Characteristics of Polymerization-Filled Polycaprolactams

V. M. CHESHKOV,[1] **M. M. NATOVA,**[1] **N. R. ASHUROV,**[2] **M. M. USMANOVA,**[2] **A. M. VEKSELMAN**[3]

[1]Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

[2]Institute of Polymer Chemistry and Physics, Uzbek Academy of Sciences, Tashkent 700128, Uzbekistan

[3]McGill University, Montreal, Quebec H3S 2K6, Canada

ABSTRACT: A polymerization filling of a base in character monomer (ε-caprolactam) was carried out using fillers with solid acid character and catalytic action such as γ-alumina and calcium phosphate. The properties and structure of the polymerization-filled polycaprolactam obtained were studied. The following characteristics were determined: melting temperature, glass transition temperature, crystallization temperature, tensile strength, and dynamic elastic modulus. The advantages of the polymerization filling method are shown as compared to conventional methods for homogeneous production of polycaprolactam. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1255–1258, 1997

INTRODUCTION

The introduction of solid acids into ε-caprolactam makes it possible to produce polycaprolactam via polymerization, only because of the catalytic action of the surface acid sites.[1,2] Thus inorganic substances applied act as both catalysts in the polymerization of the base in character ε-caprolactam and fillers of the resulting polycaprolactams. The activation of the monomer molecule is associated with its acid–base interaction with the surface of the fillers applied.

The heterogeneous polymerization reaction running with the participation of fillers with catalytic action is called polymerization filling and the resulting product a polymerization-filled polymer. The acid sites affect the kinetics and reaction mechanism on one hand and the structure and properties of the resulting polymer materials on the other.

The present article aims to reveal some intrinsic characteristics as well as structural peculiarities of polymerization-filled polycaprolactams prepared using γ-alumina and calcium phosphate.

EXPERIMENTAL

The characteristics of calcium phosphate, γ-alumina, and ε-caprolactam used throughout the experiments are given in a previous study.[1,2] The polymerization filling process was carried out in an open laboratory reactor at a temperature of 523 K under nitrogen flow until the equilibrium concentration of the monomer (approx. 10 wt %) was achieved. The reactor was supplied with a screw stirrer, and the resulting composite material was extruded into a water cooled bath. The samples were prepared through injection molding. Some of them were annealed in a vacuum at 458 K (the temperature close to the crystallization temperature of the polymer) for 20 h.

The following characteristics of the polymerization-filled polycaprolactams (of the polymer itself and of the composite material as a whole) were determined:

Table I Characterization of Polycaprolactams

	Heterogeneous Polymerization (Polymerization Filling)				
Properties	$Ca_3(PO_4)_2$ 30 wt %	γ-Al_2O_3 5 wt %	γ-Al_2O_3 10 wt %	γ-Al_2O_3 5 wt % + $Ca_3(PO_4)_2$ 20 wt %	Homogeneous Polymerization
Molecular weight, $M_\eta \cdot 10^{-3}$	43	36	30	51	15–25
Melting temperature, T_m (K)	492	494	494	492	491–498
Glass transition temperature, T_g (K)	327	340	338	333	323–330
	344[a]	347	346	345	
Crystallization temperature, T_c (K)	454	457	457	456	420–440
Degree of crystallinity (%)	39	31	34	31	22–33
	64	40	40	37	
Tensile yield strength (MPa)	58	62	64	52	40–60
Dynamic elastic modulus, $E_d \cdot 10^{-2}$ (MPa)	76	59	65	82	55–60
	132	79	84	120	

[a] When two values are reported, the second one refers to annealed samples (458 K, 20 h).

1. melting temperatures, crystallization temperatures, and degree of crystallinity were read from thermograms recorded with a Perkin–Elmer DSC-2 type differential scanning calorimeter under a heating rate of 10 K/min and nitrogen flow;
2. glass transition temperatures and dynamic elastic moduli were measured with a Metravib viscosimeter at a frequency of 7.8 Hz;
3. tensile strength was measured with an FT-10 type tension test instrument under a loading rate of 5 mm/min;
4. crystallographic forms of the surface layer (200 μm) and the bulk of samples were established by X-ray diffraction analysis carried out with a Dron-2 type diffractometer; the surface layer was cut with a microtome;
5. Molecular weights were measured by the viscosimetric method using polymer solutions in *m*-cresol after centrifugation of the filler.

