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Biodegradable anionic poly(esteramide)s. Physico-mechanical properties

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The poly(ester amide)s from ϵ–caprolactam and ϵ–caprolactone are semicrystalline materials. These types of PEAS possess partially bloky microstructure, with chains composed of –NH(CH_2)5CO– (ϵ–caprolactam) and –O(CH_2)5CO– (ϵ–caprolactone) groups. Each of the copolymers displayed a single melting point on DSC analysis. The degree of crystallinity and melting point of copolymers decreases with increasing ϵ–caprolactone initial content. The notched impact strength values of the copolymer increases, while flexural modulus decreases with increasing ϵ–caprolactone initial content. This suggests that the ester component in the copolymers act as plasticizer, reducing the degree of crystallinity of the copolymer and flexural modulus. The poly(esteramide)s were synthesized by using different monomer ratios CL/CLO: 100/0, 95/5, 90/10, 85/15, 80/20 and 75/25. The initial mold temperature (initial polymerization temperature) was kept constant at 160°C.

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1. Introduction

In the context of the explosive development of the field of the polymers the attention of the researchers has been given recently to the materials that have the ability to be compatible with living world (environment and tissues) and promote the green chemistry by controlled enzymatic synthesis and degradation.

Because the vast majority of plastic products are made from petroleum-based synthetic polymers that do not degrade in a landfill or in a compost–like environment there is an urgent need for the development of green polymeric materials that would not involve the use of toxic or noxious components in their manufacture, and could allow to composting to naturally occurring degradation products [1].

One of the solutions to the problem of plastic wastes management includes applications of biodegradable thermoplastics which degrade in soil, sea or lake water, activated sludge, or compost after their service life is over.

Aliphatic polyesters such as poly(ϵ–caprolactone) (PCLO) [–O–(CH_2)$_5$–CO–]$_n$ are an important class of biodegradable synthetic polymer, and its degradation products are biocompatible. It is very useful in biomedical applications, especially as drug delivery devices [2]. On the other hand, aliphatic polyamides such as poly(ϵ–caprolactam) (PCLA) (polyamide 6) (nylon–6) [–NH–(CH_2)$_5$–CO–]$_n$ are known for their inertness to biodegradation although present a good combination of thermal and mechanical properties [3]. It plays an important role in the field of engineering thermoplastics and has a broad processing range being compatible with additives and other materials. Also, it is known that the polyamides have biomedical application because their structure is relatively similar of proteins [4]. In this sense the study of the polymers that contain both amide and ester groups is at present of considerable interest because the properties of poly(esteramide)s are open to wide variation by structural choice. Poly(esteramide)s may have several possible distributions of the amide segments, random, uniform or alternating [5]. These copolymers range in properties from plastic to elastomer depending on the amount of lactone monomer initially incorporated into the polymerizable composition [6].

In principle, the good properties of polyamides and polyesters (melt processable, solvent resistance) may be combined in poly(esteramide)s and can be controlled by varying the proportion of functional groups in their structure. Also, these polymers retain biodegradability characteristics of the polyesters.

Both poly(ϵ–caprolactam) and poly(ϵ–caprolactone) are commercially obtained from the cyclic monomers by ring–opening polymerization. The two major commercial routes to manufacturing poly(ϵ–caprolactam) are hydrolytic polymerization and anionic polymerization.

It is well known that the anionic polymerization of lactams occurs at a significantly faster rate, reaching equilibrium conversion in only a few minutes, compared to the classical hydrolytic polymerization process which takes about 12–24 h.

The advantages of the anionic polymerization of ϵ–caprolactam have been put to use in reactive polymerization–molding processes, namely reaction injection molding (RIM) [7], rotational molding [8,9,10], centrifugal molding [11–14], and monomer casting [15] which permit direct manufacturing of large and complex shape plastic parts with a high degree of the surface finishing and control of the products characteristics [13, 14,16].

