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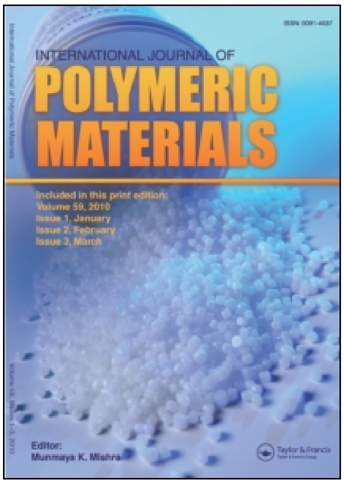

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On Liquid Water Isothermic Segregation in a Medium of Highly Elastic Hydrophobic Polymers Such as Polymethyl Methacrylate

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On Liquid Water Isothermic Segregation in a Medium of Highly Elastic Hydrophobic Polymers Such as Polymethyl Methacrylate

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Deglassifying the films of plasticized polymethyl methacrylate (PMMA) in heated water causes the spontaneous segregation of water drops of micrometer and larger radius. This process which is accompanied by a change in the film size is impossible in structureless hydrophobic systems. The phenomenon indicates a structural organization of polymer chains, which are responsible for adsorption of a certain amount of molecular water by hydrophobic PMMA. From a thermodynamic standpoint, "structural hydrophily" is of entropic nature and is provided by the micropore generation caused by fluctuations. The micropores are stabilized through the capture of water molecules. When the polymer transforms to the highly elastic state, zones of a dynamically active microporous sponge are formed with the participation of moisture. In these zones, the fluctuation results in the formation and destruction of hydrophobic slits, which ensure the appearance of the water interlayers and drops of critical size that merge into the stable water phase. A thermodynamic model of the process is considered.

KEY WORDS Polymethyl methacrylate, hydrophobic polymers, water segregation.

INTRODUCTION

Water diffusion in highly elastic hydrophobic polymers is complicated by the segregation of water drops.[1-3] This phenomenon is of practical interest because of its influence on the exploitation properties of polymeric materials. However, a theory of the water phase formation under such conditions has not been completed. All the investigations performed in this line are based on the concept of interaction between the diffusing water molecules and water-soluble impurities, which are present in the materials.

At the same time, the above phenomenon is typical for many polymers that differ in technology of their production and processing (natural and synthetic rubbers, polyolefins, polyvinyl chloride, polycarbonate, polysulfone, polyvinyl acetate, and so on[1-3]). This fact is in rather poor agreement with the presence of water-soluble impurities in all the polymers and suggests that the more common mechanism of the phenomenon exists.

In this work, the formation of the drop water phase is studied by the example of plasticized hydrophobic PMMA. The water-soluble impurities are not necessary for the realization of this process, but the high molecular-segmental mobility is required.

EXPERIMENTAL

Commercial PMMA (M_w = 135,000, M_w/M_n = 2.0, T_g = 380 K), which was produced by emulsion polymerization of MMA in the presence of lauryl peroxide and contained about 1% of residual MMA, was used both in unpurified and purified forms. The purification was conducted through the polymer precipitation from a methylene chloride solution by methanol followed by additional extraction by methanol in a Soxhlet apparatus for 6 hours. The 5–35 μm thick films were prepared from a PMMA solution in distilled methylene chloride (MC) at the polished glass surface by their exfoliation with water upon MC evaporation. Then, the films were kept in a vacuum for 24 hours. In order to accelerate the structural relaxation, a portion of the films was annealed in a vacuum at 343–353 K for eight hours.

For PMMA plasticization, spectroscopically pure dibutyl phtalate (DBP) was used, its concentration in MC solutions being 2.5, 6.0, 10.0, 20.0, and 30.0%. Dibutyl phtalate and PMMA have virtually the same solubility parameters equal to 19.3 and 19.0 $(\mathrm{J/cm^3})^{0.5}$, respectively, whereas that for water equals to 47.0 $(\mathrm{J/cm^3})^{0.5}$.[4] The above fact points to identical hydrophoby of both components; therefore, DBP cannot be considered a water-soluble impurity.

To determine the amount of liquid water segregated, the sizes and number of water drops, the method of the turbidity spectra was used, which is generally applied for such purposes.[1,3,5,6] The method is based on the difference in the indexes of refraction for water and polymer. These indexes are equal in magnitude for PMMA and DBP (1.49).

The turbidity spectra were recorded using the UV Vis Specord instrument. The film strips of size 10 × 30 mm were placed in spectroscopic cells, which were filled with distilled water and were heated in a thermostat. The volume content of water drop phase Φ% and the average radius of the drops R were calculated by formulas $\Phi = \tau/g$ and $R = \alpha\lambda/2\pi\mu_0$, where $\tau = 2.3D/l$ is the turbidity of the 1 cm thick film there, D is the optical density at λ = 546 nm, l is the film thickness, $\mu_0 = 1.33$ is the index of refraction for water, α and g are the parameters determined from the calibration graphs given in References 5 and 6. The n index, which is required for the use of these graphs, was found from logarithmic anamorphoses of the D = const λ^n relationships in the range $400 < \lambda > 700$. The relative index of refraction $m = \mu/\mu_0$ and the index of refraction μ for optically transparent PMMA saturated by water (at the water volume fraction of 0.025) are taken equal to 1.115 and 1.486, respectively.[2,7] The radius of voids, which are left upon drying out the turbid samples, was calculated by formula $R = \rho\lambda/2\pi\mu$ (λ = 500 nm, μ = 1.5, ρ was determined from the calibration plot of n versus ρ[8,9]).

