LCO AS MODIFIER OF POLYAMIDE FIBRES - THE INFLUENCE ON THE NANOSTRUCTURE AND SELECTED PROPERTIES

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Abstract

The objective of research presented in this work was to analyze of the influence of the LCO (Liquid Crystalline Oligoester) on mechanical and thermal properties of fibres formed from PA6/LCO blends. The relationship between obtained results of mechanical investigation and supermolecular structure of blend fibres was presented. This one is the consequence of specific dispersion of modifier in a matrix of thermoplastic polymer of fibres. It was stated that addition of LCO modifier causes considerable increase in values of selected mechanical parameters of PA6/LCO fibres in related to unmodified polyamide fibres.
Key words: Liquid Crystalline Oligoester, Nanostructure, Tensile strenght parameters, Polyamide6 blends,

1. Introduction

Nowadays polyamides have become essential materials in fibre production for textiles and technical uses. However, such applications require extremely high strength parameters as well as excellent dimensional stability. In order to improve polymer properties they are reinforced with glass fibres or with very high strength and high modulus liquid crystalline polymers. Blending of thermotropic LCP with semicrystalline thermoplastic polymers to form in-situ polymer composites is very attractive because LCP acts as reinforcing elements in the blends and its addition to a polymer matrix has profound impact on its physical and mechanical properties of the final product [1-3]. However, the melting temperature of liquid crystalline polymers is usually too high for processing semicrystalline thermoplastic polymers. In order to reduce the melting transition temperature new LCP having flexible units in the main chain were synthesised [4]. Blends obtained from new LCP (called liquid crystalline oligoester LCO) and semicrystalline thermoplastic polymer PA6 were used as fibroplastic materials
The mechanical and physical properties of PA6 fibres are controlled by their nanostructure, where finite sections of crystalline lamellae and amorphous polymer alternate throughout a lamellar stack.. The parameters of nanostructure based on the structural investigations using modern analytical methods such as: small angle X-ray scattering (SAXS and 2D-SAXS) and thermal (DSC) methods have been calculated. Above parameters have allowed to construct a general model of nanostructure of new PA6/LCO fibres and draw relations between the determined structural parameters and selected mechanical properties of the blend fibres.

2. Materials

Investigations were carried out for polyamide fibres (commercial Tarnamid T27 was used) and fibres from polyamide and new liquid crystalline polymer blends. Liquid crystalline polymer component of blend fibres was selected from the group of synthesized liquid crystalline oligoesters LCOs (Fig.1). The macromolecular chain of selected LCO is presented in Fig.1a.
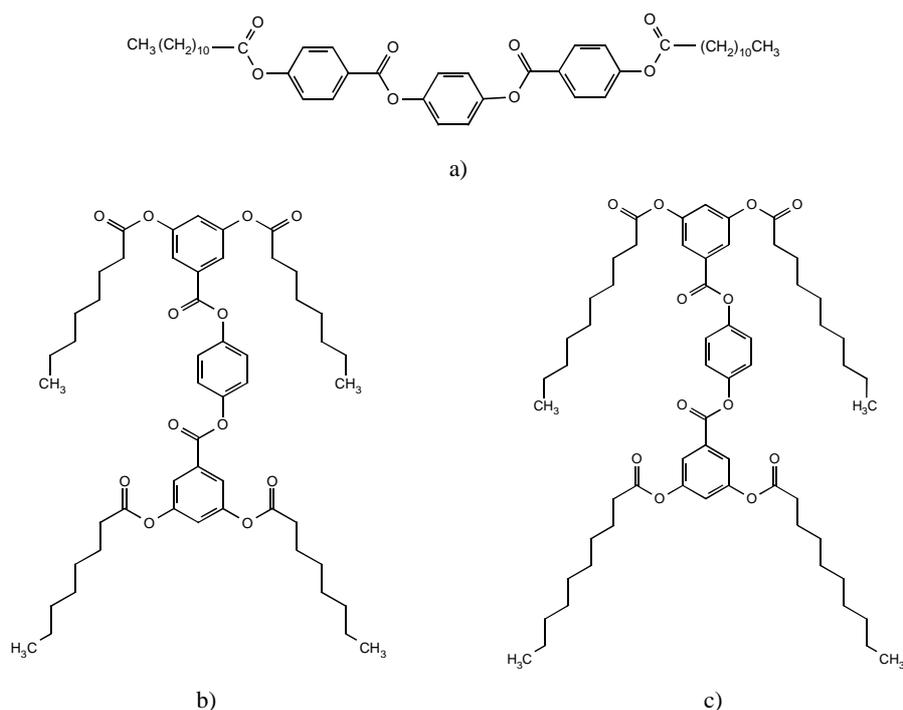
Fig. 1. The macromolecular chains of synthesized liquid crystalline oligomers. a) LCO consisting linear aliphatic end groups (11 carbon atoms) , b) LCO_1 consisting branched aliphatic end groups (7 carbon atoms), c) LCO_2 consisting branched aliphatic end groups (9 carbon atoms)

