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Block Polymers from Isocyanate-Terminated Intermediates. IV. Properties of Cured Butadiene–ε-Caprolactam Block Polymers

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Synopsis

Butadiene–ε-caprolactam block polymers containing a high proportion of 1,2 units in the butadiene segments were synthesized and physical properties were measured on the cured copolymers. Flexural strength and impact resistance both increase regularly with increasing ε-caprolactam content in peroxide cured copolymers. This behavior is explained by the higher values of flexural modulus and impact resistance for poly(ε-caprolactam) compared with peroxide-cured polybutadiene resins. Copolymers reinforced with silica showed higher heat distortion temperatures but lower impact resistance than corresponding unfilled samples. Arrhenius plots of flexural properties at various test temperatures were linear. Both flexural modulus and strength decreased regularly with increasing test temperature. Flexural properties of filled copolymers were relatively unaffected by heat aging up to 204°C for several weeks, however, dramatic decreases in these properties were noted in a matter of days when heat aging was done at 260–316°C. These results are explained by the rapid degradation of poly(ε-caprolactam) above its melting point. Block polymers whose butadiene segments contained a high proportion of 1,4 units were also synthesized. These copolymers were elastomeric when cured with either sulfur or peroxide.

INTRODUCTION

In an earlier report,[1] we described the preparation of butadiene–ε-caprolactam block polymers. It was shown then that these copolymers were actually mixtures of block polymer, homopolybutadiene, and nylon 6. The most interesting feature of these polymerization mixtures is their high pliability at room temperature even at high ε-caprolactam contents (70–80 weight per cent). Because of this, they are easily compounded and processed at ambient temperatures by ordinary milling techniques.

The present study concerns itself with the physical properties obtained from cured butadiene–ε-caprolactam polymerization mixtures. We have cured the copolymers containing a high proportion of 1,2 units in the butadiene segments with dicumyl peroxide to obtain hard resins. Copolymers having butadiene segments composed mainly of 1,4 repeat units have been cured with both sulfur and peroxide. The effects of various parameters, including copolymer composition and molecular weight, on physical properties were then investigated.

EXPERIMENTAL

Reagents

Dicumyl peroxide (98% active) was obtained from Hercules Incorporated and vinyltriacetoxysilane was obtained from Dow Chemical Company. Both were used without further purification. Silicon dioxide (silica) was obtained from Central Silica Company with particle size <44 μm.

Polymerization

All copolymers were prepared according to procedures described previously.[1]

Compounding and Molding

Compounding ingredients were added to the copolymers on a mill at room temperature. Dicumyl peroxide was used at the 2 part per hundred copolymer level, while silica was added at the 100 and 150 parts per hundred copolymer level for injection and compression molded samples, respectively. The silane was used only with copolymers containing silica (1 part silane per 100 silica). The basic recipe employed for sulfur cures was 100 copolymer, 5 zinc oxide, 2 sulfur, 2 stearic acid, and 1.2 accelerator.

Samples containing dicumyl peroxide were compression molded for 10 min at 175°C or 3 hr at 145°C (both are 10 half-lives for dicumyl peroxide).[2] Samples containing sulfur were molded for 30 min at 150°C.

Samples were injection molded with a Model 75TS New Britain unit at 182°C with a nozzle temperature of 99°C. The injection pressure was 48 MPa and the holding pressure, 34 MPa. Total cycle time was 120 sec, including 30 sec for cooling. Screw speed was 104 rpm.

Physical Property Measurements

Flexural modulus and strength were measured according to ASTM Method D-790. Heat distortion temperatures were determined by ASTM Method D-648 at 1.82 MPa stress loading and Rockwell hardness, according to ASTM Method D-785 (procedure A). Izod impact resistance was measured by the ASTM Method D-256 (procedure A). Gardner impact resistance was measured according to ASTM Method D-2794 on 3.81 cm × 2.54 cm × 0.32 cm samples. Compression strength and modulus were determined by ASTM Method D-695. Tensile properties were measured on both elastomeric copolymers and hard thermosetting resins. Tensile strength, modulus, and elongation were measured on elastomers according to ASTM Method D-412, while tensile properties on the resins were determined by ASTM Method D-638. Shore hardness values were measured according to ASTM Method D-2240. Properties were measured on both compression- and injection-molded samples.

