure and mobility of the wall layer of a liquid cannot fail to influence also its crystallisation. Indeed, in the crystallisation of piperine[15] and betol[16] in a layer with a thickness of several tenths of a millimetre between glass surfaces and also in the case of piperine between mica surfaces, the curves for the temperature variation of the rate of nucleation show two maxima. The authors of these investigations attribute the low-temperature maximum (at a distance of several degrees from the high-temperature maximum) to the effect of the solid surface, in the vicinity of which the molecules of the liquid are in a more ordered state than in deeper layers. The curves relating the rate of nucleus formation in betol to the distance from the surface of glass show a maximum, the effect of the surface extending over a distance of the order of several micrometres[17]. Brief treatment of glass surfaces with hydrogen fluoride, coating of the surface with a thin layer of lactic acid[17], and the application of a magnetic field[18] weaken the effect of the surface on the rate of nucleation while coating of the surface with a layer of collodion (10 μm thick) completely eliminates the surface effect[17]‡.

The results of many investigations demonstrate the dependence of the structure of thin metallic films, obtained by vacuum deposition on a solid support, on their thickness. Under certain experimental conditions, silver telluride (Ag_2Te) films with a thickness less than 300–350 Å are structureless, in films with a thickness of between 350 and 700 Å spherulites 100 μm and above in diameter are formed, while in still thicker layers the spherulite structure is gradually suppressed by microcrystals growing in increasing numbers[19]. Beryllium, vanadium, nickel, chromium, and cobalt films give rise to electron diffraction patterns which coincide with those of the massive specimens only when the thickness is in excess of 70–80 Å; for smaller thicknesses, the diffraction patterns show additional lines and when the thickness is 20–30 Å only diffuse rings are seen[20]. In silver films 40–50 Å thick two phases coexist at room temperature—a face-centred cubic phase and a hexagonal phase, while in thicker films (of the order of 100 Å) the hexagonal modification is unstable[21].

The above data by no means exhaust the abundance of observations on the properties of wall or surface layers of low-molecular substances and are quoted only to assist the reader gain an idea about the general occurrence of the phenomena under discussion for both high-molecular and low-molecular substances. Extensive evidence concerning the unusual properties of the wall layers of low-molecular liquids is presented in a detailed review by Henniker[22].

3. THE THICKNESS OF POLYMER WALL LAYERS AND METHODS FOR ITS DETERMINATION

Recently Kargin and coworkers demonstrated the possibility of forming large supermolecular polymer species in dilute solutions. In solutions of poly-α-butylene (M = 180 000) in rosin at a concentration of 0.1% and above supermolecular species with a length of the order of 1 μm were observed[23], while in solutions of the same polymer in propane species with a length of several tenths of a micrometre were observed at concentrations as low as 0.05%[24]; in solutions of atactic polypropylene (M = 35 000) in propane at concentrations as low as 0.2% particles with dimensions of the order of a micrometer were found[25].

So far it has not proved possible to observe directly supermolecular formations in polymer melts but there is much reliable evidence for their existence. This includes electron diffraction data showing the presence of a high degree of order in the distribution of polymeric molecules in the melt[26,27], results of studies on the sorption properties of polymers above their melting points[28], certain rheological characteristics of melts[29–34], the retention of the steric distribution of the spherulite centres after repeated fusion[35], and the high rate of crystallisation of melts[36].

The existence in melts and solutions of polymers of supermolecular formations must inevitably result in high-molecular substances having much thicker wall layers (with properties differing from those in the bulk-phase) than low-molecular compounds.

We shall examine briefly the methods used to determine the thickness of the wall layers of polymers in systems comprising a polymer solution or melt and a solid surface. Various methods for the determination of the weight of the polymer adsorbed on the surface from its solution are widely employed. Since these methods have been widely discussed in a review by Patat et al.[37], we shall not deal with them.

Viscometry

Viscometric methods are simplest; with their aid, it is possible to determine the effective change in capillary

† We restrict the review of the work of Deryagin's school to the publications quoted above, which contain the bibliography of other papers by this school on the properties of the wall layers of low-molecular liquids.

‡ In the publications quoted above[15–18] there is a bibliography of other investigations at Odessa University on the effect of surface on the crystallisation of low-molecular organic liquids.

diameter caused by the appearance of an adsorbed layer[38-42] or in the dimensions of adsorbent particles suspended in a solution or melt of the polymer[43-48].

Öhrn[38] measured the flow times of a polymer solution using a viscometer with two parallel capillaries of different diameters (0.5 and 0.2 mm). The following considerations were employed to calculate the effective thickness of the adsorbed layer. If, for a capillary with a radius r and a thickness of the adsorbed layer δ, the apparent (observed) relative viscosity of the solution is denoted by η^*_{rel}, the true relative viscosity of the solution $\eta_{rel} = \eta_{soln}/\eta_{solvent}$ is given by

$$\eta_{rel} = \eta^*_{rel}\left(\frac{r-\delta}{r}\right)^4 = \eta^*_{rel}\left(1-\frac{4\delta}{2}\right)+\cdots$$

We shall retain only the first term in the expansion and, on converting to the viscosity number (term recommended by IUPAC), we obtain the expression

$$\eta^*_{sp}/c = \eta_{sp}/c + (\eta_{rel}/c)(4\delta/r) \ .$$

If we assume that for a given concentration the effective thickness of the adsorbed layer δ is independent of the dimensions of the capiliary§, then δ may be calculated from the slope of the linear plot of η^*_{sp}/c against $1/r$.

The thickness of the adsorbed layer may be calculated also directly from the flow times of the solution in two capillaries of different diameters[40], and from the formula[42]

$$\delta = \frac{r\,\Delta t}{4t} \ ,$$

where r is the capillary radius, t the flow time of the solvent until the viscometer is filled by the test solution, and $t + \Delta t$ the flow time of the solvent after the viscometer had been used for the test solution and then washed with the solvent. The thickness of the adsorbed layer obtained by the last method is probably somewhat too low, since it is very likely that part of the adsorbed polymer is removed from the walls of the capillary when it is washed.

In the determination of the thickness of the adsorbed layer from the change in the dimensions of adsorbent particles suspended in a liquid, measurements were made either of the viscosity of such a system using the Einstein equation[43,45-49] or the rate of sedimentation of the particles[44]. The familiar Einstein equation for the viscosity of suspensions of rigid spherical particles in a Newtonian liquid[50,51] is of the form

$$\eta = \eta_0(1 + K\varphi) \ ,$$

where η is the viscosity of the suspension, η_0 the viscosity of the pure liquid, φ the volume fraction of the particles, and K a constant. If the particles are spherical and the liquid merely wets them, then $K = 2.5$. When an adsorbed layer is formed on the particles of the suspension, their effective volume increases and the viscosity of the system is described by the Einstein equation in which K (in this case the constant may be denoted by K_{eff}) is greater than 2.5. When the form of the particle deviates from the spherical, K also proves to be greater than 2.5. If this deviation is slight, the value of K characteristic of particles of a given form (it will be denoted by K_0) may be determined by measuring the viscosity of the suspensions in a suitable low-molecular liquid (transformer oil, for example, has been used for this purpose[48]).

