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Thermomechanical properties of polyamide-6/polypropylene glycol copolymers with mineral additives

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Copolymers of polyamide-6 / polypropylene glycol (PPG) were synthesized via activated anionic polymerization of ε-caprolactam in the presence of mineral additives - graphite and boron carbide. Composites structure and thermomechanical behavior were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA). The study explores the influence of both PPG soft segments and fillers onto the thermal stability, mechanical properties and structure of the composites.

Key words: polyamide-6, copolymers, graphite, boron carbide

INTRODUCTION

It is well known that the elastic properties of polyamide-6 (PA-6) could be significantly improved by activated anionic polymerization of lactams. In the recent years many studies were dedicated to investigating the copolymerization of ε-CL. Comonomers, such as rubbers, polyols, styrenics, etc., were introduced, trying to extend the properties of PA-6, either impact or tensile strength and thus to respond to the need of materials with specific properties applicable for various industries [1-7]. Most of these studies were concentrated in improving the impact strength of PA-6 by incorporating soft segments in its polymer chain, due to the fact that it is a notch-sensitive polymer. All these methods led to the creation of already commercially available copolymers such as PA-6/PA-6,6 and PA-6/polyethers, the latter being a basis for the Reaction Injection Molding (RIM) process [8].

From another perspective, polyamides properties could be improved by physical modification, fillers loading being one of the most common ways of enhancing thermal, mechanical and conductive properties of PA-6 [9-11]. Further on, nanofillers, such as graphene [12], carbon nanotubes [13], montmorillonite (MMT) [14], talcum [15] are explored as well. However, dispersion of inorganic additives in low viscosity ε-CL, could lead to segregation of the filler particles and it is important proper polymerization conditions to be followed. By that point, the behavior of a multicomponent system based on ε-CL, polyol and filler is of particular interest. Developing a technology for *in-situ* preparation of composite structures based on PA-6, will significantly reduce the energy costs of the final product and allow matching various industry specifications. In our previous study, the activated anionic polymerization of ε-CL in the presence of graphite and B_4C was investigated [16]. For the end-use application, mechanical and thermal properties of thus synthesized composites are of critical importance, therefore, the aim of this paper was to determine their thermal and mechanical properties.

EXPERIMENTAL

Materials: The monomer ε-caprolactam (ε-CL, BASF), Mw=113.16 was dried for 3 days over P_2O_5 in a vacuum oven at 60ºC. The initiator, sodium salt of ε-CL (Na-CL), was synthesized according to [17], Mw=424. Isophorone diisocyanate (5-isocyanate-1-isocyanatomethyl-1,3,3-trimethyl-cyclohexane) (IF; Merck), methanol (Fluka), n-acetylcaprolactam (AcCL); were used as received. Polypropylene glycol (PPG; Fluka) with average molecular weight 2000 was kept in a molecular sieve at 25ºC under vacuum for 10 h. Graphite with particle size (PS) = 20 µm and boron carbide (B_4C; Fluka), PS=15-62 µm were heated at 150ºC for 2 min before use.

Polymerization: Detailed study on the synthesis was described elsewhere [16]. Bulk anionic polymerization of ε-CL was carried at 180ºC using both ampule technique (samples for DSC, TGA) and mold casting (samples for DMTA). For DSC and TGA unreacted monomers were extracted in a Soxhlet apparatus with methanol for 8 h. The residue was dried in vacuum at 60ºC until constant weight was reached.

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Analysis

DSC: Calorimetric measurements of melting and crystallization behavior were handled on a DSC Q100 TA Instruments apparatus using indium as standard. Samples were heated in the range from -90°C to +250°C at a rate of 15°C min^{-1} in a nitrogen flow of 50 m min^{-1}. After that they were quenched to -90°C at 100°C min^{-1} and then reheated to 250°C, again at 15°C min^{-1}.

From the endothermic maximum of the curves the melting temperatures (*Tm*) of the composites were determined. Glass transition temperature (*Tg*) was calculated at the inflection point of the re-heating curve. DSC crystallinity was calculated from the ratio of the measured and equilibrium heats of fusion $\Delta H_f/\Delta H_f^o$, where the equilibrium one (ΔH_f^o = 230 $J.g^{-1}$) refers to a 100% crystal PA-6, taken from the literature [18].

