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Correlations between thermal and tensile behavior with friction coefficient in copolyamides 6/12

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ABSTRACT

Although polyamide 6 (PA6) obtained from ε-caprolactame (CL) is an engineering polymer with outstanding properties used in sliding applications, it exhibits low impact strength and high water absorption. Those are some of the reasons why copolymerization between CL and laurolactame (LL) is desired. In this work, copolymers from 0–100 wt% LL are prepared to evaluate crystallinity, melting behavior, tensile properties and those properties are correlated with coefficient of friction. Experimental results show that PA6 (0 wt%) crystallinity and elasticity modulus are higher than those obtained from 100 wt%LL (PA12), but friction coefficient in PA6 is lower than that of PA12. While with 60 wt% LL crystallinity and elastic modulus reach a minimum value, with 350% elongation and coefficient of friction they register a maximum value. Our results suggest that crystallinity and elastic modulus are opposed to coefficient of friction. The absence of hydrogen bonds produces irregularities in the chain, reducing the crystal formation; such behavior is a consequence of copolymerization. Our findings will help to customize copolyamide, modulate the response between mechanical properties and friction behavior, as well as evaluate when it is necessary to add lubricants in the copolymer formulations.

1. Introduction

Polyamide 6 (PA6) and Polyamide 12 (PA12) are engineering polymers used to replace metal parts because of its behavior under dry friction conditions or when low frictions are required. PA6 shows high values for modulus, wear resistance, hardness and melting temperature, but low impact resistance and low dimensional stability (high water absorption). On the other hand, PA12 exhibits high values for impact resistance, dimensional stability (low water absorption) and chemical resistance, but low melting point and modulus. It is important to combine these properties through synthesis of copolymers to maintain their advantages in order to obtain customized materials for specific applications.

PA6 can be obtained from monomer ε-caprolactame (CL) and PA12 from ω-laurolactame (LL) by means of the following reaction mechanisms: hydrolytic polymerization, cationic or anionic polymerization, being the last one the most common because the equilibrium conversion takes just a few minutes. In this reaction, the initiators used are sodium hydride (NaH), sodium or potassium caprolactame (CLNa, CLK), magnesium bromide caprolactame (CLMgBr) and ethyl magnesium bromide (EtMgBr); the activators are N-acil lactames, isocyanates and N-carbamoillactame substitutes [1,2,3,5,15]. When CLNa is used as initiator, with the polymerization temperature between 130 and 180 °C, the result is a random type copolymer in the full concentration range of 0–100 mole% [15].

For copolyamide 6/12 (PA6/12) all researchers focused on the relationships between microstructure, mechanical and thermal behavior in PA6/12, but none of them linked the effect of microstructure, mechanical properties and their coefficient of friction, which is a relevant parameter for this engineering polymer. Frunze examined the PA6/12 structure variation in the full concentration range from 0–100 mol% LL [4]. Kubota and Simunkova et al. examined the relation structure-thermal-mechanical properties of copolymers PA6/12 in the concentration range 0–30 mol% LL preparing the copolymers at a maximum temperature, lower than their melting temperature [6,7]. Kehayoglou and Garner performed extensive studies to evaluate the physical-thermal-mechanical properties of PA6/12 in the whole LL concentration range [8–10]. Budin et al. studied the effect of CLNa and CLMgBr as initiators in the structure and thermal properties [11]. Rusu et al. evaluated copolymers PA6/12 thermal, physical, mechanical and dielectric properties, obtained from anionic polymerization by using the centrifugal molding technique; they used EtMgBr and CLMgBr as initiators, at 160 °C as polymerization temperature in 0–50 wt% LL [12–14].

