Poly(urethan-urea), modifier of impact strength of poly(vinyl chloride)

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To improve the impact strength of poly(vinyl chloride), a physical mixture of polymers with powdered poly(urethan-urea) as the modifier was prepared. The distinct modifying effect has been explained by investigating the decisive criteria used for evaluation of the rubberlike component.

С целью улучшить ударную прочность поливинилхлорида, была приготовлена физическая смесь полимеров с порошкообразной полиуретанмочевиной в роли модификатора. Резкий модифицирующий эффект был объяснен в ходе исследования определяющих критериев, используемых для оценки резиноподобного компонента.

Preparation of physical mixtures with a polymer modifier is one of the ways of improving the impact strength of a glassy polymer. Production of impact poly(vinyl chloride) (i-PVC) by this method has not been wide-spread so far, mainly due to the lack of suitable polymers meeting the required criteria for the modifying rubberlike component. For this purpose many macromolecular substances, *e.g.* nitrile rubbers with different content of acrylonitrile, natural, synthetic, and chloroprene rubbers, chlorinated polyethylene, polyamides and polyacrylates, ABS and MBS terpolymers, polyurethan elastomers, and ethylene—vinyl acetate copolymers have been investigated. However, only some of them, namely, chlorinated polyethylene, found application in practice. Also the use of poly(urethan-urea) as a modifier of impact strength of PVC has been only sporadically dealt with in the literature and claimed to be little effective [1—3].

In the present communication the preparation of i-PVC in physical mixture with thermoplastic powdered poly(urethan-urea) (PURU) [4, 5], prepared by a new technological procedure [6, 7], is described and the mechanism of the effect of the modifier is investigated.

Experimental

Materials

Poly(urethan-urea), $M = 190\,000$ g mol^{-1}, content of allophanate—biuret bonds 0.1 mass % NCO, content of primary amino groups 0.02 mass %, bulk density 600 kg m^{-3}, particle size 40—250 μm, portion of particles of 40—90 μm 92 mass %.

Poly(vinyl chloride), suspension Slovinyl S-683, product of CHZWP Nováky, K value 68, bulk density 500 kg m^{-3}, intrinsic viscosity $[\eta] = 115$ cm^{3}g^{-1}.

Interstab M-195, product of AKZO AMERSFOORT, calcium-zinc soaps dispersed in soya oil.

Phosclere P-315, tris(nonylphenyl)phosphite, product of AKZO AMERSFOORT.

Wax E, montan wax, product of Hoechst, pour point 76—81 °C.

N,N-Dimethylformamide, product of Fluka A.G., b.p. = 152—154 °C, $\varrho\,(20\,°C) = 948$ kg m^{-3}, $n_D^{20} = 1.4300$.

Working procedure

Suspension PVC Slovinyl S-683 (100 g), the investigated amount of PURU, stabilizer Interstab M-195 (3 g), chelating agent Phosclere P-315 (1 g), and wax E (0.5 g) were homogenized in an ETA MIRA mixer at 5 rs^{-1} for 10 min. The obtained physical mixture was plasticized on a laboratory two-roll mill at 175 °C for 5 min. From the calendered foil (64 g) test specimens of 50 mm × 200 mm × 4 mm were prepared by compression moulding on a CBS 45-7 hydraulic press with preheating to 175 °C for 5 min; time of moulding 5 min at 180 °C and 30 MPa. The specimens were cooled to room temperature at the same pressure within 5 min.

Determination of compatibility of PVC and poly(urethan-urea) by rheoviscosimetric method

Viscosity of solutions ($w = 2.5$ mass %) was measured on a Höppler viscosimeter at (20.0 ± 0.1) °C. The solutions were prepared by dissolving the mixtures of PVC and PURU in *N,N*-dimethylformamide at 50 °C during 5 h.

Dynamic mechanical measurement of i-PVC and poly(urethan-urea)

Temperature dependences of the real part of complex elasticity modulus E', imaginary part of complex elasticity modulus E'', and tangent of loss angle tg δ were measured on a Rheovibron DDV-II-C (Toyo Baldwin Co.) apparatus at temperatures from -50 °C at linear increase 1 K min^{-1} and 110 Hz.

Preparation of electron micrographs of fracture surfaces

Fracture surfaces of i-PVC were obtained by a defined hammer blow after the Charpy method at room temperature. These surfaces were fixed onto aluminium plates and adjusted

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by coating in a sputtering Balzers apparatus to be surface-conductive. The electron micrographs were obtained with a rastering JSM 35 electron microscope at accelerating voltage of 25 kV; magnification 4000.

Measurement of notch impact strength

Notch impact strength of i-PVC was measured on test specimens No. 3 of 50 mm × 6 mm × 4 mm at 20 °C according to Czechoslovak Standard 64 0612. When measuring the temperature dependence of notch impact strength, the test specimens were kept at the measuring temperature for 4 h; 15 test specimens were used.

