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N-Acetylpolyethylenimine

A Blending Agent for Polyamide Fiber

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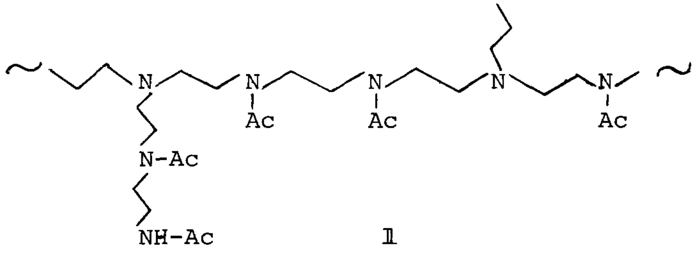
Summary

This paper describes a blending agent N-acetylpolyethylenimine(AcPEI) for polyamide fiber. Two types of AcPEI were examined; the branched one **1** which was the acetylated product of commercial polyethylenimine(PEI) and the linear one **2** prepared by the ring-opening polymerization of 2-methyl-2-oxazoline. Polyamide fibers(nylon 6) blended with a 2-10 wt % ratio of AcPEI were prepared by the melt-spinning technic. The processability of spinning was very high because **1** and **2** were very compatible with polyamide. In addition, the polyblend fibers obtained displayed good antistatic and dyeing properties, in which **1** containing tertiary amino groups was more effective than **2**. The mechanical properties were also disccussed.

Introduction

In the present study, N-acetylpolyethylenimine(AcPEI) was examined as a blending agent for polyamide fiber(nylon 6). This study was performed on the basis of an expectation that AcPEI would exhibit an anti-static property for polyamide because it was thought to be a polymeric homologue of N,N-dimethylacetamide which is highly hygroscopic and compatible with polyamide. Two types of AcPEI were examined. The one **1** was the acetylated product of commercial polyethylenimine(PEI), which had a highly branched structure. The other **2** was the polymer of 2-methyl-2-oxazoline, whose molecular structure was linear.



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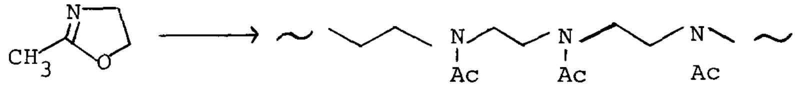

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A patent literature in 1968 described the preparation of nylon-6 fibers blended with polyethylenimine (CAMPBELL and HORNER, 1968). However, considerable decomposition of PEI did occur during spinning, and a fiber blended with 0.5 wt % PEI showed poor properties.

Blend of nylon 6 with **1** or **2** was subjected to spinning. The processability of spinning, and some properties of fibers (anti-static property, dyeability and stress-strain curve) were examined.

Experimental

Materials. Four samples of AcPEI, **1(0.6)**, **1(1.2)**, **1(10)** and **1(70)**, were prepared by the acetylation of four commercial polyethylenimines having molecular weights of 600, 1,200, 10,000 and 70,000, respectively, with acetic anhydride according to a method of JOHNSON and KLOTZ (1974). AcPEI **1** were purified by repeated (several times) reprecipitation from $CHCl_3$(solvent) to Et_2O(precipitant), which were finally dried *in vacuo*. NMR spectroscopic analysis showed that primary and secondary amino groups were completely acetylated. Two samples of linear AcPEI, **2(3)** and **2(10)**, were prepared by the ring-opening polymerization of 2-methyl-2-oxazoline(BASSIRI et al 1967). The molecular weights of **2(3)** and **2(10)** were 3,000 and 10,800, respectively. Nylon 6 chips (relative viscosity of 2.64 in 96% H_2SO_4) were provided by Unitica Co. Ltd(Japan).

Spinning. An AcPEI solution in CH_3OH was added to nylon 6 chips, and dried thoroughly at 100°C *in vacuo*. Melt spinning was carried out at 260°C with a single-screw(25 ϕ) extruder epuipped with a spinneret having 30 holes of 0.9 mmϕ. The draft ratio of spinning V_2/V_1 was determined by measuring the followings(FURUKAWA et al. 1971) :

V_1 ; the rate of polymer extrusion (m/min)

V_2 ; the rate of winding filament (m/min)

The as-spun filaments thus obtained were submitted to a 4.5-fold drawing at room temperature.

