

**Table 3.** Strength of PET Fibres with  $\Upsilon$  Profile in Dependence on the Number of Capillaries

Length mass ( $\Upsilon$ )	Tensile strength	Adhesive strength
	N	N
84/36 dtex x 1	3.1	—
84/36 dtex x 3	9.5	10.3
84/36 dtex x 6	19.0	13.6
84/36 dtex x 9	28.1	13.4
84/36 dtex x 12	37.8	13.1

this fibre position it is possible to utilize the geometrically modified profile for increasing the contact area of fibres with rubber.

### CONCLUSION

The fibre macromorphology secures a number of their functional and utility properties. By enlarging the

fibre area by means of intentional geometrical modification of the fibre profile the parameter of adhesion of fibres to rubber is considerably increased. With regard to the optimum value of the adhesion of fibres to rubber by intentional change of the macromorphology of fibres it is possible to decrease the economical demands on the fibre mass or consumption of adhesive agents.

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Translated by P. Rosner

## The Possible Application of Dissolution Measurements to the Study of Composite Films

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Received 25 November 1992

The dissolution rheoviscometric measurements were used to evaluate dissolution of films based on gelatin upon the addition of nonionic hydroxyethylcellulose and ionic carboxymethylcellulose. The method is very useful for the interpretation of the dissolving process by the quantitative parameters and can be used for a more complex evaluation of composite films.

The solid layered systems based on water-soluble polymers have many applications [1]. The study of composed polymer films is of interest with regard to many practical aspects oriented to solubility, flexibility, and other technically important properties. In this paper we want to show the possibility of study of composite polymer films using rheoviscometric dissolution measurements. A laboratory device for continuous dissolution measurements of polymers by solution viscosity recording was described earlier [2]. The nonlinear viscosity dependence on the polymer content in the solution is utilized to measure a dis-

solution by recording the driving motor power of the discs rotating within the solution.

Gelatin, which was used as the binding agent for photographic layers 100 years ago is still very common polymeric component in many layered materials. Mixing the gelatin with water-soluble appropriate polymers we can obtain layers with combined properties of individual components. In case of gelatin which is an ionic polymer we have to consider different types of interactions with different polymer components depending on their chemical nature. However, between two ionic polymers we can ex-

pect the formation of polyelectrolyte complexes [3–5]. To demonstrate the utilization of dissolution measurements for the study of composite films, we compare two systems based on gelatin upon the addition of nonionic hydroxyethylcellulose and ionic carboxymethylcellulose.

## EXPERIMENTAL

We used commercial sample of gelatin (LOBA CHEMIE — Fischamend), Prep. 18519. The sodium salt of carboxymethylcellulose (CMC, Lovosa) was precipitated by acetone (water to acetone volume ratio = 1 : 3). Molecular mass ( $M_r$ ) was about  $1.1 \times 10^5$  and degree of substitution (DS) 0.95. Hydroxyethylcellulose 250H (HEC, Hercules) had  $M_r$   $5 \times 10^5$  and DS 2.5.

The polymer solutions for the preparation of films were prepared by dissolving polymers in 0.1 M-NaCl aqueous solution. Polymers were swollen first at 20 °C and then they were dissolved at temperature 40–50 °C by intensive mixing in a water bath during 1 h. The films were prepared by water evaporating at 30 °C in thermostat chamber and kept at ambient temperature in the desiccator. It was necessary to use a thick foil ( $> 0.5$  mm) in order to attain independence of measured kinetic parameters from the sample thickness.

The viscosity was measured by a rotary disc viscometer that works also as a stirrer. Rotating discs are driven by DC motor, the power of which is a function of solution viscosity. The solution viscosity is recorded continually in time using a personal computer. The computer is recording a numerical quantity proportional to the power, which is a complicated complex function of the polymer solution mass concentration  $\rho_{p,l}$ . The measured data can be transformed by a computer through a calibration function to the required physical dimension [2].

