Journal of Engineering Physics and Thermophysics, Vol. 76, No. 3, 2003

ROLE OF THE STRUCTURAL-RHEOLOGICAL STATE OF POLY(METH)ACRYLATE SOLUTIONS IN THEIR SOAKING INTO CAPILLARY-POROUS BODIES

D. N. Yemel'yanov, N. V. Volkova,
O. I. Sheronova, and T. S. Krasil'nikova

UDC 532.135:678.026.2:621.537.67

We have investigated the influence of the structural-rheological state of solutions of poly(meth)acryl copolymers on the rate of their capillary rise and the uniformity of the polymer distribution in the bulk of porous bodies — models of monuments of art made of ceramics, terracotta, loessial and lime plaster, and concrete. It has been found that in the region of concentrations corresponding to the transition of poly(meth)acrylate solutions from the viscous-Newtonian to the structural-viscous rheological state there is a sharp decrease in the rate of capillary rise of solutions into clay, chalk, and cement-sand specimens. A worsening of the uniformity of the polymer distribution over the height of the porous specimens, a decrease in their surface wetting with copolymer solutions, and a decrease in the value of the polymer adsorption on the filler surface are also observed.

The processes of capillary soaking of liquids occur widely in nature and impregnation of fibrous materials is used in industry (impregnation of fabric and paper with solutions and dispersions of polymers). A specific but quite common field of using the process of capillary soaking of solutions of natural and synthetic polymers is the restoration and conservation of cultural and historical monuments made of various porous materials that have weakened with time. These are articles of stone, ceramics, limestone, concrete, etc. The choice of the impregnating solution and polymer solvent concentrations thereby is carried out purely empirically by trial and error. The aim of our investigations was to provide a scientific substantiation of the process of impregnating porous specimens of clay, chalk, and cement-sand mixtures — models of monuments — with solutions of poly(meth)acryl copolymers. It was also necessary to elucidate the influence of the viscous properties on the penetration rate and the uniformity of polymer distribution in the bulk of porous solid specimens.

As porous bodies, we used specimens of loessial clay and lump chalk (MK-1, GOST 17498-72) 15 × 15 × 80 mm in size and cement-sand specimens 10 × 10 × 100 mm in size. The content of river sand in the specimens was 0, 60 and 90 mass parts. The porous specimens were impregnated with solutions of polybutylmethacrylate (PBMA) and a copolymer consisting of 50 wt.% of butylmethacrylate (BMA) and 50 wt.% of methylmethacrylate (MMA). We used industrial PBMA obtained by the suspension polymerization method: the BMA + MMA copolymer was produced under laboratory conditions by the method of radical copolymerization in a block. The molecular mass of PBMA was $3.6 \cdot 10^5$ and of the copolymer — $7.5 \cdot 10^5$. The specimens were impregnated in closed vessels by means of spontaneous rise of the polymer solutions in solid body capillaries. The viscous properties of the poly(meth)acrylate solutions were changed by varying the polymer concentration and estimated by a Hoppler viscometer at 23°C. The polymer adsorption on fine-dispersed fillers was determined by the change in the concentration of the solutions, checking the refractive index of the solutions prior to and after the adsorption with the aid of an IFR-22 refractometer. To find the wetting angle of the surface of the cement-sand and clay specimens, the fine-dispersed fillers were mixed with a certain quantity of water. A thin layer of the thick paste formed was applied to glass and dried at room temperature. Then all asperities were removed by means of abrasive paper. A drop of PBMA solution in isopropyl alcohol was applied to the prepared surface of the specimens by means of an injector. Using a reading microscope, we measured the profile chord and the droplet height and calculated, by the formula given in [1], the wetting angle. The moisture capacity of the specimens of cement-sand mixtures and chalk was estimated by the method given in [2].

N. I. Lobachevskii Nizhnii Novgorod State University; email: polymer@ichem.unn.runnet.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 3, pp. 96–100, May–June, 2003. Original article submitted September 6, 2002.