RESULTS

The turbidity spectra for the films of unpurified PMMA are observed at a temperature of water above 343 K. Figure 1 shows these spectra, and Figure 2 shows the cor-

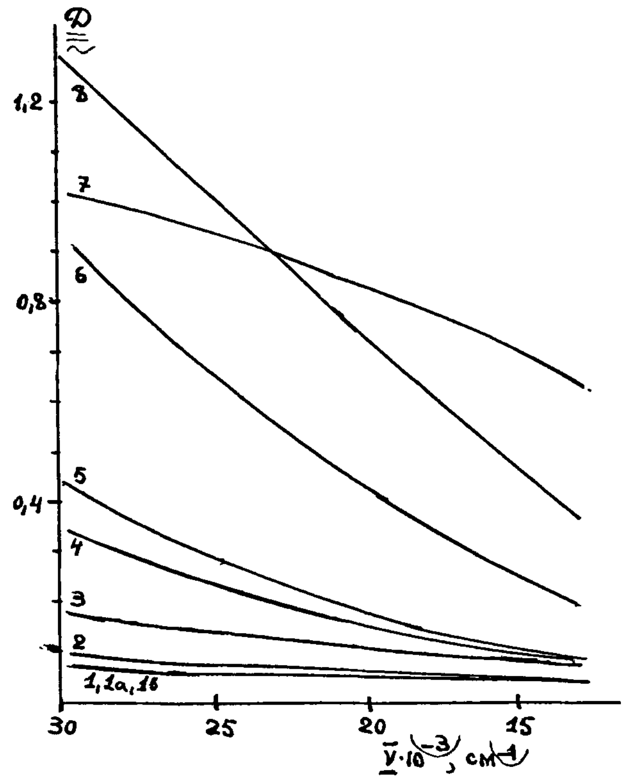

FIGURE 1 The turbidity spectra of the PMMA films: arbitrary thick (1), 10 μm thick (2) and 35 μm thick (1a, 1b, 3–8), after heating at 343 K (1a, 7), 353 K (1b, 5), 363 K (4), 368 K (2, 6), and 372 K (3) for 200 min (1a, 1b), 20 and 100 min (2), 5 and 50 min (3), 10 min (4), 20 and 200 min (5), 10 min (6), and 110 min (7) prepared from the unpurified (1a, 1b, 2, 4–8) and reprecipitated (3) polymers and from that containing 27% of DBP (7) with the preliminary annealing of the films (1a, 2b, 3) and without the anneal (2, 4–8). The spectra are obtained in an optical cell filled with water (1–7) and in air (8). The latter spectrum is recorded after drying the film exhibiting the spectrum (4).

responding $\Phi(t)$ curves. The turbidity increases as water temperature rises. This process is sensitive to the structural relaxation proceeding in the polymer. Thus, the freshly prepared films reach fast the limiting turbidity (Figure 2, curves 2a, 5–7). However, time of the attainment of the limiting value increases on prolonged keeping the films. If such samples were preliminary annealed at 343 K, these virtually do not become turbid in water at the same temperature (Figures 1 and 2, curves 1a and 1b), but lose their initial activity (Figure 1, curve 5 and Figure 2, curves 2a and 5). At elevated temperatures, this process proceeds more slowly in the annealed films (Figure 2, curves 3 and 4) compared to the unannealed ones (Figure 2, curves 6 and 7).

The decrease in the thickness of films prepared from unpurified PMMA causes a disproportionately sharp reduction of the limiting turbidity. Thus, Figure 1 (curve 2) shows the insignificant turbidity for the 10 μm thick film at 368 K. This value is rather far from 0.28 the value that to be expected from the 4, 5, and 6 curves observed at 363, 353, and 368 K, respectively, for the 35 μm thick films. The above peculiarity

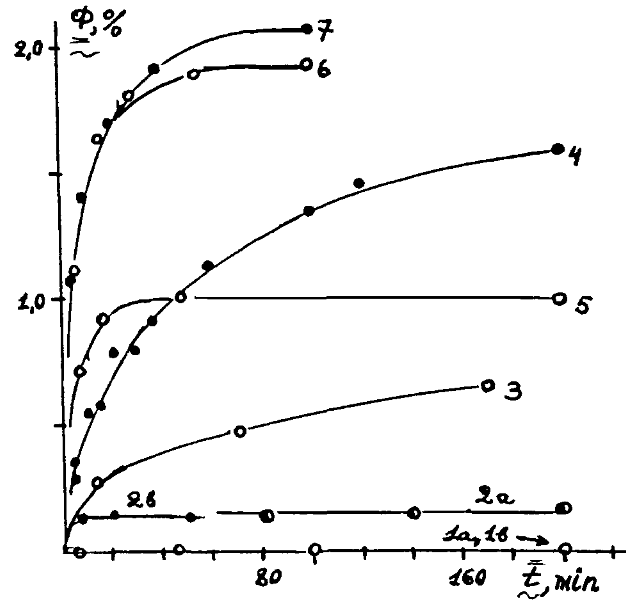

FIGURE 2 The dependence of the volume content of drop water in the polymer on heating time for the 35 μm thick films prepared: from unpurified PMMA with dry annealing of the films (1a, 1b, 3, 4) and without annealing (2a, 5–7) and from the reprecipitated PMMA with the dry film annealing (2b) at temperatures of 343 K (1a, 2a), 353 K (1b, 5), 363 K (3, 6), 368 K (4, 7), and 372 K (2b).

is connected with fast removing the plasticizer remains (MMA and MC) from the thin films. With dry annealing of samples, as opposed to annealing in water, the residual MMA and MC are poorly removed from the films. Thus, the IR absorption spectra show that the bands at 700 and 735 cm^{-1}, which are characteristic of MC, virtually do not change even after the additional film treatment in a vacuum for 10 hours. The above bands hardly decreases after the annealing but disappear completely when the films are heated in water for a short time.

