SUMMARY

FABRICATION OF OCTADECYLAMINE THIN FILMS BY DIFFERENT PHYSICAL-CHEMICAL METHODS

Thin films based on octadecylamine (ODA) material have been successfully fabricated by different methods: Langmuir-Blodgett (LB) method, spin-coating, spray-coating and dip-coating methods. The films obtained on the glass substrate were investigated for their optical properties (Uv-vis), film morphology (digital microscope, SEM) and contact angle. The solution and thin film absorption spectra of ODA and the mixtures of ODA and polymer RTV/SR do not absorb in the wavelength of the visible light region. The SEM analysis results show that the film morphology of ODA strongly depends on the nature of the ODA solution and the method of film formation and these are important factors affecting the different hydrophobicity of ODA films. Comparison of the droplet contact angle of thin films obtained by the above methods shows that the films fabricated by LB, spin-coating and spray-coating all increase the hydrophobicity of the glass substrate with the droplet contact angle range from 100^o-145^o, while dip-coating it is possible to fabricate superhydrophobic films with contact angles up to 161^o.

Keywords: *Octadecylamine, thin film, Langmuir-Blodgett, Langmuir-Schaefer, physical-chemical methods, superhydrophobic, RTV/SR.*

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EFFECT OF TITANIUM OXIDE ON THE SUPRAMOLECULAR STRUCTURE AND PROPERTIES OF POLYCAPROAMIDE

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1. INTRODUCTION

Polycaproamide (PCA) is a polymer, characterized by high wear resistance, mechanical strength, chemically resistant, resistant to most solvents. It is a promising structural material and is widely used in industry, for example, in shipbuilding, mechanical engineering, etc. [1]. However, it has several disadvantages: low values of specific toughness, elasticity and thermal stability, as well as a large water absorption, which does not allow to use products from PCA in environments with high humidity. In addition, sometimes, PCA products crack prematurely and collapse during operation. This is due to the heterogeneous supramolecular structure of the polymer, obtained by anionic polymerization in bulk [2-5].

It is possible to improve the characteristics of PCA using inorganic additives, in particular, metal oxides. Solid particles of metal oxides act as artificial nucleating agents. Addition them into the polymer can influence on the supramolecular structure and, consequently, the properties of polymers. Artificial nucleating agents in the process of polymer synthesis lead to an increase in the strength, thermal and mechanical properties, and also increase their shelf life [6-7].

It was of interest to study titanium dioxide (TD) as an inorganic addittive. TD is widely used in industry as a white pigment, in addition, it is chemically inert, non-toxic, does not dissolve in polymers. It is characterized by high thermal stability under the most severe processing conditions. TD exists in three crystalline forms, such as anatase, rutile and brookite. Brookite is rare in nature. In addition, it does not represent commercial interest [8]. Anatase and rutile forms of TD have different crystal lattices. Therefore, they have different properties. The anatase has a greater amount of oxygen vacancies than rutile, which causes its greater chemical and photocatalytic activity. It also has a higher chemical and photocatalytic activity [9]. At the same time, rutile diffuses light better than anatase, it's more stable and less photodestructive.

Mateva et al. showed that the addition rutile at a concentration of 2 wt.% in PCA leads to an increase in the molecular weight of the polymer and an increase in thermal stability [10]. The available information of the effect TD on PCA does not give a complete picture of the research topic.

In this regard, the purpose of this work was to study the effect of anatase and rutile in various concentrations (10^{-4} M, 10^{-2} M, 10^{-1} M) on thermal, physicomechanical and operational properties of PCA, obtained by anionic polymerization of ε-caprolactam.

2. EXPERIMETAL

2.1. Materials

The ε-caprolactam monomer (99%) was supplied by Sigma-Aldrich. The catalyst Bruggolen C10 (sodium caprolactamate in ε-caprolactam), activator Bruggolen C20 P (blocked diisocyanate in ε-caprolactam) were supplied by Bruggemann Chemical.

