

MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Control of Penetration of Macroglobules from Polymer Solution into the Bulk of a Porous Solid

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Abstract—Penetration of poly(butyl methacrylate) macroglobules into solid porous samples of chalk, clay, cement, and cement–river sand mixtures was studied as influenced by the macroglobule size.

Important aspects in impregnation and reinforcement of porous solids (particularly, loose materials typical of historical and cultural monuments) are the depth of penetration and uniformity of distribution of the fixing agent (e.g., polymer) in the bulk of these solids. Naturally, the above-mentioned characteristics will be governed by the properties of the impregnating solution and, above all, by the polymer macroglobule size.

The aim of this work was to study penetration of poly(butyl methacrylate) (PBMA) macroglobules from solutions in solvents of different solvency into the bulk of solid porous samples such as models of historical and cultural monuments. Poly(butyl methacrylate) is widely used for conservation and restoration of art monuments made of various materials [1].

EXPERIMENTAL

We studied suspension PBMA [TU (Technical Specifications) 6-01-240–76] with the molecular weight $M = 3.5 \times 10^5$. As solvents for PBMA served toluene, *o*-xylene, acetone, butanol, and isopropanol. The quality of the solvents with respect to the polymer used was estimated by comparison of their solubility parameters δ [2] summarized in the table below. The table shows that, in changing from toluene to alcohols, the difference in δ increases. This means that, along this series, the quality of the solvent with respect to PBMA tends to deteriorate. The quality of the solvent was also worsened by introducing a precipitating agent for PBMA [3.5 to 10.5% (hereinafter, wt %) distilled water] into isopropanol. In this case, worsened solubility of PBMA in the mixed solvent was evidenced by increased turbidity of the solution, which was estimated nephelometrically.

The rms distance between the ends of the PBMA macromolecule in θ -solvent, isopropyl alcohol, was calculated by the Flory–Fox formula [3]

$$(\bar{h}_0^2)^{3/2} = \frac{[\eta]_0 \bar{M}}{\Phi}, \quad (1)$$

where Φ is the Flory constant; \bar{M} , viscosity-average molecular weight of PBMA; and $[\eta]_0$, intrinsic viscosity of the PBMA solution in θ -solvent (isopropanol), $l\ g^{-1}$, measured at the θ -temperature of 21.5°C [2].

The swelling coefficient α^3 of the macroglobule and the rms distance $(\bar{h}^2)^{1/2}$, nm, between the ends of the macromolecule in different solvent were calculated by the formula

$$\alpha^3 = \frac{[\eta]}{[\eta]_0} = \frac{(\bar{h}^2)^{3/2}}{(\bar{h}_0^2)^{3/2}}. \quad (2)$$

Influence of the solubility parameter δ on the intrinsic viscosity $[\eta]$ of the PBMA solutions, swelling coefficient α^3 of the macroglobule, and rms distance between the ends of the PBMA macromolecule $(\bar{h}^2)^{1/2}$ [$\delta_{\text{PBMA}} = 8.70\ (\text{cal cm}^{-3})^{1/2}$]

Solvent	δ , (cal cm^{-3}) ^{1/2}	α^3	$(\bar{h}^2)^{1/2}$, nm	$[\eta]$, $l\ g^{-1}$
Toluene	8.97	5.30	46.0	0.080
<i>o</i> -Xylene	9.03	5.53	46.7	0.083
Acetone	9.74	2.53	36.0	0.038
Butanol	10.77	1.67	31.3	0.025
Isopropanol*	–	1.0	26.4	0.015

* For propanol, $\delta = 12.06\ (\text{cal cm}^{-3})^{1/2}$.

The polymer content in the solutions was varied from 1 to 16%.

As solids we used $10 \times 10 \times 100$ -mm cement-sand samples (CSSs), as well as $10 \times 10 \times 80$ -mm pressed chalk (TU 458-15-14-89) and clay samples. The cement-sand samples were prepared by mixing grade 400 Portland cement [GOST (State Standard) 10 178-85, particle size from 50 (65%) to 150 (7%) μm] with river sand [average particle size from 100 (5%)–300 (25%) to 400 (20%)–500 (15%) μm] in 18 ml of distilled water. The sand content in the samples was varied from 0 to 90%. The samples were molded at room temperature for 14 days. Clay samples were prepared by room-temperature molding, through mixing fine clay particles [from 1 (28%) to 60 (61%) μm in size] in 18 ml of water, followed by drying to constant weight at 200°C. Next, the pore size of the solid samples was estimated. To this end, we measured the rate of penetration of isopropanol into the sample pores. Then, the average pore radius r_{av} , nm, was calculated by the Washburn equation [4].

The pore radius of the solid samples r_{av} , nm, was estimated at 0.63, 0.48, 0.14, and 1.80 for chalk, clay, CSS-0, and CSS-90, respectively (the figure at the CSS designation corresponds to the river sand percentage).

