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Postdecrystallization Rates of Grafted Fibers and Their Effect on Fiber Elasticity. I. Effect of Zinc Chloride Concentration

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Synopsis

Rayon yarns grafted with poly(ethyl acrylate) become highly elastic following decrystallization in aqueous zinc chloride solutions. An increase in temperature speeds up the decrystallization rate but does not have a substantial effect on the ultimate elongation properties of the grafted fiber. Increasing the concentration of zinc chloride does not have a marked change in the extension properties of the grafted fiber until 70% zinc chloride. At this saturated concentration, there is a sudden and dramatic change in the elastic properties of the grafted fiber. In fact, the grafted fibers after decrystallization in 70% zinc chloride have elongations in excess of 800%.

INTRODUCTION

In prior communications, it was shown that wool[1] and cellulose yarns[2–6] could be rendered highly elastic by preirradiation grafting techniques. More recently, it was reported that, in the case of cellulose, the amount of graft necessary to achieve the high "rubber-like" elasticity could be greatly reduced by an appropriate postdecrystallization procedure.[2–6] In fact, the actual amount of grafting required could be lowered approximately tenfold and still obtain highly elastic properties following postdecrystallization. In the present paper, the grafting rates and details of the postdecrystallization process will be examined at various temperatures and at intermediate concentrations of the decrystallizing agent.

EXPERIMENTAL

A continuous-filament, semidull rayon was used in this work that had been thoroughly extracted with methanol prior to grafting. A 5.1-g sample was irradiated in vacuum at 0.5 megarads/hr to a total dose of 3.7 megarads. Afterwards, the sample was allowed to react for 22 hr with an emulsion of inhibitor-free ethyl acrylate (36 ml EA and 90 ml 5% Triton X-405 in water) at 45°C. Following grafting, the sample was Soxhlet extracted with acetone for 48 hr; the per cent graft on a weight basis was found to be 360%.

Approximately 1-yard samples of the 360% grafted rayon were wound onto

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glass bobbins and placed in zinc chloride solutions for various periods of time at the required temperature. At the end of the time period, the samples were thoroughly washed with water and allowed to air dry before mechanical testing. An Instron tester with a 1.0-in. gauge and a cross-head speed of 1.0 in./min was used for all mechanical property measurements.

RESULTS AND DISCUSSION

In an earlier paper, it was shown that rayon samples containing between 100% and 500% of preirradiation grafted ethyl acrylate did not change substantially in terms of their mechanical properties following the grafting process. However, when these same samples were subjected to a 70% solution of zinc chloride in water, they suddenly became highly elastic, having ultimate elongations often in excess of 500%. These dramatic increases in elasticity following removal of the decrystallizing agent have been attributed to the grafted side chains hindering normal recrystallization of the cellulose chain. The newly formed fiber extends more freely, restrained only by any residual or newly formed crystalline regions which serve as crosslinks.

In the present work, a rayon sample containing 360% grafted ethyl acrylate was subjected to decrystallization for various periods of time. Afterwards, the decrystallizing agent was thoroughly removed by water and the fiber allowed to air dry. Finally, the mechanical properties of the conditioned samples were measured. The results of the elongation studies are summarized in Figure 1. It can be seen that the breaking extension for a given zinc chloride concentration increases rapidly with time over the first few hours, but levels off to an essentially constant value after about 5 hr. It is also evident that the magnitude of the breaking elongation increases vary substantially with increasing zinc chloride concentration over the range studied. For example, the elongation increased by a factor of about 1.5 as the concentration was increased from 57.5% to 65% zinc chloride. It should be pointed out, however, that at the saturated zinc