TGA: Measurements were performed on a TGA Q500 TA Instruments apparatus, in the range from +30°C to +600°C. Heating rate was 15°C min^{-1} and nitrogen flow 40 ml min^{-1}.

Activation energy was calculated from Broido equation [19]:

$$ln[ln1/x]=-Ea/RT+const \qquad (1)$$

where, *Ea* is the activation energy ($J.mol^{-1}$), *T* absolute temperature (K), *R* gas constant (8.314 $J.mol^{-1}.K^{-1}$) and *x* is the residue:

$$x=(Wt-Wf)/(Win-Wf) \qquad (2)$$

where *Wt* is the sample weight at time t, *Win* and *Wf* are initial and final weights.

DMTA: Dynamic mechanical properties of the composites were measured with a torsional pendulum on a Rheometric Scientific apparatus in the range from -100°C to +150°C at a heating rate of 10°C min^{-1} and 1 Hz constant frequency. The storage modulus (G'), loss modulus (G") and loss tangent (tan delta) were automatically recorded during the test.

Test specimens 45mm × 10mm × 2.5mm were cut from pre-pressed films.

RESULTS AND DISCUSSION

DSC

According to the data obtained, it was observed that melting peaks of pure (without additives) PA-6/PPG-IF copolymers appear in a narrow range between 218°C and 220°C with the only exception of 3% PPG-IF, where it was shifted to 222°C.

Introduction of B_4C and graphite into the system leads to a decrease of the melting temperatures (resp. heat of fusion), due to the decrease of crystallinity, which is clearly visible at high percentages of filler loading and macroactivator concentration. Degree of crystallinity (α) and glass transition temperatures (Tg) showed similar behavior - shift to lower values with the increase in system complexity. Tg of the amorphous region of PA-6 is obviously affected by the PPG soft segments due to the fact that PPG segments are incorporated into the amorphous regions of the polymers [20]. On the other hand, compared to the first heating cycle, at the second one Tg increased while α decreased. On Figures 1-2 DSC thermograms of different composite structures at 3% macroactivator are shown. Based on these results, which correlate with other studies [20], we may conclude that both segments - rigid (PA-6 ones) and soft (PPG) are fully compatible in the amorphous region.

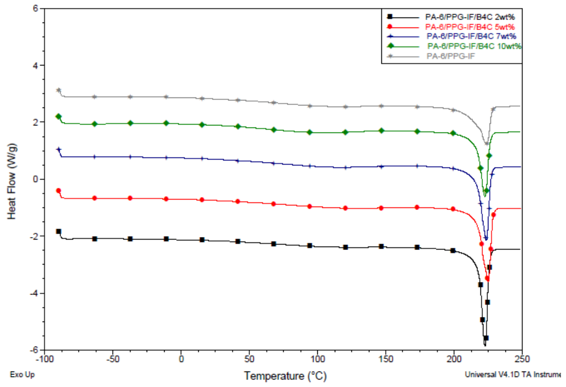

Fig. 1. DSC thermograms of PA-6/PPG/B_4C copolymers at 3% PPG.

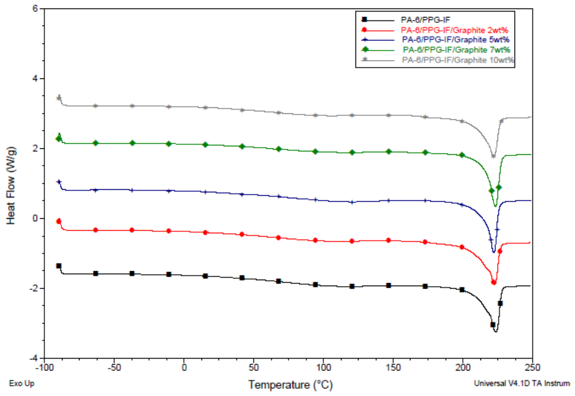

Fig. 2. DSC thermograms of PA-6/PPG-IF/graphite copolymers at 3% PPG.