In the literature are presented syntheses of poly(esteramide)s by anionic polymerization ϵ–caprolactam and ϵ–caprolactone or ϵ–caprolactam with poly(ϵ–caprolactone) using monomer casting technique. [17,18]. Goodman and coworkers [19,20] reported the polymerization of random copolymers of CL with CA in a batch glass reactor without a substantial amount of coinitiator. They confirmed a random copolymer having a slight blocklike character by finding only a single melting point of the copolymer. Also, recently X. Fang et al. [21,22] was report that the ring–opening polymerization of ϵ–caprolactam and ϵ–caprolactone can be performed efficiently and effectively by microwave irradiation without any external thermal heating in a period of only 2 h to produce poly(esteramide)s. B. J. Kim et al. [23] have performed continuous copolymerizations of ϵ–caprolactone with ϵ–caprolactam and laurolactam in a modular intermeshing corotating twin–screw extruder.

This paper deals with a study of physico–mechanical properties of some anionic poly(esteramide)s obtained as constituent materials of the parts by a reactive rotational molding process *via* anionic ring–opening copolymerization of ϵ–caprolactam with ϵ–caprolactone.

2. Experimental

2.1. Materials

monomers**:**

ϵ–caprolactam (CLA) (tehnical grade, Fibrex–Savinesti, Romania);

ϵ–caprolactone **(**CLO) (Aldrich 99%) was dried over CaH_2 and distilled under vacuum.

Ethyl magnesium bromide, (EtMgBr, Aldrich Chemical Co., Inc.) as initiator 3.0 mol L^{-1} in diethyl ether solution used without further purification.

Activator **–** *N,N′*–isophthaloyl–*bis*–ϵ–caprolactam of the formula:

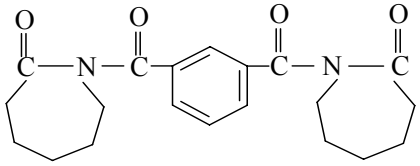

Fig. 1. Chemical structure of N,N′–isophthaloyl–bis–ϵ–caprolactam was synthesized in our laboratories from isophthaloyl dichloride and ϵ–caprolactam according to the procedure described in the literature [11,24]; m. p. (DSC), 141 °C (Ref. [25]:139.2 °C).

Sulfuric acid (97%) supplied by Riedel–de Haen – Germany and other chemicals were of reagent grade and used without further purification.

2.2. Synthesis of polyesteramides by rotational molding

The polyesteramides were synthesized as constituent polymers of the parts made by activated anionic ring–opening copolymerization of ϵ–caprolactam and ϵ–caprolactone on a laboratory rotational molding instalation. The molding–polymerization process was preformed below the melting point of the polymers.

The polyesteramides were synthesized by using different monomer ratios CLA/CLO: 100/0, 95/5, 90/10, 85/15, 80/20, and 75/25.

Grignard reagent (ethyl magnesium bromide) as initiator and *N,N′*–isophthaloyl–*bis*–ϵ–caprolactam as activator at 0.6 mol % and 0.4 mol % of reaction mixture, respectively was used.

In preparing the poly(esteramide)s, a lactam monomer and a ϵ–caprolactone monomer are weighed out and heated in separate vessels to about 110 °C. A catalytically effective amount of the initiator is added to and dissolved in the heated ϵ–caprolactam monomer and an effective amount of an activator is added to and dissolved in the heated ϵ–caprolactone monomer. The heated solution of magnesium initiator in ϵ–caprolactam monomer and the heated solution of activator in ϵ–caprolactone monomer are admixed and immediately introduced into rotated mold which was previously heated at 160 ± 2 °C (initial polymerization temperature). The polymerization–molding time was 30 min in all cases. The polymer part obtained by molding–polymerization process was allowed to cool to room temperature at a rate of about 2 °C/min before demolding, while the mold was still rotating. Finally, the mold is opening and the formed part is removed. Products with a circular section and uniform wall thickness have been obtained.