The role of residual plasticization is minimum for monomer-free samples. The turbidity of such samples is insignificant, and the process stops fast (Figure 1, curve 3 and Figure 2, curve 2b) due to the rapid removal of the residual MC.

As distinct from the above situation, the stimulating effect of the larger size DBP molecules on the process is retained also for thick films over a wide range of temperatures and long times. In particular, the curve 7 in Figure 1 was obtained at the DBP content of 27%, at 343 K in a time of 100 min, whereas the samples did not become turbid in the absence of DBP (Figure 1, curve 1a).

Figure 3 shows in coordinates Φ, $t^{0.5}$ the curves of the drop water accumulation at 363 K in the samples, containing 6–30% of DBP. The process is accompanied by a small loss of DBP only (no more than 10% for 1.5 hour at the DBP content of 30%). The shape of the curves in Figure 3 suggests the presence of two kinetic stages in the process—a fast and a slow one. These stages cannot be given a common quantitative description, because the different Φ values correspond to the same instants of time at the same DBP concentrations.

The process under study is accompanied by a characteristic change in the sample

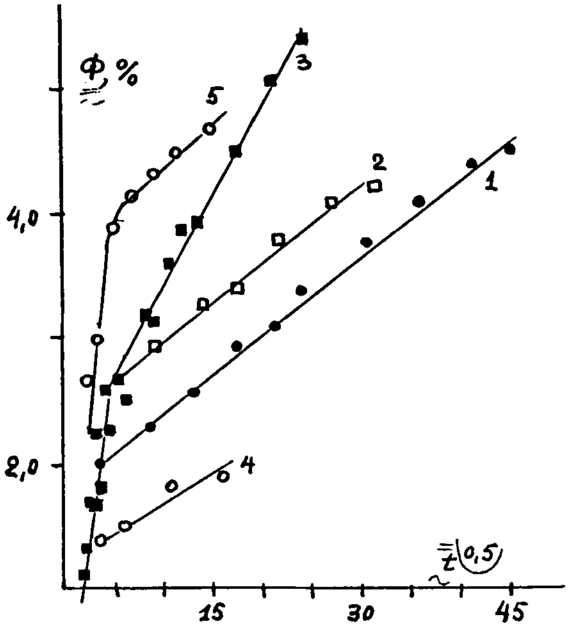

FIGURE 3 The curves of the accumulation of drop-liquid water in plasticized PMMA at the DBP content of 6% (1), 10% (2, 3), and 30% (4, 5) for the films of 18 μm (1), 16 μm (2), 25 μm (3), 5 μm (4), and 13 μm (5) in thickness.

sizes: their thickness increases in parallel with a decrease in the length and width. The thickening is especially large (up to 50%) when the film edges are not rigidly held. The rigid mounting decreases the turbidity rate. However, the resulting internal stress causes often an abrupt increase of the turbidity in the course of the experiment because the film edges are drawn from the fixing frame. Thus, the data in Figure 3 reflect not only the internal properties of the samples, but also the action of the external mechanical prevention of the deformation.

Figure 4 shows the temperature dependence of Φ for liquid water, which is accumulated for 15 min at the various DBP contents. The curves 1–5 refer to the DBP-free films, of which the curves 1–3 are obtained at 368 and 372 K and correspond to the limiting Φ value, because these characterize reprecipitated PMMA, losing fast the MC remains. The curves 4 and 5 characterize annealed and unannealed films, respectively. These films were tested at various intervals during storage at room temperature. As is seen, PMMA, whose internal structure is not completely relaxed, displays a higher activity. Thus, about 2% and 0.2–0.3% of water is segregated for 15 min in the freshly prepared films and in the annealed ones, respectively.

The relaxation is evident at low DBP content as well. As an example, we refer to the curves 6, 7 and 9, 10 that were obtained at the DBP content of 2.5% and 10.0%, respectively. Note that every point in the curves 6 and 9 was obtained using an individual sample of the freshly prepared film, and those in the curves 7 and 10 were obtained without the sample exchange, when the action of heat was completed. The curve 8 corresponds to the aged film, containing 6% of DBP. The curves 11 and 12,