RESULTS AND DISCUSSION

Table I lists the features of the polymerization-filled polycaprolactams obtained. The characteristics of polycaprolactams produced by conventional methods of homogeneous polymerization are given for comparison.[3–8] The fillers used are distinguished in respect to strength of the fillers' acid sites from pK_a = 2.0 to 4.8. The polymerization-filled polycaprolactams are not inferior but are even superior to known polycaprolactams with re-

spect to molecular weights, degree of crystallization, and dynamic elasticity modulus, in spite of a high percentage of filler. Data in the last column refer to unfilled caprolactams. Introduction of fillers to these caprolactams according to conventional procedures often causes a deterioration of the characteristics of the polymer. Abdurazakov et al.[9] reports that the introduction of 15% graphite to caprolactam produced by the conventional method causes a decrease in the tensile strength from 60 to 28 MPa. Reimschuessel[4] established a decrease in the melting temperature from 222 to 204 K with a ZrF_4 content of 15% while the crystallization temperature drops from 440 to 423 K. On introduction of 12.5% $FeCl_3$ to the polycaprolactam the degree of crystallinity drops from 31 to 16%.[10] The comparison of our data with these data gives an additional confirmation to the efficiency of the present method of polymerization filling.

It is impossible to make a correlation between all characteristics of the composite materials obtained and the strength of the acid sites on the inorganic surfaces. Data in Table I show that catalysts with stronger acid sites yield polycaprolactams with higher glass transition temperatures as compared to catalysts with weaker sites and lower molecular weight. Thus the system with γ-alumina containing acid sites of pK_a = 2.0 ÷ 3.0 yields a polymer with molecular weight of 30,000–36,000 (depending on the filler amount) and T_g = 340 K; in the presence of calcium phosphate (pK_a = 3.3 ÷ 4.8) the resulting polymer has a molecular weight of 43,000 and T_g = 327 K. In the
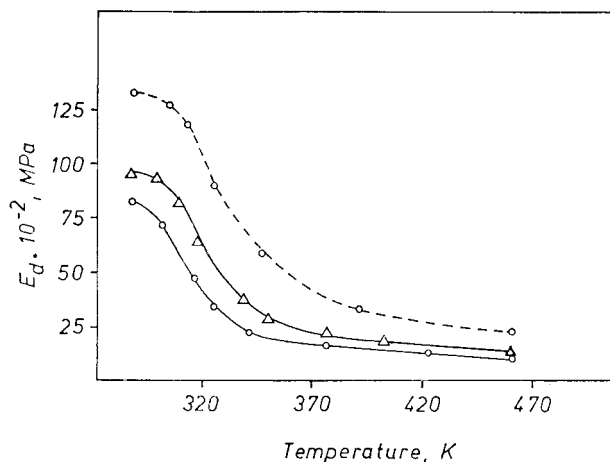
Figure 1 Dynamic elastic modulus versus temperature plot of the polymerization filled pollycaprolactam samples: $(-\triangle-)$ 10 wt % γ-Al_2O_3; $(-O-)$ 30 wt % $Ca_3(PO_4)_2$; $(--O--)$ 30 wt % $Ca_3(PO_4)_2$, annealed.

case of the mixed catalyst the polycaprolactams produced exhibit similar characteristics except for the molecular weight, which is higher as compared to single fillers. At the same time melting and crystallization temperatures as well as the degree of crystallinity of all polymerization-filled polycaprolactam samples are comparable.

All investigated samples showed a single peak of melting, regardless of the acidity of the filler–catalysts applied. Its position (in the range 492–494 K) is characteristic of the polycaprolactam crystal α form, which is most stable thermodynamically. Annealing (which is widely used in practice) at T = 458 K for 20 h led to a strong increase in dynamic elastic modulus and degree of crystallinity values. The glass transition temperatures also increased to some extent.