Results and discussion

From the relationship of notch impact strength on the PURU content follows that a relatively high notch impact strength, 15.6 kJ m^{-2}, has been achieved already with a charge of 4 mass %. Further increase of the PURU amount resulted in rapid increase of notch impact strength reaching the maximum value 62 kJ m^{-2} with 7.5 mass %. In the range of $w = 7.5$—15.0 mass % the notch impact strength was practically constant, with higher charges slightly decreased (Fig. 1). The representative curve showed a rapid increase in notch impact strength already at low charges of PURU, high value and wide plateau of the maximum, and slight decrease beyond the maximum.
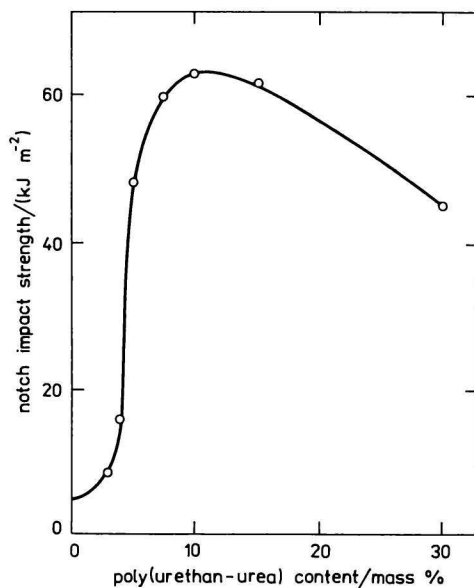

Fig. 1. Dependence of notch impact strength of i-PVC on the poly(urethan-urea) content.

PVC modified by poly(urethan-urea) is highly impact resistant not only at 20 °C but also at low temperatures. From the temperature dependence of notch impact strength of i-PVC with 7.5 and 10 mass % PURU it is evident that with decreasing temperature the notch impact strength decreases, however, it is still high enough $(40—15 \text{ kJ m}^{-2})$ in the temperature range from 0 to -20 °C (Fig. 2).
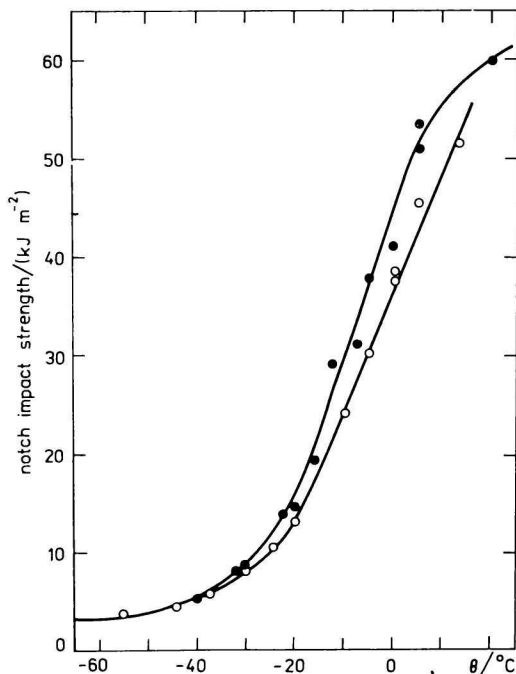

Fig. 2. Temperature dependence of notch impact strength of i-PVC containing poly(urethan-urea).
○ 7.5 mass % ; ● 10 mass %.

According to the theory of impact strength of two-phase systems, the decisive criteria for modifying rubber polymers are [8—10]: incompatibility, insolubility of polymers, good interfacial adhesion, low temperature of glass transition, and suitable size and distribution of particles.

Compatibility of PVC and PURU was determined by the rheoviscosimetric method [11]. The values of the characteristic coefficient $\Delta i/\Delta \eta$ (Δi is the difference between additive and real viscosities and $\Delta \eta = (\eta_{\text{solution of PURU}} - \eta_{\text{solution of PVC}})$ were read off from the graphical dependence of viscosity of PVC and PURU mixtures in N,N-dimethylformamide on composition of both polymers (Fig. 3). The characteristic coefficient $\Delta i/\Delta \eta$ for PVC and PURU mixtures varied in the range 0.1—0.14. Since these values are higher than 0.1, the polymers are incompatible.