TGA

Measurements confirmed the expected better thermal stability of the copolymers compared to similar PA-6 copolymers reported [1, 22-23]. Start of decomposition (*Tin*, initial decomposition temperature / at 1%) of all copolymers is above 400°C with similar behavior of both graphite and B_4C (Figs. 3-4). This indirectly proves the good dispersion of both fillers, and the improved heat transfer, thus allowing composites to withstand higher temperatures.

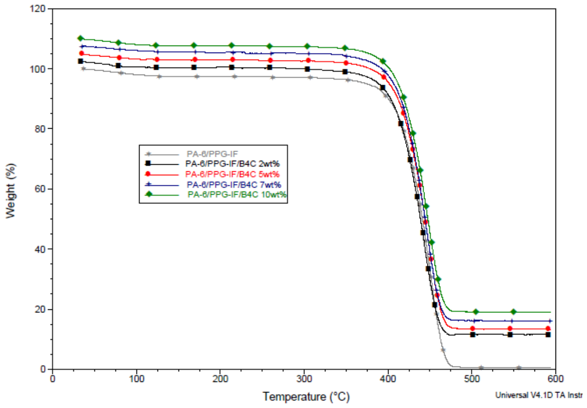

Fig. 3. TGA of PA-6/PPG-IF/B$_4$C copolymers at 3% PPG.

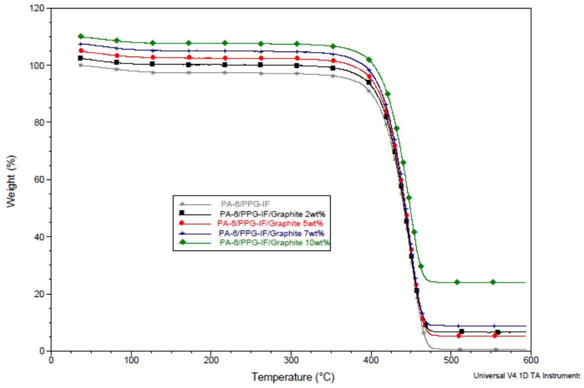

Fig. 4. TGA of PA-6/PPG-IF/graphite copolymers at 3% PPG.