§ The velocity gradient in both capillaries of Öhrn's viscometer was the same and $r \gg \delta$.

Knowing the particle diameter d and the experimental values of K_0 and K_{eff}, it is easy to calculate[47] the thickness of the adsorbed layer δ:

$$\delta = \frac{d}{2}\left(\sqrt[3]{\frac{K_{eff}}{K_0}}-1\right).$$

If a polydisperse absorbent with a specific surface S_{sp} is used, then, having calculated the effective increase of its volume in the suspension per unit weight ($\Delta\varphi_{eff}$) due to adsorption, it is possible to calculate also the thickness of the layer $\delta = \Delta\varphi_{eff}/S_{sp}$. An advantage of this method is the possibility of applying it in studies on concentrated solutions and polymer melts; the measurements must be made for low values of φ and under conditions ensuring Newtonian behaviour of the system.

The following two methods for the determination of the thickness of the wall layer based on its enhanced viscosity may also be included among viscometric methods. The dependence of the viscosity of polymer wall layers on the distance from the solid surface has been investigated by the so called "blowing off" method[52]. The essential features of this method have been described in detail in a number of papers[53-55] and are as follows. A jet of air directed onto a slit between two flat surfaces containing the liquid produces a tangential force causing the profile of the film to assume a definite form reflecting the property investigated. The steepness of the film profile at each point is proportional to the viscosity of the liquid at the corresponding distance from the surface. If the viscosity is independent of the distance from the surface, then the profile of the wedge-shaped film is linear; the increase of viscosity on approaching the surface leads to the "blunting" of the wedge. The steepness of the profile can be comparatively simply determined from the distance between the interference bands obtained on illuminating the film with monochromatic light.

Tsvetkov et al.[56] employed in the investigation of polymers a previously developed method[13,57] for the determination of the thickness of the boundary layer in low-molecular liquids. The essential feature of the method consists in the study of the variation with time of the thickness of a layer of the liquid between the parallel plates of a planar plastometer compressed by a constant force. Extrapolation of the relation to infinite times permits the estimation of the thickness of this rigid "non-fluid" layer, which may be regarded as the wall layer. It has been shown for low-molecular liquids[13,57] that the thickness of this layer depends on the pressure on the plates of the plastometer, the nature of the liquid and of the surface of the plates, and the experimental temperature. There is no doubt that these factors influence also the thickness of the polymer layer. However, one may question the validity of the extrapolation of data obtained over a period of 15 min for the highly viscous polymer melts of the kind investigated by Tsvetkov[56].

Ellipsometry

Ellipsometry is a satisfactory method permitting the measurement of the thickness of the adsorbed layer with an accuracy of several ångstroms. This procedure uses the fact that the formation of a film on the solid surface influences the optical properties of the latter—there is a change in the phase difference and the amplitude ratios of the components of the elliptically polarised light reflected

from it. The accuracy of this method is considerably reduced if the refractive indices of the film and the solution adjoining it are similar. A method has been described for the calculation (using computers) of the thickness of adsorbed films of low-molecular and polymeric substances from data obtained with the aid of an ellipsometer[58,59]. To improve the precision of the measurements, the incident beam was reflected three times from the test surfaces. Ellipsometry has been used to investigate adsorption from dilute polymer solutions[58-61]; the use of this method to investigate adsorption from polymer melts would be of great interest.

The somewhat arbitrary nature of the ellipsometric values obtained for the thickness of the wall layer is a consequence not only of the fact that these values, as in measurements by any other method, constitute merely effective quantities but also because in the calculation it is necessary to take into account the refractive index (and hence the density) gradient within the layer. In the first studies by Stromberg and coworkers[58-60] the simplest hypothesis was adopted, namely that the adsorbed film is homogeneous and that the refractive index gradient within the layer is zero. Subsequently[61] in the calculation of the thickness it was also postulated that the density gradient is exponential. The refractive index gradient in the film is at present unknown; statistical calculations show that, even for the simplest model (an isolated macromolecule of finite[62] and infinite length[63]), there is a fairly complex relation between the density of the adsorbed layer and the distance from the surface of the support, the relation being influenced by the rigidity of the chain and the adsorption energy.

Table 1. Thicknesses of polymer wall layers in various systems.

Polymer; 10^{-5} mol. wt.	Soln. concn., g litre^{-1}	Thickness of wall layer, μm	Methods for determination of layer thickness	References
Polystyrene				
4—6.2	0.2—2.0	0.08—0.25[a]	viscometric	38, 39
0.6—14	not indicated[b]	0.01—0.07[a]	ditto	47
0.8	0.18	~0.008	ellipsometric	59
0.8	2—9.7	~0.02	ditto	59
5.4—33	1—2	0.04—0.09	"	61
2.9	up to 10	up to 0.001[c]	from weight of adsorbed layer	67, 68
6	6.6—25.7	0.087—0.5[a,d]	ditto	69
Not indicated[e]	20	0.3	viscometry of suspensions	48
Not indicated	1.6—14	0.03—1[a,d,f]	from weight of adsorbed layer	70, 71
4.4 and above	melt; 227°	7—9	extrapolation of distance between plates of plastometer	56
	melt; 296°	~2		
Poly(vinyl acetate)				
8.8	0.11—0.18	0.47—0.66	viscometric	40
0.8—12	not indicated	0.01—0.09	ditto	41, 47
0.45—9	0.35—2.0	0.025—0.074[g]	from weight of adsorbed layer	72, 73
7.7	not indicated	0.15[d]	ditto	75
7.7	2.7—31.0	0.06—0.72[a,d]	"	69
0.32	80	2[r]	"	66
Poly(methyl methacrylate)				
0.75—66	not indicated	0.01—0.4[h]	viscometric	47, 74
0.44—15	3.3—56.2	0.048—0.72[d]	from weight of adsorbed layer	69, 75
Not indicated	0.3—13.1	0.02—0.76[d,f]	ditto	70, 71
Poly(lauryl methacrylate)				
3.3 or 11.9	not indicated	0.0025	from measurement of of rate of sedimentation	44
Copolymer of stearyl methacrylate and *N*-vinyl-2-pyrrolidinone (5:1)	not indicated	0.021	ditto	44
Polyvinylpyrrolidinone 6	18	0.75[d]	from weight of adsorbed layer	69, 75
Poly(vinyl chloride) 0.7-0.8	0.01—0.5	0.14—0.33	viscometric	76
Poly(vinyl alcohol)				
Not indicated	not indicated	1.2[d]	from weight of adsorbed layer	75
Polyisoprene				
0.22-0.32	70	>2.7[d]	ditto	66
Guttapercha	20—40	0.9—3.6	viscometry of suspension	48
Ditto	melt; 75°	3.2—8[i]	ditto	48
Butadiene-styrene (GR=S)	0.1—0.2	0.015—0.010	"	43
Poly(ethylene glycol) 0.3	90	>3[d]	from weight of adsorbed layer	66

Table 1 (contd.)