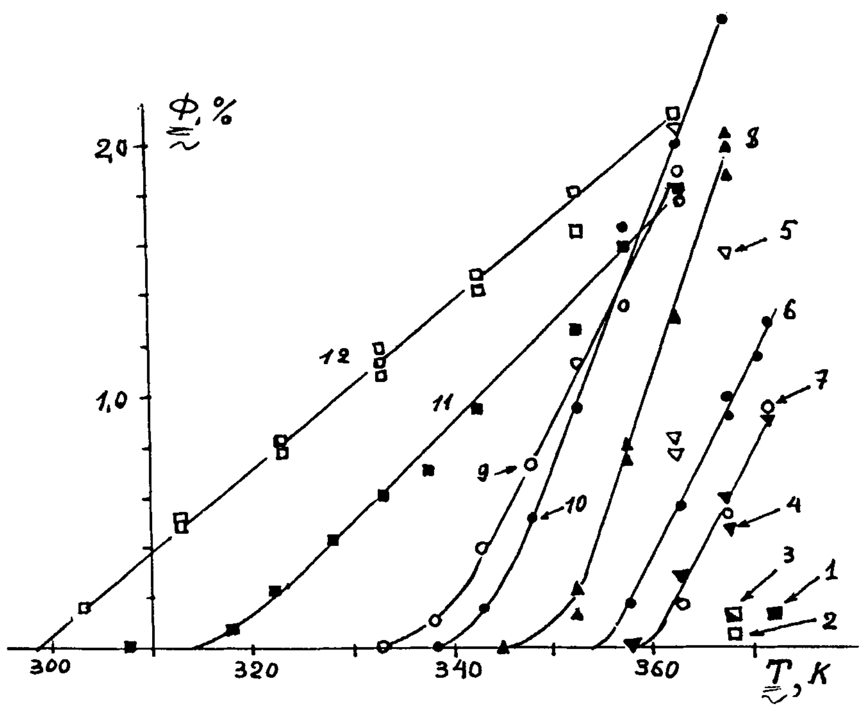

FIGURE 4 The temperature dependence of the amount of drop-liquid water segregated for 15 min in the films prepared from reprecipitated (1) and unpurified (2–12) PMMA at the DBP content of 0% (1–5), 2.5% (6, 7), 6% (8), 10% (9, 10), 20% (11), and 30% (12) after dry annealing of film (1, 4), without annealing (2, 3, 5, 6, 8, 9, 11, 12) and with a stepwise increased temperature of the single sample (7, 10). The thickness of the films is: 10 μm (2), 13 μm (12), 17 μm (3), and 30 μm (5–11).

which were obtained for the samples with 20 and 30% of DBP, respectively, are identical for the freshly prepared and aged films.

The date presented in Figure 4 show that drop water appears in plasticized samples at glass transition temperatures, T_g, which are determined for analogous samples by the DSC method[4] and equal to 355–360, 345–350, 333–338, 315, and 300 K at the DBP content of 2.5, 6.0, 10.0, 20.0, and 30.0%, respectively. Thus, DBP displaying the identical hydrophoby as PMMA, causes the segregation of liquid water drops on deglassification of the polymer. It is notable that as the DBP content increases, and the T_g value is correspondingly reduced, the slope of the straight-line portions of the 8–12 curves decreases, i.e., the temperature sensitivity of the developed process is diminished.

The following may be mentioned regarding the average radius of water drops *R* and their number *N* in unit volume. In the absence of DBP, the *R* value is constant from start to finish of the process and is the same for unannealed and annealed films: 210 ± 20 and 310 ± 20 nm, respectively, at 353–363 and 368–372 K. In the initial stage of the process, the *N* number in the unannealed polymer grows more sharply compared to that in the annealed one. For example, at 368 K, *N* equals to 1.0×10^{11} and 0.1×10^{11} cm^{-3} (within 5 min), 1.8×10^{11} and 0.9×10^{11} cm^{-3} (within 100 min) for the unannealed and annealed polymers, respectively (Figure 2, curves 7 and 4). At the same instants of time at 363 K, the corresponding *N* values equal to 2.8×10^{11} and 0.5×10^{11} cm^{-3}, 5.0×10^{11} and 1.4×10^{11} cm^{-3} (Figure 2, curves 6 and 3). Thus, a change in the internal structure, which is caused by the dry annealing, decreases the number of drops.

In the presence of DBP, the average radius of drops in PMMA increases during the process in the ranges 300–450, 400–700, and 300–1000 nm at the DBP content of 2.5, 6.0 (10.0), and 20.0 (30.0)%, respectively. That is, the R value varies in magnitude (as the Φ factor does) as a result of mechanical action preventing the deformation of the visco-elastic material.

The considerable resemblance of the liquid water segregation in deglassified PMMA to the corresponding process in elastomers[3] should be noted. However, the turbid elastomers become transparent reversibly as a result of their drying, whereas this process in PMMA is hindered by glass transition. On the contrary, the turbidity of dry PMMA even increases when the DBP content is low or equal to zero (Figure 1, curves 4 and 8). This phenomenon results from an increase in light scattering due to the replacement of liquid water with air. The calculations by the method described in References 8 and 9 showed that the average radius of voids in dry DBP-free films equals that of segregating water drops. Repeated wetting of the dry turbid films brings about their initial turbidity (Figure 1, curve 4), but the drop radius remains unchanged. The above result indicates that interaction between the PMMA transparent films and water is not limited to filling the available voids and is connected with the displacement of the polymer matter from the zones of growing drops. This result is also indicative of the absence of dissolved macromolecules in the drops.