The porous samples were impregnated until complete saturation with the polymer solutions in closed vessels, by immersing samples, suspended by wires from their face side, by 1 cm of their height in the impregnating liquid. Next, the samples were dried at room temperature under slow solvent evaporation. The uniformity of distribution of the polymer in the bulk of the porous samples was monitored by the procedure from [5]. It is underlain by the fact that the water absorption in the open pore space of the solid sample varies with the extent of pore filling with the penetrated polymer.

The solvent quality will, above all, affect the size of the polymer macroglobule. Grosberg and Khokhlov [6] found that, with deteriorating solvent quality, the macromolecular globule gets contracted. The volume occupied by the macromolecule decreases by a factor of several tens. The table below shows that, in changing from "good" (*o*-xylene or toluene) to "bad" (butanol or isopropanol) solvents, the rms distance between the ends of the PBMA macromolecule decreases by a factor of 1.5–2.

It could be expected with a good reason that, the smaller the globule, the easier and faster its penetration into pores (capillaries) of a solid. However, our

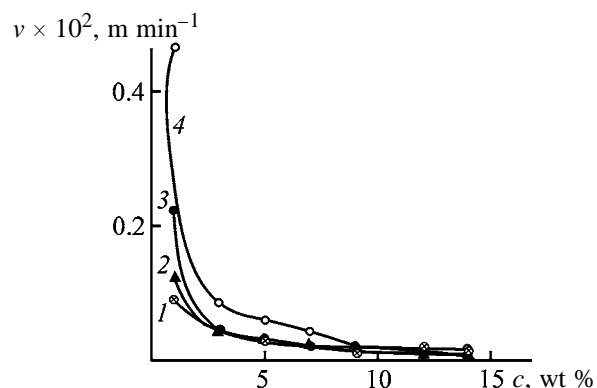


Fig. 1. Influence of the PBMA concentration c in the impregnating solutions in different solvents on the rate of their capillary rising v in CSSs containing 90% river sand. (1) Isopropanol, (2) butanol, (3) *o*-xylene, and (4) toluene.

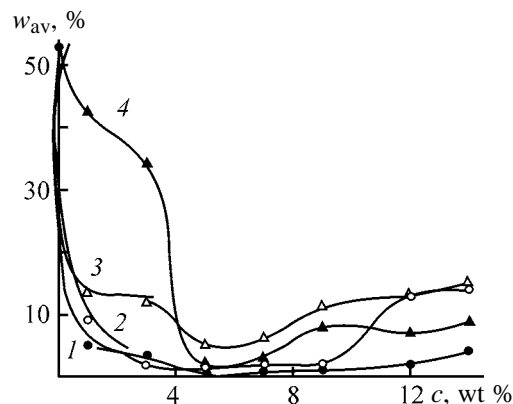


Fig. 2. Average water capacity w_{av} of CSSs containing 90% river sand as a function of the concentration of the impregnating solution c . (1) *o*-Xylene, (2) acetone, (3) butanol, and (4) isopropanol.

study showed that the rate of the capillary rising of the solution is larger (Fig. 1) and the degree of penetration of the polymer into CSSs with larger pores is greater (Fig. 2) when the PBMA macroglobules occur in the swollen state. The degree of penetration of the polymer into pores of solid samples was estimated from the amount of water w , %, able of penetration into the sample pores that remained open after impregnation with the polymer. The larger the amount of water absorbed by the sample, the lesser the amount of the polymer it contains. Evidently, in the case of loose globules, the globules extend and get oriented along the flow under the influence of the capillary pressure of absorption. This favors faster and deeper penetration of the globule into the sample pores.

When penetrating into surface pores of the sample, compressed PBMA macroglobules in isopropanol, evidently, plug them, thus preventing further penetration of PBMA into porous solids. This assumption is

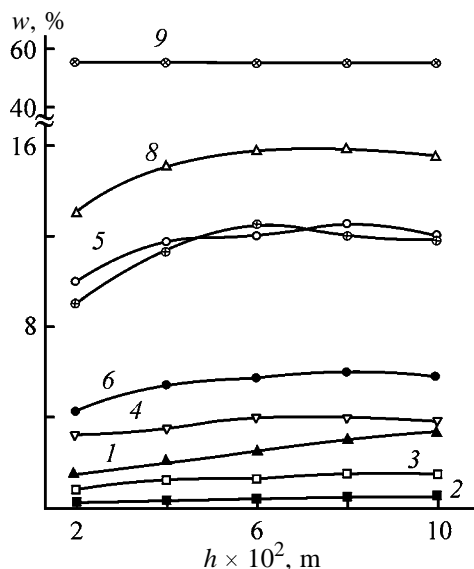


Fig. 3. Variation of the moisture capacity w of CSSs containing 90% river sand along the sample height h . (1–4) *o*-Xylene, (5–8) butanol, and (9) unimpregnated sample. Impregnating solution concentration, %: (1, 5) 3, (2, 6) 5, (3, 7) 9, and (4, 8) 14.