Polymer; 10^{-5} mol. wt.	Soln. concn., g litre^{-1}	Thickness of wall layer, μm	Methods for determination of layer thickness	References
Poly(butyl vinyl ether)				
0.006	melt	>5[k]	"blowing off" of film	52
	ditto	up to 18[l]	ditto	52
Poly(neopentyl phthalate) 0.02	0.1—10	0.0004—0.0035[c]	from weight of adsorbed layer	77
Polyepoxide [from 4,4'-bisglycidylphenyl-2,2'-propane and hexane-1,6-diamine]	filled system	0.05—0.15	from sorption of solvent vapour	64, 78
Cellulose trinitrate 22	0.005—0.12	0.05—0.1	viscometric	42

a. This range of thicknesses includes results obtained using various solvents.
b. Concentration not indicated in the paper; however, there is no doubt that the behaviour of dilute solutions was investigated.
c. The thicknesses are much too low, since in the calculations the authors assumed that the entire surface of the sorbent (carbon black, titanium dioxide, etc.), determined from the extent of adsorption of nitrogen, is available for the adsorption of the polymer and the density of the adsorbed layer is equal to that of the solid polymer.
d. Thickness of the layer estimated assuming that its density does not differ from that of the solid polymer; this method of estimation yields low results.
e. Isotactic polymer.
f. This range of thicknesses includes results obtained at different temperatures.
g. The layer thickness was estimated by the present author from the weight adsorbed per unit surface area of the adsorbent using[40] 0.17 g ml^{-1} as the density of the layer.
h. It has been stated[74] that the layer thickness fails with increasing concentration of the solution; this range of thicknesses includes the results obtained by extrapolation to zero concentration.
i. The layer thickness decreases with increasing shear stress.
j. From the difference between the viscosities of the wall layer and the bulk-phase polymer.
k. From the zone corresponding to the breakdown of interference bands.

Sorption

An unusual method for estimating the thickness of polymer layer immobilised by the surface of a filler is based

on the extent of sorption of the solvent vapour by the filled system at a temperature greater than T_g for the polymer[64]. In the calculation it was assumed that at the experimental temperature the immobilised polymer layer sorbs like the initial polymer in the vitreous state and the remaining polymer in the filled system does not differ in its sorption capacity from the unfilled polymer; it was also assumed that, for low vapour pressures, sorption by the vitreous polymer may be neglected. It is noteworthy that these assumptions lower the thickness of the immobilised layer.

Table 1 presents data for the thicknesses of the wall layers of various polymer–solid surface systems obtained by different methods. A striking feature of the results in Table 1 is their considerable scatter, which is due primarily to the different concentrations of the polymers in the systems to which the particular data refer. Layer thicknesses of the order of tenths and hundredths of a micrometer occur in dilute polymer solutions at concentrations ranging from a fraction of a gramme to several grammes per litre; in all cases where melts were investigated the thickness of the wall layer amounted to several micrometers. It is appropriate to mention here that, in the determination of the extent of adsorption of the polymer from solution over a wide range of concentrations, saturation was not observed with increase in concentration[65,66]. The thickness of the wall layer depends not only on the concentration of the solution, the nature of the solid surface, the molecular weight, and the nature of the polymer and solvent (if it is present in the system) but also on experimental conditions such as temperature, pressure, shear stress and shear velocity, and the method used to determine it (see above, p. 704). It may be supposed that in those cases where the thickness of the wall layer of the polymer is comparable to the dimensions of the solid particles round which the layer is formed (for example in systems with a highly dispersed filler), the thickness of the layer is directly related to the particle diameter.

Table 1 shows also the extreme paucity of information at present available about the thickness of the wall layer in polymer melts.

4. CHARACTERISTICS OF RELAXATION PROCESSES IN POLYMER WALL LAYERS

A solid surface in contact with a polymer can influence the wall layer via two mechanisms¶: as a result of a purely steric effect—by restricting the volume occupied by the units of the macromolecule and the larger kinetic units during their thermal motion, and as a result of an energy effect—by bonding via an intermolecular interaction directly to certain units of the macromolecules adjacent to the surface, via chemical bonding to macromolecules comprising these units, and via intermolecular bonding to supermolecular formations (naturally not only those of which such molecules are constituent parts but also the adjacent formations). As a result, the majority of the relaxation processes in the wall layer are slower than in the bulk of the polymer.

The data on the relaxation times and activation energies for isothermal compression obtained in the study of the unfilled systems poly(methyl methacrylate)–nitron or fibre glass and polystyrene–quartz or nitron lead to the conclusion that in these systems the principal factor responsible for the reduced mobility of the structural units in the polymer wall layers is the decrease of the number of possible conformations of the macromolecules and not their energy interaction with the surface[84]. However, it may be supposed that in certain other systems this energy factor will predominate. The reduced mobility in polymer wall layers is associated with the expansion of the relaxation spectrum towards longer times[85–87].

Effect of the Solid Surface on the Packing Density and Orientation in Wall Layers

The lack of correspondence between the steric disposition of the centres of intermolecular interactions on the solid surface on the one hand and in the polymer on the other, which usually obtains, leads to a lowering of the packing density of the polymer in its wall layers compared with bulk phase. The results of sorption measurements[84,88–90], direct determinations of the deviation of the density of the mixture from additivity[84,88,91,92], and the increase in the coefficient of volume expansion on filling[93] indicate a loosening of the polymer bulk phase in the systems poly(vinyl acetate)[92] and vinyl acetate-vinyl chloride copolymer[88]–titanium dioxide, polystyrene and poly(methyl methacrylate)–fibre glass[89] or quartz powder[84,93], isotactic polypropylene–glass powder[90], and natural rubber–zinc oxide[91]†. The increase of the rate of dissolution of small particles of dye in the melt of isotactic polypropylene on increasing the distance between such a particle and a glass surface, starting with a distance of 30 μm, observed in our experiments[90], also confirms that the density of the polymer in the wall layer is reduced.

