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DETERMINATION OF COMPOSITION, MELTING HEAT AND THE CRYSTALLINITY DEGREE OF POLYAMIDE PHASE IN POLYAMIDE-6/BARIUM TITANATE SYSTEM

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The method of determination of ceramics contents and melting heat of polymer phase in composite PA-6/BaTiO$_3$ has been suggested. Samples of composite have been obtained by polymerization of caprolactam in which the fine particles of barium titanate were dispersed. The obtained samples have been characterized by means of specific volume measurements and the DSC technique. Contents of barium titanate and melting heat of polyamide phase have been calculated using suitable equations.

Keywords composite materials, composition of polyamide-ceramic composites

1. INTRODUCTION

In the past couple of years, one has observed an increased interest in new composite materials which have specific properties. It is because of their wide application in many fields; for example, electrostatic filters are used in environmental protection. The composite materials are two or multilayer systems, in which individual phases are matched so that the composite has proper physical properties (for example, good electret-piezoelectric properties) [1-4]. Some of the polymer and polymer-ceramic systems demonstrate these qualities. Other polymer piezoelectric known systems contain PVDF, but the piezoelectric activities are present in some of the polyamides, for example polyamide-9, and polyamide-11.[3-6]. Polymer-ceramic systems in which the powdered ferroelectric ceramics are dispersed in polymer matrix are of particular interest [1]. Aforementioned electrized systems adopt fairly large electrical charges on the phase boundaries. In the final effect, the composites are characterized by electret and also piezoelectric properties, and therefore, they are becoming to be widely adopted in industry (electromechanical transformers, electrostatic filters, etc.). It is a known fact that polyamide-ceramic composites can be classified as electret-piezoelectric materials, especially when one will use barium titanate as a ceramic phase; barium titanate is known to have good piezoelectric properties.

Polyamide-11, polyamide-9, and even polyamide-6 could serve as a polymer phase in these composites [3-9]. There are other known techniques of introducing powdered ferroelectric ceramics into the polymer matrix. One of the techniques is monomer polymerization in the presence of powdered ferroelectric substance. As a result, one obtains the polyamide-ceramic composite. Depending on the preparation conditions, the composite product is usually not uniform in regard to the ceramics location in the polyamide matrix. Therefore, the composition of the final product is not uniform.

The purpose of the study was to create the method which would allow to determine the contents of the ceramic phase in any given place of the composite and, concurrently, more precisely characterize polyamide phase by determining its melting heat and the degree of crystallinity.

2. MATERIALS AND EXPERIMENTAL CONDITIONS

The determination method of the composition, melting heat and the crystallinity degree was tested for the polymer-ceramic composite in which polyamide-6 was applied as a polymer phase, and barium titanate was applied as a ceramic phase. In order to achieve PA-6/$BaTiO_3$ composite, barium titanate (Radio Ceramics Manufacturing, Warsaw) was used in its powdered form in which the individual granules were not bigger than 0.075 mm. Pure PA-6 and PA-6/barium titanate mixture was prepared by an anion polymerization of caprolactam in the presence of adequate catalysts. The exact laboratory procedure of the production of pure PA-6 and PA-6/ $BaTiO_3$ with the proper composition was described in a previous study [10]. The final products of the composites preparation had the shape of a cylinder (diameter – 8 mm, height – 30 mm), from which additional samples were taken from the middle part of the cylinder for further studies. In the case of the composite, a series of samples were prepared in which the contents of barium titanate was gradually increased in subsequent samples. The contents value, however, was not exceeding 45% of composite's weight. Samples that exceeded the barium titanate 45% weight limit were fragile and breakable and were not suitable for further studies which were indented to determine their piezoelectric activities [10].

In order to determine the structure of the aforementioned composites and more narrowly characterize their polyamide structures, it was necessary to determine their specific volume and the melting heat of the tested samples. The specific volume of PA-6 and their composites were determined by density measurements in the hydrostatic method [11]. The density of barium titanate was determined by a pycnometric method [11]. The melting heat of the polyamide phase in the tested samples was determined by DSC with a Perkin-Elmer DSC-2 calorimeter [12].