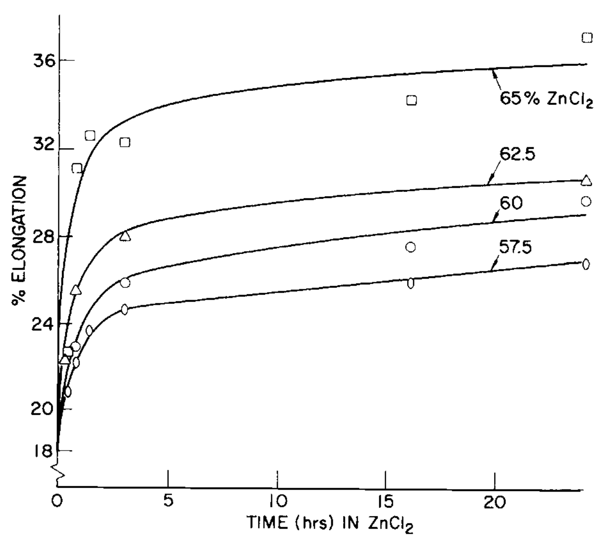

Fig. 1. Effect of postdecrystallization time on % elongation at break of 360% ethyl acrylate-grafted rayon.

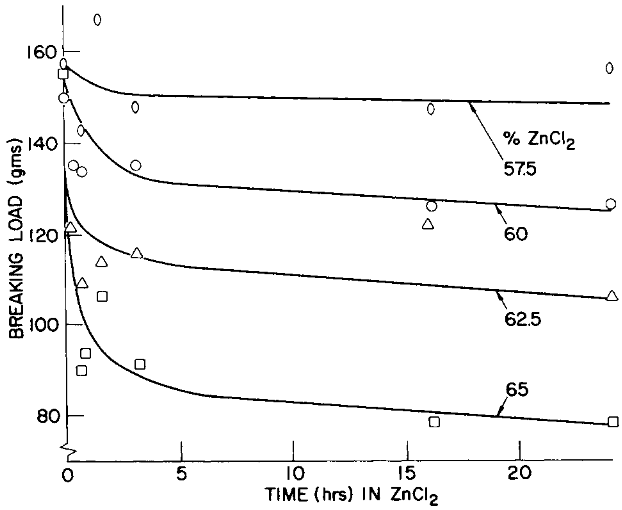

Fig. 2. Effect of postdecrystallization time on breaking strength of 360% ethyl acrylate-grafted rayon.

chloride concentration, 70%, the extension increases even more dramatically by a factor of at least 20.

The results of the corresponding curves for breaking strength are shown in Figure 2. These curves are similar, but in the opposite sense to the extension curves. Initially, the strength drops rapidly with time but levels off to a lower rate of drop after about 5 hr of contact time. In this case, the breaking strength drops by about a factor of 2 as the concentration is increased from 57.5% to 65% zinc chloride.

In a separate set of experiments, time was held constant at 3 hr, and the effects of postdecrystallization on the breaking extension were examined over the entire

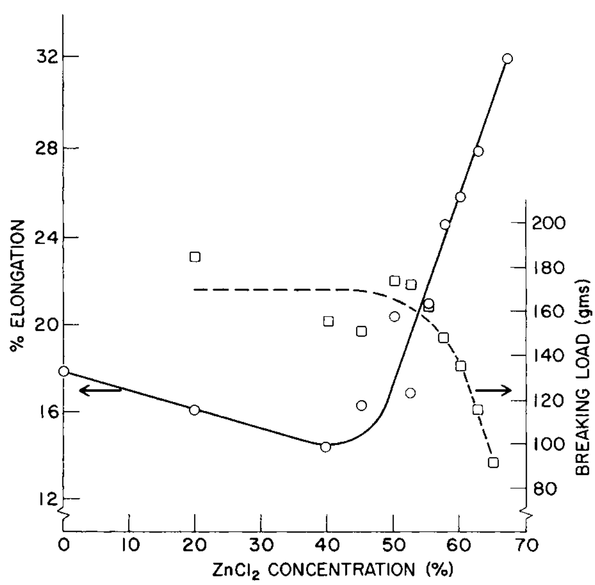

Fig. 3. Effect of $ZnCl_2$ concentration on breaking extension and strength of 360% ethyl acrylate-grafted rayon after postdecrystallization for 3 hr at 25°C.