A solid surface interacting fairly strongly with the polymer can orient to some extent its molecules and supermolecular formations in the wall layer. In the limiting case this orientation leads to epitaxy‡, which will be considered in the next section. It has been established by electron diffraction that guttapercha is oriented on aluminium[94]; Kozlov et al.[95] concluded, on the basis of studies of the strength, swelling, and contraction of films of cellulose ethers on the surface of glass that the orientation of such films is planar. Calculation, based on data for the sorption of water showed that, when a polyepoxide [from 4,4′-bisglycidylphenyl-2,2′-propane and hexane-1,6-diamine] is filled with titanium dioxide (arutile modification with an average particle size of 0.2 μm), there is a

¶ We are not discussing here the chemical interaction between the polymer and the material with which it is in contact nor the effect of the solid surface on polymerisation, polycondensation, and cross-linking processes, which have been described in a number of publications[79–83].

† The observed[92] decrease of the coefficient of volume expansion of poly(vinyl acetate) at 40°C (slightly above the glass point T_g) as a result of the introduction of 12.1% of titanium dioxide is not inconsistent with the hypothesis that the density of the polymer decreases on filling. If at a temperature below T_g the free volume of a filled polymer is significantly greater than that of an unfilled polymer, then, despite the decrease of the coefficient of volume expansion, there is a certain range of temperatures fairly close to T_g where the free volume of the filled polymer will still remain higher than that of the unfilled polymer.

‡ Epitaxy is the formation at the boundaries of the crystals of one substance of oriented crystals of another.

decrease of the free energy and enthalpy (by 2 cal g^{-1}) and of entropy (by 5×10^{-3} cal g^{-1} deg^{-1}) of the polymer, which also indicates some ordering of the latter[78].

The conclusion that the configurational entropy of poly(vinyl acetate) may increase when it is filled with titanium dioxide was also based[92] on a considerable (almost by a factor of 2) decrease of the activation energy for the diffusion of oxygen and argon (at temperatures above T_g) on filling.

The orientation obtained when the polymer is extended may lead to both an increase and a decrease of the packing density of the polymeric molecules[96,97]. By analogy, we must suppose that the orienting effect of the solid surface on the polymer can also lead either to an increase or a decrease of the packing density of the wall layer. Since the molecular attractive forces of the solid act not only on the nearest layer of units of the macromolecules but also on the more remote layers, an enhancement of the interaction between the polymer and the solid surface should favour an increase in packing density; more favourable conditions for relaxation have a similar effect. It can also be supposed that in certain cases filling leads to an increase in the packing density of the polymer at temperatures above T_g, but lowers it below T_g. Indeed, it has been established in a number of studies that above T_g the swelling of the polymer or the sorption of water vapour decrease on filling. This has been observed in the study of the systems natural rubber or polyisobutylene–colloidal nickel or cobalt[98], natural rubber–carbon black[99], poly(vinyl acetate) or polyepoxide–titanium dioxide or copper-phthalocyanine[64], and gelatine–glass[100] (in the last case gelatine sorbed such an amount of water long before the attainment of equilibrium swelling that T_g fell considerably below the experimental temperature).

The packing density of the wall layer can also be influenced by the conditions of its formation. Thus it has been shown[101] that, when a mixture of poly(methyl methacrylate) or polystyrene with a glass powder is obtained from solutions in different solvents (by evaporating the solvent), then, as a rule, with enhanced thermodynamic effectiveness of the solvent (estimated from the second virial coefficient of the osmotic pressure), the packing density of the polymer falls and the capacity for swelling increases correspondingly. This is due to the fact that in thermodynamically more effective solvents the macromolecules are in more extended conformation than in less effective solvents and it has been established by electron microscopy[102] that the initial conformation of the polymeric chains influences their interaction with the solid surface. It has also been observed[99] that the introduction of carbon black into a solution of natural rubber with subsequent evaporation of the solvent yields a mixture which swells much less than the mixture obtained by rolling. It is interesting to note that, after standing at room temperature, the density and degree of ordering of rubber in the mixture increase in the first tens of minutes after the termination of rolling (as shown by the decrease of the capacity for swelling).

Effect of the Solid Surface on Relaxation Processes in Wall Layers

The solid surface, which interacts with polymers and restricts by its steric effect the mobility of the macromolecules and supermolecular structural elements (as already mentioned above), retards the relaxation processes in the wall layer. The decrease in packing density in the polymer wall layer (which occurs at temperatures below T_g) has the opposite effect on relaxation processes, accelerating them[103-105]. The opposing effects of these factors which act simultaneously (the packing density also depends on the polymer–solid surface interaction) greatly complicates the observed situation.

The study of the temperature variation of the tangent of the dielectric loss angle of poly(methyl methacrylate) ($M \simeq 8 \times 10^4$) and polystyrene ($M \simeq 8 \times 10^5$) filled with a quartz powder having a particle diameter of about 4 μm showed[86] that filling (up to 24 vol.%—average distance between particles 4 μm) hardly affects the temperature of the maximum dipole–elastic losses in poly(methyl methacrylate) and greatly increases this temperature in polystyrene; at the same time the temperature of the maximum of the dipole–radical losses for [poly(methyl methacrylate)] falls. These results apparently contradict the dilatometric data showing a considerable increase of T_g for poly(methyl methacrylate) ($M_{visc} \simeq 3 \times 10^4$ and 6×10^6) filled by the same quartz powder[93], according to which the introduction of 30 wt.% of quartz increases T_g by 24°C. These findings found a natural explanation based on the concept of the packet structure of polymers[36,106], taking into account the contribution by the mobility of particular structural units of the polymer to the observed effect.

Not only segments and macromolecules but also various supermolecular formations (packets and in certain cases more complex species) interact with the solid surface, only a small fraction of the functional groups of the polymer being linked directly to the surface§. The side chains of the macromolecules containing the remaining functional groups are not directly influenced by the surface and therefore, on lowering the packing density with the associated increase of free volume[93], may exhibit in the vicinity of the solid surface a greater mobility than further away from it. The increase of the mobility is responsible for the decrease of the corresponding dielectric relaxation time, which is reflected in a lowering of the temperature of the maximum in dipole–radical losses[110].

As already mentioned above, the interaction of the solid surface with the functional groups of the polymers leads to a lowering of the mobility of the packets (and larger structural formations if they are present); Lipatov[86] in fact explained the observed increase of T_g of a polymer interacting with a solid surface by such lowering of the mobility of the packets.

The lack of dependence on the degree of filling of the temperature of the maximum dipole–elastic losses for the systems investigated[86] of shows, that, despite the decrease of the mobility of the packets, the mobility of the segments of the macromolecules in the wall layers does not change or changes only slightly.