Table 1. DSC data of PA-6 composites

	T'm, °C[1)]	ΔH'm, J/g[2)]	T'g[3)]	T"m, °C[4)]	ΔH"m, J/g[5)]	T"g, °C[6)]	α 'DSC, %[7)]	α "DSC, %, [8)]
PA-6/AcCL	220.96	92.24	44.91	219.84	68.98	44.23	40.10	29.99
PA-6/PPG-IF=97/3	222.41	73.81	36.51	214.55	48.53	38.67	32.09	21.10
PA-6/PPG-IF/B4C=95/3/2	222.74	86.70	27.11	215.78	41.28	46.09	37.70	17.95
PA-6/PPG-IF/B4C=92/3/5	224.53	83.30	35.46	214.66	45.97	40.52	36.22	19.99
PA-6/PPG-IF/B4C=90/3/7	223.70	87.23	35.90	215.05	45.37	38.83	37.93	19.73
PA-6/PPG-IF/B4C=87/3/10	222.48	72.88	37.99	213.91	36.61	41.49	31.69	15.92
PA-6/PPG-IF/Graphite=95/3/2	221.54	68.14	30.30	213.80	41.89	40.61	29.63	18.21
PA-6/PPG-IF/Graphite=92/3/5	221.08	58.64	26.77	214.69	41.47	40.38	25.50	18.03
PA-6/PPG-IF/Graphite=90/3/7	221.55	62.68	37.82	214.48	43.76	42.67	27.25	19.03
PA-6/PPG-IF/Graphite=87/3/10	216.89	51.94	27.42	215.43	46.51	31.51	22.58	20.22
PA-6/PPG-IF=95/5	218.68	80.74	56.19	214.89	42.24	34.00	35.10	18.37
PA-6/PPG-IF/B4C=93/5/2	220.39	70.32	39.43	217.76	47.17	43.40	30.57	20.51
PA-6/PPG-IF/B4C=90/5/5	222.49	78.91	31.10	215.16	43.65	44.35	34.31	18.98
PA-6/PPG-IF/B4C=88/5/7	222.05	77.94	18.01	214.53	39.03	45.66	33.89	16.97
PA-6/PPG-IF/B4C=85/5/10	221.81	63.87	31.13	213.78	29.19	44.78	27.77	12.69
PA-6/PPG-IF/Graphite=93/5/2	223.01	77.80	31.64	214.31	34.19	44.26	33.83	14.87
PA-6/PPG-IF/Graphite=90/5/5	221.29	62.49	38.10	214.06	36.64	43.58	27.17	15.93
PA-6/PPG-IF/Graphite=88/5/7	221.28	67.68	30.01	214.59	37.71	44.32	29.43	16.40
PA-6/PPG-IF/Graphite=85/5/10	220.45	60.14	37.79	214.28	33.83	44.00	26.15	14.71
PA-6/PPG-IF=90/10	219.67	81.14	32.25	214.44	32.34	43.01	35.28	14.06
PA-6/PPG-IF/B4C=88/10/2	220.15	80.30	28.40	215.15	37.78	38.42	34.91	16.43
PA-6/PPG-IF/B4C=85/10/5	219.80	81.57	27.62	215.14	39.18	36.81	35.47	17.03
PA-6/PPG-IF/B4C=83/10/7	218.74	86.01	32.59	214.27	38.43	43.51	37.40	16.71
PA-6/PPG-IF/Graphite=88/10/2	207.39	72.17	37.38	209.07	38.58	37.99	31.38	16.77
PA-6/PPG-IF/Graphite=85/10/5	214.73	74.15	39.59	213.56	49.24	33.84	32.24	21.41
PA-6/PPG-IF/Graphite=83/10/7	216.38	73.86	37.70	213.88	51.25	39.06	32.11	22.28
PA-6/PPG-IF/Graphite=80/10/10	215.78	38.55	23.73	213.35	41.20	38.56	16.76	17.91

[1)] Melting temperature at first heating
[2)] Heat of fusion at first heating
[3)] Glass transition temperature at first heating
[4)] Melting temperature at second heating
[5)] Heat of fusion at second heating
[6)] Glass transition temperature at second heating
[7)] Degree of crystallinity at first heating
[8)] Degree of crystallinity at second heating

DMTA

In order to define the combined effect of soft block and additives concentration of copolymers the mechanical properties - mechanical loss tangent (Tan delta) and storage modulus (G’) are presented on Figs. 5-8.

At the same concentration of macroactivator, the following effect on G’ is observed: increase of B_4C content resulted in an increase of copolymers stiffness, whereas graphite followed a similar trend but with lower absolute values. As a result highly loaded (10% B_4C) composites show increased (40%) stiffness compared to the corresponding graphite ones (Figs. 5-6).

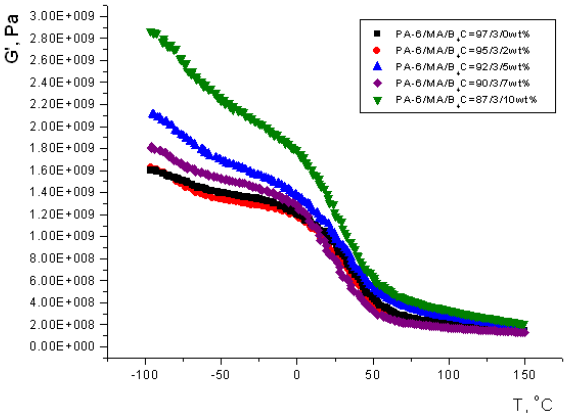

Fig. 5. Storage modulus of PA-6/PPG-IF/B_4C copolymers as a function of temperature.