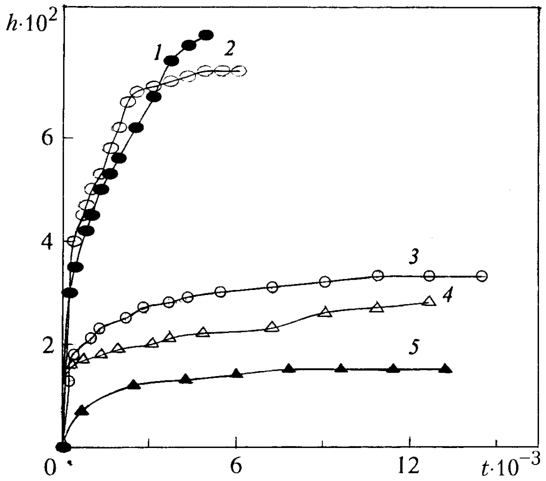


Fig. 1. Kinetics of the capillary rise of PBMA solutions in isopropyl alcohol into a cement-sand specimen containing 90 mass parts of river sand and 10 mass parts of cement at various concentrations of solutions: 1) C = 0; 2) 1; 3) 5; 4) 7; 5) 12 wt.%. h, m; t, sec.

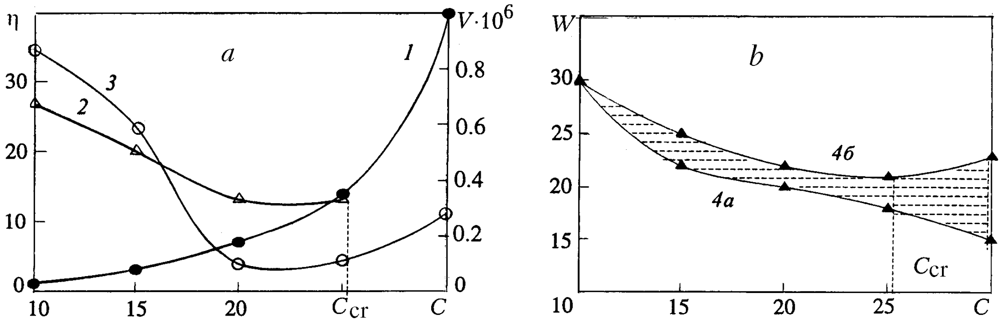


Fig. 2. Influence of the concentration of solutions of 50% of BMA + 50% of MMA copolymer in acetone on its effective viscosity (1), the rate of capillary rise of solutions into clay (2) and lump chalk specimens (3), and the moisture capacity of chalk specimens impregnated with copolymer solutions (shaded zone 4ab) (a, moisture capacity of end parts of the specimen; b, same for central parts). W, wt.%; C, wt.%; V, m/sec; η, mPa·sec.

According to the Washburn theory, the rate of capillary rise of a liquid is inversely proportional to its viscosity [3]. It is quite natural that the impregnation rate of the porous specimens under investigation decreases on passing from the solvent to the polymer solution and with increasing concentration of the impregnating solution (Fig. 1). This is explained by the fact that an increase in the concentration of the impregnating solution leads to an increase in the viscosity of the solutions. However, as seen from Figs. 2 and 3, with increasing polymer concentration the viscosity of the solutions and the rate of their rise into porous solid specimens of clay, chalk, and cement-sand mixtures changes nonmonotonically. The intensity of growth of the polymer-solution viscosity sharply increases and the intensity of decrease in the impregnation rate of the cement-sand, clay, and chalk specimens sharply decreases, approaching a constant value after some critical polymer concentration in the solution.

In [4], it is shown that in the process of homogeneous polymerization of vinyl monomers the change in the complex of rheological properties of the reaction mass occurs stage by stage. The characteristic changes in the complex of rheological parameters have made it possible to break down the polymerization process into a number of conversion regions with transition parts between them (Fig. 4). Since reaction masses are polymer solutions in its monomer, the obtained laws can be extended to solutions of polymers in "alien" solvents. It may be considered that the region of conversions $\Pi_{\mathrm{cr}1}$ corresponds to the region of $C_{\mathrm{cr}1}$ for polymer solutions and means the transition of the