The compatibility of polymers can be reliably determined only from the properties of the final polymer composite. From dynamic mechanical properties of
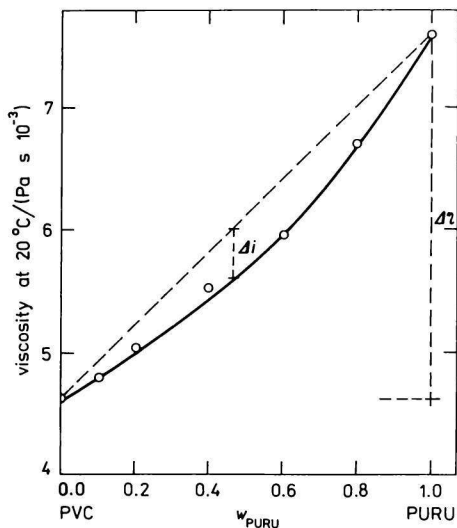
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Fig. 3. Dependence of viscosity on the composition of PVC and poly(urethan-urea) mixtures.

impact PVC with 7.5 mass % PURU it is evident that the real part of the complex elasticity modulus E' decreases monotonously up to 80 °C and on the curves of temperature dependences of imaginary part of the complex elasticity modulus E'' and tangent of loss angle tg δ two maxima appeared (Fig. 4). The first one,
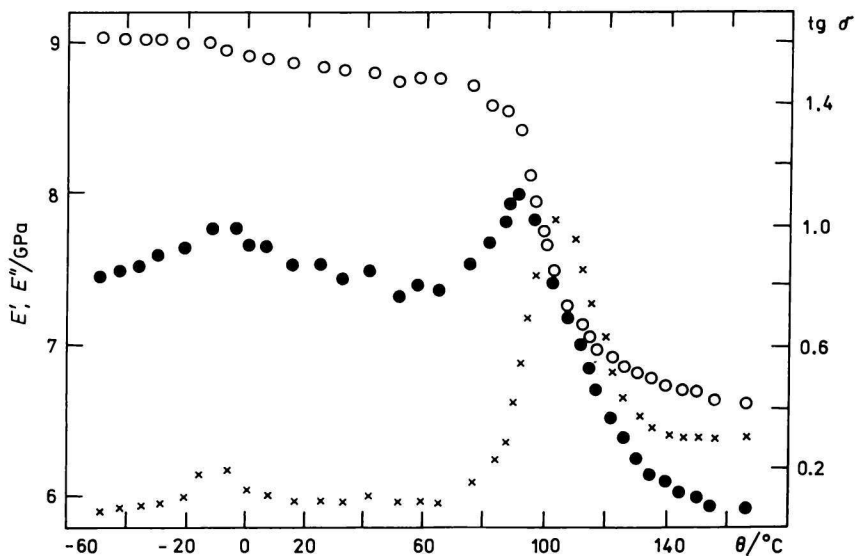

Fig. 4. Dependence of the real part of complex elasticity modulus E' (○), imaginary part of complex elasticity modulus E'' (●), and tangent of loss angle tg δ (×) on temperature of impact PVC containing 7.5 mass % poly(urethan-urea).

a slightly distinct maximum, appearing at -12.5 °C belonged to transition temperature of the modifier PURU, the second pronounced transition with the maximum at 103 °C belonged to PVC. The positions of both maxima of transition temperatures were independent of the PURU content (5—30 mass %), which indicated a two-phase system of incompatible polymers.

The second decisive parameter for an effective modifier is good adhesion between the separated phases. In the investigated PVC—PURU system the sufficiently high interfacial adhesion is conditioned by hydrogen bond between the chlorine atom of the PVC chain and the strongly polar hydrogen on the nitrogen atom bound in the urethan bond —NH—COO—, disubstituted urea —NH—CO—NH—, and terminal primary amino group —NH$_2$ of poly-(urethan-urea).
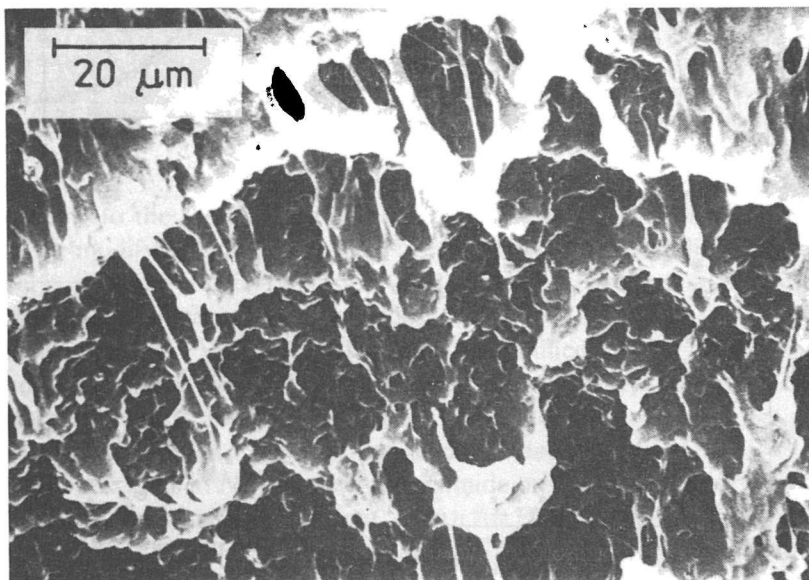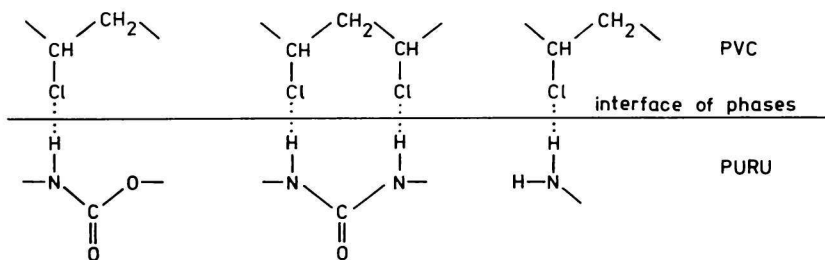