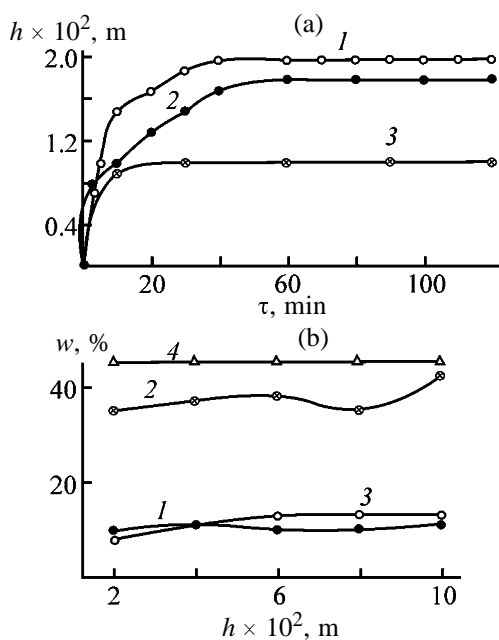


Fig. 4. (a) Kinetic curves of the capillary rising h of 3% PBMA solutions into cement samples and (b) variation of the moisture capacity w of the samples impregnated with 3% PBMA solutions along their height h . (τ) Time of rising of PBMA solutions into the samples, min. (1) *o*-Xylene, (2) isopropanol, (3) butanol, and (4) samples untreated with PBMA solution.

confirmed by Fig. 3 which suggests that the moisture capacity of the CSSs impregnated with PBMA solutions in *o*-xylene (a “good” solvent) is virtually invariant along the sample height. This means that the polymer is uniformly distributed over the sample. At the same time, the samples impregnated with PBMA solutions in butanol (a “bad” solvent) are characterized by a much lower moisture capacity of that segment of the sample through which impregnation was performed, compared to that at the opposite end. This suggests that the polymer is nonuniformly distributed over the CSS height and is, most probably, concentrated primarily in the surface pores. Evidently, the internal pores occurring in the middle part of the sample remained unimpregnated with the polymer. This is also confirmed by the fact that the moisture capacity of the samples impregnated with PBMA solutions in butanol significantly exceeds that of the samples impregnated with PBMA solutions in *o*-xylene.

In the case of impregnation of solid samples having small pores, the difference in the rates of rising of solutions in solvents with low and high solvency is virtually leveled off (Fig. 4a). The polymer is uniformly distributed along the height of the samples from both “bad” and “good” solvents (Fig. 4b). However, the degree of its penetration into the sample from the *o*-xylene solution significantly decreases, approaching that of the polymer penetrating from solutions in “bad” solvents. Thus, in both cases the polymer occurs in the surface pores of solids. Penetration of the polymer into sample pores is evidenced by a significant decrease in the moisture capacity relative to the untreated sample.

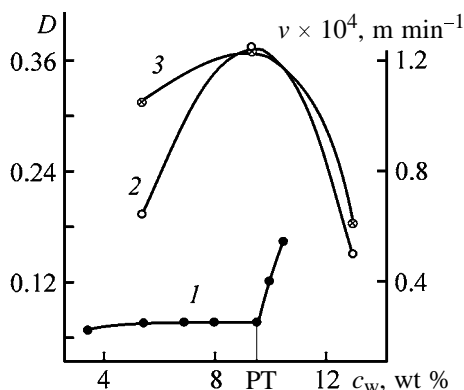


Fig. 5. (1) Optical density D of 2% PBMA solution and (2, 3) rate of capillary rising of solutions v into (2) clay and (3) chalk samples as functions of the water content c_w in mixtures with isopropanol. (PT) Precipitation threshold for the polymer.

When a precipitating agent is added to a "bad" solvent for PBMA (e.g., water to isopropanol), the macroglobules get contracted, and the solution becomes turbid. We found that, in this state, the rate of impregnation of solid clay and chalk samples with small pores sharply increases (Fig. 5). Decrease in the rate of impregnation of the clay and sand samples after passing the precipitation threshold can be explained by formation of large agglomerates from adhering globules.

Thus, the penetrability of the pores of a solid with large pores by the polymer can be increased by converting the macroglobules into the swollen state. In the case of samples with small pores, the globules should be compressed to the maximal extent.

CONCLUSIONS

(1) In changing from good (*o*-xylene, toluene) to bad (butanol, isopropanol) solvents, the rms distance between the ends of the poly(butyl methacrylate) molecule decreases by a factor of 1.5–2.

(2) The rate of the capillary rising of the poly(butyl methacrylate) solution is higher, and the penetration depth and uniformity of distribution of the polymer within the bulk of a solid with large pores is greater in the case of a swollen globule, i.e., that penetrating from a good solvent.

(3) For samples with small pores, the impregnation rate and uniformity of distribution of poly(butyl

methacrylate) along the sample height is independent of the quality of the solvent: The polymer occurs in the surface pores of the samples. Impregnation of the samples with small pores sharply accelerates upon contraction of poly(butyl methacrylate) globules.

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