The conclusion that there is a sharp decrease in the mobility of the structural elements of the wall layers of polymers also follows from the results of Deryagin and coworkers[111], who investigated the self-adhesion of thin

§ Since the thickness of the wall layer exceeds by several powers of ten the diameter of the macromolecules, only a small fraction of the functional polymer groups present in this layer can interact directly with the surface. This conclusion is also a direct result of a number of experimental studies[44,107-109].

layers of natural or butadiene rubbers deposited on quartz filaments. For films with a thickness less than 0.3 μm, the adhesive force was small and, in contrast to thicker films, hardly changed with the duration of contact. Such a weak dependence of the adhesive force on the duration of contact can be accounted for by a considerably reduced mobility of the structural elements in films with this thickness, which leads, on the one hand, to a virtually unchanged area of contact of the films and, on the other hand, to a suppression of the diffusion of macromolecules and their segments, which is known to be responsible[112] for the dependence of the effect of the adhesive bond on the duration of contact of the test specimens.

The results of studies on stress relaxation by the method described previously[114] in the system polyarylate N-1 (obtained from phenolphthalein and the chloride of isophthalic acid[113])–copper powder showed that the initial activation energy for the relaxation process U_0¶ diminishes with increasing degree of filling up to a certain limit and then remains virtually unchanged[117]. A similar variation of the activation energy for deformation with the degree of filling was established for the system polystyrene–fibre-glass[118]. The curve relating the constant γ to the filler content in compositions based on polyarylate N-1 passes through a minimum corresponding approximately to 40 wt.% of the copper powder[117]. This form of the curve may be due to the fact that for comparatively low contents of the filler, partial breakdown of the supermolecular structural elements produces a more uniform distribution of stresses despite the appearance of inhomogeneities such as the filler particles. When the filler content is greater than 40 wt.%, the effect of the concentration of stresses in the vicinity of filler particles predominates.

Effect of the Specific Features of the Relaxation Processes in Wall Layers on Certain Properties of Heterogeneous Polymeric Systems

The expansion of the spectrum of relaxation times towards longer times caused by the solid surface of the filler particles or of the support produces significant change in many properties of polymers.

The glass point of the majority of the systems investigated increases with the filler content. This happens in the systems polystyrene–fibre-glass[118], glass powder[122], kaolin[119], colloidal lead[120], and bentonite[121], poly(methyl methacrylate)–glass powder[101,122], bentonite[121,123,124], and kaolin[119], poly(vinyl alcohol), polyvinylbutyraldehyde, and poly(vinyl acetate)–fibre-glass[125], polyisobutylene–glass microspheres[85,126], polyurethane rubber–glass microspheres[126] and sodium chloride[127], polyamide 6,6–fibre-glass[128], phenolformaldehyde resins–highly dispersed iron powder[129] and graphite[130], poly(vinyl chloride)–graphite[130], alkyd-melamine resin–titanium dioxide[131], and epoxy-resin–titanium dioxide[132].

In many cases T_g is found to remain constant or to decrease on introduction of a filler. Thus T_g did not change or changed only slightly on introduction of carbon black into the following elastomers: natural rubber (up to 18 vol.% of carbon black)[133], polyisobutylene (up to 50%)[134], butadiene–styrene (SKS-30) and nitrile (SKN-40) vulcanised rubbers (up to 30 vol.%)[135,136], and fluororubber SKF-6 (up to 15 vol.%)[135]. Similarly chalk, kaolin, and lithopone (20 vol.%) hardly altered T_g for SKS-30 vulcanised rubber; chalk (20 vol.%) T_g had very little effect on T_g for SKN-40 vulcanised rubber[135,136]. Introduction of up to 50 parts by weight of aluminium powder into 100 parts of SKMS-10 butadiene–methylstyrene vulcanised rubber mixture did not increase T_g.[135]

The introduction of 10% of chalk into poly(methyl methacrylate) reduced T_g by 10 deg[137]; when the polymer is plasticised to some extent, the filling of polystyrene and poly(methyl methacrylate) with glass powder also lowers T_g.[122] Carbon black slightly decreased T_g for vulcanised *cis*-polybutadiene[134]. It has been reported that the introduction into polystyrene of 30% of iron powder appreciably lowered T_g for the composition[138], but the lowering is undoubtedly due to the degradation of the polymer on mixing with the filler.

There is no doubt that the absence of an effect or only a slight effect of inert fillers (chalk, kaolin, aluminium powder) on T_g for rubbers is due to the absence of a strong interaction between the rubber molecules and the surface of the fillers. The paucity of the experimental data precludes at present a reliable explanation of the independence of T_g for rubbers of the carbon black content over a fairly wide range of concentrations and there are even fewer grounds for an explanation of the lowering of the temperature as a result of the introduction of carbon black. Possibly the reason for this consists in the high flexibility of rubber macromolecules; another explanation is based on the hypothesis that in filled vulcanised rubber the density of cross-links is somewhat lower than in unfilled rubbers, or they are distributed less regularly[134].

Table 2. Effect of the filler (TiO_2) on the glass points of the vinyl acetate–vinyl chloride copolymer[109].

TiO_2 content, vol.%	0	1.1	3.0	4.8	6.5	12.8	19.1
Glass point, °C	30 and 77	32 and 73	27 and 62	28	48	51	51

* The volume concentration was calculated for 25 °C.

An unusual effect of fillers on the glass point of copolymers was observed in dilatometric studies on the system vinyl chloride–vinyl acetate (9 : 1 molar ratio) copolymer–rutile (with a mean particle diameter of 0.220 μm)[109]. Table 2 shows that, for a comparatively low degree of filling (up to 4.8 vol.%), the upper T_g, due to the presence of vinyl chloride units, increases, while the lower T_g, reflecting the mobility of the vinyl acetate units, changes only slightly. Further increase of the filler content leads to some increase in the glass point (now a single point) for the system and finally to its independence of the degree of filling. According to the authors[109], the lowering of the upper T_g can be accounted for by the adsorption of the acetyl group on the filler and the dissociation of the intermolecular bonds formed by these groups, thereby increasing the mobility of the vinyl chloride units. An increase of

¶ One of the constants of the familiar Aleksandrov–Gurevich equation[115,116] $\tau = \tau_0 \exp[(U_0 - \gamma\sigma)/RT]$, where τ is the relaxation time, σ the stress, T the temperature, R the gas constant, and U_0, γ, and τ_0 are constants characterising the relaxation properties of the polymeric material.

the TiO_2 content above 4.8 vol.% leads to the binding of a large number of acetyl groups and an increase of the lower T_g. One may expect that different effects of the filler on the upper and lower glass points will be shown also on filling other copolymers the units of the macromolecules of which differ appreciably in chemical nature and polarity.