## RESULTS AND DISCUSSION

The dissolution curves of composite films HEC–gelatin and pure components at two temperatures are shown in Figs. 1 and 2. The differences in solubility are more expressive at lower temperature. The highest solubility is recorded for the composed film. A different behaviour can be seen for the composed films CMC–gelatin (Figs. 3 and 4). The solubility of composed films is lower comparing with the films made of pure CMC at both temperatures. The effect is more recognized at lower temperature.

The dissolution of composite polymer films has some typical features when compared to dissolution of films made from a single polymer. The transport

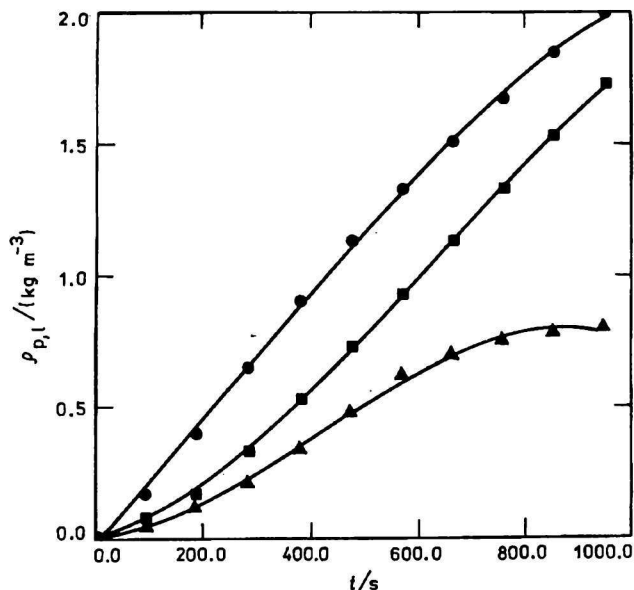


Fig. 1. Dissolution curves of films prepared from the mixture HEC–gelatin and from pure components at 45 °C. ● HEC–gelatin, ■ HEC, ▲ gelatin.

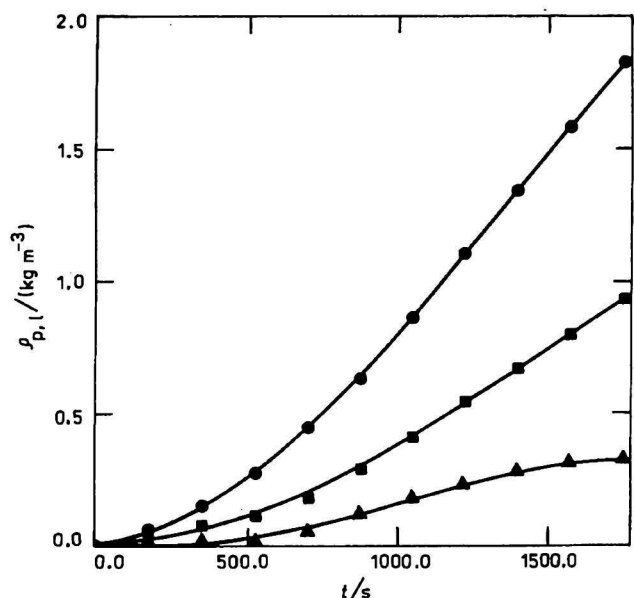


Fig. 2. Dissolution curves of films prepared from the mixture HEC–gelatin and from pure components at 22 °C. Denotation as in Fig. 1.

of polymer into solvent does not take place immediately after contacting with solvent. One of the characteristic kinetic parameters of the dissolution process is an induction period,  $t_0$ , which generally depends on temperature, the polymer characteristics, kinetic and thermodynamic properties of solvent and also on the method of film preparation [6, 7].

