Properties of concentrated solutions of polyvinyl chloride

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SUMMARY
The influence of the molecular weight of suspension polyvinyl chloride on the rheological characteristics of solutions based on it in solvents of different nature is established.

At present, vinyl chloride homopolymers of different grades with a Fikentscher’s constant $K_f$ in the range 50–80 are being produced on an industrial scale. The $K_f$ characterises the molecular weight of polyvinyl chloride: the greater the $K_f$, the higher is the molecular weight of the PVC. Polyvinyl chloride, in compound form, is processed by extrusion, calendering, injection moulding, atomisation, and moulding of plastisols, but it has not been used hitherto as a film former for lacquer coatings, although it is a good anticorrosion material, resistant to many corrosive media, and relatively cheap. In lacquer coatings, instead of PVC, use is made of copolymers based on vinyl chloride and chlorinated polyvinyl chloride, which are 5–10 times more expensive than PVC. The reasons for this have traditionally been considered to be the strong tendency of PVC to form associates of macromolecules in solutions, the increase in viscosity of the solutions with time, and subsequent gelation [1, 2]. However, in the literature, the question of the influence of the molecular weight of PVC on processes of dissolution and gelation has hardly been considered, while available experimental data are fragmentary and contradictory in nature and mainly concern polymers with a narrow range of molecular weights corresponding to $K_f$ values in the range 55–80.

We had already estimated the influence of the molecular weight of industrial specimens of suspension PVC with $K_f$ values of 60, 70, and 80 on the intrinsic viscosity $[\eta]$ and parameter $k_H$ in the Huggins equation [3] at a temperature of 25°C:

$$[\eta_{rel}] / c = [\eta] + k_H [\eta]^2 c$$  \hspace{1cm} (1)

Traditional plasticisers for PVC were used as solvents: dibutyl phthalate (DBP); diocyl phthalate (DOP); diocyl sebacinate (DOS); and KhP-418 chlorinated paraffin, and also cyclohexanone (CH) as the reference solvent for estimating the molecular weight of PVC and the magnitude of $K_f$ by the ISO 1628-2 procedure.

The results obtained are presented in Figures 1a and 1b and indicate the following:

1. In the thermodynamically “poor” solvents DOS and KhP-418, the values of the intrinsic viscosity of PVC are considerably lower than for the “good” solvents DBP, DOP, and CH, as expected from the theory of Flory–Huggins solutions [1, 3].

2. In “poor” solvents DOS and KhP-418, the influence of the molecular weight of the polymer on the magnitude of the intrinsic viscosity is considerably weaker compared with the “good” solvents DBP, DOP, and CH.

3. In the “poor” solvents DOS and KhP-418, the parameter $k_H$, which indirectly characterises the compatibility of the polymer with the solvent, decreases with reduction in the molecular weight of the PVC, approaching the corresponding $k_H$ values of the good solvents DBP, DOP, and CH.

All this enabled us to assume that, with reduction in the
molecular weight of the PVC, concentrated solutions of the polymer in “poor” solvents can differ considerably, in terms of their behaviour with time, from the traditionally held belief that gradual gelation of PVC in solutions occurs.

To investigate the properties of such solutions, specimens of PVC with \(K_F\) of 36–84 were specially synthesised. A mixture of acetone and toluene in a mass ratio of 26:74 was used as the “poor” solvent. The dissolution of PVC was conducted during mixing for 3 h at a temperature of 60 ± 5°C, and then the solution was cooled to 20°C, and the nominal and relative viscosity of the solution were determined using a VZ-246 viscometer with a nozzle diameter of 4 mm (GOST 8420-74). The solutions were stored at room temperature, and periodically during storage their viscosity was assessed.

With increase in the concentration of solutions for PVC with different \(K_F\) values, starting with a certain concentration, the viscosity of freshly prepared solutions begins to increase sharply, and rapid gelation is observed in the system. We termed the minimum concentration of solutions with which the relative viscosity has values of 1.4–2.2 and gelation of the freshly prepared solution does not occur the critical concentration of gelation for PVC of the given molecular weight. The dependence of the critical concentration of gelation on the magnitude of \(K_F\) of the polymer is presented in Figure 2. The results obtained make it possible to conclude that PVC with a \(K_F\) of below 45 is capable, in principle, of yielding gelation-resistant solutions with a concentration of 13–22%. It is this solution concentration range that is of interest and that is used in industry in the production of lacquers and enamels based on copolymers of vinyl chloride and chlorinated PVC.

Investigation of the viscosity properties of solutions of PVC with a \(K_F\) value of 36–48 with a concentration of 13 wt% during storage for 2 years showed that, in PVC solutions with \(K_F > 45\), the viscosity increased fairly rapidly, and gelation is observed in the system; and conversely, PVC solutions with \(K_F < 45\) are stable with time.

A possible reason for stability of these solutions is believed by the present authors to be as follows. Macromolecules of low-molecular-weight PVC with \(K_F < 45\) in solution comprise slightly swollen coils in solvent; the coefficient of swelling of coils \(\alpha \to 1\). In all likelihood, PVC macromolecules are strongly associated. Here, coils in solution behave like rigid balls: the dependence of the relative viscosity of solutions on concentration (the volume fraction of the polymer) is in practice determined by the well-known Einstein equation [4] for calculating...
the relative viscosity of a suspension of particles of spherical shape:

$$\eta_{rel} = 1 + 2.5^2$$

For PVC with $K_F > 45$, the relative viscosity of the solution increases much more rapidly with increase in concentration, and this probably results in greater swellability of the PVC in solution and increases the effective volume fraction of the coils, and ultimately leads to the coalescence of coils and to gelation.

Thus, the possibility of producing concentrated solutions of polyvinyl chloride that are stable during storage has been shown for the first time. On the basis of the results obtained, technology for the production of low-molecular-weight PVC for lacquers according to TU 2212-026-10641390-2004 and the formulation and technology for lacquer of grade KhV-701B based on PVC have been developed. Lacquer KhV-701B is intended for the long-term protection of concrete, brick, metal, and wood, both in above-ground and below-ground structures, against the constant and variable action of corrosive media, including media characteristic of natural groundwaters and storm run-offs. The development is protected by a Russian patent [5].

REFERENCES