The present author's investigations[139-141] established that the temperature variation of the strength of adhesive junctions tested under conditions of a very non-uniform distribution of stresses (tearing away, separation of separate layers, etc.) passes through a maximum in the region of glass formation. The presence of this maximum was explained by the fact that, on approaching the glass formation region from the low-temperature side, the rate of decrease of excess stresses increases in the vicinity of the apex of the growing crack as a result of the acceleration of relaxation processes and the decrease of such stresses leads to an increase of the load necessary to break the specimen. On further increase of temperature, the breaking load diminishes in consequence of the usual temperature-induced decrease of cohesive or adhesive strength. It was found that a decrease in the thickness of the layer of polymeric adhesive in the junction from 30 to 3 μm increased the temperature of the maximum strength of the junction by 10 deg. A similar effect was obtained when, instead of a homogeneous adhesive, a filled adhesive was employed, in which the average distance between the filler particles was close to 2 μm.[140] The observed increase in the temperature of maximum strength can be reasonably attributed to the retardation of relaxation processes in the vicinity of the solid surface.

The yield point (T_y) of filled polymeric systems is even more sensitive to filling than the glass point. This is because fairly large doses of filler in many cases produce a three-dimensional network apart from changing the number of conformations of the macromolecules and the spectrum of relaxation times[125,142-145]. The ability to form a three-dimensional structural network is clearly shown by fibrous and carbon black fillers. Thus the introduction into polystyrene of 20% fibre-glass hardly alters T_g but increases T_y by 40–50 deg[145,146]. The introduction of a filler increases T_y in the systems poly(methyl methacrylate)–fibre-glass[125], kaolin[119], and bentonite[121,124,137], polyisobutylene–Lavsan fibres[147] [a variety of nylon produced in the USSR (Ed. of Translation)], and mixed polyamide G-548–powdered metal oxides in large amounts (CaO, ZnO, MgO, and VO_3).[148] In certain systems the curve relating T_y to the filler content passes through a minimum in the region of low concentrations. This happens in mixtures of poly(methyl methacrylate) with kaolin[119], of polystyrene with bentonite[121], of polyisobutylene with very short (length 25–75 μm) Lavsan fibres[149], and of polystyrene containing 5% of a plasticiser with fibre-glass[146]; the introduction of 10% of chalk lowers T_y for poly(methyl methacrylate) approximately by 25 deg.[137] It may be that at least in some if not all systems the decrease of T_y is caused by the disruptive effect of the filler on the supermolecular structural formations in the polymer[149]. It must be emphasised that the introduction into polyisobutylene of longer Lavsan fibres (3 and 10 mm) as well as filling with fibre-glass of polystyrene not containing a plasticiser or containing more than 10% of a plasticiser inevitably leads to an increase of T_y.

It is known that in the deformation of homogeneous polymers in the state corresponding to rubber elasticity intermolecular bonds are broken as are a certain number of chemical bonds[150]. During the deformation of filled polymeric systems some of the polymer–filler bonds are also broken and in certain cases, in particular in rubbers filled with carbon black, also of filler–filler bonds[151]). After the removal of the load, the relaxation process tending to return the system to the initial state is accompanied by the reformation of the polymer–filler bonds (and also of the bonds between the filler particles in the relevant systems). Then part of the macromolecules and their aggregates are fixed in non-equilibrium positions. As a result, filled polymers exhibit some thixotropy[143,145,152]; the dissociation and reformation of the bonds and the fixation of a certain fraction of deformations of the rubber-elastic type result in a greater similarity of the behaviour of filled systems to that of polymeric materials under conditions of "chemical flow"[36,153-156].

Since the polymer interacts with the surface of solid particles, an increase of the degree of dispersion of the filler enhances its influence on the relaxation properties of the system. This was observed, in particular, in mixtures of poly(methyl methacrylate) or polystyrene with bentonite or kaolin[157] and on introduction of aminated bentonite into methyl methacrylate and subsequent polymerisation of the monomer[158]; for mixtures of polyethylene or butadiene–styrene or natural rubber with a number of mineral fillers, a linear relation has been established between certain properties associated with strength and deformation and the reciprocal of the filler particle dimensions (in the range of dimensions <0.2 μm)[159].

5. CHARACTERISTICS OF STRUCTURE-FORMATION PROCESSES IN POLYMER WALL LAYERS

In the previous section it was shown that wall layers differ from the bulk phase of a polymer in packing density and orientation and by a reduced rate of relaxation. These differences must influence also the structure-formation processes†. The looser packing and lower rate of relaxation should hinder both the formation of crystal nuclei and the growth of crystalline structures; on the other hand, orientation may favour crystallisation. The surface of an extraneous solid may affect the nucleus-formation processes also by influencing the change in surface energy on formation of a nucleus of the crystalline phase. As a result of the different contributions by these factors in various systems, in some cases the solid phase favours crystallisation to some extent while in others it hinders it up to complete suppression; in a comparatively small number of systems polymer crystals oriented in accordance with the crystal structure of the support (epitaxy) are formed at the crystal–support boundaries.

Promotion of Crystallisation in Wall Layers and Its Influence on the Properties of Polymeric Materials

In recent years the possibility of regulating the dimensions (and number) of spherulites in polymeric materials by introducing into the polymers a small amount of a finely dispersed additive[160-204] has been attracting the

† We are not considering the differences in the structures and properties of wall layers caused by the differences in the thermal history of these layers and the bulk phase of the polymer (in many cases the rates of change of the temperature of wall and bulk-phase layers differ significantly).

attention of investigators and technologists to a considerable degree. Kargin, Sogolova, and coworkers[174,175,182-184,187,190] showed that the mechanism by which these additives act involves the formation (by adsorption) on the surface of the solid particles of the nucleating agent of ordered regions of the polymer, which act as crystallisation centres. Such ordered regions are retained on the surface of the nucleating agent at high temperatures of the polymer melt when homogeneous crystallisation centres (in the bulk of the melt) are completely decomposed. When the number of added particles is sufficiently large, the number of heterogeneous centres of the surface greatly exceeds the number of homogeneous centres formed in the bulk of the polymer throughout the crystallisation. It has been shown that nucleus-forming agents do not affect the rate of the linear growth of spherulites. An increase in the number of crystallisation centres in combination with a constant rate of linear growth in fact leads to a decrease of the dimensions of the spherulites‡ and an increase of the rate of crystallisation. It is interesting to note that nucleating agents which alter the dimensions of polyethylene spherulites altogether fail to influence the formation and dimensions of its single crystals.[190]

Several hundreds of compounds, mainly organic[161-163,166,168-175,178,183-186,195,202], have been tested as nucleating agents. These investigations established that the effectiveness of the nucleation depends primarily on the physicochemical nature of the polymer and the nucleator. The particles of a satisfactory nucleating agent should be readily wetted by the polymer melt above its melting point (T_f) and should interact fairly strongly with it below T_f, but they should not dissolve in the polymer at T_f or below it; the melting point of the nucleus-forming agent should be higher than that of the polymer§. The similarity between the crystal structures of the polymer and the nucleating agent is not essential.

