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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Effect of Mixture Components on the Rheological Characteristics of the Composite

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Abstract—Rheological characteristics and properties of composites prepared from tanning industry wastes were studied in relation to the ratio and composition of components in the mixture.

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Any production involves formation of wastes whose certain fraction is recycled, whereas the other fraction is dumped, polluting the environment. Therefore, utilization of collagen-containing wastes (chrome leather chips, hide crops, etc.) formed in significant amounts in the course of the rawstock treatment is an urgent problem from both commercial and environmental viewpoints.

An alternative solution of the problem of utilizing collagen-containing wastes can be based on modern procedures developed for processing of polymeric and biopolymeric systems [1, 2]. New polymeric materials with a wide range of service properties can be prepared from compounds of various chemical nature, including wastes from the tanning industry. These materials can be most efficiently used in production of insole and support materials, especially for sports, childhood, and orthopedic footwear.

Elucidation of the relationship between the composition and structural and mechanical properties of the composites is one of the main problems in production of composite materials with required characteristics [3]. However, data on the rheological properties of mixtures for preparing composites based on the protein–polymer matrix and collagen-containing filler are scarce.

In this study we examined the elastoplastic and heat-protecting properties of composites prepared from disperse systems containing latexes, products of collagen dissolution (PCD), products of collagen hydrolysis (PCH), and polyethylene glycol oleate (PEGO) plasticizer. The following latexes were used: Lenteks A5 (acrylate–styrene), Lenteks AN7 (terpolymer of acrylate with styrene and acrylonitrile), BS-50 (butadiene–styrene), and BN3 (copolymer of acrylate with acrylonitrile). As a filler, we used chrome leather chips, wastes from shaving of the chroming half-finished product, preliminarily ground to 1.0–1.5 mm size, with water and chromium oxide contents of ≥30 and ≥3.8–4.3%, respectively. The dry residues of PCD and PCH were 2.81 and 8.57%, respectively.

The rheological properties of the mixtures were determined on a DV-II Brookfield viscometer at a shear rate of 30 s^{-1}. First, we studied the rheological properties of mixtures of the initial components. The viscosity of the protein-containing solutions is plotted in Fig. 1 vs. the content of chrome leather chips. As seen, with increasing content of the chips in the mixture its viscosity increases. The strongest increase in the viscosity of the PCH- and PCD-containing systems is observed at the chip content of 20–25 and 10–20 wt %, respectively. Probably, at these compositions fine chips are saturated with macromolecules of hydrolyzate and PCD, whereas further linear increase in the viscosity is due to the system thickening. At the viscosity of the chrome leather chips–PCD system higher than 8000 mPa s, casting of the resulting mixture to prepare the composite material is complicated by its poor distribution in the mold.

Changes in the viscosity of the chrome leather chips– PCD system also depend on the content of PCD (Fig. 2).

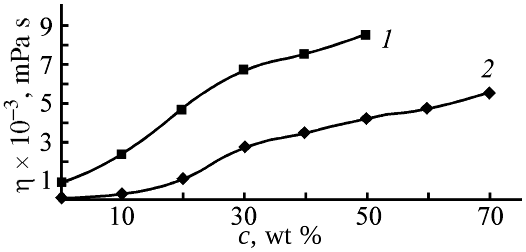

Fig. 1. Viscosity η of (*1*) PCD and (*2*) PCH systems as a function of the chip content c.

Table 1. Properties of composites in relation to the ratio of the initial components

Sample no.	Chips : PCD : AN7 latex ratio	Volume, cm^3	Thickness, cm	Weight, g	Specific density, g cm^{-3}	Heat conductivity, W m^{-1} deg^{-1}
1	1 : 1 : 0.1	16.06	0.3	6.8	0.42	0.059
2	1 : 1 : 0.5	23.59	0.4	11.4	0.48	0.047
3	1 : 1 : 1.3	46.07	1.0	23.2	0.50	0.168
4	1 : 0.5 : 0.1	18.28	0.3	6.4	0.35	0.079
5	1 : 0.5 : 0.2	20.90	0.4	8.2	0.39	0.086
6	1 : 0.5 : 0.5	26.12	0.4	12.0	0.42	0.104
7	1 : 0.5 : 1	37.21	0.7	16.6	0.45	0.138