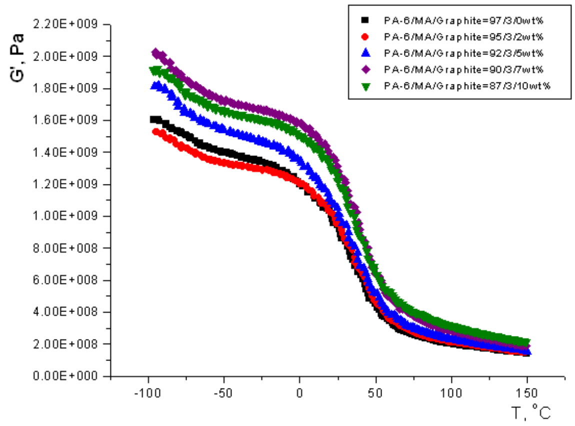

Fig. 6. Storage modulus of PA-6/PPG-IF/graphite copolymers as a function of temperature.

As PA-6 has two mechanic relaxation peaks: α around 50ºC, corresponding to glass transition temperature (Tg) and β around -80ºC, which overlaps with Tg of PPG around -75ºC [24], on Tan delta curves two Tgs were observed: in the range -72ºC to -84ºC, corresponding to PPG and PA-6 segments and 42ºC to 57ºC, belonging to PA-6 ones. Results confirmed the DSC data that both polymers are fully compatible in the amorphous region. Practically, both fillers are not showing a significant effect on both PPG and PA-6 segments mobility, which indirectly confirms their good dispersion into the system.

Taking into account the magnitude of the Tan delta peaks (Figs.7-8), the effect of PPG and fillers onto the amorphous phase of PA-6 can be seen. Since the soft PPG segment with both fillers is one and the same, the impact is different - B_4C in general follows the expected trend - with increase of PPG soft segments Tan delta peaks around -80ºC increase their magnitude, resp. amorphous phase of copolymer to transform into rubbery state. Same could be observed for PA-6 ones around 50ºC.

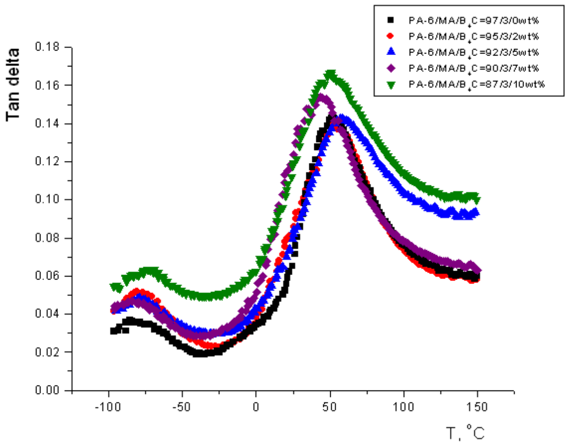

Fig. 7. Tan delta temperature dependence for PA-6/PPG/B_4C copolymers.

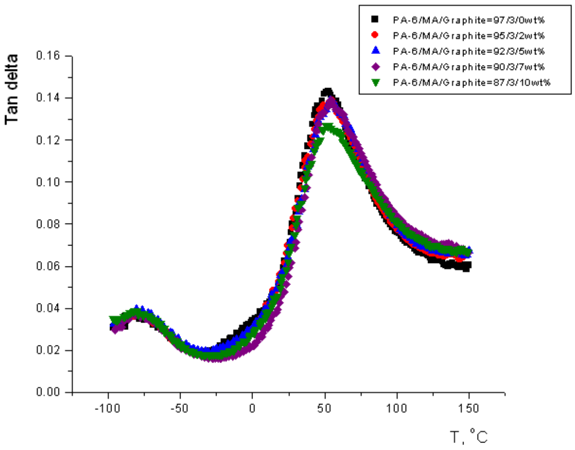

Fig. 8. Tan delta temperature dependence for PA-6/PPG/graphite copolymers.

Graphite effect is somehow an opposite one since there is no impact on PPG segments for PA-6 ones to decrease with increase of filler concentration Tan delta, which could be explained by the fact that graphite has certain energy dissipation effect allowing PA-6 polymer chains to better respond to external loads. From another perspective, the observed two Tg peaks confirmed the presence of block copolymers.

