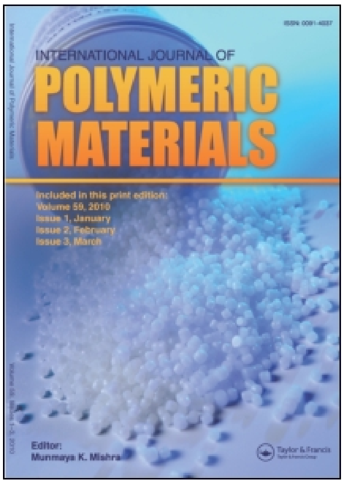

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Properties of Polycaprolactam Polyethyleneimine Graft Copolymers

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Caprolactum has been grafted onto polyethyleneimine. The mechanical properties of the resulting polycaprolactam polyethyleneimine graft copolymers were studied as a function of the number average molecular weight in the polycaprolactam side chain and compared to those of linear nylon 6.

INTRODUCTION

The mechanical properties of nylon 6 depend on a number of factors, among them the type and amount of crystalline structure, molecular weight and moisture. It has been reported that nylon 6 can crystallize in the pseudohexagonal form as well as in the monoclinic form.[1] These structures will be referred to in this paper as the gamma and alpha structure respectively. The gamma and alpha structures represent different degrees of packing. Their densities have been estimated from crystallographic data at 1.155 and 1.23 g/cc for the gamma and alpha structure respectively. The density of the amorphous phase is 1.10 g/cc.

Moisture affects the mechanical properties of the amorphous phase as well as that of the gamma phase. It increases the segmental mobility of the amorphous phase by plasticizing the hydrogen bond junctions between interchain amide-linkages, and as a consequence the glass transition tempera-

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ture is reduced from +50 to about −50°C as the moisture content increases from 0 to 9 wgt %. It furthermore appears to plasticize the more open gamma structure more readily than the alpha structure, as must be concluded from yield stress data in Table I.

TABLE I

Yield stress as a function of crystalline structure and moisture in nylon 6 at 23°C

% RH	High gamma (~50 %) Yield stress, psi	High alpha (~60 %) Yield stress, psi
0	10,000	12,300
50	4600	9400
93	2500	6300

The difference in temperature dependence of the mechanical properties of samples containing a high content of gamma structure as compared to samples containing a high alpha content is shown for the yield stress in Table II. The experimental facts suggest that the alpha structure is the most desirable structure for obtaining the maximum strength in nylon 6 polymer.

TABLE II

Yield stress as a function of crystalline structure and temperature

Test temperature	High gamma (~50 %) Yield stress, psi	High alpha (~60 %) Yield stress, psi
23	10,000	11,000
100	2900	—
150	1600	—
175	1150	6100
210	—	4450

Extensive studies on the rate and mode of crystallization in nylon 6 revealed that the alpha structure is formed in the temperature range of 225°C, the melting point, to about 150°C, while the gamma structure is formed from 150°C down to +50°C, the T_g of the nylon 6, as shown in Figure 1. The rate of crystallization for the gamma structure was obtained by heating a quenched amorphous film, using a hot stage microscope technique.

The alpha structure is thus formed only in a narrow temperature range from 150 to 225°C.