The initial optical transmittance of the dry turbid films is restored by heating. The films become transparent at the marked rate at temperatures close to the T_g value (380 K), but the process slows down rapidly, because for the process to take place an additional rise of a temperature is required. At 393 K, the process is completed in about 0.5 hour. The analysis of turbidity spectra by the method[8,9] showed that clarifying of the films proceeded through a reduction of the void number, while the R value decreased insignificantly. That is, this process occurs not at the expense of a viscous flow of the material into the voids, but by the "unfreezing" the stored elastic deformation and a fast collapse of voids. Indeed, a prolonged decrease in the R value over a period of many tens of hours suggests to the mechanism of the flow of a very viscous polymer.[10]

DISCUSSION

According to the above considerations, the high molecular-segmental mobility in PMMA causes an isothermic interaction between the water and polymer represented by the following scheme:

$$\text{external volume of water} \xrightarrow{\text{I}} \text{molecular surface water} \xrightarrow{\text{II}} \text{molecular dissolved water} \xrightarrow{\text{III}} \text{drop size liquid water.}$$

An important point is that the phase transition of molecular water diffusing in the polymer is not connected with water-soluble impurities or with filling the initially existed voids and occurs at the expense of mechanical work.

The diffusion coefficient for the water molecules in PMMA, d, at T_g is known to be equal to 3.3×10^{-8} cm^2/s and to increase as a temperature rises.[11] Time, $t = x^2/6\alpha$,[12] of saturation of the films 40 μm (l) in thickness ($x = 0.5l$) by molecular water should be less than 20 s. Therefore, the segregation of drop size water (stage III), which is continued for many hours, is not limited by the diffusion stage (II) and is determined by the specific structural properties of the polymer. Note that in a homogeneous structureless medium, such a process is impossible because of the absence of supersaturation of the medium by dissolved water under isothermic conditions and violation of the second thermodynamic low.[13]

As was mentioned above, this problem is considered in various publications applying the concept of a low degree of structure of a medium. This hypothesis postulates the formation of osmotic cells involving water-soluble impurities, which are heterogeneously distributed in the structureless medium.[1-3,13] This assumption is unsuitable for our case. We believe that the reason for the observed phenomenon must lie in the peculiarities of the supermolecular structure that ensures the occurrence of stage III.

Obviously, the structural element—generator of the initial water drops—should operate in the following way. First, it will accumulate a needed amount of water molecules (despite the inherent hydrophobia of the macromolecules) and then will segregate the accumulated water as drops, realizing the hydrophobia of the macromolecules. The above scheme involves a microporous sponge formed from the dynamically mobile polymer chains. The affinity of the sponge to water depends on the appearance of fluctuation micropores. It is precisely these micropores that sorb water in hydrophobic highly elastic polymers.[14]

The function of the water drop generator of can be described assuming that the main structural element of noncrystalline polymers is a "superglobule," which is formed from a large number of macromolecules.[15] The PMMA globules observed in the electron-microscopic photographs are 10–15 nm in diameter.[16,17] According to References 18 and 19, every globule is insulated by a shell of the tightly packed segments of polymer chains. Assuming further that the molecules are in random coil conformation, the chains must undergo considerable stretching in the radial direction of the globule, thus redistributing the load on the shell.

For glassy PMMA and PS, the stretch of macromolecular coils is proved by the methods of small-angle X-ray scattering and neutron scattering[20-22] (their radii are larger than those of coils in a Θ-solvent by 10–20%). The above stretch is also demonstrated by a jump of an internal pressure at a temperature close to T_g, which is connected with the storage of the energy of the elastic chain tension amounting to 25–30 cal/cm^3 in PMMA and PS glasses.[23]

Glassy PMMA falls in the category of nonporous sorbents.[24] However, mechanical processing of the polymer in a ball mill at 77 K increases its sorption capacity with respect to nitrogen to the level of activated carbon.[25] This suggests that the expended work results in loosening of the globule packing to the state of a microporous sponge.

The free volume, fraction at T_g for a typical PMMA, equals 0.019 (the method of small-angle X-ray scattering[26]) or 0.021 (the procedure of hydrostatic compression[27]). At the same time, the relationships of water vapor sorption indicates that the structural voids stored in PMMA are not filled. Thus, the polymer and water volumes are approximately additive until the water content attains 2 wt.%,[7] and the heat of sorption equals to zero. At the relative moisture $P/P_s > 0.95$, a deviation from the Henry' low is observed owing to the appearance of internal structural surfaces in PMMA, which separate water clasters consisting of some molecules and molecular chains with the hydrogen bonds.[2] It appears to be advantageous for the chain sponge to physically bind a certain amount of water molecules to form associates. This process results in a change in the chain conformation and in a decrease of the elastic load in the sponge. The entire energy of such interaction goes into the work directed against the structural forces. This phenomenon makes itself evident in the zero heat effect and in the formation of a colloidal solution of osmosis-bonded water.[28]

Let us consider the system, containing a constant number of particles, using the method of thermodynamic potentials. From the basic thermodynamic relationship $TdS = dU + PdV + \delta W$, where δW is the elementary work against structural forces, the following expressions for the Gibbs' energy and the enthalpy, respectively, can be written: $dG = -SdT + VdP - \delta W$ and $dH = d(U + PV) = TdS + VdP - \delta W$. Hence, we obtain for the isobaric-isothermic process $-dG_{P,T} = \delta W$. Because in the case considered $dH = 0$ and $dU = 0$ ($PdV = 0$ due to additivity of the bulks of the components), we have $-dG_{P,T} = TdS = \delta W$ or $-\Delta G_{P,T} = T\Delta S = W$. Thus, the driving force of the adsorption of molecular and cluster water by a hydrophobic polymer when the sorption heat equals to zero is a decrease in the Gibbs' energy caused by an increase in the entropy of the system due to the growth of the entropy of the polymer-chain network and to mixing of the components.