Table 2. Activation energy of destruction.

	Tin, ^oC	*T_{Wmax}, ^oC*	*Ea, kJ/mol*
PA-6/AcCL	412.22	462.65	12.60
PA-6/PPG-IF=97/3	418.61	466.2	12.84
PA-6/PPG-IF/B$_4$C=95/3/2	413.05	459.73	7.49
PA-6/PPG-IF/B$_4$C=92/3/5	415.83	463.87	8.04
PA-6/PPG-IF/B$_4$C=90/3/7	415.11	462	7.89
PA-6/PPG-IF/B$_4$C=87/3/10	417.22	464.35	7.57
PA-6/PPG-IF/Graphite=95/3/2	417.31	463.67	10.07
PA-6/PPG-IF/Graphite=92/3/5	417.8	463.83	13.58
PA-6/PPG-IF/Graphite=90/3/7	417.64	462.94	12.28
PA-6/PPG-IF/Graphite=87/3/10	418.56	462.88	5.93
PA-6/PPG-IF=95/5	413.74	461.19	8.71
PA-6/PPG-IF/B$_4$C=93/5/2	419.14	465.64	13.67
PA-6/PPG-IF/B$_4$C=90/5/5	417.52	463.32	12.91
PA-6/PPG-IF/B$_4$C=88/5/7	417.42	463.46	8.64
PA-6/PPG-IF/B$_4$C=85/5/10	416.86	463.26	7.84
PA-6/PPG-IF/Graphite=93/5/2	414.87	462.87	9.08
PA-6/PPG-IF/Graphite=90/5/5	410.87	460.52	9.48
PA-6/PPG-IF/Graphite=88/5/7	418.31	462.5	4.96
PA-6/PPG-IF/Graphite=85/5/10	419.4	464.52	7.24
PA-6/PPG-IF=90/10	406.59	457.86	10.59
PA-6/PPG-IF/B$_4$C=88/10/2	413.26	462.8	13.05
PA-6/PPG-IF/B$_4$C=85/10/5	413.18	463.84	12.20
PA-6/PPG-IF/B$_4$C=83/10/7	412.6	461.39	10.98
PA-6/PPG-IF/B$_4$C=80/10/10	412.72	461.8	9.85
PA-6/PPG-IF/Graphite=88/10/2	415.99	461.17	9.08
PA-6/PPG-IF/Graphite=85/10/5	412.58	458.38	8.37
PA-6/PPG-IF/Graphite=83/10/7	415.84	460.39	11.63
PA-6/PPG-IF/Graphite=80/10/10	406.61	455.73	5.82

CONCLUSIONS

The synthesis of PA-6/PPG copolymers via activated anionic polymerization of ε-CL in the presence of mineral fillers- graphite and B$_4$C, permits to produce composite materials which are obtained *in-situ* during the polymerization process. The polymerization rate is determined by the presence of the macroactivator (PPG-IF in our case). The effect of fillers loading is different:

At high concentration of macroactivator (10%), increasing the graphite content results in increasing the polymerization rate (higher yields), and graphite bejng considered as an active additive, while B$_4$C is practically inert. On the other hand, at certain levels of loading (3-5%), both fillers are contributing to the better mechanical properties of the composites.

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ТЕРМОМЕХАНИЧНИ СВОЙСТВА НА ПОЛИАМИД-6/ПОЛИПРОПИЛЕН ГЛИКОЛ СЪПОЛИМЕРИ С МИНЕРАЛНИ ПЪЛНИТЕЛИ

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(Резюме)

Съполимери на полиамид-6/полипропилен гликол (ППГ) бяха синтезирани по пътя на активираната анионна полимеризация на ε-капролактамв присъствие на минерални пълнители- графит и борен карбид. Структурата и термомеханичните отнасяния на композитите бяха изследвани чрез диференциално сканираща калориметрия (ДСК), термогравиметричен анализ (ТГА) и динамимичен механичен термичен анализ (ДМТА). Статията изследва влиянието на еластомерните ППГ сегменти и пълнителите върху термичната стабилност, механичните характеристики и структурата на композитите.