Polymer Characterization

NMR spectra were measured at 60 MHz for all polybutadienes in CCl_4 at room temperature to investigate polymer microstructure. Peak areas of signals for terminal and nonterminal olefinic protons were analyzed according to the method of Senn.[3]

GPC measurements were made with a Waters Model 200 GPC unit. Four crosslinked polystyrene columns with nominal pore sizes of 10^4, 3×10^3, 10^3, and 2×10^2 Å were used. Copolymer compositions were determined by elemental analyses on a Hewlett-Packard Model 185 analyzer.

RESULTS AND DISCUSSION

Unfilled Copolymers

A series of butadiene–ε-caprolactam copolymers was prepared and characterized. The compositions, microstructures, and molecular weights are presented in Table I. The molecular weights of the polybutadiene segments (M_2) were determined by GPC. The molecular weights of the block nylon 6 (M_1) were then calculated from the molecular weights of the polybutadiene segments, copolymer composition, and molar ratio (M) of toluene diisocyanate (TDI) to polybutadienyl lithium (PBL) as described previously.[1]

TABLE I
Characterization of Butadiene–ε-Caprolactam Copolymers

Sample no.	ε-Caprolactam in Copolymer, (wt. %)	$M_2 \times 10^{-3}$, (g/mole)	M	$M_1 \times 10^{-3}$, (g/mole)	1,2 Content of Butadiene Seg., (wt. %)
1	26.2	16.0	1.18	4.2	76
2	26.2	56.2	1.03	13.6	83
3	35.3	24.0	1.26	8.6	82
4	35.3	51.5	1.00	28.1	80
5	50.0	26.2	1.53	11.9	82
6	50.0	22.8	1.14	17.8	79
7	64.7	19.3	1.21	24.0	83
8	64.7	20.0	1.04	36.5	80
9	73.8	8.1	1.33	13.7	84
10	73.8	14.0	1.03	37.0	78

TABLE II
Physical Properties of Cured Butadiene–ε-Caprolactam Copolymers

Sample no.	Flexural		Rockwell hardness E scale	Heat dist. temp. @ 1.82 MPa, °C	Gardner impact, J	Izod impact, J/m	
	Modulus GPa	Strength, MPa				Notch.	Unnotch.
2	1.3	49	63	163	0.35	31	165
3	1.3	52	63	—	0.40	30	219
4	1.3	45	64	161	0.34	51	128
5	1.6	65	64	182	0.40	37	224
6	1.6	66	64	189	0.52	59	203
7	1.4	66[a]	65	172	0.95	75	646
8	1.4	63[a]	61	186	0.97	96	416
9	1.1	54[a]	60	156	1.47	107	854
10	1.2	54[a]	59	161	1.13	133	1060

[a] Yield Strengths.

Physical properties of the copolymers described in Table I are listed in Table II. These were obtained from samples cured with dicumyl peroxide for 3 hr at 145°C. The cured copolymers were hard resins. This was not unexpected since the butadiene segments contain a high proportion of 1,2 units.[4] There is little variation in flexural properties as well as heat distortion temperature with copolymer composition. Impact resistance as measured by both the Gardner falling dart and Izod methods was quite sensitive to copolymer composition. The values were quite low at 26 wt-% ϵ-caprolactam but increased dramatically in copolymers having >50% ϵ-caprolactam content. This trend is probably due to the fact that homopoly(ϵ-caprolactam) has considerably greater impact resistance than highly crosslinked resins made from polybutadiene having a high proportion of 1,2 units.