The theoretical background of the diffusion process of dissolution is introduced in [2]. The dissolution kinetic curve following the mathematical curve is shown in Fig. 5. Putting the polymer in a contact

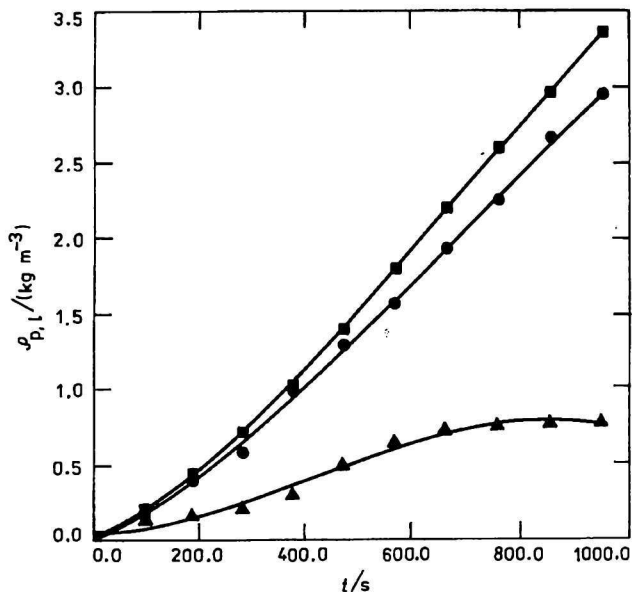


Fig. 3. Dissolution curves of films prepared from the mixture CMC-gelatin and from pure components at 45 °C. ● CMC-gelatin, ■ CMC, ▲ gelatin.

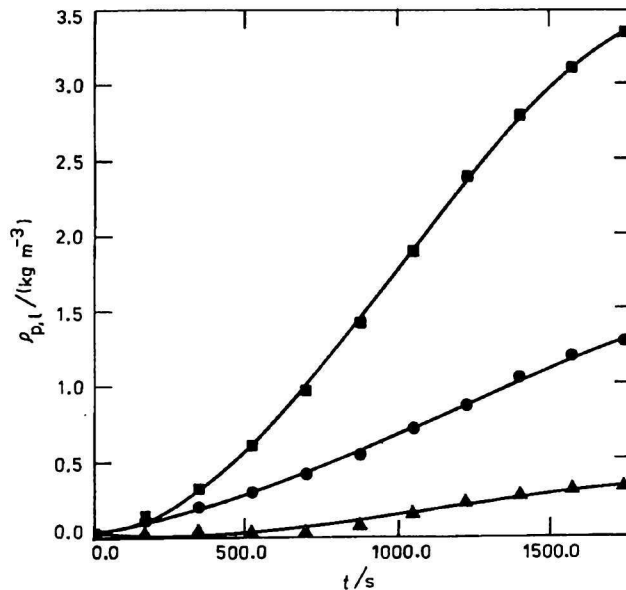


Fig. 4. Dissolution curves of films prepared from the mixture CMC-gelatin and from pure components at 22 °C. Denotation as in Fig. 3.

with solvent, swelling starts in the first period of the process. The dissolution is described in the first approximation as quasi-stationary in a time region when  $\rho_{p,i}(t) \ll \rho_{c,i}(\text{saturated})$  which is the initial stage of dissolution with a sufficient volume of the solvent. Steady-state dissolution is defined by the constant rate of dissolution,  $d\rho_{p,i}/dt$ . The diffusion coefficient is expressed by the equation

$$D = 3/2 t_Q [ |(V_s/Aq) (d\rho_{p,i}/dt)|_{t \rightarrow t} ]^2$$

where  $A$  is the area of the interfacing surface,  $V_s$  is the solution volume, and  $q$  is density of the polymer film.

The kinetic parameters of dissolution of compos-

ite films and pure polymers were analyzed on the basis of this model. The data are summarized in Table 1.

By this way the systems can be compared quantitatively. Evaluating the parameters separately, it can be seen that time of swelling is shortened with increasing temperature for all systems and thickness of the surface swollen layer is proportionally diminished. Besides, the velocity of dissolution increases with temperature.