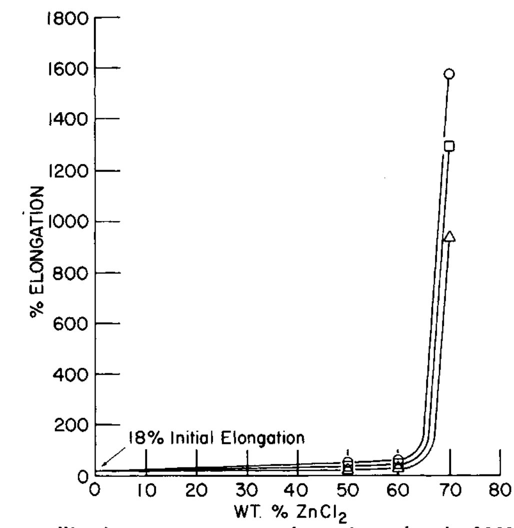

Fig. 4. Effect of decrystallization temperature on elongation at break of 360% ethyl acrylate-grafted rayon after postdecrystallization for 4 hr at various concentrations of zinc chloride: (Δ) 25°C; (□) −40°C; (○) −60°C.

range of zinc chloride concentrations. These results are presented in Figure 3, where it can be seen that there is a small decrease in the breaking extension up to about 45% zinc chloride concentration. This is presumably due to some increased crystallization. At higher concentrations, the breaking extension increases very rapidly with increasing concentration of zinc chloride, reaching eventually the "rubber-like" elastic properties. The corresponding curves for breaking strength are also summarized in Figure 3 and show that the two parameters go hand-in-hand with a substantial decrease in strength evident after circa 45% zinc chloride.

In a separate set of experiments, the effect of decrystallization temperature on breaking extension was examined at various zinc chloride concentrations. These results are summarized in Table I and Figure 4 for 50%, 60%, and 70% zinc chloride solutions, respectively. It is apparent from Table I that increasing the decrystallization temperature from 25°C to 60°C does not increase the breaking elongations substantially, even after 8 hr of exposure to zinc chloride at 50% and 60% concentrations. There is, however, a dramatic increase in elongation using 70% zinc chloride (Table I). In this case, an increase in temperature decreases the time required to achieve the high, rubber-like elastic properties. This effect may be due to increased diffusion rates at the higher temperature since essentially the same degree of elasticity can be achieved for longer reaction times at the lower temperature.

The strong increase in elasticity with zinc chloride concentration is summarized in Figure 4. After decrystallization for 4 hr in 70% zinc chloride, all the grafted samples become highly elastic. At the lower concentrations, however, the breaking elongations are to a first approximation the same as unmodified rayon. From Figure 4, it is evident that this transition to high elasticity is abrupt and is directly associated with the zinc chloride concentration required to "dissolve" the cellulosic crystallites. This sudden change in mechanical properties at the higher concentrations of zinc chloride can be understood best by consideration of the changes in crystallinity of cellulose with higher concentrations of zinc

TABLE I
Effect of Temperature on Per cent Elongation at Break of Rayon Grafted with 360% Ethyl Acrylate Decrystallized with Aqueous Zinc Chloride Solution

Zinc chloride, %	Temperature, °C	Elongation, %			
		0.25 hr[a]	1.0 hr	2.0 hr	8.0 hr
50	25	30	27	25	30
	40	20	—	18	22
	60	—	22	—	—
60	25	50	45	38	29
	40	35	30	35	—
	60	—	43	—	42
70	25	100	550	1150	1400
	40	380	1200	1300	1680
	60	800	1320	1420	1720

[a] After treatment for indicated time.

chloride. For example, Patil and co-workers[7] have shown that the crystallinity of cellulose remains essentially unchanged up to about 55% zinc chloride, but then drops suddenly to almost zero crystallinity at circa 70%. In the present work, similar results are also observed for the grafted cellulosic fibers, with the initial changes beginning to take place at 40% zinc chloride and the more dramatic changes occurring with saturated (70%) zinc chloride.

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