2.3. Sample preparation

In order to obtain samples for the determination of polymer yield and viscosity measurements the 'as molded' part was dried, cut, ground up and submitted to a Soxhlet extraction with methanol for 24 h. Subsequently the samples were dried at 95 °C for 48 h and stored in a desiccator over phosphoric oxide. The samples for the determination of mechanical properties were prepared by cutting and milling to dimensions required by the standards (see below) and then were dried at 60 °C, to constant weight and stored in a desiccator over phosphoric oxide. The film samples of poly(esteramide)s for the FT–IR spectral measurements were obtained by casting the formic acid polymer solutions (10 wt.–%) on glass plates followed by drying at 120 °C for 15 min.

2.4. Methods of investigation

The reduced viscosity of nylons solutions (0.5 g dL^{-1}) in sulfuric acid (97 %) was determined with a suspended level Ubbelohde viscometer thermostatted at 25±0.1°C.

Densities of the samples were evaluated at 23 °C by means of a density gradient column. The 1 m–high column, covering the range from 1.000 to 1.200 g cm^{-3}, was filled with a mixture of toluene and carbon tetrachloride (dried by 5 Å molecular sieve).

A Vertex–70 spectrometer was used to acquire FT–IR data, over a range 400–4000 cm^{-1}, at a resolution of 4 cm^{-1} and co–addition of 100 scans.

Differential scanning calorimetry (DSC) was performed by METTLER DSC 112E, under nitrogen atmosphere, at a heating rate of 10 $^oC\ min^{-1}$, with a temperature range from 25 to 250 ^oC. The measuring cycle of all samples consisted of three scans: heating (of as–received sample), cooling (crystallization under identical conditions for all samples) and heating (see Fig. 2). The heats of fusion the crystalline region of PCLA and PCLO were considered to be 45.6 [10,11,13] and 32,5 cal g^{-1} [22,26], respectively. The values of the heat of fusion for the 100% crystalline CLA–CLO copolymers were calculated based on the contributions of the mole percent of each homopolymer in the respective copolymer. Thermogravimetric analysis (TGA) of the extracted samples was carried out on a F. Paulik Derivatograph at a heating rate of 10 $^oC\ min^{-1}$, in air.

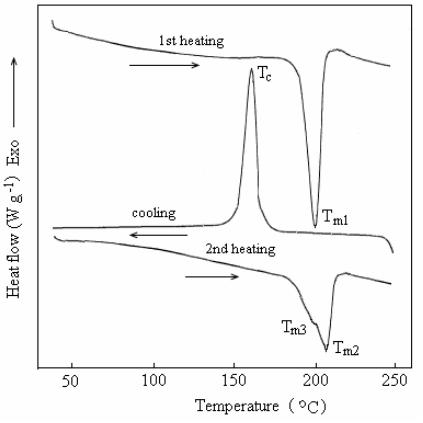

Fig. 2. DSC curves of poly(esteramide) (PEA–10).

The notched impact strength was measured by means of the Charpy pendulum testing machine PSW 1.5 (Werkstoff Prufmaschinen, Leipzig, Germany) at 23 °C according to ASTM D256–70 (with an accuracy of ± 10%). The tests for the determination of flexural modulus were performed as previously reported [9,13].

3. Results and discussion

The polymerization system consists of a combination of monomers, ϵ–caprolactam and ϵ–caprolactone, respectively, initiator and activator which form poly(esteramide)s and follows an activated anionic ring–opening mechanism.