The ε-caprolactam was dried in a vacuum oven at 45°C for 48 h before use. Anatase (Purity: 99%, APS: 30 nm, SSA: 210 m^2/g, Color: white, Morphology: spherical, Bulk density: 0.25 g/cm^3, True density: 3.9 g/cm^3, Sigma Aldrich) and rutile (Purity: 99%, APS: 45 nm, SSA: 30 m^2/g, Color: white, Morphology: spherical, Bulk density: 0.4 g/cm^3, True density: 4.3 g/cm^3, Sigma Aldrich) TD powder was used as a modifying additive. TD was dried 48 h at 100-120°C in the air.

2.2. Anionic polymerization

PCA was synthesized by anionic polymerization of ε-caprolactam [3]. The reaction was carried out in a three-necked flask with stirrer, reflux condenser and nitrogen inlet system. The ε-caprolactam with catalyst (1 wt.%) was melted at a temperature of 100°C, then the temperature was raised to 180°C, and activator was added. The fine dispersed TD was added into the polymerization system simultaneously with the activator. The reaction was conducted for 180 minutes. The resulting product was extracted in acetone, dried (at the vacuum to a constant weight at 60°C), weighed and analyzed. In order to avoid experimental errors, each sample was synthesized three times.

2.3. Measurements and equipment

PCA samples was examined on the D8-Advance Bruker diffractometer with CuKα radiation, scan speed was 5 second/step. Each sample was measured three times, and then data of three diffractograms were summarized. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer Instrument system (STA6000) at a heating rate of 3°C/min under a dinitrogen atmosphere, in the range of room temperature to 450°C. Thermomechanical curves was obtained on the TMA 402F (Netzsch, Germany) under nitrogen flow at a heating rate of 3°C/min. Constant load was 1 N. Differential scanning calorimetric analysis (DSC) was performed on a DSC-1STARe System (Mettler Toledo, USA). The heating rate of the sample was 5°C/min. Melt flow index (MFI) was determined by capillary viscometer IIRT-5 M (Russia). The diameter of a capillary was 0.2095±0.0005 cm. MFI was measured at the temperature of 230°C and the load of 2.16 kg. The measurements of the elongation at break (ε) and tensile strength (σ) were carried out on the Inspekt mini 3 kN tensile testing machine (Trilogica, Germany). The traveling speed of clamps was 100 mm/min. Micrographs of the samples were obtained on Olimpus BX51 polarizing microscope. Water absorption was determined by keeping the obtained samples in distilled water until the weight of the sample ceased to change. Water absorption was calculated using the following formula:

$$M = \frac{m - m_0}{m_0} \, x \, 100\% \quad (1)$$

where M is water absorption; m is mass of the polymer after swelling in water; m_0 is the mass of the dry polymer.

The study of samples by each method was carried out at least three times independently of each other. The arithmetic mean value was taken as the test result.

3. RESULTS AND DISCUSSION

The anionic polymerization of ε-caprolactam in the presence of anatase and rutile showed the influence of selected additives on the morphology of the PCA. As seen from Figure 1, the TD leads to the fact that the structure becomes more uniform over the entire cross section of the sample.

DSC curves of PCA samples containing anatase and rutile have a second melting peak which is absent in the unmodified sample of PCA. The presence of the second peak is observed in all samples obtained by repeated synthesis. Moreover, this melting peak persists during the repeated cycle of cooling and heating of the sample (Figure 2).

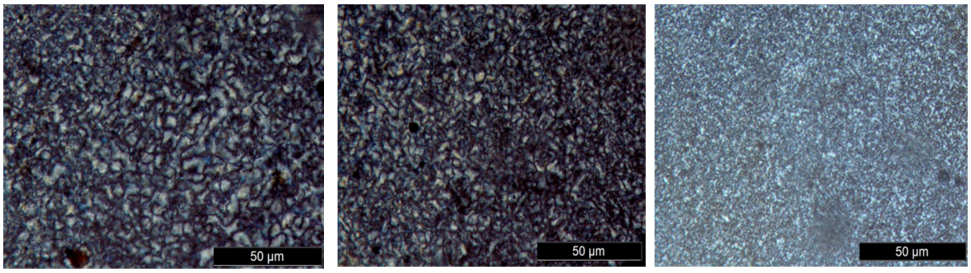

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Figure 1. Micrographs of polycaproamide samples: without additives (1), modified with rutile (2) and anatase (3) at a concentration of 10^{-4} M