3. THE METHODOLOGICAL BASIS FOR DETERMINATION OF THE COMPOSITE COMPOSITION, MELTING HEAT, AND THE DEGREE OF CRYSTALLINITY OF THE POLYMER COMPONENT

The described method can be applied with the assumption that the polymer-ceramic composite is a two phase structure (two components), in which the polymer matrix is a semicrystalline polymer with a defined melting heat, which is associated with the specific volume of the polymer. In addition, the polymer component should also contain amorphous and crystalline regions. Crystalline regions are formed by one well defined crystallographic form, which melts in the process of heating but does not transform itself into yet another form. The ceramic component, within the range of the applied temperatures, should not exhibit any thermoeffects; only under these conditions the curves achieved in the DSC techniques correspond with the rearrangement and melting processes of the crystallites of the polymer component. It can be assumed that the tested system PA-6/$BaTiO_3$ satisfies all of the aforementioned conditions. Below, we outline the symbols of the physical quantities used in the equations of the study.

V, V_p, V_c – Volume of composite, polymer phase, ceramic phase
m, m_p, m_c – Mass of composite, polymer phase, ceramic phase
$\upsilon, \upsilon_p, \upsilon_c$ – Specific volume of composite, polymer phase, ceramic phase
x_c, x_p – Mass fractions of ceramic phase and polymer phase in the composite
x_k – Crystallinity degree of polymer phase
ΔH – Melting heat determined for the composite sample
ΔH_p – Melting heat of polymer phase
ΔH^o – Melting heat of fully crystalline polymer phase
$\upsilon_{p,a}$ – Specific volume of fully amorphous polymer phase
$\upsilon_{p,k}$ – Specific volume of fully crystalline polymer phase
a,b,A,B,C – Constants

If we assume that the tested composite is a two phase system, in which each phase is realized through a given component, then:

$$\begin{gathered} V=V_p+V_c \\ V=\upsilon_p m_p+\upsilon_c m_c \\ \upsilon=\upsilon_p x_p+\upsilon_c x_c \\ \upsilon_p=(\upsilon-x_c\upsilon_c)/(1-x_c) \end{gathered} \tag{1}$$

We can also assume, that in the case of some semicrystalline polymers, there is a linear correlation between their melting heat and the specific volume [13].

$$\upsilon_p=a-b\Delta H_p \tag{2}$$

In the case of polymer/ceramic system, the melting heat of the polymer phase is associated with the melting heat determined for the composite sample through the concentration of the polymer (or ceramic) phase.

$$\Delta H_p=\Delta H/x_p=\Delta H/(1-x_c) \tag{3}$$

Based on equations 2 and 3, we can conclude that:

$$\upsilon_p=a-b\Delta H/(1-x_c) \tag{4}$$

When one will compare the sides of equations 1 and 4, one can achieve the following:

$$x_c=(a-\upsilon-b\Delta H)/(a-\upsilon_c) \tag{5}$$

In the composite which includes a given polymer phase (PA-6) and a given ceramic phase ($BaTiO_3$), in addition to the a and b constants, we have a determined value υ_c, and therefore the following determined values:

$$a/(a-\upsilon_c)=A,\quad 1/(a-\upsilon_c)=B,\quad b/(a-\upsilon_c)=C$$

The equation, therefore, takes the form of:

$$x_c=A-B\upsilon-C\Delta H \tag{6}$$

Having studied the literature data [13], one can assume that in the case of poliamide-6 $a=\upsilon_{p,a}=0.910\ cm^3/g$, $b=5\cdot10^{-4}\ cm^3/J$. Moreover, $\upsilon_c=0.178\ cm^3/g$ (Table 1), and therefore :

$A=1.2435$, $B=1.3665\ g/cm^3$, $C=6.8\cdot10^{-4}\ g/J$, and finally for the studied composite of polyamide-ceramic PA-6/$BaTiO_3$ the contents of the ceramic $BaTiO_3$ can be derived from the following equation:

$$x_c=1.2435-1.3665\upsilon-6.8\cdot10^{-4}\Delta H \tag{7}$$

Knowing the contents of ceramic (x_c) in the composite, one can calculate:

- mass fraction of the polymer phase $x_p=1-x_c$
- melting heat of the polymer phase (ΔHp) according to the formula (3)
- crystallinity degree (x_k) of polyamide component based on the equation:

$$x_k=\Delta H_p/\Delta H^\circ=\Delta H/[188(1-x_c)] \quad (8)$$

concurrently, adopting $\Delta H^\circ=188$ J/g for polyamide-6 [13].