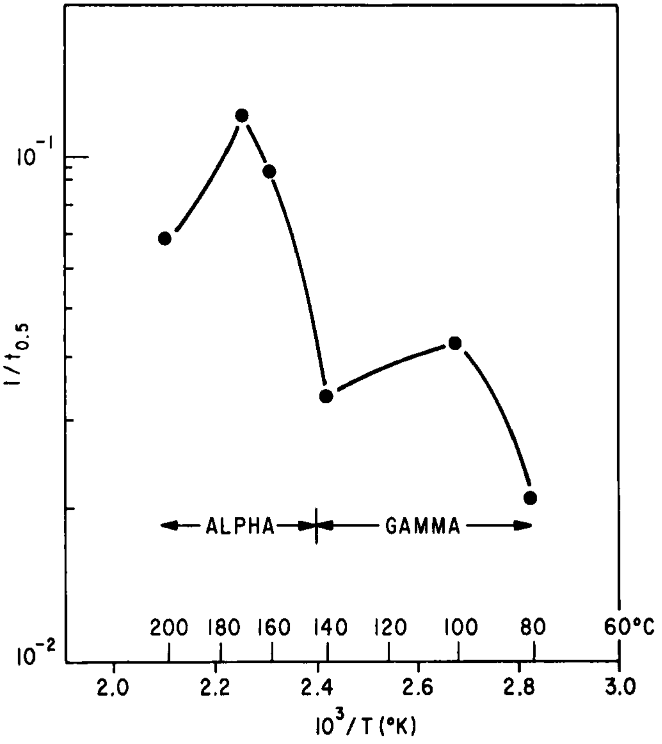

FIGURE 1 Crystallization kinetics nylon 6. Reciprocal half times (sec.$^{-1}$) as a function of temperature.

Other approaches must thus be sought to increase the alpha content in the short time intervals available during the cooling cycles in commercial forming processes.

Nucleating agents can be used, of course, to increase the amount of alpha structure.[2] In this paper we shall describe another approach to the problem of high alpha content in nylon 6 moldings. It is based a on polyethyleneimine-polyamide graft copolymer. The graft copolymer consists of short polycaprolactam side chains grafted to a polyethyleneimine backbone. The short nylon 6 side chains provide for a higher rate of crystallization, while the polyethyleneimine backbone provides the tie molecules between the crystallite domains for strength in the crystallized solid.

EXPERIMENTAL PART

The synthesis of the polycaprolactam polyethyleneimine polymer has been described in U.S. Patent 3,442,975. The synthetic procedure is essentially the same as for standard nylon 6 polymers, except for the addition of polyethyleneimine. The polyethyleneimine polymer itself has a branched structure. It was reported to contain approximately one branch point at the nitrogen atom for every 4 monomer units, and 70% of the nitrogen containing groups in the polymer are available for substitution reactions.[3]

For the discussion of the graft copolymers it is important to note that the mole ratio of caprolactam to imine structures in the polyethyleneimine determines the degree of polymerization in the polyamide side chains of the graft copolymer. All graft copolymers contained about 9–12 wgt % water extractables depending on the polymerization conditions. This is the same as for pure nylon 6.

The experimental polycaprolactam polyethyleneimine graft copolymers were extracted with water and analyzed for carboxyl acid and amine endgroups by the following standard methods:

Carboxyl acid endgroups: 1–2 grams of polymer is dissolved in benzyl alcohol under refluxing conditions for about 20 minutes and titrated with 0.01N KOH solution in benzyl alcohol at 60°C using phenolphthalein as an indicator.

Amine endgroups: 1–1½ grams of polymer are dissolved in trifluoroethanol and titrated potentiometrically with 0.01N paratoluene sulfonic acid in TFE at room temperature. The precision of both methods is ±0.005 meq/g.

A typical polymer containing 2 wgt % PEI would contain 0.303 meq/g amine endgroups and 0.008 meq/g carboxylic endgroups. Its reduced viscosity was 1.02 dl/g.

The solution viscosity was determined in meta cresol at 25°C for a 0.5 wgt % solution. The melt index number was determined by an extrusion plastometer (ASTM-D-1238). The conditions were modified to 235°C and 325 g load to accommodate nylon 6 properties.

Rates of isothermal crystallization were measured by employing a method that is based upon the depolarization of light by birefringent materials.[4] A polarizing microscope equipped with a hot stage, a photocell and a recorder was used to measure the increase in birefringence of the crystallizing specimen.

To determine the rate of crystallization for the γ structure, quenched amorphous nylon 6 film was used and heated rapidly from room temperature to the crystallization temperature. To study rates of crystallization in the temperature range in which the α structure is formed, specimens were melted between cover-glasses and quenched to the crystallization temperature. Half times of crystallization were calculated from the recordings obtained.