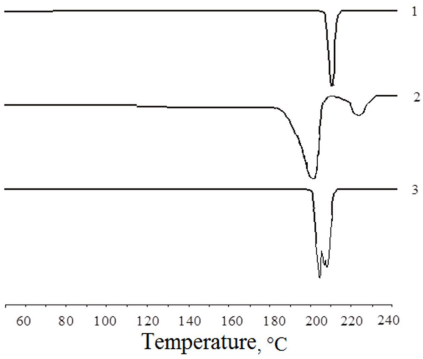

Figure 2. DSC curves of polycaproamide: without additives (1) containing anatase (2) and rutile (3) at a concentration of 10^{-4} M

Most likely, the appearance of the second melting peak is due to the fact that the nucleation process during crystallization of the polymer containing TD proceeds via two possible mechanisms: homogeneous and heterogeneous. As a result of only

homogeneous nucleation for unmodified polycaproamide, the crystallite size (L) is characterized by a large value (192 Å) compared with the modified sample (Table 1). The crystallite size of polycaproamide obtained in the presence of 10^{-4} M of TD is 48 Å for the rutile and 45 Å for the anatase.

An increase in the concentration of titanium dioxide from 10^{-4} to 10^{-1} M leads to the formation of smaller crystals (35 Å and 39 Å, respectively, for the rutile and anatase). Most likely, this is due to the fact that a large number of nucleating agents interferes with the growth of crystals in the polymer.

Table 1. Characteristics of the supramolecular structure of the polycaproamide, calculated according to X-ray structural analysis

Modifier	Concentration, M	L^*, Å	χ_c^{**}, %
-	-	192	63
Anatase	10^{-1}	35	61
	10^{-2}	41	62
	10^{-4}	45	65
Rutile	10^{-1}	39	55
	10^{-2}	44	58
	10^{-4}	48	67

*L is crystallite size; **χ_c is degree of crystallinity.

The presence of crystals of different sizes in the polymer structure should lead to a change in the diffusion of melting (Table 2). In this case, small-sized crystals melt at lower temperatures than large ones.

The presence of TD in the polymer system at a concentration of 10^{-4} M leads to an increase in the degree of crystallinity, as evidenced by the amount of energy consumed to melt 1 g of the substance, as determined by DSC.

Table 2. Effect of titanium dioxide on melting energy, diffusion of melting (ΔT) and equilibrium melting temperature (T_m) of polycaproamide

Modifier	Concentration, M		Relative weight of each peak, %	Melting energy J/g	T_m, °C	ΔT, °C	Yield, %
-	-		100	97.28	220	25	99
Anatase	10^{-1}	1 peak	16	122.03	198	10	98
		2 peak	84		215	11	
	10^{-2}	1 peak	81	124.11	212	19	98
		2 peak	19		219	3	
	10^{-4}	1 peak	75	156.09	212	35	99
		2 peak	25		228	12	

Modifier	Concentration, M		Relative weight of each peak, %	Melting energy J/g	T_m, °C	ΔT, °C	Yield, %
Rutile	10^{-1}	1 peak	14	63.24	178	5	98
		2 peak	86		215	20	
	10^{-2}	1 peak	80	104.50	213	21	98
		2 peak	20		219	5	
	10^{-4}	1 peak	69	175.51	211	15	99
		2 peak	31		226	8	

As shown in the Table 2, the yield of all polymers was above 97%.

The addition of TD leads to an increase in the thermal stability of the samples. The TGA curves show that samples containing rutile at a concentration of 10^{-4} M and anatase at 10^{-4}, 10^{-2} M lose weight at a higher temperature than PCA sample without additives (Figure 3, 4).

