IRREVERSIBILITY OF DEGRADATION OF POLYMER SOLUTIONS

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The degradation of polymer solutions of different concentration was investigated. It was found that a polymer solution that has been degraded by prolonged subjection to shear stress does not recover its drag-reducing properties after freeze-drying and re-solution.

It is known that dilute polymer solutions capable of drag reduction lose this ability when they are subjected to shear stress over a long period. These changes are referred to as "degradation" or "destruction" of polymer solutions.

An investigation of the degradation of dilute polymer solutions is of great interest; the main aim of such investigations is to determine for how long polymer additives can continue to affect the flow characteristics. This problem has been widely investigated and is the subject of a large number of studies. So far, however, there is no unified viewpoint on the mechanism of this effect.

A number of authors maintain the view that degradation is due to irreversible changes directly affecting the polymer macromolecules [1, 2] and probably involving bond rupture and reduction of molecular weight. Others believe that the supramolecular structure of the solution is destroyed by a change in the characteristics of the macromolecules. This means either untangling of the molecular aggregates or the destruction of fluctuational kinetic structures [4, 5].

If degradation is due entirely to destruction of the supramolecular structures that are formed by solution, then by obtaining the polymer from the degraded solution and dissolving it again we would expect that a solution "restored" in this way would recover its drag-reducing properties. In the opposite case degradation could be attributed to irreversible changes occurring in the macromolecules.

In the present work we investigated the ability of aqueous solutions of polyethylene oxide WSR-301 that had been mechanically degraded to recover the properties responsible for the Toms effect after "restoration."

We determined the drag reduction coefficient f for freshly prepared aqueous PEO solutions of different concentration on an apparatus consisting of coaxial cylinders. The diameter of the inner stationary cylinder was 36 mm and its height was 30 mm. The gap between the cylinders was 2 mm. The experiment was conducted in developed turbulent conditions. The solutions were then subjected on the same apparatus to prolonged shear stress, which led to their degradation, after which they were converted to a powder by freeze-drying at 45°C. The polymer obtained in this way was again dissolved in water to the same initial concentrations. We again determined the drag reduction coefficient f for the "restored" solution.

The values of f for freshly prepared and "restored" degraded solutions of different concentrations are given in Table 1. This table also gives values of f for control undegraded solutions which had been evaporated in the same conditions and dissolved again to the initial concentrations. The error of measurement of f was 10%.

Table 1 shows that a "restored" degraded solution had the same diminished properties as before evaporation. This was the case in the whole range of concentration. In the case of the control solution the drag-reducing ability was almost completely restored.

We also investigated the values of the coefficient for freshly prepared, degraded, "restored," and control solutions of a prescribed weight concentration (C = 500 ppm) in relation

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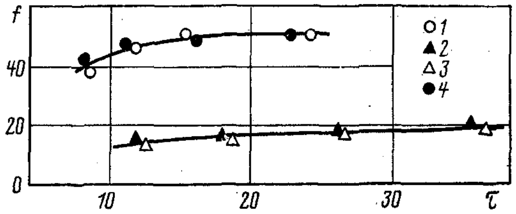

Fig. 1. Plots of drag reduction coefficient f, %, against shear stress τ, N/m^2, on wall of inner cylinder for polyethylene oxide solutions with concentration C = 500 ppm; 1) freshly prepared; 2) degraded; 3) "restored"; 4) control solutions.

TABLE 1. Values of Drag Reduction Coefficient f for Freshly Prepared, Degraded, "Restored," and Control Solutions of Different Concentration

Solution	Polymer concn. C, ppm	Drag reduction coeff. f, %	Solution	Polymer concn. C, ppm	Drag reduction coeff. f, %
Freshly prepared	1000	48	"Restored"	1000	18
	500	51		500	15
	100	49		100	16
	50	43		50	10
Degraded	1000	20	Control	1000	46
	500	17		500	50
	100	14		100	48
	50	11		50	44

to the shear stress τ on the wall of the inner cylinder. These results are presented in Fig. 1, which shows that the tabulated data are valid for different τ.

Thus, the re-solution of dry residue obtained from a degraded polyethylene oxide solution does not lead to restoration of the properties of the solution responsible for drag reduction. This indicates that degradation causes irreversible changes in the polymer macromolecules.

NOTATION

τ, stress on wall of inner cylinder, N/m^2; f, drag reduction coefficient, %; C, concentration of polyethylene oxide WSR-301 in solution, ppm.

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