Filled Copolymers

In an effort to determine the influence of a filler on physical properties, each of the copolymers described in Table I was compounded with 150 parts of silica in addition to the peroxide curative. Small quantities of silane coupling agent (1.0 parts per hundred silica) were also employed. These filled copolymers were cured at 175°C for 10 min, and then physical properties were measured on the cured resins. These properties are summarized in Table III. As with the unfilled copolymers, flexural modulus was relatively insensitive to copolymer composition; however, flexural strength is dependent on copolymer composition in these filled systems. It is seen to increase regularly as the ϵ-caprolactam content is increased. This trend is explained by the fact that poly(ϵ-caprolactam) possesses a much higher flexural strength than peroxide-cured polybutadiene.[5] As mentioned above, this trend is not apparent in the unfilled copolymers. This is not unreasonable, however, when one considers that at high ϵ-caprolactam contents (>50%), we are measuring flexural yield strengths rather than failure points in the unfilled copolymers. Although heat distortion temperatures are again insensitive to copolymer composition in these filled copolymers, it is important to note that heat distortion temperatures are considerably higher in silica-loaded copolymers than in those copolymers without filler. In fact, in the silica-

TABLE III
Physical Properties of Filled Butadiene–ϵ-Caprolactam Copolymers

Sample no.	Flexural Modulus, GPa	Flexural Strength, MPa	Rockwell hardness E scale	Heat dist. temp. @ 1.82 MPa, °C	Gardner impact, J	Izod impact, J/m Notch.	Izod impact, J/m Unnotch.
1	3.4	62	47	230	0.40	28	224
2	4.4	68	66	230	0.35	20	64
3	4.4	72	62	251	0.35	24	155
4	4.3	74	68	220	0.38	23	160
5	5.4	79	72	250	0.35	24	224
6	5.4	88	71	220	0.44	24	192
7	5.2	96	68	230	0.63	27	288
8	5.1	97	67	220	0.62	24	251
9	4.7	108	58	197	0.71	28	390
10	4.9	101	64	220	0.70	29	352

filled samples, a 0.254-mm deflection was measured in one case only (sample 3 of Table III). All other samples were removed from the test bath before 0.254-mm deflection was reached. The same dependence of Gardner impact resistance on copolymer composition is seen in these filled copolymers as was noted in the unfilled systems. Values increase with increasing ε-caprolactam content. In addition, Gardner impact is generally lower in filled copolymers than for corresponding unfilled samples. Izod impact resistance shows little if any variation in the notched Izod impact resistance with copolymer composition. Unnotched values, however, showed the same tendency to increase with increasing ε-caprolactam content as did Gardner impact resistance. The values measured for notched impact resistance were considerably lower than corresponding values measured on unnotched samples. This illustrates a high notch sensitivity for these filled butadiene–ε-caprolactam copolymers.

With the exception of samples 1 and 2 of Table III, there does not seem to be any dependence of physical properties on the molecular weight of the copolymers. Sample 1 is a particularly low molecular weight copolymer. After cure, it gave much lower values for both hardness and flexural modulus than sample 2 at the same copolymer composition. Apparently, sample 1 was simply not as highly cured as sample 2. This conclusion is supported by the fact that impact resistance is considerably higher for sample 1 than sample 2.

Effect of Temperature

The flexural properties of a silica-filled copolymer containing 74 wt-% ε-caprolactam were also measured at elevated test temperatures. Arrhenius plots of these data are shown in Figures 1 and 2. As might be expected, a steady decrease in both flexural modulus and strength with increasing test temperatures was noted. These properties were measured on silica filled samples (150 phr) containing a small amount of silane (1.5 phr).

In addition to measuring flexural properties at elevated temperatures, this sample was heat aged in a forced-air oven for several weeks at various temperatures. The per cent weight loss as well as changes in physical properties were then measured at various times. Flexural properties were relatively unaffected at temperatures up to 204°C for several weeks. In fact, flexural modulus was seen to increase initially and then remain relatively constant. Weight losses were also minimal, generally in the 2–6% range over an eight-

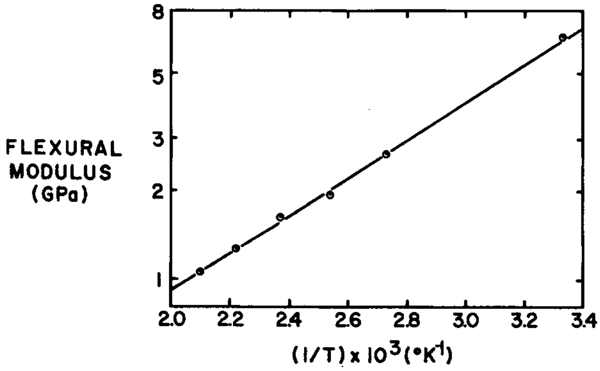

Fig. 1. Flexural modulus vs. test temperature.