Evaluating the experimental results, it is interesting first to compare the data of the induction period and velocity of dissolution between the composed system with HEC and CMC. The system CMC-gelatin falls into the region between the data of the pure

Table 1. Kinetic Parameters of Dissolution Measurements

$\theta$ °C	Layer	$t_Q$ s	$d\rho_{p,i}/dt$ $\text{kg m}^{-3} \text{s}^{-1} \cdot 10^{-4}$	$D$ $\text{m}^2 \text{s}^{-1} \cdot 10^{-12}$	$q$ $\text{m} \cdot 10^{-6}$
22	CMC	350	27.21	2.77	154
	CMC-gelatin	376	10.35	0.43	62
	Gelatin	613	3.95	0.10	40
45	CMC	128	40.97	2.30	85
	CMC-gelatin	142.5	36.94	2.08	85
	Gelatin	171	16.45	0.49	44
22	HEC	507	7.48	0.30	60
	HEC-gelatin	420	13.66	0.84	90
	Gelatin	560	3.57	0.07	30
45	HEC	133	21.24	0.64	46
	HEC-gelatin	38	26.32	0.28	16
	Gelatin	171	15.79	0.46	44

$t_Q$  — time of swelling (induction period),  $d\rho_{p,i}/dt$  — velocity of dissolution (quasi-stationary),  $D$  — the diffusion coefficient of the solvent into polymer,  $q$  — thickness of the surface swollen layer.

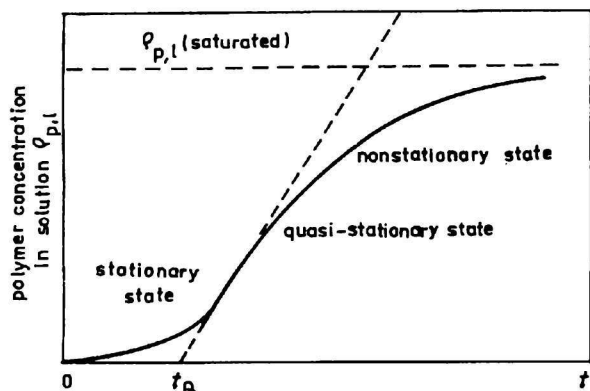


Fig. 5. Dissolution kinetic curve;  $t_0$  – time of swelling (induction period).

components. This is evident especially at lower temperature (Fig. 4). The solubility of the film CMC–gelatin increases with higher temperature and can be more compared with pure CMC (Fig. 3). On the other hand, comparing the system HEC–gelatin with pure components, we can see that the composed system is swollen more rapidly at both temperatures (Figs. 1 and 2). Particularly at 45 °C the process of dissolution starts almost immediately without a marked stationary state of swelling and so it probably does not comply with the proposed model. This could explain a very low value of the calculated diffusion coefficient for the system HEC–gelatin at 45 °C (Table 1). The values of diffusion coefficients as well as the values of thickness of the surface swollen layer correspond with the times of swelling and the velocities of dissolution for all further evaluated systems.

The different behaviour of the complex system HEC–gelatin and CMC–gelatin is caused by different chemical character of the components. In case of CMC and gelatin, both are ionic polymers. A mutual influence and probably the formation of polyelectrolyte complexes can lower dissolution. The explanation of the behaviour of HEC–gelatin film can be seen in comprehensive decreasing of cohesive energy due to the addition of the nonionic polymer HEC to gelatin.

Changes of gelatin film solubility by the addition of different water-soluble derivatives of cellulose are a good example of how the dissolution measurements can be used for the study of such systems. In other words, the dissolution measurements interpreted by the quantitative parameters of the dissolving process can help to evaluate the structure of composite films as well as interactions between the components. Theoretical working out of these problems is a subject of the next paper.

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Translated by D. Bakoš