Fibres were formed from the melt in laboratory condition using prototype one-head laboratory extruder. Fibre-forming material (fiber masterbatch) was melted in mass cylinder of extruder's melting-block. To overpress of melting material compressed neutral gas (nitrogen) was used. Mass cylinder is one-zone device electrically heated. An extruder head consist of static mixer as well as spinneret with one hole $\phi = 0,2$mm. Fibres were formed near following parameters of work of spinning machine: gas pressure - 0,5 MPa, melt temperature - 240°C. The fibres were spun with a take-up velocity of 26m/min. New PA6/LCO blend fibres were formed using 95% of PA6 and 5% of LCO by weight [5].

3. Experimental methods

Nanostructure of polyamide fibres was analysed by means of SAXS (small-angle scattering) methods, thermal properties of fibres was analysed by means of DSC (differential scanning calorymetry) method and mechanical properties was analysed

3.1. SAXS

Small-angle X-ray scattering investigations for fibers were performed by means of MBraun camera with conventional Kratky collimation system. The front of the camera was directly mounted on the top of the tube shield of the stabilized Philips PW 1830 X-ray generator. The X-ray tube was operated at a power of 1200W. Cu Kα radiation was used. Monochromatisation was performed by Ni β filter and a pulse-height discriminator. Scattered radiation was recorded by means of MBraun PSD50 linear position-sensitive detector. The experimental SAXS curves were corrected for sample absorption and de-smeared from collimation distortion by means of the 3DVIEW MBraun computer program.

2D-SAXS measurements were carried out by means 2D-SAXS camera with Philips PW 1830 X-ray generator. Cu K$_\alpha$ radiation was used at 40kV and 30mA. Scattered

radiation was recorded by means of Fuji IP detector with sample detector distance 495 mm. Exposure time was set at 40 min.

3.2. DSC

Differential Scanning Calorimetry investigations were carried out with a TA Instruments Thermal Analysis System 5100 equipped with a Differential Scanning Calorimeter model 2920.The linear function of temperature increase was used. The samples of fibres were heated at a rate of 10°C/min (atmosphere N_2; flow 40ml/min) in wide temperature range suitable for given sample. The heats and temperatures of transitions were calculated by means of the computer program Universal V2.6D TA Instruments.

3.3. Mechanical tests

Tensile strength parameters of the undrawn fibres were defined by means of the tensile testing machine INSTRON 5544 Single Column. The machine consisted of press- stretching head for fibres of static load cell rating ±10N with indication error 1,0%. The tensile testing machine was connected to the computer equipped with MERLIN software. The measurements were taken in normal climatic conditions for samples length 10mm. The tensile speed was 30 mm·min^{-1} and 20 tests were made for each sample. On the basis of the measurements taken, we defined: breaking tenacity, breaking elongation and modulus of elasticity (modulus).

4. Results and discussion

4.1. Thermal properties of LCO modifier

The results of thermal properties of liquid crystalline oligoester was analyzed in the aspect of possibility to use it as proper compound for blends with semicrystalline thermoplastic PA6 polymer .
The basic thermal parameters of LCO modifier are presented in Table 1.

Table 1. Temperatures and enthalpies of phase transition of LCO: T_g, T_m, T_c, T_i - glass transition, melting, crystallization and isotropization temperature respectively, ΔH_m, ΔH_c, ΔH_i - enthalpy of melting, crystallization and isotropization, respectively

Heating					Cooling			
T_g [°C]	T_m [°C]	ΔH_m [J/g]	T_i [°C]	ΔH_i [J/g]	T_c [°C]	ΔH_c [J/g]	T_i [°C]	ΔH_i [J/g]
56,0	118,7	17,5	156,6	2,3	114,8	11,0	155,0	2,6

The results listed in the above table shows that the oligoester has relatively low melting temperature and exhibit the ability to form the thermotropic mesophase in the wide temperature range (118-156°C).