Figure 1 illustrates some typical changes in dynamic elastic modulus of polymerization-filled polycaprolactams (annealed and unannealed) as a function of temperature. The most significant changes are observed in the range of glass transition.

Figure 2 presents a tangent of the angle of mechanical loss versus temperature plots for annealed and unannealed samples of the composite material that point out the molecular mobility in the crystalline and amorphous parts of the polymer. Two main temperature transitions are observed that are characteristic of polycaprolactams produced by conventional procedures as well. The first one at 205–225 K is associated with the molecular mobility of the amide groups not bound through hydrogen bonds. The second transition

(320–345 K) is attributed to segmental mobility of the amorphous phase of the polymer; that is, it presents the glass transition temperature.

Figure 3 presents diffraction patterns typical of all samples of the composite material. Two peaks are observed at 2θ = 20.2° and 23.6°, characteristic of α-crystal modification of polycaprolactam (bulk samples), and a peak at 2θ = 21.2°, characteristic of γ^* modification (surface layer).[6] The latter is characteristic of the stable γ-crystal form of polycaprolactam as well, but its presence should be accompanied by a peak at 2θ = 11°, which was not observed in our case. Another confirmation to the suggestion that the peak at 2θ = 21.2° is provided by the presence of unstable γ^* modification is the fact that it disappeared on annealing of the samples, which is not typical of the γ form, while new peaks at 2θ = 20.2° and 23.6° appeared; that is, a γ^* modification to the α-form transition occurred. The presence of various crystal modifications can be attributed to varying crystallization conditions under which the materials are produced, the so-called "ad-wall" effect. Another interesting phenomenon is the appearance of a sharp peak at 2θ = 25° in all diffraction patterns of polymerization-filled polycaprolactams, which corresponds to an interplanar distance of 3.55 Å. This peak was not observed either in the diffraction patterns of filler–catalysts applied or in the patterns of known crystal forms of polycaprolactam. Hence, the appearance of this unknown peak can be associated with the develop-
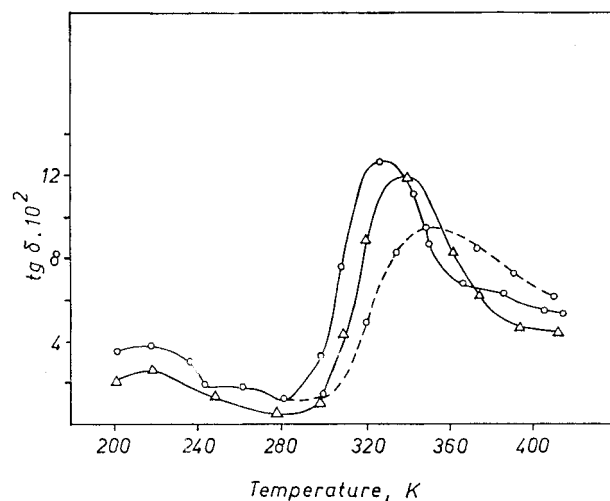

Figure 2 Tangent of the angle of mechanical loss versus temperature dependence for polymerization filled polycaprolactam samples: $(-\triangle-)$ 10 wt % γ-Al_2O_3; $(-O-)$ 30 wt % $Ca_3(PO_4)_2$; $(--O--)$ 30 wt % $Ca_3(PO_4)_2$, annealed.