For example, the viscosity strongly decreases with adding AN7 latex at a small content of PCD. This suggests that, under the given experimental conditions, the system viscosity decreases due to the plasticization of the chrome leather chips with the polymer. With increasing PCD content in the system, the dependence becomes more complex, probably due to the interaction between PCD and latex (solutions of protein and acrylonitrile polymer), and this interaction determines the viscosity of the system. First, the polymeric complexes exhibiting no plasticizing effect are formed, and, as a result, the viscosity increases. Then, due to the affinity for the chromic collagen, certain fraction of the hydrolyzate is adsorbed on the chip surface, plasticizing the system and decreasing its viscosity. The system stabilizes at a PCD : latex ratio of 1 : 1, and its viscosity decreases with further addition of the polymer. In excess PCD, the maximal viscosity is observed at the polymer content of 5 wt %.

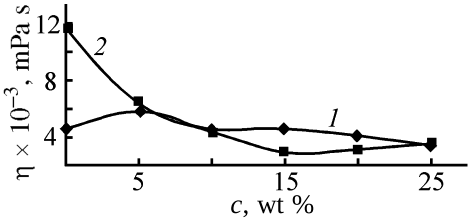

Fig. 2. Viscosity η of the system as a function of the AN7 latex content *c*. PCD content, wt %: (*1*) 12.8 and (*2*) 6.4.

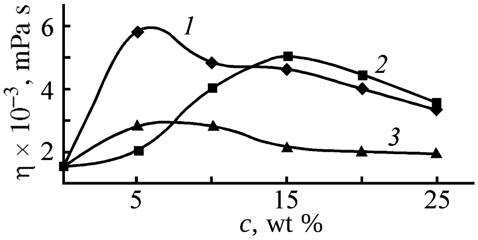

Fig. 3. Viscosity η of the system as a function of the latex content *c*. Latex: (*1*) AN7, (*2*) BN3, and (*3*) BS-50.

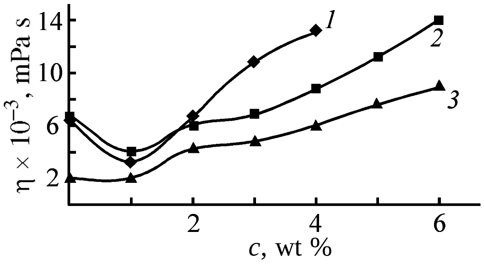

Fig. 4. Viscosity η of the system as a function of the plasticizer content *c*. PCD content, wt %: (*1*) 3.2, (*2*) 6.4, and (*3*) 12.8.

The effect of various latexes on the rheological properties of the system is illustrated in Fig. 3. In all the systems, the viscosity passes through a maximum, though at different polymer concentrations. The best structuring effect is observed for AN7 latex exhibiting the maximal viscosity of 6000 mPa s at its content in the system of 5 wt %. Slightly lower viscosities are typical of the mixtures with BN3 latex at its content of 15 wt %. BS-50 latex is efficient in the concentration range 5–10%, but the system viscosity does not exceed 3000 mPa s, i.e., it is lower by a factor of 2 as compared to the system with AN7 latex. These data suggest intermolecular interactions between the protein functional groups and polar groups of the latexes in the systems studied.

Study of the rheological characteristics of the system in the presence of PEGO (Fig. 4) showed that the viscosity of the system first decreases and then increases upon addition of the plasticizer, and the system becomes thickened. Since the viscosity range is limited, 2 wt % plasticizer content was suggested.

As seen from Table 1, sample nos. 4 and 5 have the smallest density, and sample nos. 1 and 2, the lowest heat conductivity. The use of these materials as insoles would provide the comfortable conditions of shoe wearing [4].