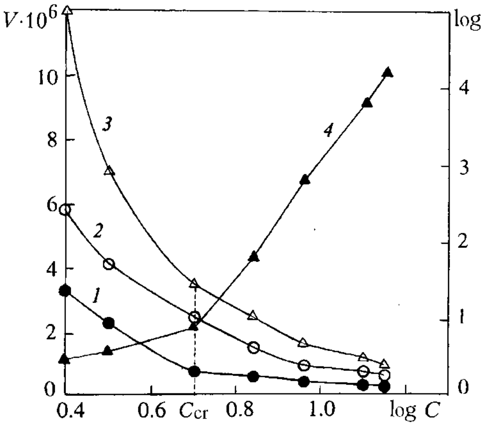


Fig. 3. Influence of the PBMA content in isopropyl alcohol on the rate of capillary rise of solutions into cement-sand specimens (1–3) and the effective viscosity of these solutions (4) at a content of sand in the cement-sand specimen of: 1) 0 mass parts; 2) 60; 3) 90. V, m/sec.

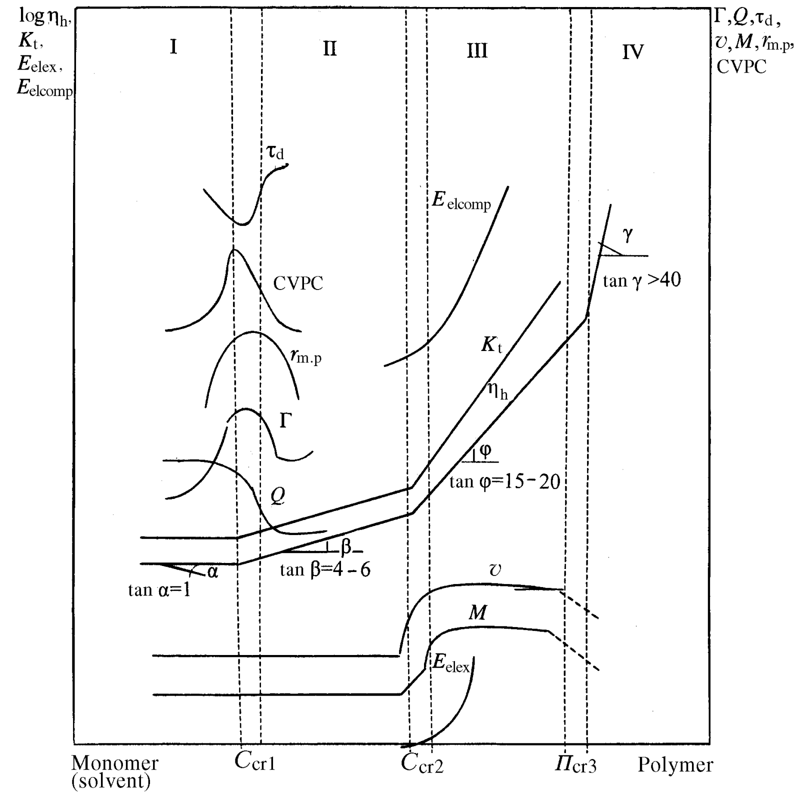


Fig. 4. Basic diagram of the conversion change in rheological ($\log\eta_h$, K_t, E_{elex}, E_{elcomp}), structural-kinetic, colloidal-chemical properties (Γ, Q, τ_d, M, $r_{m.p}$, CVPC), and the rate of polymerization v in different structural-rheological states: I) viscous-Newtonian state; II) structural-viscous state; III) highly elastic state; IV) glassy state.

solution from the viscous-Newtonian state to the structural-viscous rheological state, and the region Π_{cr2} corresponds to the region C_{cr2} for solutions and means the transition of the polymer solution from the structural-viscous to the highly elastic state. As is seen from the schematic diagram given in Fig. 4, in the transition critical regions, a change in both the rheological and colloidal-chemical properties of polymer solutions is observed. We have established that in