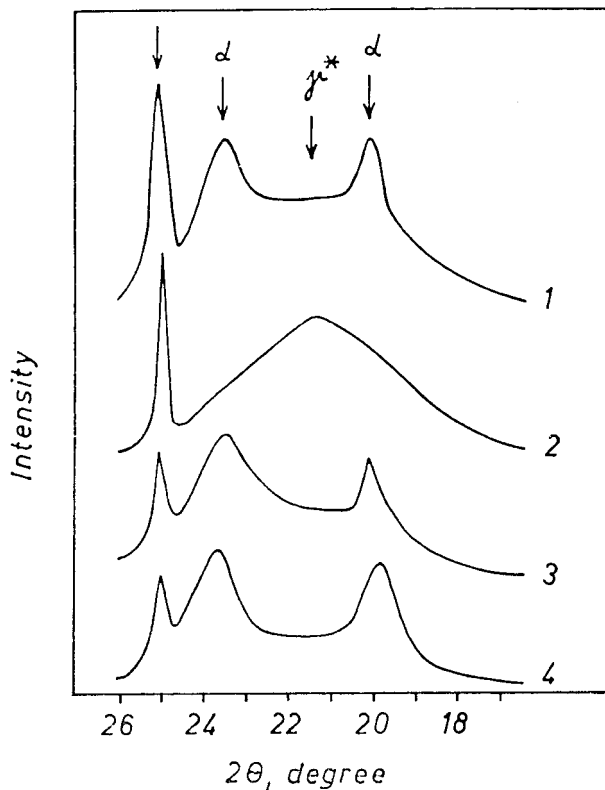**Figure 3** Typical X-ray diffraction pattern of polymerization filled polycaprolactam (30 wt % $Ca_3(PO_4)_2$): (1,3) interior parts of samples before and after annealing, respectively; (2,4) surface layers before and after annealing, respectively.

ment of a definite ordering (structurizing) of the polymer at the interface between the polymer and filler particles. The fact that this interplanar distance is unique and appears as a very narrow diffraction maximum is very likely due to the very regular orientation of polymer molecules toward the active filler surface. It can be suggested that this ordering resembles the epitaxial type crystallization and is provided by the presence of acid sites on the filler surface. On annealing of the samples the intensity of this peak decreased, which according to the suggestion about its nature can be explained with a partial disorientation of polymer molecules on the interface.

CONCLUSION

It was established that the active role of acid sites on the surface is not limited in their catalytic ac-

tion in the process of polymerization filling but affects the properties and structure of resulting composite materials as well. The polymerization-filled systems exhibited very good physicochemical and physicomechanical characteristics. Some parameters (molecular weight, degree of crystallinity, and dynamic elastic modulus) were superior to that of polycaprolactams produced by homogeneous catalysis. It is noteworthy to point out that the polymerization filling yielded polycaprolactams of the most thermodynamically stable α-crystal modification.

A new unknown interplanar distance of polycaprolactam crystal modifications was observed. It was probably provided by the interaction of the polymerizing ε-caprolactam with the filler surface, resulting in a strong orientation of macromolecules toward the acid sites. The characteristics of polymerization-filled polycaprolactams were considerably improved on annealing.

REFERENCES

1. V. Cheshkov, M. Natova, N. Ashurov, M. Usmanova, and A. Vekselman, *Eur. Polym. J.,* **27,** 205 (1991).
2. M. Natova, V. Cheshkov, N. Ashurov, M. Usmanova, and A. Vekselman, *Eur. Polym. J.,* **29,** 653 (1993).
3. A. Fichera, V. Malta, C. Marega, and R. Zannetti, *Makromol. Chem.,* **189,** 1561 (1988).
4. H. K. Reimschuessel, *Colloidal Polym. Sci.,* **260,** 842 (1982).
5. A. J. Kobljakov and A. G. Barteneva, *Vȳsokomol. Soedin.,* **A28,** 785 (1986).
6. G. Gurato, A. Fichera, F. Z. Grandi, R. Zannetti, and P. Canal, *Makromol. Chem.,* **175,** 953 (1975).
7. D. W. Van Krevelen and P. J. Hoftyzer, *Properties of Polymers: Correlations with Chemical Structure,* Elsevier Publishing Co., New York, 1972.
8. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Karauchi, and O. Kamigaito, *J. Polym. Sci., Part A: Polym. Chem.,* **31,** 983 (1993).
9. M. Abdurazakov, I. P. Gomza, S. D. Petrenko, V. N. Volkov, N. R. Ashurov, V. V. Shilov, and I. S. Lipatov, *Mekh. Kompoz. Mater.,* **2,** 257 (1988).
10. L. C. Chao and E.-P. Chang, *J. Appl. Polym. Sci.,* **26,** 603 (1981).