4.2. Nanostructure of modified polyamide fibers

The results of SAXS and 2D-SAXS measurements were analyzed in the aspect of nanostructure changes caused by addition of LCO modifier
The comparision of SAXS curves obtained for investigated fibres (Fig 2) shows the lamellar structure of PA6 matrix in all sample. For PA6/LCO 95/5 sample the additional diffraction

peak appeared. Its origin is result from presence of LCO modyfier.Furthermore investigations not reported in this paper shows that position of this peak is the same as in case of SAXS curve for LCO, which is outside of polymer matrix. The angular position of the LCO peak in Fig.2 is connected with the supermolecular structure of modifier with different electron densities of phases, which are seperated by a repeated distance. The value of repeated distance (d-space) was evaluated using Bragg's law [6], and it is characteristic of solid state.
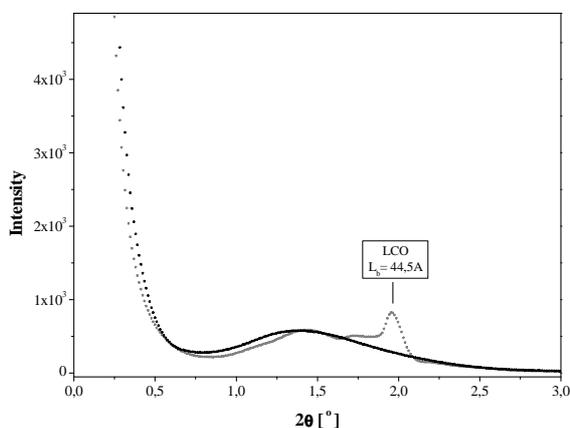

Fig. 2. Comparison of SAXS curves for modified PA6/LCO 95/5 (gray) and unmodified PA6 100 (black) fibres

Parameters of lamellar structure of PA6 matrix of investigated fibres, calculated from Bragg's law and from corrleation function [7-9], are presented in Table 2.

Table 2. Parameters of nanostructure of polyamide fibres: L_p - long period, L_c – lamellar thickness, L_a - amorphous layer thickness

S.n.	Sample	L_p [nm]		L_c [nm]	L_a [nm]
		Bragg's law	Correlation function		
1	PA6 100	5,4	5,2	2,0	3,2
2	PA6/LCO 95/5	5,7	5,3	1,9	3,5

The results listed in the table, indicate that the addition of LCO modifier has not significantly effected the lamelar structure of PA6. The values of nanostructure parameters are comparable for both modified and unmodified fibres.

Particularly the interesting information concerning the location (dispersion) of LCO domains in polymer matrix of PA6/LCO 95/5 fibres was obtained by 2D-SAXS measurements. The 2D-SAXS patterns for investigated fibres (Fig. 3) exhibits meridian peaks (connected with lamellar structure of polymer matrix) but in the case of modified fibres the additional four diagonal-peaks are observed. The angular positions and the orientation of these peaks was determined. The angular position is connected to d-space of LCO modifier and orientation correspond to distribution of orientation of the mesogens in the molecules of LCO.
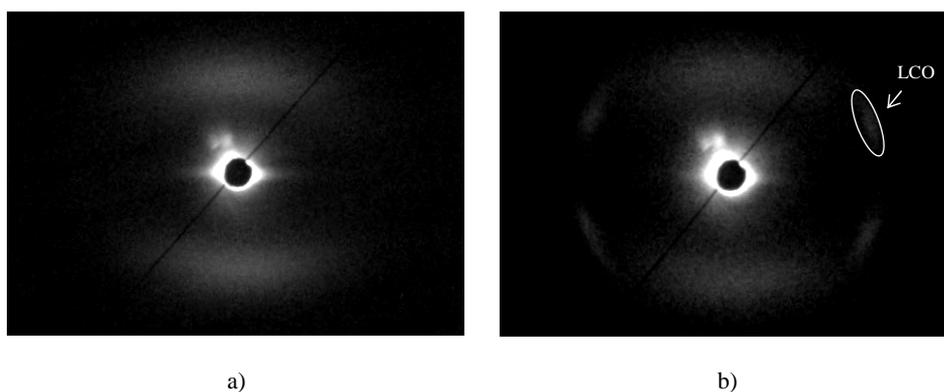
a)   b)

Fig. 3. Comparision of 2D-SAXS patterns for unmodified (a) and modified (b) polyamide fibres