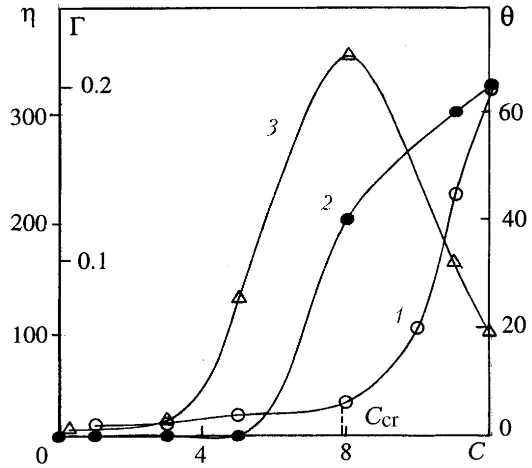
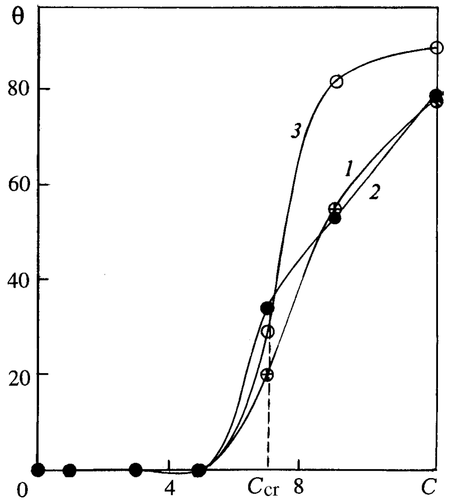


Fig. 5. Influence of the concentration of PBMA solutions on their viscosity (1), wetting angle of the clay surface with polymer solutions (2), and the value of equilibrium polymer adsorption by clay (3). C, wt.%; θ, deg; η, mPa·sec; Γ, g/g.



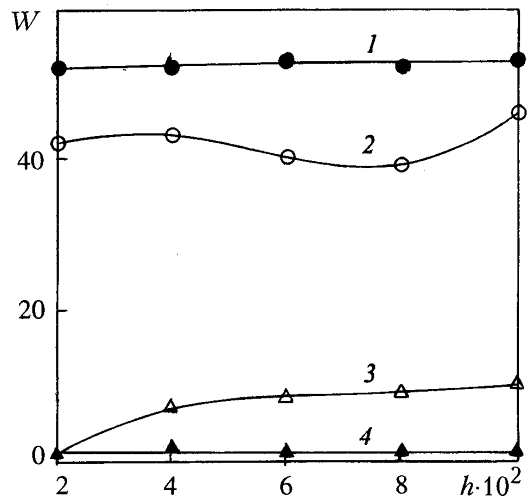


Fig. 6. Influence of the concentration of PBMA solution in isopropyl alcohol on the wetting angle of cement-sand specimens at a content of river sand in them (mass parts) of: 1) 0; 2) 90; 3) 60. θ, deg; C, wt.%.

Fig. 7. Dependence of the moisture capacity on the height of cement-sand specimens impregnated with PBMA solutions in isopropyl alcohol at a content of river sand in specimens of 90 mass parts and different concentrations of the polymer: 1) C = 0; 2) 1; 3) 12; 4) 5 wt.%. W, wt.%; h, m.

the region of transition of the impregnating polymer solution from the viscous-Newtonian to the structural-viscous state, along with a sharp increase in the solution viscosity and a decrease in the rate of its capillary rise into porous solid specimens, there are also a sharp decrease in the value of the equilibrium adsorption of PBMA on clay (Fig. 5, curve 3) and an increase in the angle of wetting of the surface of clay (Fig. 5, curve 2) and cement-sand specimens (Fig. 5, curve 6) by PBMA solutions in isopropyl alcohol.

It is known that sharp changes in the properties of solutions of polymers are associated with a change in their structure. In going from the viscous-Newtonian state to the structural-viscous rheological state, large associates consisting of several macroballs are formed. Naturally, it is more difficult for them to penetrate into the pores (capillaries) of solid specimens than for individual macroballs. Therefore, in the structural-viscous region the rise of the solution up the specimen is hindered and the adsorption interaction of large associates with the filler surface worsens, since the number of polymer–filler contacts decreases due to the steric factor.