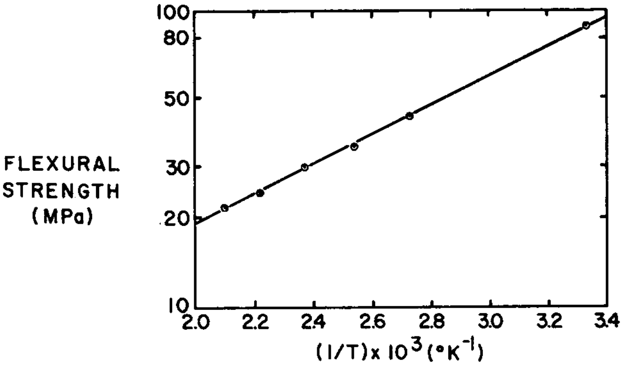

Fig. 2. Flexural strength vs. test temperature.

TABLE IV
Physical Properties of Butadiene—ϵ-Caprolactam Copolymers After Heat Aging

Aging time, wks.	Wt. loss, %	Flexural properties		Gardner impact, J
		Modulus, GPa	Strength, MPa	
@ 149°C				
1	2.3	6.97	108	0.57
2	2.2	8.55	91	0.47
3	2.5	8.48	85	0.52
4	2.5	9.03	83	0.51
5	2.5	8.90	86	0.42
6	2.5	8.83	76	0.33
7	2.5	7.93	82	0.40
8	2.5	7.86	81	0.48
@ 177°C				
1	2.9	7.38	86	0.44
2	3.0	7.38	82	0.41
3	3.0	7.86	91	0.41
4	2.9	9.10	90	0.23
5	3.1	8.48	91	0.36
6	3.2	7.86	88	0.27
7	3.3	8.48	90	0.36
8	3.3	7.79	89	0.37
@ 204°C				
1	3.0	6.34	105	0.26
2	3.1	7.72	102	0.25
3	3.2	7.38	110	0.23
4	3.5	7.10	105	0.21
5	3.9	8.48	101	0.19
6	4.5	8.28	91	0.17
7	5.2	8.07	83	0.23
8	6.0	6.69	68	0.20
Initial properties		6.55	87	0.49

week aging period. Impact resistance did decrease with increasing periods of aging with the largest decreases coming at the highest aging temperatures. A summary of these heat aging studies in given in Table IV.

It should be pointed out that the heat aging studies summarized in Table IV were done at temperatures below the melting point of poly(ϵ-caprolactam)

TABLE V
Physical Properties of Butadiene—ε-Caprolactam Copolymers Heat Aged at Elevated Temperatures

Aging time, days	Wt. loss, %	Flexural properties Modulus, GPa	Flexural properties Strength, MPa	Gardner impact, J
@ 260°C				
1	2.9	7.17	118	0.44
2	2.6	7.52	110	0.42
4	3.4	6.55	101	0.29
7	5.9	1.93	18	0.23
@ 316°C				
1	7.1	3.45	41	0.21
2	11.4	2.00	21	0.23
4	23.9	1.10	8.3	0.10
7	28.6	.83	7.6	0.08

(ca. 216°C).[6] When samples were heat aged at 260–316°C, large decreases in flexural properties were noted in a matter of days. At 316°C, the decrease in flexural properties was accompanied by significant weight losses. A summary of these results is compiled in Table V.

The rapid loss of properties noted in samples aged above the melting point of the poly(ε-caprolactam) portion of these copolymers was not unexpected. Molten poly(ε-caprolactam) has been shown to degrade rapidly by such heat treatment.[7] Since no attempt was made to stabilize the poly(ε-caprolactam) portion of these copolymers, the decay of physical properties with high-temperature aging is quite reasonable.