Fig. 5. Electron micrograph of fracture surface of impact PVC containing 7.5 mass % poly(urethan-urea).

The electron micrograph of the fracture surface of i-PVC obtained by rastering electron microscope pointed to good adhesion between the PVC and PURU phases. On the electron micrograph of the fracture surface of i-PVC with 7.5 mass % PURU (notch impact strength 63 kJ m^{-2}) a clear plastic deformation connected with increased orientation and fibrillation of the material and high density of distinct oriented fibres can be seen (Fig. 5). With lower amount of the modifier PURU in the composite the density of fibres is proportionally lower, which points to the fact that the formation of fibres is initiated by the modifier particles.

Should the modified poly(vinyl chloride) be impact resistant, *i.e.* the impact stress applied be dispersed by relaxation mechanisms, the side dispersion region of the composite must be effective at lower temperatures, *ca.* $-10\,°C$ [12]. By measuring the dynamic mechanical properties of the real part of complex elasticity modulus E', imaginary part of complex elasticity modulus E'', and tangent of loss angle tg δ in dependence on temperature it was shown that the glass transition to
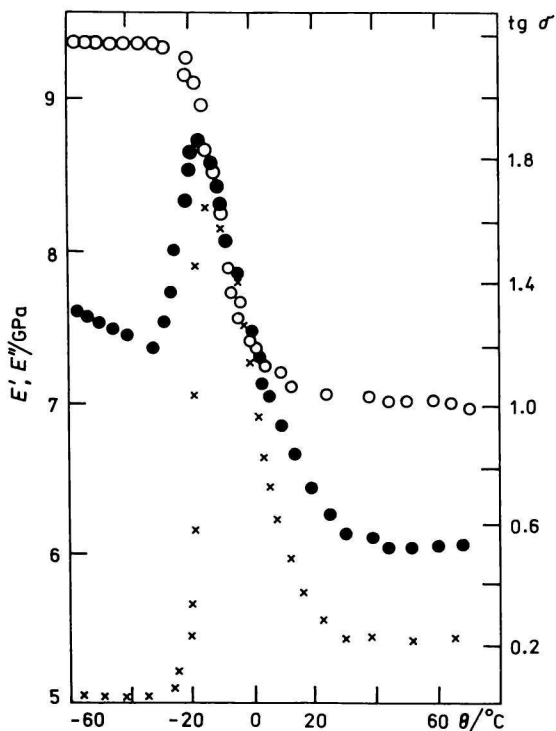

Fig. 6. Dependence of the real part of complex elasticity modulus E' (○), imaginary part of complex elasticity modulus E'' (●), and tangent of loss angle tg δ (×) on temperature of poly(urethan-urea).

viscoelastic state of poly(urethan-urea) was at sufficiently low temperature − 12.5 °C (Fig. 6). Comparison of dynamic mechanical properties of E'' and tg δ of PURU and i-PVC (Figs. 4 and 6) revealed that the maximum of transition of the modifier appeared at the same temperature both with i-PVC and PURU itself.

The properties and homogeneity of i-PVC are affected also by morphology of the modifier particles. By proper choice of technological conditions it is possible to prepare PURU of 25—1000 μm, while the particle size of the individual charges is in the range of maximum 50 μm. It was found that the particle size in the mentioned range had practically no effect on notch impact strength when processing the physical mixture by rolling. In spite of this finding it is probable that the effect of particle size will be more pronounced when physical mixtures will be treated by other technologies. Besides, the particle size affects the preparation of physical mixtures, their homogeneity, and stability against segregation and separation.

Powdered poly(urethan-urea) meets the required criteria for the rubber component and is a highly effective modifier of impact strength of PVC. The elaborated procedure for the preparation of PURU widened the sortiment of modifiers for impact PVC mixtures. On the basis of the obtained results this modifier can be attributed a prominent place among polymer modifiers.

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