An important characteristic of the strengthening process of porous materials of art monuments is the penetration depth of the polymer and the uniformity of its distribution in the bulk of a porous body. If the polymer is concentrated near the surface, this can lead to a change in the color of a painting, e.g., on loessian plaster, which is prohibitive. Moreover, in so doing, the lower layers of the object being restored will remain unfixed, which too can subsequently lead to destruction of the momentum. We judged the polymer distribution uniformity in a porous specimen by the change with specimen height in its moisture absorption. We assumed that the content of absorbed water corresponded to the volume of polymer-free pores. Naturally, the more polymer absorbed, the smaller the number of free open pores remaining. In Fig. 2, the dependence of the distribution uniformity of the BMA + MMA copolymer over the height of the chalk specimen is represented by zone 4ab. The lower boundary of the zone 4a shows the values of moisture absorption by the ends of lumps of chalk through which impregnation was carried out. The upper boundary 4b shows the moisture absorption of the mid-height part of the chalk specimen. It is seen that after the concentration portion corresponding to $C_{\mathrm{cr}1}$ zone 4ab widens, which points to a worsening of the polymer distribution uniformity. This means that when a porous specimen is impregnated with polymer solutions with a concentration higher than the critical one, the absorbed polymer is predominantly concentrated near the ends. Consequently, the following conclusion can be drawn: the strengthening of the impregnating solution structuring is accompanied by an impairment of the polymer distribution uniformity over the height of a porous specimen. However, if the polymer solution is in the viscous-Newtonian state and its concentration is small, then a nonuniform distribution of the polymer over the height of a porous specimen is observed (Fig. 7, curve 2). And, as is seen from Fig. 7, only in the region of polymer concentrations corresponding to the transition of the system from the viscous-Newtonian to the structural-viscous state is a more uniform distribution of the polymer over the height of cement-sand specimens observed.

Thus, the foregoing shows that to impregnate solid porous bodies — models of stone monuments of art and culture — it is essential that the impregnating polymer solution be in the critical concentration region corresponding to the transition of the solution from the viscous-Newtonian to the structural-viscous rheological state.

This work was supported by the Russian Basic Research Foundation (grant No. 01-06-80328).

NOTATION

$C_{\mathrm{cr}1}$ and $C_{\mathrm{cr}2}$, critical concentrations of polymer solutions corresponding to the transition from the viscous-Newtonian to the structural-viscous state and from structural-viscous to the highly elastic rheological state; $\Pi_{\mathrm{cr}1}$, $\Pi_{\mathrm{cr}2}$, and $\Pi_{\mathrm{cr}3}$, critical conversions corresponding to the transition of the polymerized mass from the viscous-Newtonian to the structural-viscous state, from the structural-viscous to the highly elastic state, and then from the highly elastic to the glassy rheological state; V, rate of capillary rise of the polymer solution into the porous specimen, m/sec; C, polymer concentration in the solution, wt.%; h, height of the specimen, m; t, impregnation time, sec; η, viscosity of solutions, mPa·sec; θ, wetting angle, deg; Γ, equilibrium absorption of the polymer, g/g; W, moisture capacity, wt.%; η_{h}, highest Newtonian viscosity, Pa·sec; K_{th}, thixotropy coefficient; $\gamma_{\mathrm{m.p}}$, most probable size of associates in the solution, Å; E_{elcomp} and E_{elex}, elastic moduli of compression and extension, Pa; Q, rate of sedimentation, m/sec; M, molecular mass; v, rate of polymerization, mole·l/sec; CVPC, critical volume pigment concentration, volume %; τ_{d}, ultimate strength at destruction of the solution structure, Pa. Subscripts: cr, critical; h, highest; th, thixotropy; elex, elastic in extension; elcomp, elastic in compression; d, destruction; m.p, most probable.

REFERENCES

1. A. D. Zimon, *Adhesion of Liquid and Wetting* [in Russian], Moscow (1974).
2. A. V. Ivanova, *Khudozh. Nasledie*, Issue 2(32), 33 (1977).
3. S. S. Voyutskii, *Physicochemical Principles of Soaking and Impregnation of Fibrous Systems with Water Dispersions of Polymers* [in Russian], Leningrad (1969).
4. D. N. Yemelyanov, I. E. Smetanina, and G. V. Vinogradov, *Rheol. Acta*, **221**, 280 (1982).