Copolymerization ϵ–caprolactam with ϵ–caprolactone, using rotational molding technique was preformed below the melting point of the polymers. The initial polymerization temperature was kept constant at 160 ± 2 ^oC for all tests. Grignard reagent (ethyl magnesium bromide) as initiator and *N,N'*–isophthaloyl–*bis*–ϵ–caprolactam as activator at 0.6 mol % and 0.4 mol % of reaction mixture, respectively were used. The systems involving the higher concentrations of ϵ–caprolactone (>25 wt.–%) in total monomer feed presented some problems due to depress of the degree of crystallinity of copolymers that making demolding process difficult. The polymer part obtained by molding–polymerization process was allowed to cool to room temperature before its removal from the mold. The mold rotation continues during the cooling phase. Finally, the mold is opening and the formed part is removed.

All analyses were performed on the 'as–molded' and extracted samples as is presented in Section 2.3.

The effect of ϵ–caprolactone initial concentration on polymer yield, reduced viscosity and density of CLA–CLO copolymers are shown in Table 1

The data related to ϵ–caprolactam homopolymer (PCL) prepared in the same conditions as caprolactam–caprolactone copolymers are presented for comparison. As shown in Table 1 the polymers were obtained in high yields. However, the yield values corresponding to copolymers were somewhat lower than that of pure nylon 6 and decrease with increasing of ϵ–caprolactone initial content in the comonomer feed. The effect of variation in ϵ–caprolactone initial concentration on reduced viscosity and density are also surveyed in Table 1. It can be observed that the reduced viscosity (η_{sp}/c) and density of poly(esteramide)s decrease with increasing initial ϵ–caprolactone concentration. The poly(esteramide)s exhibited copolymer yield in the range of 81.8 to 96.07 and reduced viscosities in the range of 1.38 to 2.19 g dL^{-1}, respectively (see Table 1).

Table 1. Characteristics of the CLA–CLO copolymers.

Sample	CL/CLO[a] feed ratio (wt%)	Copolymer yield[b] (%)	Reduced viscosity[c] (g dl^{-1})	Density (g cm^{-3})
PEA00	100/0	98.2	2.6735	1.1556
PEA05	95/5	96.7	2.1915	1.1413
PEA10	90/10	95.8	1.9330	1.1339
PEA15	85/15	93.3	1.7710	1.1219
PEA20	80/20	91.7	1.5991	1.1083
PEA25	75/25	81.8	1.3850	1.0962

[a]CLA= ϵ–caprolactam, CLO= ϵ–caprolactone, composition by weigth

[b]Methanol–insoluble polymer (wt %)

[c]Determined at 25^oC with a polymer concentration of 0.5 g dL^{-1} in H_2SO_4 (97%) .

It is well known that the nylons present in the IR range stretching and bending vibrations characteristic to essential structural element of polyamides, amide group –CO–NH– existing in the *trans* planar conformation. The IR spectrum of nylon 6 presents a strong and sharp absorption band at 3299 cm^{-1} (amide A, =N–H stretching). Another two strong bands at 1651 cm^{-1} and 1547 cm^{-1} are assigned to the amide I band and to the amide II band, which have main contributions of the C=O stretching and the NH deformation, respectively. The weak absorption at 1265 cm^{-1} is associated with the amide group and is sometimes called an amide III band. The IR bands present at 1463 and 1417 cm^{-1} are attributed to $–CH_2–$ units adjacent to NH and C=O groups in the extended conformation of the chain in the α crystal modification of the obtained nylon 6. In the IR spectra are also observed bands associated with hydrogen–bonding between the NH and C=O groups at about 3400 cm^{-1} (3460 cm^{-1} – *trans*, non–bonded amide group; 3420 cm^{-1} – *cis*, non–bonded amide group) [27].

The IR characteristic bands of nylon 6 and of the copolymer PEA25 containing 25wt–% CLO are given in Fig. 3.