It has been noted[206-208] that carbon black present in considerable amounts (tens per cent) promotes the crystallisation of vulcanised rubbers and in some cases[206] larger crystals with more regular shapes are formed in carbon-filled rubbers on extension than in unfilled vulcanised rubbers. Possibly the higher rate of crystallisation in vulcanised rubbers is due to the lowering of the density of cross-links in them as a result of the adsorption of vulcanising agents on the carbon black[208].

The considerable reduction of the dimensions of supermolecular formations achieved by the use of nucleating agents leads to a significant improvement of a number of properties of finished articles. There is an increase in transparency[160,164,169-172,176,178,185,186,197], strength and capacity for deformation and extension[169,173,176,181,183-187,198,200], stress resulting in the formation of a "neck"[176,200], resistance to long-acting[199] and impact loads[164,166,168-172,176,188], hardness[161,169,176,186], and resistance to wear[188] and there is a decrease in the coefficient of friction[164] and in the evolution of heat on cyclic application of loads[200]. The presence in the polymer system of nucleating particles stabilises the supermolecular structure and properties of the material at elevated temperatures[184]; it has been shown that thermal-oxidative degradation of polyethylene takes place more slowly when an antioxidant with a nucleating action is introduced into the polymer[201]. This is evidence that the use of nucleating agents improves certain technological properties of polymeric materials[169,176,186], but an increase in the viscosity of the polymer melt has also been observed following the introduction of nucleating agents[191-195].

Inhibiting Effect of the Solid Surface on the Crystallisation of Polymers in Wall Layers

Apart from the present author's investigations[90,209,210], it was possible to find only a few unsystematic data concerning the retarding effect of the solid surface on crystallisation in the adjacent layer of polymer. To account for the protecting effect of carbon black in the thermal oxidation of polyethylene, it was suggested[211] that near the surface of the carbon black particles the concentration of the amorphous polymer phase is above average. On the basis of a study of the mechanical properties of mixtures of polyarylate F-1 with powders of various metals and mineral fillers, Korshak and Slonimskii concluded that the filler particles to some extent prevent the natural development of structure-formation processes in the polymers[117,212]. In contrast to the effect of carbon black on vulcanised rubbers mentioned above, the introduction of 50 wt.% of particles of carbon black into non-vulcanised natural rubber reduced the rate of its crystallisation (the introduction of 2% of carbon black did not alter appreciably this rate)[213]. This observation is related to the conclusion, based[214] on the results of an electron-microscope study of mixtures of natural rubber with carbon black and activated silica gel, that in the vicinity of the particles of these fillers there is a layer 0.03–0.05 μm thick in which rubber does not crystallise¶. Schoon and Adler[214] suggested that crystallisation is hindered by mixtures adsorbed on the surface of the filler but did not put forward any facts in support†.

The effect of the thickness δ of the polymer layer between two glass surfaces on the kinetics of the crystallisation of certain polymers has been investigated[90] by microcinematographic techniques. The Figure presents curves characterising this effect for isotactic polypropylene; similar curves were obtained for guttapercha and cellulose tribenzoate. Curve *2* shows that a linear rate of growth of spherulites, which is low at low values of δ, increases with δ, and, for a certain thickness of the film when the effect of the surface no longer operates, ceases to depend on δ.

The minimum in curve *3* describing the effect of δ on the rate C_3 of nucleus formation calculated per unit volume of the polymer can be explained as follows. C_3 is the sum of the rates of nucleation on the polymer–glass interface and in the bulk of the film. Nucleus formation on the surface is slower than in the bulk phase. In the region of low values of δ surface nucleation predominates; in this range of thicknesses, an increase of δ favours a more

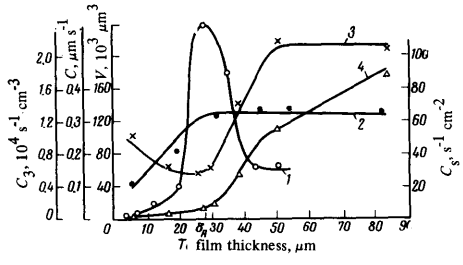
‡ The method of modifying the structure and properties of polymeric materials by introducing into the polymer surface-active substances[205] yields a result similar in many respects, but it is based on a different mechanism of action on crystallisation.

§ Amorphous polymers, liquids, and even air exhibit some nucleus-forming properties[184,187,192,193,195].

¶ The photographs quoted by Schoon and Adler[214] are insufficient to determine the validity of this conclusion.

† There exist data of the opposite kind[199]—crystals of natural rubber which do not melt up to 125°C (the usual crystals of natural rubber melt[215] at 28°C) grow on the surface of amorphous carbon.

rapid increase in the volume of the film than in the number of nuclei and the C_3 curve moves downwards. The minimum in curve *3* corresponds to a thickness δ_A for which the contribution of the bulk-phase nucleus formation to C_3 begins to increase sharply. For sufficiently thick films, bulk phase nucleation plays a significantly more important role than surface nucleation and the number of nuclei in the film increases in proportion to its thickness, like its volume. This results in C_3 being independent of δ. This explanation is confirmed by the form of curve *4*, which shows the variation of the rate of nucleation C_S, calculated per unit surface, with δ. C_S is almost independent of film thickness up to δ_A and, when δ_A is reached, the slope of curve *4* rises sharply.



Effect of the thickness of the polypropylene layer, on the volume of spherulites (V, curve *1*), linear rate of growth of spherulites (C, curve *2*), and rate of nucleus formation (C_3, curve *3*—rate calculated per unit volume of the polymer; C_S, curve *4*—rate calculated per unit surface of the specimen).

The variation with thickness of the rate of linear growth of spherulites (curve *2*) and nucleus formation (C_3; curve *3*) is responsible for the maximum (observed in this investigation and previously[209]) in the curve relating the volume of the spherulites to δ (curve *1*) in the region of thicknesses for which the crystallisation behaviour of the polymer layer is determined by the crystallisation in surface layers.

In the case of isotactic polystyrene the linear rate of growth of spherulites depends on δ similarly, but, probably owing to the low rate of homogeneous nucleus formation in this polymer[183], C_S is independent of δ.

