Physical Chemistry

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Fixation of the Porosity of Condensation Structures from Synthetic Polymers

Fixation of a porous structure in order to preserve the necessary vapor permeability, sufficiently high porosity, and a set of required mechanical characteristics is one of the most important physicochemical problems of leather manufacture ($^{1-3}$), but recently it has acquired a more general significance; it is encountered both in attempts to obtain porous artificial leather and in a number of other areas of technology.

A three-dimensional fibrous collagen network (dermis), without special treatment, is incapable of resisting the capillary pressure developing in the region of the menisci of evaporating moisture—more precisely, the forces of capillary contraction (^{4}), including the forces of interaction between the elements of the structure. Upon drying it shrinks strongly in volume and turns into a nonporous, semitransparent, hornlike mass almost impermeable to water vapor. Tanning, i.e., treatment with aldehydes, polyphenols, basic salts of chromium, aluminum, etc., leading, on the one hand, to partial hydrophobization of the fibers and, on the other, to increased strength, reduced elasticity, and capacity for autohesion, is usually regarded as a very specific procedure in the technology of natural leather, for which it is difficult to find an analogue in the technology of synthetic polymers.

Fig. 1. Change in vapor permeability $j_{\mathrm{H_2O}}$ (bold curves) and in the reciprocal of the apparent specific weight $1/\gamma_{\mathrm{k}}$ (thin curves) of condensation structures formed in a solution containing 1.83 g-equiv/l polyvinyl alcohol, 2.52 mol/l H_2SO_4, and 2.62 mol/l CH_2O, at different temperatures as a function of the duration of acetalization. 1, 2 —at 55°; 3, 4 —at 45°; 5, 6 —at 40°C.

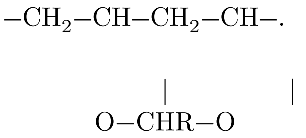
The use of the principle of condensation structure formation for obtaining, from supersaturated solutions of synthetic polymers, three-dimensional structures formed by coalesced and interlaced fibers of a new polymer phase has made it possible to obtain synthetic porous materials which, in a number of properties, successfully model natural leather (^{5}).

Fig. 2

Figure 2: Fig. 2

In a mixture of aqueous solutions of polyvinyl alcohol, aldehydes, and acids (as catalyst), an acetalization reaction takes place, substituting the free hydroxyl groups of polyvinyl alcohol (CH_2—CHOH—CH_2—

–CHOH–$)_n$ acetal rings



$$\begin{array}{l}-CH_2-\underset{|}{CH}-CH_2-\underset{|}{CH}-. \\ \quad\; O-CHR-O\end{array}$$

At a sufficiently high degree of acetalization (in the case of formaldehyde, 15-30%) the polymer loses solubility; a metastable system is formed, from which a spatial condensation network grows.

Fig. 2. Change in the vapor permeability of condensation structures formed at 45° in solutions containing 1.83 g-eq/l of polyvinyl alcohol, 2.52 mol/l H_2SO_4, and various concentrations of formaldehyde: 1 –3.3 mol/l; 2 –2.62 mol/l; 3 – 2.00 mol/l; 4 –1.50 mol/l.

The solution turns into an opaque white mass possessing considerable strength and elasticity. However, if the condensation structure that has just formed is washed free of excess acid and aldehyde and then dried, its porosity and permeability practically disappear completely. The white microheterogeneous mass in the swollen state, upon drying, turns into a homogeneous glassy material. (Repeated swelling in water leads to restoration of the microheterogeneity.) If the structure remains in the acid-aldehyde medium, the acetalization process continues, although its rate under the conditions of a heterogeneous system decreases.

One of the important characteristics of porous materials (including natural leather) is vapor permeability, which is determined by a standard method (6) from the rate of evaporation of water from aluminum cups tightly covered with a layer (about 1 mm) of the material under study and kept over concentrated sulfuric acid in a desiccator at 29°. Natural leather that has not been subjected to tanning has a vapor permeability of about 0.4 $mg/cm^2 \cdot h$. Approximately the same is the vapor permeability of a condensation structure of polyvinyl alcohol partially acetalized with formaldehyde (by 30%) that has just formed, been washed, and dried in air.