Fibers Properties. Half-life time of leakage of electrostatic charge was measured at 20°C and under 60% relative humidity (SHASHOUA 1958) using an instrument having a trade name of "Static Honest Meter" (S-4104 Shishido Shokai. Japan). The charged voltage was 10,000 volt. The stress-strain curve was obtained with an Autograph(Shimazu M-100, Japan). Washing test was made in a 0.2% soap solution at 80°C using a standard launder meter(Suga Test Instruments Co., Japan). One washing cycle was 30 minutes.

Dyeability. One gram of filament was dipped in a bath containing 0.03 g of Orange II. The bath ratio was 1:400, and pH was adjusted to 4.7 by the addition of acetic acid. The concentration of Orange II in the bath was determined by UV spectroscopy at 482 nm.

Results and discussion

Compatibility of AcPEI with Nylon 6. Results of spinning experiment(draft ratio), DSC curve and microscopic observation all showed that AcPEI was quite compatible with nylon 6. Table 1 shows the results of spinning experiments in which nylon 6

Table 1. Spinning of nylon 6 blends with AcPEI (2.0 wt %) at 260°C.

AcPEI	$\eta sp/c^{a}$	Draft Ratios	Compatibilities	Water Regains $\%^{b}$
1(70)	0.32	28.5	very good	4.0
(10)	0.22	14.7	good	4.1
(1.2)	0.057	9.8	good	4.5
(0.6)	0.045	6.2	good	4.1
2(10)	0.22	27.8	very good	4.7
(3)	0.098	28.0	very good	4.8
blank		28.0	very good	4.0

a) In methanol at 30°C, at 0.40 g/100 ml.
b) At 20°C, 60% relative humidity.

was blended with 2 wt % of AcPEI. In all cases, colorless mulitifilament fibers were obtained. Draft ratio values are taken to indicate the extent of spinnability or compatibility of AcPEI.. With branched AcPEI **1**, a higher draft ratio was obtaineu when had a higher molecular weight. The draft ratio of a blend with **1(70)** was similar to that of the unblended sample. With **1(0.6)** and **1(1.2)**, spinning was difficult because of decreased melt viscosities of the blends.

Linear AcPEI was easily blended, and high draft ratio was obtained with both **2(10)** and **2(3)**.

Spinnabilities of Polyblends with 10 wt % of **1(70)** and of **2(10)** were worse as indicated by the draft ratios lower than 12. Especially a blend with **1(70)** (10 wt %) turned yellow when it was spun, probably due to the slight decomposition at the tertiary amino group.

DSC curve also showed good compatibility, i.e., the filaments of the blends with **1(70)** and with **2(10)** (10 wt %) showed the same melting zone as that of unblended sample of nylon 6. No other endotherm and exotherm peak was observed up to 200°C. Especialy it is important to note that no endotherm due to cristalline AcPEI **2(10)**, whose melting temperature was known to be 200°C, was observed.

Microscopic observation (100 magnifications) of filament surface did not detect any phase-separation nor bleeding out of AcPEI.

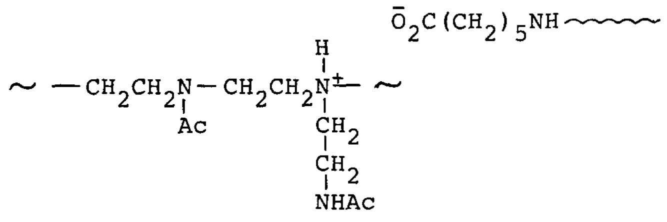
Antistatic and Dyeing Properties. Antistatic property of blended fibers (2.0 wt % AcPEI) was examined semi-quantitatively by the value of half-life time of leakage of electrostatic charge of fibers (Table 2). It is seen in Table 2 that the half-life time was much decreasea by blending of AcPEI. The water regain property, however, was not much improved by blending (Table 1).