Based on the thermodynamic theory of vacancy solutions for nonporous, wide-porous, and microporous sorbents,[30,31] one can consider that the moistened intraglobular filling is turned into a sponge with an ideal vacancy solution over the interval, wherein the Henry's low is valid ($P/P_s \leq 0.95$). As the clusters and chains of associated water molecules appear, the vacancy solution ceases to be ideal. In accordance with the concept developed in References 30 and 31, a binary solution, comprising an adsorbed substance and adsorption vacancies, is always at osmotic pressure equilibrium with the adsorption vacancies.

In other words, the globule filling of a hydrophobic polymer carries a structural (entropic) "water-soluble" component produced by the elastic tension and by the flexibility of the polymer chains. Adsorption vacancies—fluctuation micropores—act as such a component. Due to the capture of water molecules and clusters, the micropores are stabilized as elementary osmotic cells and create the osmotic pressure in the moistened sponge. However, the vacancy-entropic hydrophilia by itself cannot ensure the integration of colloidally dispersed water in the body of the sponge, into the drops of the stable liquid phase. The realization of this phase transition is impossible without supersaturation of the sponge medium by water.

The mechanism of the supersaturation comes into effect with the availability of a high molecular-segmental mobility of the polymer ($T \geq T_g$), if the sponge structure enables the cooperation of the chain segment movements under the water action. In circumstances where cooperative fluctuations oscillations of hydrophobic segments occur; sufficiently broad slits can open and collapse in the sponge matrix due to the fluctuation. These slits can accumulate water in the amount required for the appearance of the water interlayers and drops. As this takes place, the factor of supersaturation appears as a result of the manifestation of hydrophobic forces.[32]

The thermodynamic parameter π connected with the colloidal state of a substance constitutes of a variety of components.[32] For this consideration, the negative component resulting from the forces of the molecular attraction of the slit walls and the structural one connected with the structure of the water interlayer are of importance. The latter component is different in its structure for hydrophobic and hydrophilic slits, the wall attraction to one another and the wall repulsion. The point is that the water density is reduced near the hydrophobic walls, and that is enhanced in the bulk between the walls. In this case, the attraction force of the walls exceeds considerably that of the homogeneous water interlayer. On the contrary, in hydrophilic slits, water is strongly linked to the walls, forming thick adsorptive layers, mutual overlapping of which ensures a total positive disjoining pressure.[32]

According to Reference 32, in the general case of thermodynamic equilibrium, the disjoining expression pressure

$$\pi = P - P_v, \tag{1}$$

where P and P_v, respectively, are pressures at the interlayer surface and in the bulk, which is bonded with the interlayer. However, with overlapping the ordered adsorptive layers, the possibility of unbonded water to form drops is excluded in hydrophilic slits. (Note that the drops do not form in a wood with the slits attaining a width of 10 nm.[28]) For such layers, which are in equilibrium with vapor, the π value is determined by the expression identical to that for osmotic pressure P_{os}[32,33]:

$$\pi = P_{os} = RT \ln(P_s/P)/V_m \geq 0,$$

where V_m is the molar volume of film water. The relative vapor pressure $(P/P_s) \leq 1$ points to the absence of slit supersaturation by unbonded water. If a portion of water molecules unites accidentally into a germ drop, then the latter, exhibiting an elevated vapor pressure $P/P_s > 1$,[33] will immediately evaporate into the layer of bonded water.

In the case mentioned above, the subtrahend in Equation (1) disappears ($P_v = 0$), and the thermodynamic equilibrium is realized under conditions of balance between the external and internal pressures, which are identical to the swelling pressure: $\pi = P_{os} = P$.

In accordance with these considerations, the polymer-chain sponge formed from hydrophilic slits is in a state of quasi-equilibrium interaction with water and should swell uniformly in any arbitrarily taken region.

As distinct from the above situation, entropic hydrophilia of a hydrophobic sponge is realized in the form of the identity of π with P_{os} only on a limited scale of swelling, which is nonuniform in various zones of the matrix. The swelling is limited because the opening of hydrophobic slits results in negative disjoining pressure. The latter causes the reverse collapse of slits under conditions of the high structural dynamics and in doing so prepares the new alternation of the sign of the disjoining pressure. The quasi-equilibrium state of the hydrophobic slit can be ensured by a stretching pressure that is equivalent to $-\pi$. As this takes place, the following conditions will be fulfilled for the water interlayer: $\pi = -P_{os} = -RT \ln(P_s/P)/V_m < 0$ and $P/P_s > 1$ (the latter points to slit supersaturation by unbonded water). Such a situation is unstable, but that is possible, when the stretching of a zone is temporarily stabilized through the compression of the adjacent material.

The above combination of the polymer chain displacements is unlikely in the bulk of the uniformly swollen hydrophilic sponge; however, that is realized in the hydrophobic sponges due to the formation of waves of medium expansion and compression in the neighboring zones under the interchange of the π sign in opposed phases of the oscillation. Accidental synchronization of such structural oscillations can result in fluctuations of capillary water. As this takes place, the expanded regions, will draw the interlayer water from the neighboring zones that are in compression. This, in turn, leads to fluctuation water drops segregation during the next compression cycle.