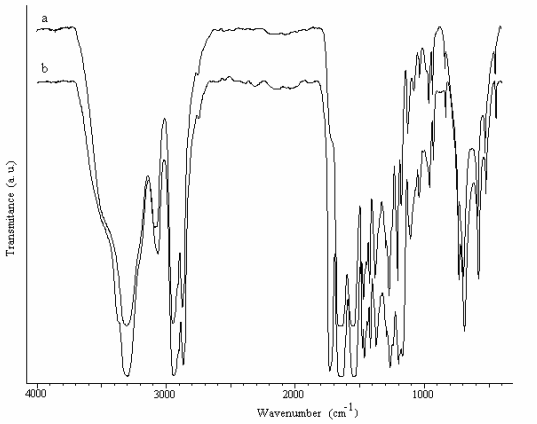

Fig. 3. FT–IR spectra of (a) PEA0 and (b) PEA25.

The spectrum of the copolymer shows characteristic absorptions of the poly(esteramide) i.e. the absorption band of ester carbonyl groups shifted to a lover wave number compare with that of PCLO (1732 cm^{-1}), while the absorption band of the amide groups is shifted to a higher wave number compared with polyamide 6 (1651, 1547 cm^{-1} assigned to amide I and amide II, respectively).

The strong absorption band at 3302 cm^{-1} (ν_{NH}) indicated that the amide NH groups of copolymers are substantially of *trans* form and completely hydrogen–bonded. The ester absorptions ($\upsilon_{C=O}$, *ca* 1732 cm^{-1};υ_{C-O}, *ca* 1169 cm^{-1}) increasing as the CLO content increases whilst the principal amide absorptions (amide A, *ca* 3302 cm^{-1}; amide B, *ca* 3061 cm^{-1}; amide I, *ca* 1651cm^{-1}; amide II, *ca* 1547 cm^{-1}) diminish correspondingly. Absorbance at *ca* 731 cm^{-1}, due to the polyester sequences, is apparent for ϵ–caprolactone contents ≥10 wt–%.

Also other characteristic bands for ester linkage appear in the range 1260–1100 cm^{-1}.

The evaluation of the thermal behavior of poly(esteramide)s was carried out using the data obtained from measurements by thermogravimetry (TGA) and differential scanning calorimetry (DSC) at heating rates of 10 ^oC /min. From TGA experiments, carried out in air in the 20 to 600 ^oC temperature range it can be observed that polyesteramides PEA 0–25 showed good thermal stabilities.

Fig. 4 display the thermograms of extracted poly(esteramide) (PEA15) as illustrative example.

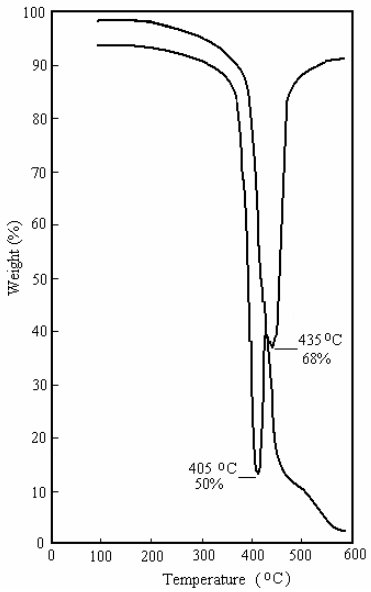

Fig. 4. Thermogravimetric analysis of the poly(esteramide) (PEA15).

An examination of data reveals three degradation steps detected at ca. 332 (7.1 % weight loss), 405 (50%) and 435 ^oC (68%). This behavior suggest that the structure of the polyesteramides could be partially blocky. The degradation of PCLO proceeds at a temperature lower than that of the PCLA. The thermal degradation of copolymers start at 332°C. This first peak could be mainly due to the degradation of PCLO sequences while the last degradation should be essentially due to that of PCLA blocks. A slightly decreased thermal stability of copolymers in comparison with that of the polyamide 6 (with about 20°C) was observed.

The results related to the thermal behavior of copolymers, thermal transition (peak values) and melting and crystallization enthalpies, observed during first and second heating and during cooling, together with data for nylon 6 are presented in Table 2.