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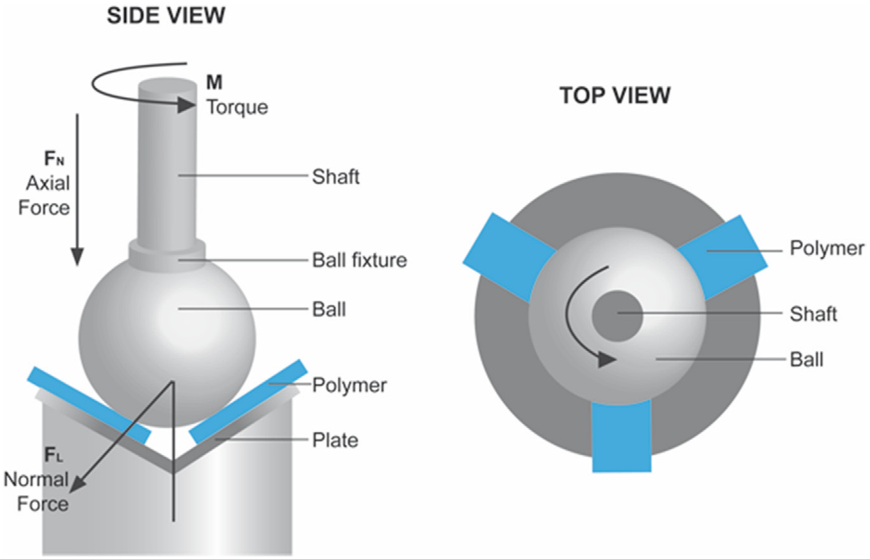

Fig. 1. Set-up of the tribology cell.

Cast PA6 is applied today as a replacement for metal parts; the selection of the appropriate polyamide grade is difficult because the sliding mechanisms are still unknown. Kang and Chung added to cast PA6 different components, such as mineral oils or wax [17] and they found that the coefficient of friction did present a significant improvement when the PA6 was filled. When graphite was added to cast PA6, the coefficient of friction did not improve [18]. Samyn et al. studied the friction, wear and transfer of pure and internally lubricated cast PA6 at different testing scale, but they did not find a unique correlation for friction regarding testing scale [19]. Morioka et al. determined the correlation between the abrasive wear, fatigue and tensile properties in PA6 with dispersed titanium carbide particles, aluminum borate whiskers and vapor-grow carbon fibers. They found a positive correlation between the low sliding velocity, wear resistance and the low stress fatigue life. During the surface wear test, high-aspect ratio fillers are detached from the film, reducing the wear resistance [20].

Sliding and wear behavior was studied for PA6 with a significant number of additives, but for copolyamide 6/12 there are no reports investigating the specific features of these polymers with the friction behavior. The aim of this work is to evaluate the PA6/12 formulations without lubrication in order to know their mechanical and thermal behavior and to correlate them with the coefficient of friction. These new materials have outstanding properties to be used in engineering contact applications like gears and bearing elements.

2. Experimental

2.1. Materials

The monomers were commercial materials, ε-caprolactame (CL) with melting point 69 °C and ω-laurolactame (LL) with melting point 153 °C used as received. Sodium salt of ε-caprolactame (CLNa) was the initiator.

2.2. Preparation of nylon 6/12 copolymers

Anionic polymerization between ε-caprolactame (CL) and ω-laurolactame (LL) were performed in two steps: each monomer was heated separately, and then they were cast in a metallic mold until the reaction took place. Copolymers were synthesized adding 10 wt% of LL from 0 wt% LL (PA6) up to 100 wt% LL (PA12). In this work the copolymer label will be described according its LL content, e.g CP10 means a copolymer with 10 wt% LL.

2.3. Evaluation of copolymer properties

2.3.1. Thermal analysis

Thermal properties were evaluated by DSC Q200 (TA Instruments) in the temperature range of 0–240 °C, at 10 °C/min in N_2 atmosphere. Crystallinity was evaluated with the heat fusion obtained by DSC, rationing the heat fusion copolymer with PA6 100% crystalline (190 J/g) and PA12 100% crystalline (220 J/g) average [15].

2.3.2. Tensile mechanical properties

The experiments were carried out using an Instron machine model 3366 with hydraulic grips, according to ASTM D 638-10, with type I specimen (This is the preferred specimen when sufficient material is available) [16]. All probes were conditioned at 60 °C during 24 h in a vacuum oven. Each material was measured five times within an interval of confidence of 95%. Tensile stress and strain were measured at 50 mm/min and elastic modulus was measured at 5mm/min.

2.3.3. Coefficient of friction test

Since this work was fundamental research, small-scale tests were used and the tribo-test conditions were selected to compare the effect of the copolyamide microstructure with the friction behavior.