When a slit containing a water interlayer is expanded, the cooperative movement of the polymer links can result in a complete release of the pressure on water, so that the slit is converted into a domain where the water from the zones in compression is collected. In the latter zone, the total pressure exerted on the water interlayer can be doubled in the limiting case due to the sign change of the external (relative to the interlayer) pressure, which initially counteracted the collapse pressure $-\pi$.

A new metastable state of the mechanical equilibrium is characteristic for the situation in consideration. In this state, the doubled pressure on the water interlayer in contact with a fluctuation drop, is balanced by the opposing pressure exerted by a drop (the latter pressure is generated by the force of interfacial tension). This state is destroyed in the course of structural fluctuations, it returns to the molecular-cluster dispersion or leads to the coalescence of the fluctuation drops into the stable liquid phase.

The fluctuation events do not change the internal energy of the system ($dU = 0$). Therefore, it follows from the expression for the first thermodynamic law $\delta Q = dU + PdV$ that the fluctuation work should be provided by the isothermal consumption of the heat, when the drops are formed, and by the release of heat when the reverse dispersion occurs to form clusters and interlayers.

According to the fluctuation theory of phase transitions,[33] the formation of drops of critical size is connected with an increase in the Gibbs' energy (ΔG) by one third of their surface energy. This excess should be compensated by the isothermic work of a hydrophobic sponge, which is required to maintain a critical drop at the metastable equilibrium. Taking into account the above considerations, we can write the following equation:

$$\Delta G_c = (4/3)\Pi r_c^2 \sigma_c = P_c V_c = \Delta Q_c,$$

where r_c and V_c are the radius and the volume of the critical drop, respectively, σ_c is interfacial tension at the polymer-critical drop boundary, and $\Pi = 3.14$. From this equation, we have

$$P_c = -2\pi = 2P_{os} = \sigma_c/r_c. \tag{2}$$

The P_{os} value can be estimated from the isotherm of water sorption by PMMA,[7] if in accordance with the concept of vacancy solutions,[30] P_{os} is expressed via Gibbs' integral

$$P_{os} = \int_0^{(P/P_s) = 1} C(P/P_s)\, d\mu;$$

where $C(P/P_s)$ is the equilibrium molar concentration of water sorbed by the polymer, μ is the chemical potential of the adsorbate. Hence, we arrive at

$$P_{os} = RT \int_0^{(P/P_s) = 1} C(P/P_s)\, d\ln(P/P_s); \tag{3}$$

As was mentioned above, the isotherm of sorption given in Reference 7 does not depend on T and deviates only slightly from the Henry's law in the range of the P/P_s values from 0.95 to 1. Therefore, we can neglect the fact that a vacancy solution forming in PMMA is not ideal and express the isotherm by the equation of a straight line

$$C = C_1(P/P_s), \tag{4}$$

where $C_1 = 1.5$ mol/l (0.023 wt.%) is the value of water concentration obtained by extrapolation to the value $(P/P_s) = 1$. Integration of Equation (3) in view of (4) leads to $P_{os} = C_1RT = 1.25 \times 10^4$ T, which coincides with the van't Hoff's equation for an ideal liquid solution. According to this formula, the estimated values of the osmotic pressures are equal to 3.78, 4.15, and 4.53 MPa at 303, 333, and 363 K, respectively.

Using the well-known expression for the disjoining pressure, $\pi = A/h^3$[28] (where $A = 5 \times 10^{-14}$ erg and h is the thickness of the water interlayer), we found the average value of h for fluctuating slits, which lies in the range 1.10–1.03 nm at 303–363 K. This value corresponds approximately to four water molecules.

The radius of a fluctuating drop of critical size can be estimated provided the interfacial tension σ_c depends on the surface curvature $\sigma_c = \sigma/(1 + 2l/r_c)$,[33] where $l = 0.5$ nm is the thickness of a surface layer of liquid water, σ is the interfacial tension calculated by the Owence-Vendt's formula[12] based on the surface tension values for PMMA and water.[34] The calculated σ values are equal to 26.3, 22.8, and 19.0 dyne/cm at 303, 333, and 363 K, respectively. According to Equation (2), we have $P_c = 2P_{os} = \sigma/(r_c + 2l)$; hence, the r_c values are equal to 2.50, 1.75, and 1.10 nm at 303, 333, and 363 K, respectively. Note that the values found should be related to deglassified PMMA. At the temperatures used this is achieved by applying DBP as plasticizer; DBP should not influence the σ value, because its solubility parameter is identical with that for PMMA.[12]

The critical drops formed take up a part of the free volume, the fraction of which in PMMA (0.021 at T_g) leads to the formation of caverns 2.7 and 6.9 nm in radii inside the globules of respective diameters of 20 and 50 nm. These values are large enough for the spatial redistribution of polymer chains without increasing their loads.

As a result of integration of the critical drops in the course of the structural fluctuations, the stable water drops are formed. These drops continue to grow overcoming the elastic viscous resistance of the polymer matrix, because the condition expressed by formula (2) is not fulfilled. At this stage, a new quasi-equilibrium state is established, when an excess (Laplace) pressure P_L (generated by the interface forces) on the drop is balanced by the pressure P_c, which favors an increase of the interface:

$$P_c = P_L = 2\sigma_e/r, \tag{5}$$

where r is the radius of the growing drop, σ_e is the interfacial tension at the boundary of the elastically compressed polymer matrix. The σ_e value can exceed considerably the σ value that is characteristic of the not deformed plane surface.[33] In the case considered, the drop radius determined at the early stage of the water segregation, when elastic-deformation phase of the process prevails, is 300 nm. Using formula (5), we can find the σ_e values, which are equal to 43σ, 54σ, and 70σ at 303, 333, and 363 K, respectively.