4. DISCUSSION OF RESULTS AND CONCLUSIONS

Analyzing equation (5), one has to conclude that

- In the case of a sample that does not contain ceramic component: $\upsilon = \upsilon_p$, $\Delta H = \Delta H_p$ and $x_c= 0$
- In the case of a sample that does not contain polymer component: $\upsilon = \upsilon_c$, $\Delta H = 0$ and $x_c=1$
- In the case of composite samples: $\upsilon_c< \upsilon < \upsilon_p$ and
  if $\upsilon_p= \upsilon_{p,a}$ then $\Delta H = 0$ and $0 < x_c<1$
  if $\upsilon_p= \upsilon_{p,k}$ then $\Delta H = x_p\Delta H^\circ$ and $0 < x_c<1$
  if $\upsilon_{p,k}< \upsilon_p<\upsilon_{p,a}$ then $0 < \Delta H < x_p\Delta H^\circ$ and $0 < x_c< 1$

Examined system PA-6/$BaTiO_3$ is, of course, characterized by the following set of inequalities: $\upsilon_c< \upsilon <\upsilon_p$, $\upsilon_{p,k}< \upsilon_p< \upsilon_{p,a}$, $0< \Delta H < x_p\Delta H^\circ$.

Because of the above mentioned reasons, assumed contents of barium titanate in the composite should be within the limit of $0 < x_c< 0.45$.

The results of the measurements and calculations are presented in Table 1.Based on the results in Table 1, it can be clearly concluded that the contents of ceramics in the examined composite sample is always lower than the assumed (expected) contents. Such a result is predictable because barium titanate is not equally dispersed in the total volume of the polymerizing mixture despite the process of intensive mixing. Because of the relatively high density of barium titanate (5.613 g/cm^3), the lower parts of the reacting mixture contain higher contents of ceramics than the middle and higher parts. It is necessary to indicate that in order to determine the specific volume and the melting heat, the samples were taken from the middle part of the composite. What can be expected in the determination of melting heat and specific volume of the composite samples? Higher values of melting heat characterize samples of lower ceramic fraction because the melting effect is the result of the contents of polymer phase (Figure 1). It is necessary to add that the melting heat in relation to polymer phase (ΔH_p) increases in proportion to the decrease of ceramics contents in the composite (Figure 1), which is probably the result of a higher contents of ceramics in the composite blocks hindering the crystallization and crystallization rearrangement processes of crystal regions in the polymer component [10].

Table 1. The characteristics of polyamide-6, barium titanate and polymer-ceramic composites.

Sample index	$x_{c,z}$	ΔH [J/g]	υ [cm ^{3}/g]	x_c	x_p	ΔH_p [J/g]	x_k
P	0.000	86.8	0.867	0.000	1.000	86.8	0.462
P/C-1	0.100	72.6	0.815	0.080	0.920	78.9	0.420
P/C-2	0.150	67.5	0.791	0.117	0.883	76.4	0.406
P/C-3	0.250	57.7	0.741	0.192	0.808	71.4	0.380
P/C-4	0.350	48.1	0.677	0.286	0.714	67.4	0.358
P/C-5	0.450	39.4	0.606	0.389	0.611	64.4	0.342
C	1.000	-	0.178	1.000	0.000	-	-

P – polyamide-6, C – barium titanate $BaTiO_3$, P/C-1, P/C-2, P/C-3, P/C-4, P/C-5: polyamide-ceramic composites of PA-6/$BaTiO_3$ type, $x_{c,z}$ – assumed fraction of ceramics in the composite, x_c – determined fraction of ceramics in the composite.