Table 2. Half-life time of leakage of electrostatic charge and change by washing.

AcPEI	Washing Cycles[a]				
	0	1	5	10	15
1(70)	0.7	1.7	1.5	1.4	1.8
(10)	0.8	1.7	1.5	1.0	1.7
(1.2)	1.8	3.6	10.8	>30	>30
(0.6)	1.4	3.5	11.5	11.4	>30
2(10)	3.4	3.5	—	5.0	4.5
(3)	2.8	3.3	—	15.3	>30
blank	>30				

a) By 0.2% soap solution at 80°C. One cycle is for 30 min.

Superior antistatic properties of branched AcPEI **1** in comparison with those of linear AcPEI **2** may be ascribed to the presence of tertiary amino group which forms a strongly hydrophilic ammonium salt with the carboxylic end of nylon 6.



Linear AcPEI **2** has not free amino group available for the above salt formation.

Both AcPEI **1** and **2** of lower molecular weights were removed by repeated washing (Table 2). However, those of higher molecular weights, both of linear and of branched structures, were retained. Wash-resistant property may be ascribed to the entanglement of AcPEI chain with polyamide chain.

Dyeing property of nylon 6 toward an acid dye, Orange II, was improved by blending with AcPEI. Here, a branched AcPEI **1** is more effective, probably because of the presence of free

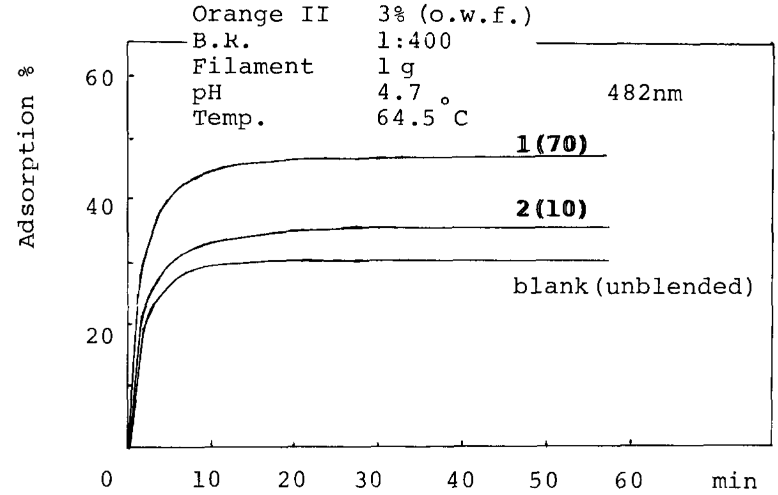


Figure 1. Curves of dye-uptake rate of nylon 6 fibers blended with 2.0 wt % AcPEI **1(70)** and **2(10)**.

tertiary amino group (Figure 1).

Stress-Strain Curve

Figure 2 shows typical stress-strain curves of filaments blended with 2.0 wt % of AcPEI. The decrease of strength of filaments of blends is noted, especially in the blends with **1(0.6)** and **1(1.2)**.

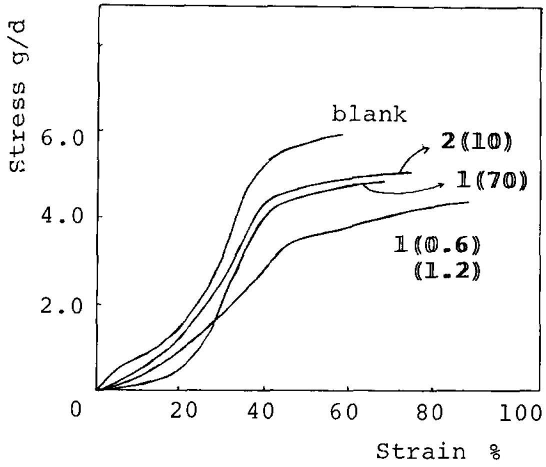


Figure 2. S-S-curves of nylon 6 filaments blended with AcPEI (2.0 wt %).

Probably, these samples of AcPEI of lower molecular weights had functioned as a plasticizer.

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