The graft copolymers have been evaluated as plastics and fibers. To this purpose, the washed and dried polymer was injection molded in a laboratory pneumatic plastic injection press (manufacturer Simplomatic Mfg. Co.—

model PRO–1–57) which was fitted with a mold for long impact type L samples, the dimensions of which adhered to the ASTM-D-1822 specifications. The heat was supplied by cartridge heaters and controlled to ±3°C. A number of the injection molded samples were conditioned to 100% RH before testing. To assure moisture equilibration the samples were submersed in water at 50°C for 5 days and then allowed to cool to 23°C.

Fiber properties were evaluated on monofilaments, which were spun from the melt and drawn in the conventional manner.

An Instron was used to obtain the stress–strain curves. The plastic samples were evaluated with a 0.05 in/min head speed, the monofilaments at 100% extension/min with a 5 in gauge length fiber. The environmental conditions were controlled as indicated in the Tables.

RESULTS AND DISCUSSION

Characterization

Experimental polycaprolactam-polyethyleneimine graft copolymers containing PEI in the range of 8.3 to 0.35 wgt % were used for our evaluation as they represent the most interesting range of graft copolymers. It is important to note that all graft copolymers contain essentially zero to a very low concentration of carboxyl endgroups and nearly exclusively amine endgroups. This indicates that all polycaprolactam units exist as grafted polymer. Assuming that the amine endgroups represent the ends of the polycaprolactam side chains, one can calculate the number average degree of polymerization of the polycaprolactam portion of the graft copolymer. The results are listed in Table III together with those calculated by assuming all available imine groups of the polyethyleneimine participated in the grafting reaction. The close agreement between the two methods of calculating the $\overline{DP}_n$ of the polycaprolactam side chain and the above-mentioned very low concentration of acid endgroups indicates that we have indeed the proposed graft structure we set out to obtain.

Additional characterization data such as melting points, solution viscosity and the melt index as a measure of fluidity, are included in Table III. For comparison, the same data are listed in Table III for a standard molding grade linear polycaprolactam and a very low molecular weight acetic acid terminated polycaprolactam.

Mechanical Properties—Injection Moulded Samples

The mechanical properties of injection molded samples of the graft copolymers are compared with those of linear polycaprolactam under bone dry and

TABLE III

Characterization data, PEI-polycaprolactam graft copolymers and linear nylon 6 polymers

Polymer	PEI content wgt %	Polycaproclatam side chain calc $\overline{DP}_n$-$\overline{M}_n$	Polycaproclatam side chain meas $\overline{DP}_n$-$\overline{M}_n$[c]	Mp °C	Red Visc. in m-cresol	Melt index 225°C & 325g
A	8.15	5.3-600	7.08-800	210	0.43	too fluid
B	3.70	14.6-1600	14.2-1610	216.5	0.61	860
C	1.84	27.0-3060	27.4-3100	225	0.89	50
D	0.70	68.2-7750	58.9-6650	225	1.20	6.6
E	0.35	137.0-15,400	135.0-15,200	224	1.74	1.0
F	0	—	32.7-3.700[a]	225	0.34	too fluid
G	0	—	177.0-20,000[b]	225	1.8	1.9

[a] N-acetyl terminated low mwt linear polycaprolactam, $\overline{M}_n$ (g/mole) by acid endgroup titration.

[b] Standard N-6 molding grade resin.

[c] $\overline{M}_n$ (g-mole) by amine endgroup titration.

100% RH conditions in Tables IV and V respectively. Structural data, i.e. type and amount of crystalline forms, and the moisture content for the 100% RH conditions are included in the Tables. It should be noted that the samples conditioned to 100% RH, showed additional crystallization during conditioning at 50°C, submersed in water.