A sliding test was performed in a tribology cell, mounted as an accessory onto a rotational rheometer (Haake Mars III) that controls the normal force; it consists of an upper holder with a flexible shaft and an adapter for 100Cr6 steel bearing balls (ISO 1.3505), 1/2 in. in diameter, with 50–60 RC hardness, which are used as a counterface. A polymers probe, with a flat geometry, is placed in the lower holder. This set-up is based on the ball-on-three-plates principle (see Fig. 1).

Three different roughnesses were created in the polymers surface probes to evaluate the effect of this variable and were measured perpendicular to the sliding direction. Surface profile roughness (Ra) was measured by means of a Mitutoyo surftest SJ-201P/4mN, the detector was set to record data every 0.8 cm of displacement and the Ra reported is the average value of five

Table 1
Sliding conditions for friction test.

Parameters	**Values**
Contact type	Sphere on flat
Sample dimensions (mm)	4 × 4 × 15 mm
Counterface roughness Ra (μm)	0,9
Polymer roughness Ra (μm)	1,5–2,5
	3–4
	5–6
Surface finishing	By polishing
Sliding time (h)	3
Normal load Fn (N)	3
Sliding velocity (m/s)	0,047
Sliding distance (m)	508
Frequency (RPM)	100

registers. The roughnesses, sliding time, distance, velocity and normal force are described in Table 1. Each test was repeated three times, under controlled atmospheric temperature and relative humidity (23 °C and 60%) with a maximum standard error of 3%. With these test conditions, it was not possible to have a significant material loss, so wear rate was not observed.

3. Results and discussion

3.1. Thermal analysis

In the first heating for all the copolymers (Fig. 2), only a single endotherm (T_m) shows up, fairly sharp between 40–80 wt% LL content, and also a single T_g starts to appear in this range. This behavior was reported previously as a classical eutectic pattern, characteristic of random copolymers with a single crystalline phase corresponding with that of the most abundant component [1,2,8,11]; in our case the eutectic composition occurs in the 60–70 wt% LL content. For materials rich in CL (PA6 until CP50), T_m reduces up to 30% and when they are rich in LL (CP80 until PA12), the reduction is just 9%.

Homopolyamides crystallinity is due to the hydrogen bonds. The amide group is a polar structure and leads to much larger secondary attractive force; in this case PA6 presents the highest value of crystallinity (54%). When we add the 60 wt% LL, crystallinity is reduced up to 84%; when the copolymers are rich in LL (from 60 to 90 wt% LL), crystallinity is approximately 60% lower than PA6. In this case, it is possible to assume that amide groups that promote H-bonds are not aligned to create crystal and remain free resulting in increased surface energy.

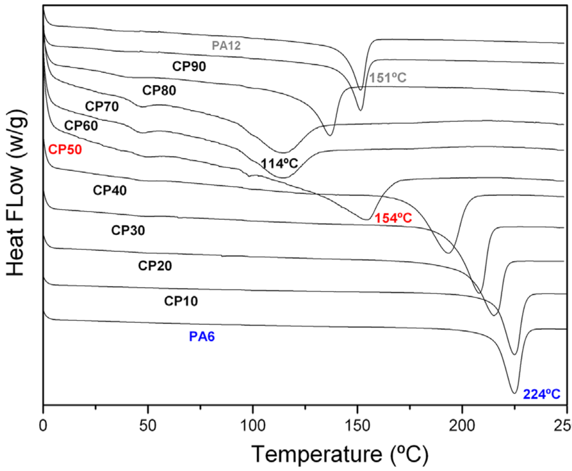

Fig. 2. Thermal transition behavior for all the copolymers.

Table 2
Mechanical and physical properties of the tested polymers.

LL [%wt]	Tensile stress σ_y [MPa]	Maximum tensile strain [%]	Elastic modulus (MPa)	Hardness (Shore D)	Crystallinity[a] (%)
0	97.33 ± 0.79	20–25	3428 ± 79	85 ± 0.7	54
10	83.92 ± 0.85	20–25	3183 ± 123	83 ± 0.6	41
20	75.56 ± 0.85	20–25	2690 ± 98	81 ± 0.5	37
30	64,51 ± 1.38	150–200	1979 ± 116	81 ± 0.5	25
40	43.27 ± 1.78	> 300	963 ± 64	78 ± 0.9	16
50	42.41 ± 2.12	> 400	834 ± 30	74 ± 0.5	11
60	41.60 ± 1.39	> 350	811 ± 64	70 ± 0.7	9
70	46.76 ± 0.56	> 350	897 ± 22	73 ± 0.3	11
80	50.23 ± 0.88	> 350	1212 ± 80	75 ± 0.3	18
90	56.47 ± 2.11	60–100	1513 ± 58	77 ± 0.9	23
100	58.58 ± 1.44	50–100	1773 ± 34	77 ± 0.8	24