Injection Molding

The physical properties discussed above and measured on butadiene–ε-caprolactam copolymers whose butadiene segments contain a high proportion of 1,2 units were obtained from compression-molded samples. Since there is a wide interest today in thermosetting resins which can be easily injection molded, we also obtained physical properties on injection-molded samples. These properties were obtained on a copolymer containing 67 weight per cent ε-caprolactam and are summarized in Table VI. As might be expected, modulus values are most affected by silica filler. These are about twice as high for silica-filled copolymers compared with unfilled samples. Other properties are relatively unaffected by silica filling, although hardness increases and Gardner impact resistance decreases in filled samples. The moldability of these copolymers is quite good, giving shiny smooth surfaces.

Elastomeric Properties

Until now, we have reported the physical properties of those copolymers whose butadiene segments contain a high proportion (>75%) of 1,2 units. We have also investigated the properties of copolymers in which about 80–90% of the butadiene repeat units have a 1,4 microstructure. As might be expected, the physical properties of these latter copolymers cured with both sulfur and peroxide were elastomeric, having much higher elongations than

TABLE VI
Physical Properties of Injection Molded Butadiene—ε-Caprolactam Copolymers[a]

Properties @ 4 min, 175°C Cure	Units	Unfilled copolymer	50/50 Copolymer + silica
Tensile strength	MPa	53	62
Tensile modulus	GPa	1.81	3.92
Flexural strength	MPa	90	101
Flexural modulus	GPa	2.30	5.08
Compression strength	MPa	106	143
Compression modulus	GPa	2.07	3.81
Rockwell hardness	E Scale	50	67
Izod impact	J/m notched	27	21
Gardner impact	J	0.76	0.31
Heat Dist. temp.	@ 1.82 MPa, °C	—	208
Elongation	%	4.8	3.0

[a] Butadiene segments contain 78% 1,2 repeat units.

TABLE VII
Characterization of Butadiene—ε-Caprolactam Copolymers

Sample no.	ε-Caprolactam in copolymer, wt-%	$M_2 \times 10^{-4}$, g/mole	M	$M_1 \times 10^{-4}$, g/mole	1,2 Content of butadiene segments, wt-%
11	64.7	1.7	1.0	3.12	11
12	64.7	3.3	1.0	6.04	9
13	64.7	3.8	2.2	2.05	10

TABLE VIII
Physical Properties of Cured Butadiene—ε-Caprolactam Copolymers

Sample no.	Shore hardness, A scale	E_b, %	σ_5, MPa	σ_b, MPa
Peroxide Cured				
11	89	150	1.31	28.8
12	91	155	1.76	34.8
13	91	160	2.83	37.2
Sulfur Cured				
11	87	160	1.31	24.0
12	88	200	1.52	27.4
13	92	210	1.79	29.3

the hard thermosetting resins discussed above. Table VII lists the characteristics of three such copolymers.

The copolymers listed in Table VII were cured with either dicumyl peroxide or sulfur to give the physical properties shown in Table VIII. Samples containing peroxide were cured for 10 min at 175°C, while those containing sulfur were cured for 30 min at 150°C. The numbers in the third column (E_b) of Table VIII are the elongations measured at break. The values reported in the last two columns (σ_5 and σ_b) are the stresses measured at 5% elongation and at break, respectively. Ultimate properties are moderately improved by increasing the molecular weight of the polybutadiene segments.

In addition, the low strain modulus σ_5 was seen to increase when the TDI/PBL molar ratio M was increased. This latter effect is probably due to the fact that an increase in M provides an increase in the amount of poly(ε-caprolactam) homopolymer present in these polymerization mixtures. In an earlier report,[8] we pointed out that an increase in M results in a decrease in the amount of coupled polybutadiene and an increase in the amount of isocyanate-terminated polybutadiene. However, when $M > 1.0$, there are TDI molecules present which are not bound to polybutadiene chains. These "free" TDI molecules together with N-lithiocaprolactam are capable of initiating nylon 6 chains. The result is the formation of poly(ε-caprolactam) homopolymer. The amount of homopolymer formation is directly proportional to the "free" TDI or M.

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