Continuation of the treatment with formaldehyde and acid for some time (the "induction period") does not give any noticeable change in vapor permeability (Fig. 1). The vapor permeability of the washed and dried samples then begins to increase regularly with increasing duration of acetalization, until it reaches a limiting value (~5.5 $mg/cm^2 \cdot h$), as in good natural chrome-tanned leather. This limiting value is reached when the samples are kept in the acetalizing bath

Fig. 3

Figure 3: Fig. 3

Fig. 4. Change in vapor permeability of condensation structures formed at 45° in solutions containing 2.52 mol/l H_2SO_4, 2.62 mol/l CH_2O, and various concentrations of polyvinyl alcohol: 1—0.45 mol/l; 2—0.98 mol/l; 3—1.42 mol/l; 4—1.97 mol/l; 5—2.41 g-eq/l

Figure 4: Fig. 4. Change in vapor permeability of condensation structures formed at 45° in solutions containing 2.52 mol/l H_2SO_4, 2.62 mol/l CH_2O, and various concentrations of polyvinyl alcohol: 1—0.45 mol/l; 2—0.98 mol/l; 3—1.42 mol/l; 4—1.97 mol/l; 5—2.41 g-eq/l

for periods of time several times longer than the time required for formation of the condensation structure from the solution.

Fig. 3. Change in the vapor permeability of condensation structures formed at 45° in solutions containing 1.83 g-eq/l of polyvinyl alcohol, 2.62 mol/l CH_2O, and various concentrations of H_2SO_4: 1 —3.50 mol/l; 2 —3.00 mol/l; 3 —2.80 mol/l; 4 —2.52 mol/l; 5 —2.00 mol/l.

The true specific gravity of the polymer subjected to additional acetalization changes only slightly (1.17-1.27), while the apparent specific gravity of the dried samples decreases noticeably, which reflects an incre—

increase in porosity (the fraction of the volume occupied by pores). The porosity of structures subjected to sufficiently prolonged treatment with aldehyde and acid can reach 80-90% (apparent specific weight 0.2-0.3). Thus, by the method of condensation structure formation, porous materials can be obtained that are close in apparent specific weight to foamed plastics, but possess finer porosity.

The increase in porosity and vapor permeability upon additional acetalization is noticeably accelerated with increasing temperature, with increasing formaldehyde concentration (Fig. 2) and acid concentration (Fig. 3). The final porosity and permeability of the structure are apparently determined by the average degree of acetalization, i.e., by the degree of hydrophobization of the polymer and, in particular, of the surface of the fibers forming the structure. The value of the average degree of acetalization required to impart to the structure resistance to capillary-pressure forces is about 70-80%. To preserve coarse pores or, correspondingly, coarse structural elements of the polymer phase, on which smaller capillary pressures act during drying, a considerably lower degree of hydrophobization is sufficient; therefore, in the course of additional acetalization they acquire stability more rapidly. This is confirmed by data on the kinetics of the increase in permeability in specimens obtained from solutions of polyvinyl alcohol of different concentrations and kept in solutions with the same acid and aldehyde content (Fig. 4).

Fig. 4. Change in vapor permeability of condensation structures formed at 45° in solutions containing 2.52 mol/l H_2SO_4, 2.62 mol/l CH_2O, and various concentrations of polyvinyl alcohol: **1** –0.45 mol/l; **2** –0.98 mol/l; **3** –1.42 mol/l; **4** –1.97 mol/l; **5** –2.41 g-eq/l.

The degree of acetalization attained does not depend on the polymer concentration; condensation structures from solutions of polyvinyl alcohol of different concentrations are formed practically simultaneously, but their subsequent fate is different. Structures obtained from dilute polymer solutions rapidly acquire stable porosity and immediately reach the greatest permeability. The pores in such structures have diameters measured in tens of microns and are readily observed with an ordinary (light) microscope. Structures obtained from more concentrated solutions require a considerably deeper and longer additional treatment in the acetalizing bath, after which they give dry materials whose pore diameter (as determined by electron-microscopic examination of replicas) does not exceed several hundred angstroms.

The data presented show that the fixing treatment of fibrous-porous condensation structures, which leads to their additional partial hydrophobization and increases their resistance to the action of capillary pressure during drying, has a significant effect on the porosity and permeability of the polymer materials obtained.

Further study of the features of such fixing treatment of various high-molecular-weight structures should be essential both for realizing all the possibilities inherent in such synthetic structures—

types, and also for further progress in the study of the physical chemistry of the processes of tanning natural leather, which, as follows from what has been set forth, are a particular case of such fixing treatment.

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REFERENCES

1. P. A. Rebinder, *Leather and Footwear Industry*, No. 7, 381 (1935).
2. A. N. Mikhailov, *Chemistry of Tanning Substances and Tanning Processes*, Moscow, 1953.
3. G. I. Kutyanin, *Investigation of the Physicomechanical Properties of Leather*, Moscow, 1956.
4. M. S. Ostrikov, G. D. Dibrov, E. P. Danilova, *Doklady Akademii Nauk SSSR*, **118**, 751 (1958).

5. I. N. Vlodavets, P. A. Rebinder, *Doklady Akademii Nauk SSSR*, **145**, 617 (1962).

6. *Chemical-Analytical Control in Leather and Tanning-Extract Production*, Part 1, 1955, p. 201.

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