[a] Calculated by DSC. The enthalpy of fusion for 100% crystalline of PA6 and PA12 was considered to be 191 $J\,g^{-1}$ and 225 $J\,g^{-1}$ respectively [14].

3.2. Tensile properties

Copolyamides 6/12 disclose a performance opposite to that of homopolyamides. They present a maximum reduction in tensile stress to 133%, and its strain can be 400% of its original shape (see Table 2). Particularly in 40–70 wt% LL compositions, copolymers behave with high plasticity, high deformation and low recovery.

Elastic modulus also presents low values, between the 40–70 wt% LL, with a reduction of 80%. This tensile behavior is related to the reduction in crystallinity; a decrease of just 54% in copolymers can cause a significant change in the mechanical behavior of these materials.

3.3. Coefficient of friction

When a thermoplastic is in contact with steel, two mechanisms contribute to friction behavior: adhesion in the contact zone and deformation of the polymer [21,22]. This contribution depends on the load level as well as on the roughness, the energy surface and the mechanical properties.

In this test, we did not change the counterface roughness in order to explore indirectly the adhesion ability of these copolyamides. Although PA6 and POM have the highest surface energy [22], copolyamide with 60 wt% LL shows a maximum value coefficient of friction of 0.516, 59% higher than PA6, so we predict that copolyamides, rather than PA6, have a higher energy surface.

In all friction curves plotted, a steady state is generally seen a few seconds after the start of the test. For the tribo-test conditions selected, roughness in the polymer surface does not have a significant effect in the coefficient of friction (Fig. 3).

3.4. Correlation between crystallinity and elastic modulus with coefficient of friction

Our results suggest that coefficient of friction is higher in the composition between 40–80 wt% LL; correlating these results with thermal and mechanical behavior, we see that friction behavior is opposite to elastic modulus and crystallinity (Fig. 4). In this case, lower elastic modulus creates a higher sliding resistance increasing the real contact area and, as a consequence, the coefficient of friction increases too. Since crystallinity decreases by 80% when we add 50–70 wt% of LL, it is feasible to say that in this range there are H-bonds not involved in the crystallinity, so there are free H-bonds that raise the surface energy and the coefficient of friction as well.