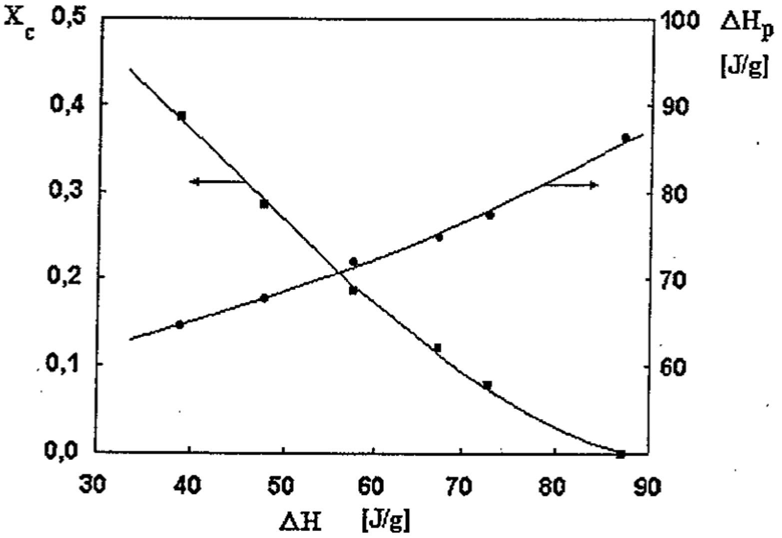

Fig. 1. The correlation between the composite melting heat and ceramics contents $BaTiO_3$ and the melting heat of polymer phase PA-6.

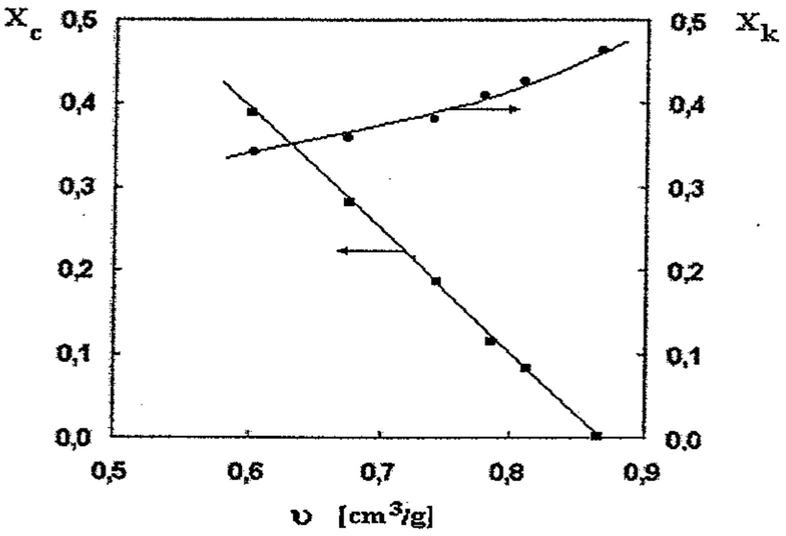

Fig. 2. The correlation between the specific volume of the composite and the contents of barium titanate $BaTiO_3$ and the degree of crystallinity of polyamide phase PA-6.

Figure 2 demonstrates that, in the case of the examined samples, the specific volume of the composite is linearly correlated with the contents of the ceramics in the composite. It is necessary to observe that the influence of the changes of phase PA-6 specific volume on the value of x_c is not particularly high. It is clear, also, that the increase in the specific volume of the composite, as a result of the decrease of the ceramics contents, causes an increase in the degree of crystallinity of the polyamide phase.

Based on the presented results and the discussions, one has to conclude that:

- composite samples based on polymer/ceramic systems may by characterized by internal non-homogeneity related to the diversity of the ceramic contents in a given volume of the polymer matrix,
- using certain specified conditions, one can determine the ceramics and polymer contents in the composite samples using the technique of DSC and measurement of specific volume,
- one can also additionally determine and properly characterize polymer component by specifying its melting heat and the degree of crystallinity.

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WYZNACZANIE SKŁADU KOMPOZYTU ORAZ CIEPŁA TOPNIENIA I STOPNIA KRYSTALICZNOŚCI FAZY POLIAMIDOWEJ W UKŁADZIE: POLIAMID-6/TYTANIAN BARU.

Streszczenie

Zaproponowano metodę wyznaczania zawartości ceramiki $BaTiO_3$ i ciepła topnienia fazy polimerowej w kompozycie typu: PA-6/$BaTiO_3$. Próbki kompozytowe otrzymywano na drodze polimeryzacji kaprolaktamu w obecności sproszkowanego tytanianu baru. Uzyskane próbki charakteryzowano wykorzystując pomiary objętości właściwej oraz technikę DSC. Zawartość tytanianu baru i ciepło topnienia fazy poliamidowej obliczano stosując odpowiednie równania.