The melting temperatures T_{m1} (first run), T_{m2} (second run), degree of crystallinity, nonisothermal crystallization temperature T_c, and the heats of fusion ΔH_{m1} and ΔH_{m2} of unextracted nylon 6 and poly(esteramide)s were evaluated by differential scanning calorimetry (DSC). Parameters

such as heat of fusion (ΔH_m) and heat of crystallization (ΔH_c) were used to determine the melting and crystallization behaviour of the nylon 6 and polye(steramide)s with various ϵ–caprolactone content. The results related to the melting and crystallization behaviour of polyesteramides, observed during first and second heating and during cooling, together with data for nylon 6 are presented in Table 3.

DSC thermograms of poly(esteramide)s recorded on the first run display a single melting endotherm peak (noted as T_{m1}), associated with the α–form crystals of poly(esteramide)s [28–30] in the 178–208 °C temperature range. This single melting temperature and its decrease with increasing initial CLO concentration suggest that poly(esteramide)s with distinct random structure are formed [31]. On the second heating scan, the melting peak (T_{m2}) of α–form crystals slightly shift to a lower temperature value (see Table 3). The values of melting temperatures of poly(esteramide)s were slightly below the melting temperature reported for neat (pure) nylon 6 (i.e. 225 °C – first scan, 220 °C – second scan) and diminish progressively with the ϵ–caprolactone content. Besides T_{m1} and T_{m2}, another lower endothermic peaks, T_{m3} (second run) occur as shoulders and they are associated with the melting of γ–form crystals of poly(esteramide)s as suggested by different research groups [28,29,32].

Also, an evaluation of the melting temperature indicate that the values corresponding to poly(esteramide)s found in the second (182–214 °C temperature range) are slightly higher than those obtained in the first heating (178–208 °C temperature range) (see Table 2). This behavior can be attributed to the fact that the conditions during cooling scan (non–isothermal crystallization) are much more favorable, in comparison with those in the course of the molded–polymerization, and therefore bigger spherulites can develop and higher values of melting temperatures are observed.

The degree of crystallinity of polyamide 6 and poly(esteramide)s was calculated from ratio of the measured enthalpy of fusion of the sample and the enthalpy of fusion of a completely crystalline polymer by using the following equation:

$$\alpha_{DSC}\% = \Delta H_f/\Delta H_{f,c} \times 100 \quad (1)$$

where ΔH_f is the enthalpy of fusion of the sample, and $\Delta H_{f,c}$ is the enthalpy of fusion of 100% crystalline sample of the same copolymer.

Table 2 shows that the degree of crystallinity of poly(esteramide)s decreased as the initial concentration of the ester units incorporated into the polyamide 6 was increased (the degree of the ordering of the system distinctly decreases).

Also, the values of degree of crystallinity of the poly(esteramide)s are lower than that of the pure polyamide 6 (see Table 2).

Table 2. Thermal properties and degree of crystallinity of the nylon 6 and poly(esteramide)s with varying concentrations of ϵ–caprolactone.

Sample	*First heating*			*Cooling*		*Second Heating*		
	T_{m1} (°C)	ΔH_{m1} (J/g)	[a] α_{1DSC} *(%)*	T_c (°C)	ΔH_c (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	[a] α_{2DSC} *(%)*
PEA00	225.0	98.62	*51.6*	180.0	65.38	220.0	62.64	*33.5*
PEA05	208.0	86.04	*44.6*	170.0	60.59	214.0	57.29	*29.7*
PEA10	199.0	78.77	*40.3*	158.0	53.76	205.0	53.38	*26.8*
PEA15	195.0	67.46	*34.1*	145.5	49.32	197.0	47.68	*24.1*
PEA20	187.5	54.53	*27.2*	140.0	43.69	189.5	41.09	*20.5*
PEA25	178.0	38.82	*19.1*	120.5	27.81	182.0	23.58	*11.6*

Heating/cooling rate 10 °C min^{-1} (1 and 2 mean first and second heating, c means cooling)
[a] Degree of crystallinity by DSC measurements

Mechanical properties were measured for dry samples only. The crystallinity is important for the mechanical properties of the articles produced from poly(esteramide)s.