The elastoplastic characteristics of the resulting composites were studied on a Relaks apparatus [5]. It is known that comparison of the deformation and

Table 2. Elastoplastic properties of the composites

Sample no.	Modulus of Hookean elasticity E_1	Modulus of hyperelasticity E_2	Viscosity coefficient N_1	Viscosity coefficient N_2	Viscoplasticity coefficient N_3
	MPa		MPa s		
1	55.3	159	2.74	354	15192
2	52.4	120	14.6	366	7203
3	229	513	151	1809	13428
4	24.9	55.1	3.51	154	2858
5	11.1	23.1	5.41	55.9	1073
6	11.0	25.9	10.2	89.5	666
7	73.6	169	77.25	656	4261

strength properties of the composites allows evaluation of the contribution of one or another component to formation of the structure and properties of the materials. The relaxation spectra of the composites prepared using AN7 latex with various ratios of the initial components are shown in Fig. 5. The elastoplastic characteristics of the composites are listed in Table 2. Figure 5 shows a strong effect of the latex content on the composite properties. At a small latex content, the relaxation spectra have two maxima characterizing various structural levels, which indicates that the composite structure in this case most strongly resembles natural leather. These relaxation maxima suggest formation of the developed inner surface of the composite and high porosity, which is confirmed by the data on air permeability (maximal value 36000 ml cm^{-2} h^{-1}) and density of the samples (minimal value, Table 1).

Comparison of these results with the rheological characteristics of the mixtures suggests that, to prepare composites with high molding properties, low heat conductivities, and small densities, the composition viscosity should vary within the 3000–4500 mPa s range.

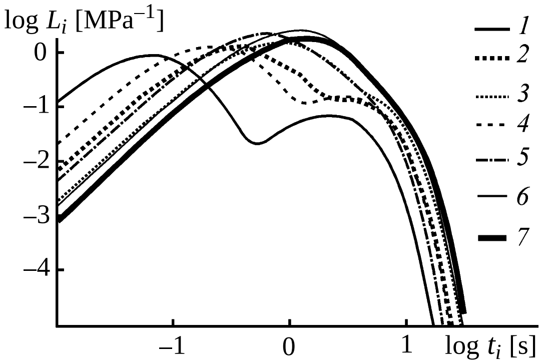

Fig. 5. Relaxation spectra of the composite samples in log t_i–log L_i coordinates. (t_i) Relaxation time and (L_i) ductility. Numbers at the curves correspond to the sample nos. in Table 1.

As seen, with increasing content of AN7 latex (sample nos. 1–3), the viscosity coefficient of the rapid relaxation processes N_1 increases, and at a latex content of 25 wt %, N_1 increases by an order of magnitude. The elasticity characteristics also sharply increase. In the systems with smaller content of PCD (sample nos. 4–7), with increasing content of the latex from 6 to 25 wt %, the moduli of Hookean elasticity and hyperelasticity first decrease and then increase. As shown previously, these trends are due to the interaction of the protein and acrylonitrile polymer in solutions. The moduli of Hookean elasticity and hyperelasticity are the most informative in evaluation of the effect of the polymer content on the composite properties.

Using the rheological characteristics of the systems studied, we determined the optimal ratios of the initial components to prepare the mixtures with high moldability. Variation of the chrome leather chips : PCD : latex ratio allows control of the properties of the composite materials. The composites prepared from the tanning industry wastes show promise for the development of the modern footwear design and production of building and decorative panels with high heat-protection properties.

CONCLUSIONS

(1) Viscosity of the mixtures is determined by both the ratio of the initial components and their chemical nature. Styrene and acrylate latexes exhibit different structuring effect. The optimal viscosity of the system studied varies within 3000–4500 mPa s.

(2) The heat conductivity of the composite increases with increasing latex content in the mixture.

(3) Moduli of Hookean elasticity and hyperelasticity strongly increase and the heat-protection properties decrease with increasing latex content in the mixture over 25 wt %.

REFERENCES

1. RF Patent 2 018 540.
2. RF Patent 2 198 225.
3. Gol’dman, A.Ya., *Prognozirovanie deformatsionno-prochnostnykh svoistv polimernykh i kompozitsionnykh materialov* (Prediction of the Deformation and Strength Properties of Polymeric and Composite Materials), Leningrad: Khimiya, 1988.
4. Vershinin, L.V., Repina, N.S., and Burtseva, I.V., *Kozh.-Obuv. Prom-st.*, 2002, no. 4, pp. 19–20.
5. Burmistrov, A.G., Chursin, V.I., and Manukyan, A.N., *Kozh.-Obuv. Prom-st.*, 2000, no. 4, pp. 21–30.