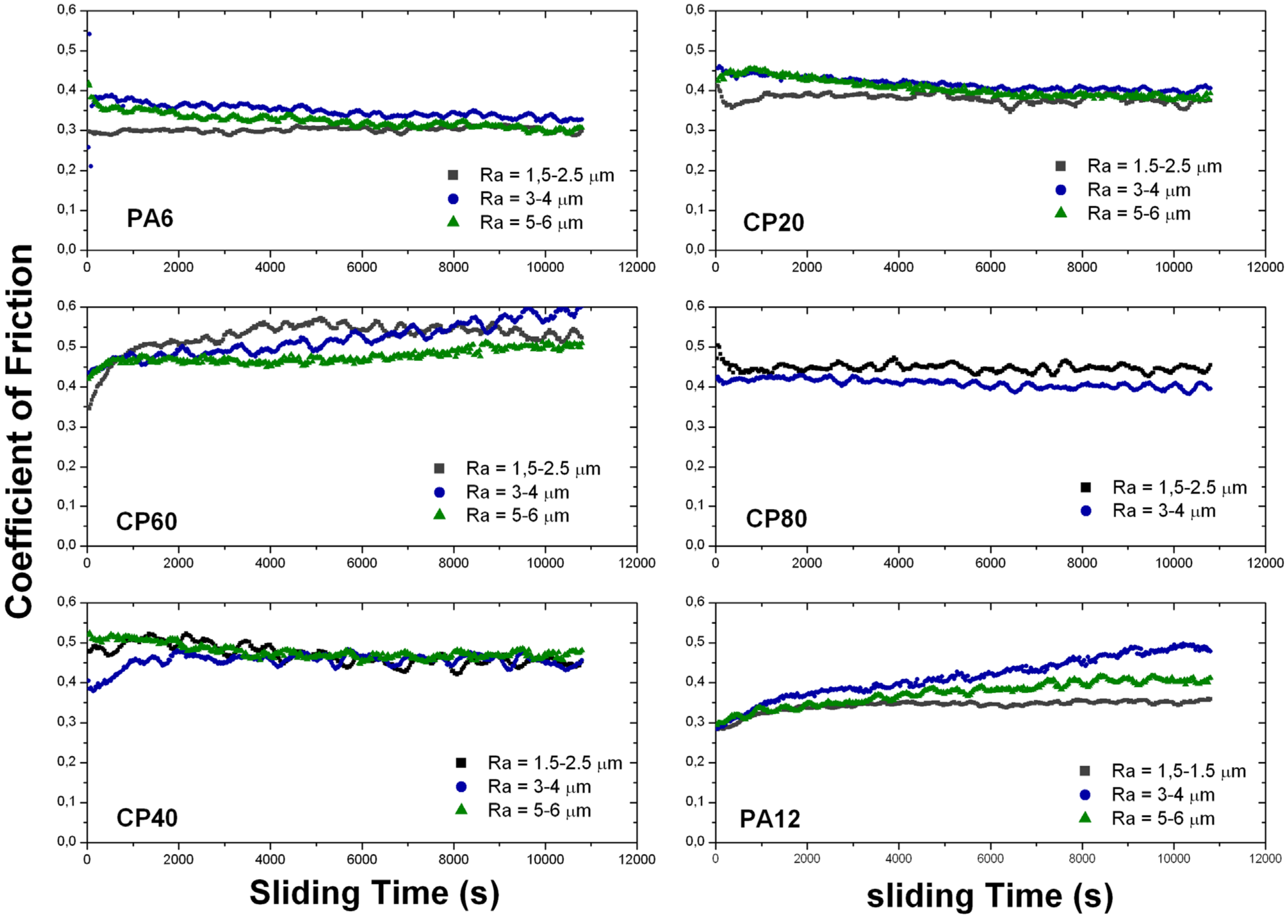

Fig. 3. Dynamic coefficient of friction as a function of time and roughness.

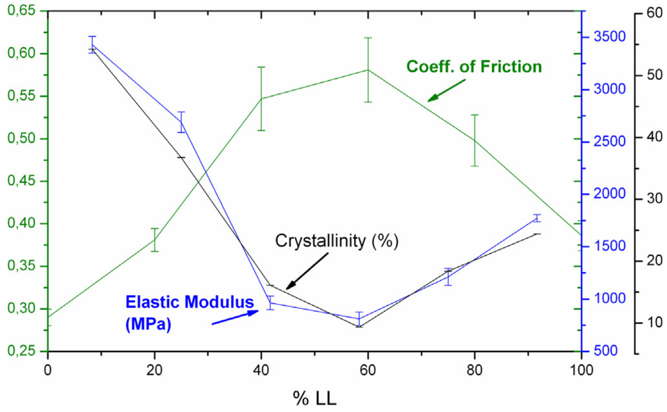

Fig. 4. Correlation between elastic modulus, crystallinity and coefficient of friction in copolymers 6/12.

4. Conclusions

In this work, the specific features of the copolyamides are used to show a correlation with friction behavior. The experimental data suggest the following conclusions:

1. In this work, adding laurolactame (LL) in caprolactame (CL) has significant changes in thermal and mechanical properties and, as a consequence, the copolymer-metal sliding also changes.
2. In homopolyamides, the amide group creates a stronger secondary attractive force (H-bonds) for the ordering and crystallization of the polymer chain. However, during the copolymerization between CL an LL, there is a range (equimolar composition) where H-bonds are not completely involved in the crystallinity and remain free, increasing energy surface. Consequently, elastic modulus decreases, while coefficient of friction increases.
3. Our results suggest a new way for design engineers to select copolyamides 6/12, e.g.

- Between 10–30 wt% LL they show good tensile properties and low adhesional work. Nonetheless, coefficient of friction could be improved by adding lubricant in the formulations.
- Between 50–60 wt% LL they could be used when high adhesional work is needed.

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