The effect of initial content of ϵ–caprolactone on notched impact strength and flexural modulus for caprolactam–caprolactone copolymers is shown in Fig. 5.

A decrease in crystallinity degree and a gradual increase in the notched impact strength of the molding samples occur by addition of ϵ–caprolactone units in the copolymer backbone [33].

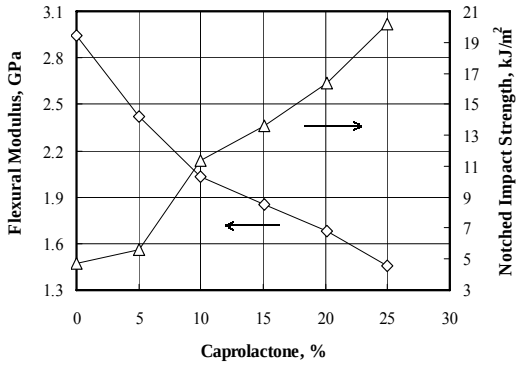

Fig. 5. Notched impact strength and flexural modulus versus ϵ–caprolactone content for poly(esteramide)s

The notched impact strength decreases with increase in crystallinity, because outside effort which acts on the sample is rapidly propagated into the crystalline region and caused breaking at interface of the crystallites. The effect of ϵ–caprolactone initial content was particularly notable at 15wt–% ϵ–caprolactone where copolymer achieved impact strengths nearly twice those of pure nylon 6. It is evident from DSC results (Table 2.) that the crystallinity of poly(esteramide)s is lower than that of pure nylon 6 while the poly(esteramide)s exhibited improved impact properties (Fig. 5) in comparison with pure nylon 6. This behavior is in accordance with data published in the literature [30].

The flexural modulus of polymers increases, generally, by increasing the degree of crystallinity [34]. The addition of the ester units in the nylon 6 structure seems to have resulted in a decrease in flexural modulus of the samples. This fact is due to the decrease in crystallinity of copolymers because the ester component in the copolymer acts as an effective plasticizer and decreased number of NH–CO groups available for crystallization [35].

4. Conclusions

A series of CLA–CLO copolymers was obtained as polymer constituent of parts obtained by rotational molding *via* activated anionic copolymerization of caprolactam with ϵ–caprolactone.

The presence of ϵ–caprolactone moieties in the nylon 6 backbone determines modification of physico–chemical and mechanical properties of polyamides. The characteristics of CLA–CLO copolymers were compared with those of the polyamide 6.

The reduced viscosity, density and melting temperature of CLA–CLO copolymers decrease with an increase in the comonomer content of the copolymer.

The reduction of degree of crystallinity accompanied by a decrease in flexural modulus and increased in impact strength at higher concentration of ϵ–caprolactone indicates that the modification of mechanical properties is due to the ester component in the copolymer that acts as plasticizer and decreased number of NH–CO groups available for crystallization.