The accumulated data lead to a number of interesting observations. Polymer F, representing a linear polyamide of low molecular weight with a $\overline{DP}_n$ of 32.7, is brittle and exhibits very low strength notwithstanding its high alpha crystallinity of 60%. Its properties compare to that of a standard nylon 6 molding resin of about 5.5 times higher molecular weight, $\overline{DP}_n$ of 177 in the same way that a polyethylene wax does to its polyethylene molding resin counterpart. Grafting polyamide chains of approximately the same $\overline{DP}_n$ to a polyethyleneimine backbone, polymer C—$\overline{DP}_n = 27.4$, yields a graft copolymer which exhibits stress–strain properties characteristic for a highly annealed nylon 6 plastic. Other experimental graft copolymers not shown in this paper reveal that a $\overline{DP}_n$ of 20 in the polycaprolactam side chain is sufficient to yield nylon 6 type of plastic properties, provided they are grafted to a polymeric backbone such as polyethyleneimine. At still lower DP's of the side chain, the tensile properties of the graft copolymer fall in between those of a nylon 6 wax and nylon 6 plastic properties.

Increasing the $\overline{DP}_n$ of the polycaprolactam side chain in the graft copolymers to 58.9 and higher, samples D and E respectively, results in increased ductility. The higher modulus and yield stress for the conditioned graft copolymer

TABLE IV

Mechanical properties of dry PEI-caprolactam graft copolymers and linear nylon 6 at RT and 0% RH

Polymer	PEI content wgt %	$\overline{DP}_n$ of caprolactam side chain	Cryst index		Modulus 2% secant psi	Yield stress psi	Yield elong %	Ultimate		Tensile impact ft lb/in^2
			%α	%γ				strength psi	elong %	
A	8.15	7.08	63	0	72,600	1700	2.5	1700	2.5	3.3
B	3.70	14.2	57	0	100,800	7500	8.4	7500	8.4	4.8
C	1.84	27.4	47	0	115,500	10,700	12.6	9300	11.9	7.2
D	0.70	58.9	48	5	125,600	10,000	10.9	10,100	100	24
E	0.35	135.0	51	5	112,000	9500	11.5	9900	260	20
F	0	(32.7)[a]	60	0	80,700	—	—	1500	1.6	0.2
G	0	(177.0)[b]	28	23	111,100	9700	11.9	9900	260	~340

All samples injection molded with 0.5 min cycle and 155°C mold temperature. Instron test conducted with 0.05 in/min head speed. [a,b] Polymers F and G as in Table III, are linear nylon 6. $\overline{DP}_n$ is number average degree of polymerization.

TABLE V

Mechanical properties of wet PEI-caprolactam graft copolymers and linear nylon 6 at 23°C and 100% RH

Polymer	PEI content wgt %	Caprolactam side chain $\overline{DP}_n$	H_2O uptake wgt %	Cryst index		Modulus 2% secant psi	Yield stress psi	Yield elong %	Uultimate strength psi	elong %	Tensile impact ft lb/in²
				%α	%γ						
A	8.15	7.08	14.4	76	0			too brittle for testing			
B	3.70	14.2	10.1	68	0	30,500	2700	17.9	2700	17.9	176
C	1.84	27.4	8.8	64	0	36,300	4800	64.9	5200	200	286
D	0.70	58.9	8.4	60	0	24,800	4400	77.7	7900	310	662
E	0.35	135.0	6.3	60	0	26,000	4300	87.7	8500	330	532
F	0	(32.7)[a]	4.7	70	0	18,900	—	—	380	1.3	0.2
G	0	(177.0)[a]	8.4	—	—	16,000	4100	77.7	9800	370	> 900

All samples conditioned by submersing for 5 days at 50°C in water. Samples cooled to 23°C at 100% RH before testing. All other specifications as in Table IV.

samples can be accounted for by the higher content of alpha crystallinity. It should be noted that the number average molecular weight of the nylon 6 side chain in the graft copolymer samples C and D, $\overline{DP}_n$ 27.4 and 58.9 respectively, is still rather low compared to the $\overline{DP}_n$ of 177 of the linear standard molding grade nylon 6 resin. It can be concluded that the polyethyleneimine backbone polymer in these graft copolymers provides for a large part the necessary "tie" molecules between the crystalline polycaprolactam domains in these highly crystalline samples.