The decrease in the thickness of the polypropylene layers achieved by increasing the extent of its filling with glass powder influences the crystallisation kinetics in the same way as the decrease (described above) of the distance between the comparatively large glass surfaces confining the film.

The same surface may influence in opposite ways the crystallisation of different polymers. Thus the inhibiting effect of the glass surface on the crystallisation of certain polymers has been described. However, in the study of a film of polyamide 66 compressed between glass surfaces it was established that a decrease of its thickness from 30 to 10 μm results in an increase of the rate of linear growth of spherulites[216].

A solid surface can influence not only the rate of crystallisation processes but also the morphology of thin films. Thus in guttapercha[90,209,217], cellulose tribenzoate, and isotactic polypropylene and polystyrene[90,217] films with a thickness less than several micrometres imperfect crystalline formations were observed, while spherulites were formed in thick layers. For $\delta < 1-1.5$ μm, no structures could be observed at all with the aid of a light microscope. Similarly, films of many polymers with a thickness less than 0.1 μm on metallic surfaces did not exhibit a spherulite structure, in contrast to thicker films[218]. In films of mixtures of poly(ethylene adipate) or poly(ethylene sebacate) with poly(methyl methacrylate) or certain other amorphous polymers with a thickness amounting to several hundreds of ångstroms, no structure was observed either, while films with a thickness in excess of 20–30 μm were crystalline[219]‡.

The crystallinity of polypropylene films with a thickness of 1–1.5 μm was also not observed in the studies of polypropylene by differential thermal analysis and by X-ray diffraction[90,217]. Crystallisation does not occur in such thin films, possibly as a result of the strong interaction of the macromolecules, packets, and other structural elements of the melt with the solid surface, which is so pronounced that the activation energies for nucleus-formation processes become very high and the rates of these processes are correspondingly negligible. It is also possible that the change in surface energy in certain solid–polymer systems during the crystallisation of the polymer in thin layers is so great that this phase transition becomes thermodynamically unfavourable.

It may be supposed that in the presence of a very weak interaction between the polymer and the surface of an extraneous body the surface does not affect the crystallisation processes, when the interaction is very pronounced the processes are retarded, and for moderate interactions the surface exhibits a nucleus-forming effect§.

Epitaxy of Polymers

As already mentioned above, in certain systems thin polymer films have an epitactic structure. Thus on freshly cleaved (001) surfaces of the crystals of certain alkali metal halides, usually sodium chloride, oriented crystallisation of polyethylene[222–226], isotactic polypropylene[226,227], poly-3,3-bischloromethylcyclobutane (pentone), poly(ethylene terephthalate), isotactic polystyrene[226], polyoxymethylene and polyoxypropylene[227], polyamides 6.66 and 610, [228] polyamides 7 and 8, [229] polyacrylonitrile[230], and polyurethane[229] was observed. Epitactic crystallisation of polyacrylonitrile on a freshly etched surface of crystalline quartz has also been observed[231]. A case of the epitaxy of polyethylene on stretched films

‡ These relations are closely related to the findings described above (p. 704) namely a sharp transition from a structured film of silver telluride on glass to a structureless form when the thickness is 300–350 Å and the variation of the structure of vacuum-deposited films of a number of metals with their thickness in the range up to 70–80 Å; a similar variation is observed also for tantalum up to a thickness of 250 Å. [220]

§ This hypothesis is fully consistent with the results of the calculations of Moazed[221], who showed that a stable epitactic nucleus of a low-molecular substance can be formed from its vapour only when the angle between the surfaces of the nucleus and the substrate is in the range 10–40°.

of polyoxymethylene has been described, the needlelike crystals of polyethylene being oriented perpendicular to the direction of the stretching of the support[232].

The crystallisation of polyethylene, pentone, and polystyrene (on alkali metal halides) begins with the formation of needlelike crystals arranged along the [110] direction on the support; subsequently these crystals grow, giving rise to an oriented network structure. Polypropylene forms squares with dimensions of up to 20×20 μm with the sides parallel to the [100] and [010] directions of the salt crystals and poly(ethylene terephthalate) and polyoxymethylene form long (up to 100 μm for PETP and up to 6 μm for POM) needles along the [110] direction on the alkali metal halide crystals. It has been established by electron diffraction that molecular chains in polyethylene, polystyrene, and pentone crystallites are oriented preferentially parallel to the surface along the [110] direction of the support, while in polyoxymethylene, polypropylene, and polyoxypropylene crystallites the chains are arranged perpendicular to the surface of the support.

Two explanations are possible for the orienting effect of the surface of alkali metal halide crystals[227]. One possibility involves the attribution of the orienting effect to sequences of similarly charged ions arranged along the [110] direction of the (001) plane. Another explanation is based on the nucleus-forming effect of dislocations, formed in large amounts when small crystals are cleaved, extended along the [110] direction; each of these dislocations contains a multiplicity of sections with an enhanced surface energy.

For epitaxy (as for the nucleus-forming agent–polymer systems), there is apparently no obligatory requirement of a correspondence between the dimensions of the crystal lattices of the support and the polymer. Thus polyethylene exhibits epitaxy on lithium fluoride, sodium chloride, sodium bromide, sodium iodide, potassium chloride, and potassium iodide despite the considerable differences in the lattice dimensions of these crystals (the lattice constant a_0 for the crystals varies from 4.01 to 7.05 Å).[226]

As a result of the presence in polymers of supermolecular formations, each of which behaves in many processes as a single kinetic entity, the wall layers of the polymer at its boundary with the solid surface differ in some of their properties from the bulk-phase layers and their thickness may exceed that of wall layers in low-molecular substances.

The relaxation processes in the wall layers of the polymer are retarded. This is because the solid surface in contact with the polymer not only restricts the volume accessible to the kinetic units of the polymer in their thermal motion, but also combines with them via intermolecular interaction forces. Interaction of the solid surface with the polymer can result in a partial orientation of the polymer in the wall layer and also in a lowering of the packing density.

The different contributions of these factors (rate of relaxation and orientation and packing density) in various polymer–solid surface systems give rise to a wide range of effects of solid surfaces on relaxation and structure-formation processes in wall layers of polymers. In some systems the solid surface promotes to some extent the crystallisation of the polymer while in others it either retards or even completely suppresses the crystallisation.

Further theoretical and experimental studies of wall layers of polymers are essential, in particular with the aid of methods such as nuclear magnetic resonance, infrared spectroscopy, radiothermoluminescence, and a combination of these methods, and also electron and light microscopy together with the investigation of the mechanical, electrical, and physicochemical properties of heterogeneous polymeric systems. Such study will not only throw light on certain fundamental characteristics of polymers but will help develop technological processes for the preparation of new materials of importance in engineering.

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