References

[1] R. S. Sinha, K. Yamada, M. Okamoto, K. Ueda, Polymer **44**, 857 (2003).
[2] L. Piao, M. Deng, X. Chen, L. Jiang, X. Jing, Polymer **44**, 2331 (2003).
[3] B. Lanska, In: R. Puffr, V. Cubenek, (Eds.), "Degradation and stabilization Lactam–based polyamides", vol. 1 Boca Raton: CRC Press (1991).
[4] E. Rusu, D. Dorohoi, Gh. Rusu, I. Hurjui, Mater. Plast. **42**, 252 (2005).
[5] K. Bouma, "Polyesteramides based on PET", Doctoral thesis of Twente Univerisity, Enschede (1999).
[6] L. R. Stabbins, K. Udippi, EP 0556170A1, (assigned to Monsanto Company) (1993).
[7] C. W. Macosko, "RIM Fundamentals of Reaction Injection Molding" Munich: Hanser Publishers, (1989).
[8] E. Harkin–Jones, R. J. Crawford, Polym. Eng. Sci. **36,** 615 (1996).
[9] Gh. Rusu, E. Rusu, High. Perform. Polym. **16**, 569 (2004).
[10] Gh. Rusu, E. Rusu, High. Perform. Polym. **18,** 355 (2006).
[11] Gh. Rusu, K. Ueda, E. Rusu, M. Rusu, Polymer **42,** 5669 (2001).
[12] Yu. N. Kostenko, Y. T. Kravet, L. F. Lopina, E. A. Merkulov, A. V. Strigin, Plast. Massy. **10,** 41 (1967).
[13] Gh. Rusu, M. Rusu, E. Rusu, A. Stoleriu, C.– A. Teaca, Polym. Plast. Technol. Eng. **39,** 233 (2000).
[14] Gh. Rusu, M. Rusu, E. Rusu, V. Nuta, Mater. Plast. **36,** 48 (1999).
[15] K. Kircher, "Chemical Reaction Plastics Processing", Munich: Hanser Publishers, (1989).
[16] T. M. Frunze, T. M. Shleifman, T. M. Babchinitser, V. V. Kurashev, V. V. Zaitsev, Vysokomol. Soed. **13A,** 103 (1971).
[17] A. –C. Draye, O. Persenaire, J. Brozek, J. Roda, T. Kosek, Polymer, **42**, 8325 (2001).
[18] A. Bernaskova, D. Chromcova, J. Brozek, J. Roda, Polymer, **45**, 2141 (2004).
[19] I. Goodman, R. N. Vachon, Eur. Polym. J. **20**, 529 (1984).
[20] I.Goodman, Eur. Polym. J. **20**, 549 (1984).
[21] X. Fang, R. Hutcheon, D. A. Scola, J. Polym. Sci. Part A: Polym Chem **38**: 1379 (2000).
[22] X. Fang, Ch. D. Simone, E. Vaccaro, S. J. Huang, D. A. Scola, J. Polym. Sci. Part A: Polym Chem **40**, 2264 (2002).
[23] B. J. Kim, J. L. White, J. Appl. Polym. Sci. **88**, 1429 (2003)
[24] Gh. Rusu, Mater. Plast. **38,** 222 (2001).

[25] K. Udipi, R. S. Dave, R. L. Kruse, L. R. Stebbins, Polymer **38,** 927(1997).
[26] I. Engelberg, J. Kuhn, Biomaterials **12,** 292 (1991)
[27] H. K. Reimschuessel, J. Polym. Sci. Macromol. Rev. **12,** 65 (1977)
[28] L. M. Liu, Z. N. Qi, X. G. Zhu, J. Appl. Polym. Sci. **71,** 1133 (1999).
[29] T. M. Wu, C. S. Liao, Macromol. Chem. Phys. **201,** 2820 (2000).
[30] T. X. Liu, Z. H. Liu, K. X. Ma, L. Shen, K. Y. Zeng, C. B. He, Composit. Sci. Technol. **63,** 331(2003).
[31] A. Bernaskova, D. Chromkova, J. Brozek, J. Roda, Polymer, **45**, 2141 (2004)
[32] L. P. Cheng, D. J. Lin, K. C. Yang, J. Membr. Sci. **172,** 157 (2000).
[33] I. Arvanitoyannys, E. Psomiadou, J. Appl. Polym. Sci. **51,** 1883 (1994).
[34] L. E. Nielsen, "Mechanical Properties of Polymers", London, Reinhold, (1962).
[35] K. E. Gonsalves, X. Chen, J. A. Cameron, Macromolecules **25**, 3309 (1992).

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