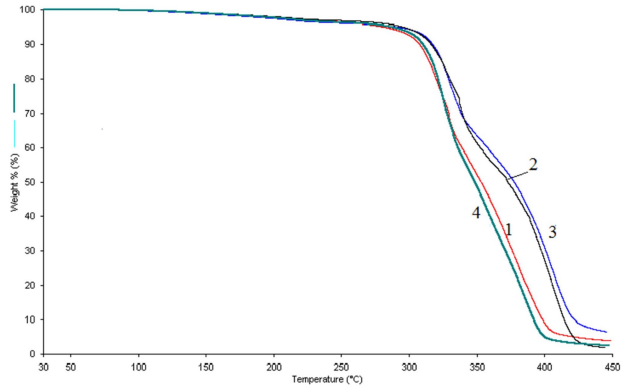

Figure 3. TGA curves of polycaproamide containing anatase at a concentration: 0 M (1); 10^{-4} M (2); 10^{-2} M (3); 10^{-1} M (4)

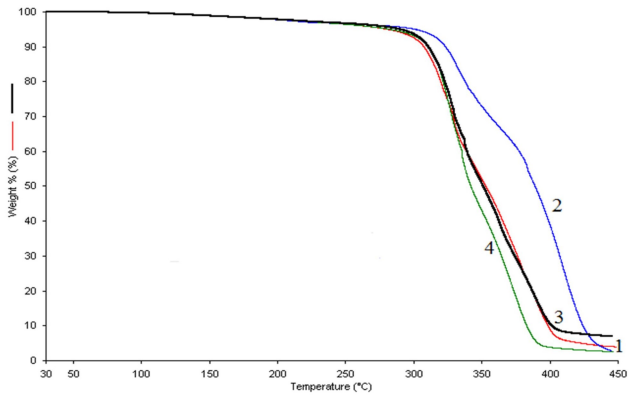

Figure 4. TGA curves of polycaproamide containing rutile at a concentration: 0 M (1); 10^{-4} M (2); 10^{-2} M (3); 10^{-1} M (4)

The best thermal stability of PCA modified with anatase and rutile in a concentration of 10^{-4} M can be explained by the uniform distribution of modifier particles between spherulites, which leads to a lower density, a decrease in the boundary voltage between two phases and difficulty in their growth. This, in turn, will lead to a higher strain resistance of the polymer obtained due to the low degree of crystallinity and the smaller size of the crystals. Anatase, in contrast to the rutile, in a concentration of 10^{-2} M also increases the thermal stability of PCA. Most likely, this is due to the fact that in anatase is more active and exhibits a greater affinity for the electron than rutile [11].

TD has not significantly effect on the water absorption and the hardness of the polymer (Table 3). Analysis of the physico-mechanical properties of the synthesized polymers showed that the anatase and rutile at a concentration of 10^{-4} M allow to increase the strength properties of PCA, at the same time increasing the concentration to 10^{-1} M leads to a decrease in physical and mechanical properties (Table 3).

Table 3. Physico-mechanical properties, melt flow index, water absorption and shore D hardness of polycaproamide

Modifier	**Concentration, M**	**MFI, g/10 min**	**Physico-mechanical properties** ***			**Water absorption**	**Shore D hardness**
			ε, %	σ, MPa	E(b), MPa		
-	-	2.49	180	38	240	1.9	84
Anatase	10^{-1}	2.79	71	32	238	2.4	82
	10^{-2}	2.05	175	41	257	1.5	83
	10^{-4}	1.07	215	53	310	1.4	84
Rutile	10^{-1}	3.74	130	32	242	2.1	80
	10^{-2}	2.38	272	43	260	1.7	82
	10^{-4}	1.85	286	54	320	1.6	84

***σ - tensile strength; ε-elongation at break; E(b)- elastic modulus.

4. CONCLUSION

It was shown that anatase and rutile have an influence on the supramolecular structure of PCA, obtained by anionic polymerization of ε-caprolactam. Thermal stability and strength properties of PCA containing anatase and rutile at 10^{-4} M. are higher than for unmodified samples.

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SUMMARY

The effect of anatase and rutile forms of titanium oxide on the thermal, physicomechanical properties, water absorption and hardness of polycaproamide was studied. It was shown that titanium dioxide has an influence on the degree of crystallinity and the crystallite size. TGA method shows that samples containing rutile and anatase lose weight at a higher temperature than polycaproamide sample without additives. Analysis of the physicomechanical properties of the synthesized samples showed that titanium dioxide in a concentration of 10^{-4} M increases the strength properties of polycaproamide. At the same time increasing the concentration of titanium dioxide to 10^{-1} M leads to a decrease in physical and mechanical properties. Anatase and rutile do not have a significant effect on water absorption and polymer hardness.

Keywords: *Additives, thermal properties, supramolecular structures, polyamides.*

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