All of the graft copolymers exhibit rather low tensile impact strength, Tables IV and V. The question remains whether this is due to the high crystallinity or an insufficient number of tie molecules, i.e. low molecular weight of the N-6 portion. In Figure 2, the effect of crystallinity or density is shown for

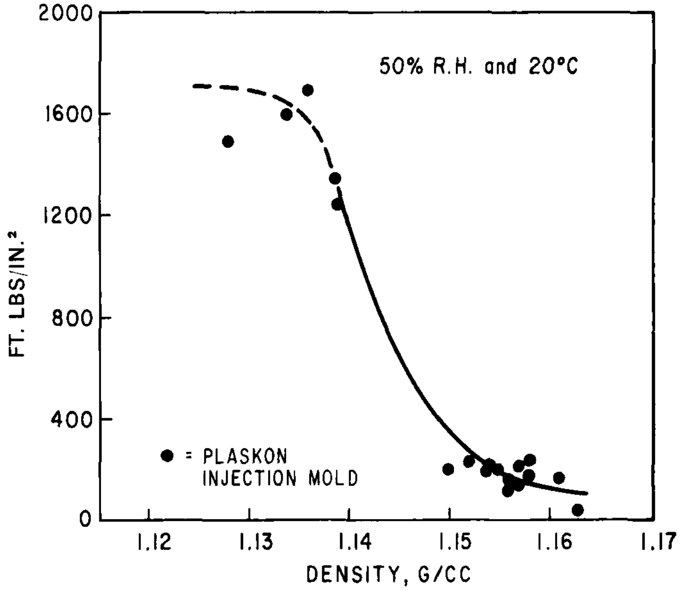

FIGURE 2 Tensile impact strength as a function of nylon 6 density (crystallinity).

high molecular weight linear nylon 6 samples, which were conditioned to 50% RH before testing. The samples were polymerized anionically under controlled semi-isothermal conditions. The density, i.e. crystallinity, is controlled by the casting time. The degree of polymerization of the samples in Figure 2 falls in the $\overline{DP}_n$ range from 570 to 870. The impact values did not show any particular trend with the molecular weight of the samples. The impact values in Figure 2 thus show clearly that the density, i.e. crystallinity, as well as the molecular weight are factors in determining the impact strength in semi-crystalline polyamide polymers under a specific set of temperature and moisture conditions.[5] The molecular weight appears to be the predominant factor at low crystallinity, the density, and to a minor degree the molecular weight, are controlling factors in highly crystalline samples.

Elevated Temperature and Fiber Properties

The graft copolymers have been evaluated as fibers and compared for their drawability and elevated temperature properties to a standard nylon 6 resin. The results, tabulated in Table VI, confirm the previous results obtained on injection molded samples. Polymer D, with a polycaprolactam side chain $\overline{DP}_n$ of 58.9, exhibits properties at room and elevated temperature which are equivalent to those of a linear standard nylon 6 polymer with a $\overline{DP}_n$ of 177. Both graft copolymers exhibit good drawability. It is interesting to note that the strength of oriented graft copolymers is sensitive to $\overline{DP}_n$ in the side chain. A similar sensitivity of the strengths on $\overline{DP}_n$ is observed for linear polymers in the low $\overline{DP}_n$ range.[6]

TABLE VI

Properties of monofilaments from PEI-polycaprolactam graft copolymers and linear nylon 6 as function of temperature at 0% RH

Polymer		H	D	G
PEI-wgt %		1.84	0.70	0
Polycaprolactam side chain, $\overline{DP}_n$		27.4	58.9	(177)
Drawing conditions:				
Draw ratio/temp °C		5.6/190	6.5/190	5.4/180
	Testing temp °C			
Tensile modulus, g/den	23	93	74	85
	75	—	32	29
	150	—	17	18
	200	—	9	12
Tenacity, g/den	23	4.1	7.5	7.6
	75	—	5.9	6.0
	150	—	4.0	4.3
	200	—	3.1	3.5
Ultimate elongation, %	23	6.7	12	13.6
	75	—	15	15.8
	150	—	23	19.7
	200	—	41	36.2

It should be mentioned that the linear polycaprolactam with a $\overline{DP}_n$ of 32.7 could not be spun into a monofilament, its melt strength was too low and this sample is in the "non fiber forming" range.