The isothermic phase-forming work of the highly elastic polymer-chain sponge is highly sensitive to mechanical obstacles because of its fluctuation origin. This is noted when the internal stress is opposed by the force caused by the mechanical fixation of films or by additional ordering of the internal structure caused by the annealing of samples. Moreover, the growing drops by themselves decrease the intensity of the fluctuations and the rate of the liquid segregation because of elastic loads on the matrix and deformation of the latter. Therefore, there are two stages of the process, one in which the deformation is essentially elastic and the other where a viscous flow takes place. The Figure 3 demonstrates the influence of the above change in the deformation regimes on the rate of the liquid water segregation.

The elastic compression of the polymer containing a great number of water drops differs little from the compression by a hydrostatic pressure, P_h. This fact allows us to estimate the bulk modulus of elasticity (usually determined by formula $K_h = P_h/(\Delta V/V_0)$, where $\Delta V = V_h - V_0$; V_0 and V_h are the bodies of the polymer in the initial and compressed states, respectively) via the volume fraction of liquid water Φ_e, which is segregated at the stage of elastic deformation of the matrix

$$K_h = P_c/\Phi_e. \tag{6}$$

The Φ_e values found from Figure 3 by extrapolation of the straight-line portions (corresponding to the second stage of the process) to the ordinate axis have the scatter from 0.013 to 0.036. This scatter appears to reflect both the difference in the internal structure and in the force of mechanical fixation of the samples. Consequently, the calculation by formula (6) results in the K_h values for plasticized PMMA at 363 K ranging from 700 to 250 MPa (for unplasticized PMMA, $K_h \approx 2000$ MPa[27]).

The appraised value of the Young's modulus obtained using $E = 3K_h(1 - 2\nu)^{12}$ (where $\nu = 0.495$ is the Poisson ratio characterizing the rubber-like state) lies in the range 21–7.5 MPa. Another method of the Young's modulus estimation, taking into account the size of water drops by means of $E = 6P_c/(5 - 4/\lambda - 1/\lambda^4)^3$ (where the coefficient $\lambda = 100$ corresponds to the degree of increasing the radius of a cavern driven apart by water from 3 to 300 nm), results in the value of $E \approx 11$ MPa. These results obtained on the basis of the water phase characteristics confirm that the plasticized PMMA is a rubber-like materials and that the interpretation of the deformation regimes for both portions of the curves in Figure 3 is correct.

Taking into account that the osmotic pressure increases with increasing temperature, we can write Equation (6) in the form

$$\Phi_e = P_c/K_{h\mathrm{DBP}} = C_1RT/K_{h\mathrm{DBP}}, \tag{7}$$

which is qualitatively comparable with the straight lines 8–12 in Figure 4.

It should be emphasized that the data presented in Figure 4 are not in agreement with the condition of the thermodynamic equilibrium and, consequently, with Equation (7). (Note that the rate of the growth of Φ can increase by a factor of two or three as a temperature rises by 10°.)

However, the decrease in the slopes of the straight lines 8–12 with increasing the DBP content in the films points clearly to the thermodynamic nature of the observed phenomenon. The slope decrease may be caused either by decreasing the concentration C_1 for molecular-cluster water dispersed in a sponge in the presence of a large amount of hydrophobic DBP [C_1 appears in the numerator of Equation (7)] or by increasing the bulk modulus of elasticity $K_{h\mathrm{DBP}}$ [which appears in the denominator of Equation (7)], if plasticization reduces the compressibility of the sponge under the acion of a hydrostatic pressure.

Once the maximum retardation of the structural fluctuations in the plasticized matrix due to compression by growing water drops is attained, the process turns into the regime of viscous flow of the polymer, and does not stop. The point is that as soon as the σ_e value [Equation (5)] starts to decrease because of the relaxation displacement of the polymer chains, the fluctuation mechanism, restoring the σ_e value caused by "pumping" of the sorbed water into the growing drops, comes into effect immediately.

The forces generated by a large number of drops results in specific directionality of the resulting forces. As a result, the sample material flows, increasing its thickness and decreasing the area. Such a situation is rather common in actual practice, for example, when breaks and exfoliations appear on coatings of water-emulsion and oil paints.

As was mentioned above, the DBP-free samples of PMMA undergo only the short-time activations of the structural fluctuations in heated water, which terminate on the completion of the relaxation process of swelling and removing the monomer and MC remains. This results from the PMMA transition to the glassy state and, therefore, from the appearance of structural impediments, which prevent the formation of the expansion and compression waves of the required size, involving the capillary fluctuations of liquid water, inside the polymer sponge. It is these waves which are responsible for the separation of impurities consisting of the mobile molecules of the MMA and MC type from the polymer.

It should be emphasized that the segregation of drop water in hydrophobic elastomers is always accompanied by the exclusion and redistribution of impurities.[3] In such elastomers, the relationships of this phenomenon closely resemble those observed in plasticized PMMA. We believe that this resemblance reflects the same structural-fluctuation properties of the sponge structures consisting of flexible hydrophobic polymer chains.

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