The results mentioned above have allowed to construct a schematically model of nanostructure of PA6/LCO 95/5 fibres, which is presented in Fig 4. Liquid crystalline oligoester domains which are situated into interfibrillar area of PA6 matrix is characteristic of the structure of this fibres. Moreover LCO modifier domains are characterized by diagonal arrangement in relation to fiber axis direction
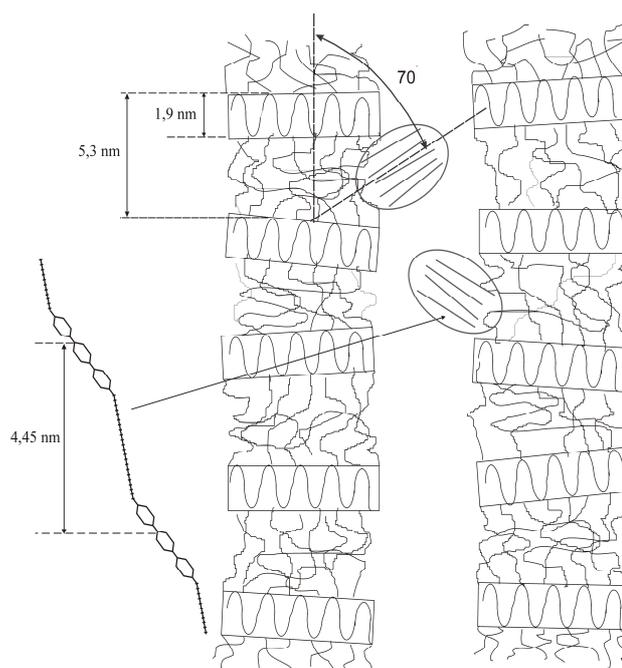

Fig. 4. Schematically model of nanstructure of PA6/LCO 95/5 fibres based on results derived from SAXS measurements

4.3. Thermal properties of modified polyamide fibers

The basic thermal parameters – the melting temperature T_m, melting enthalpy ΔH_m, crystallization temperature T_c and crystallization enthalpy ΔH_c of the investigated polyamide fibres are presented in Table 3.

Table 3. Values of T_m, ΔH_m, T_c, ΔH_c and crystallinity κ determined from DSC measurements during heating and cooling of polyamide fibres.

S.n.	Sample	T_m [^{o}C]	ΔH_m [J/g]	T_c [^{o}C]	ΔH_c [J/g]
1	PA6 100	221,5	81,0	187,1	75,6
2	PA6/LCO 95/5	221,9	76,0	186,9	78,0

Obtained results indicate that the presence of LCO modifier causes decrease of melting enthalpy (correspond to decrease of degree of the supermolecular structure arrangement), however almost equal the melting-points T_m (correspond to largest speed of melting of crystallites) for both studied fibres was observed.

The results obtained from the analysis of the non-isothermal crystallization process shows the difference in the values of enthalpy of the phase transition ΔH_c (calculated only in respect to the PA6 matrix).

4.4. Mechanical properties of modified polyamide fibers

Specific dispersion of the LCO domains in polymer matrix mentioned before has profound impact on mechanical properties of modyfied fibres.Fig.2 summarizes the results of the mechanical tests. The comparative analysis of the results shows that presence of liquid crystalline oligoester has positive influence on the tensile strenght parameters of undrawn fibres. Higher modulus for modyfied polyamide fibres means of high stiffnes in the range of elastic deformations. LCO domains are located into interfibrillar area of PA6 matrix of fibres and the extending of intermolecular bonds of macromolecular chains of polyamide are difficult. In the case of unmodified PA6 fibres the extending of these bonds should be more effective.
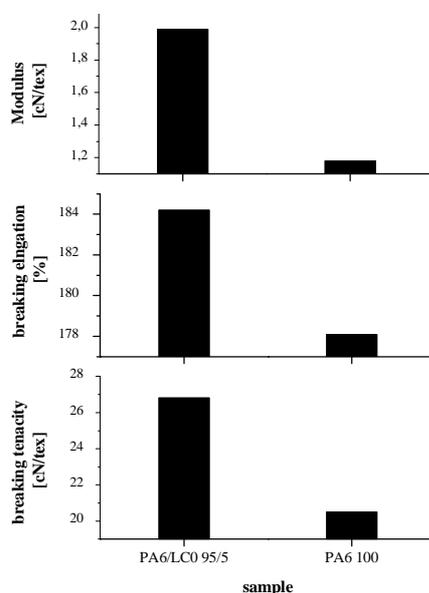

Fig. 7. Comparision of selected tensile strenght parameters of polyamide fibres.

4. Conclusions

Investigations into the nanostructure and selected physical properties of new PA6/LCO modified fibres shows that liquid crystalline oligoester has significant influence on changes of mechanical properties in reference to unmodified PA6 fibres. Changes are consequence of

the specific dispersal of LCO modifier domains in thermoplastic polymer matrix of fibres. Based on SAXS investigation schematically model of nanostructure of modified fibres was proposed. Model of the structure of PA6/LCO fibres indicate that oligoester domains are situated into interfibrillar area of PA6 matrix. Results of mechanical investigation of blend fibres shows that dispersal of stiff and strong rigid rod macromolecules of LCO causes considerable increase in value of tensile strength parameters.

5. References

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