Structure as a Function of Mould Temperature

In Figure 1, the crystallization behavior of polycaprolactam under isothermal conditions was plotted against the temperature of crystallization. In addition to the effect of temperature on rate of crystallization, it was shown that nylon 6 crystallizes in the α or *monoclinic* form above 150°C, while in the temperature range of 50 to 150°C it crystallizes in the γ or pseudohexagonal form. To study the behavior of the polycaprolactam polyethyleneimine graft copolymers, the polymers discussed in the previous sections, were injection molded with mold temperatures controlled at 50 and 150°C respectively. The structure in the samples was determined by broad angle X-ray analysis and the results are listed in Table VII together with the results for standard linear nylon 6 polymer. The injection molding cycle time was 30 seconds for all samples and the different mold temperatures essentially represent different rates of cooling.

TABLE VII

Crystalline structure of PEI-polycaprolactam craft copolymers at mold temperatures of 50 and 155°C with 0.5 minute injection molding cycles

			Mold temperature			
			50°C		155°C	
Polymer	PEI content wgt, %	Polycaprolactam side chain $\overline{DP}_n$	%α	%γ	%α	%γ
A	8.15	7.08	2	49	63	0
B	3.70	14.2	2	42	57	0
C	1.84	27.4	5	45	47	0
D	0.70	58.9	0	45	48	5
E	0.35	135.0	0	45	51	5
G[a]	0	(177.0)	0	47	28	23

[a] Standard linear N-6 molding grade resin.

The structural analysis revealed that the graft copolymers listed in Table VII crystallized essentially exclusively to the alpha form at the 155°C molding condition. The resulting total α-crystallinity decreases with increasing $\overline{DP}_n$ of the polycaprolactam side chains. The standard linear polycaprolactam polymer, (G), exhibits a much lower α-crystallinity. The gamma form exhibited by samples D, E and G at the 155°C molding condition must have occurred by a secondary crystallization upon cooling to room temperature outside the mold. It is only significant in the case of sample G. At the 50°C mold condition, the graft copolymers and the linear standard molding grade nylon 6 exhibit the gamma form nearly exclusively.

The cooling rate through the 225–150°C temperature range was thus too fast for the graft copolymers at the 50°C mold temperature condition to form any appreciable α-crystallinity.

It is interesting to note that the lower $\overline{DP}_n$ side chains afford a faster rate of crystallization at elevated temperatures, but that the increased mobility of the side chains, because of fewer entanglements of the side chains, is not sufficient to overcome the energy barrier of the hydrogen bonding of the gamma form in the temperature range below 150°C. Consequently the graft copolymers crystallize in the gamma form when cooled at a sufficiently fast rate.

Conclusions

Polycaprolactam polyethyleneimine graft copolymers have been evaluated in which essentially all the polycaprolactam units are contained in short side chains grafted to a polyethyleneimine backbone. It was found that the graft copolymers exhibit mechanical properties equivalent to those of a standard linear polycaprolactam plastic when the $\overline{DP}_n$ of the side chains is greater than 20 monomer units. The graft copolymers exhibit wax-like properties at a lower $\overline{DP}_n$ in the side chain. The polyethyleneimine backbone provides, exclusively or at least to a large degree, the essential "tie" molecules between the polycaprolactam crystalline domains in the critical $\overline{DP}_n$ range of 20 to 100 monomer units in the side chains.

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References

1. L. G. Roldan and H. S. Kaufman, *Polymer Letters* I, 606 (1963).
2. G. A. Toelcke, M. N. Riddell, G. W. Bellucci, R. J. Welgos, and J. L. O'Toole, *Modern Plastics* **45,** No. 16, 117–126 (1968).
3. Chemirad – Company bulletin on Polyethyleneimine.
4. J. H. Magill, *Polymer* **2,** 1968, 221–233.
5. V. Silvar and I. Boukal, *Kunststoffe* **59-5**, 313–318 (1968).
6. B. T. Hayes, P. V. Papero, and D. C. Prevorsek, Factors affecting strength of nylon 6, paper presented at 37th TRI – New York meeting, April 7, 1967.