INVESTIGATION OF INFLUENCE OF BARRIER DISCHARGE PLASMA ON BARIUM TITANATE PARTICLE DOPED POLYETHYLENE BY DSC METHOD

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Composite films based on high-density polyethylene and barium titanate particles before and after treatment with a dielectric barrier gas discharge were studied by differential scanning calorimetry. The values of critical temperatures, changes in entropy, enthalpy, and degree of crystallinity before and after the action of the gas discharge are found. It is shown that the critical temperature after the action of a gas discharge decreases during heating, and increases during cooling, except for the concentration of barium titanate particles of 5 vol. %. In addition, the change in entropy and enthalpy during discharge processing increases as well as the degree of crystallinity. As the filler concentration increases, the change in enthalpy, entropy, and the degree of crystallinity decrease.

Keywords: barium titanate, high density polyethylene, dielectric barrier discharge plasma; enthalpy, entropy, crystallinity.
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1. INTRODUCTION

Surface modification by electric discharge plasma is one of the most interesting applications compared with other techniques which require vacuum conditions. Under electric discharge plasma treatment, the polymeric surface undergoes a functionalization process which includes the formation of various polar groups containing oxygen [1-2]. Authors of the work [3] used the corona discharge plasma technique to modify the properties of low density polyethylene film. The results obtained show good treatment homogeneity and an improvement of adhesion properties by the functionalization and etching of the film surface. In the work [4], low pressure glow discharge O_2 plasma has been used in order to improve adhesion properties and make it useful for technical applications of low-density polyethylene (LDPE) film using differential scanning calorimetry. The results show that low pressure O_2 plasma improves wettability in LDPE films and no significant changes can be observed at longer exposure times. The fluorine-containing polymer composite filled with piezo-ceramics were prepared by a hot pressing method in the work [5]. According to the obtained experimental results, the stability of the electret charge of a composite based on F42 + PZT-5A is better than a composite based on F3 + PZT-8. The polyethylene porous films were treated by dielectric surface barrier discharge plasma in the work [6]. The significant increase of the surface energy and its polar component of polyethylene porous films were observed. The LDPE films modified by barrier discharge plasma were investigated to improve surface properties and adhesion of LDPE in the work [7]. It was shown that the topography of modified LDPE was significantly changed and the surface of modified polymer exhibited higher roughness in comparison with unmodified polymer. In the paper [8] plasma processing of polymer films and particles is examined by coating and noncoating plasmas. The authors believe that the difference by a factor of three in the etching rate between films in ammonia plasma is the consequence of their quasi-crystalline arrangement, compared to the amorphous PE films. In the paper [9], modification of the surface properties of PE films is studied using air dielectric barrier discharge plasma at atmospheric pressure. It is shown that air plasma can dramatically improve the wettability of PE surfaces. High-density polymer composites with semiconductor or dielectric fillers were prepared by the hot pressing method [10]. The results of the study indicate that, with increasing filler volume fraction, the thermal conductivity of the samples also increased.

Two possible mechanisms have been proposed in the article [11]: an increase in surface energy, and the anchor effects imparted by plasma etching. Independently from these mechanisms, reactions between free radicals, generated by plasma irradiation and adhesives are also likely to affect the adhesive properties of polymer materials. In the work [12], an atmospheric pressure glow-like dielectric barrier discharge in argon with small admixtures of hexamethyldisiloxane is employed for the deposition of thin polydimethylsiloxane films. This paper shows that the deposition rate and the chemical composition of the deposited films are strongly affected at which plasma-polymerization is performed. Two special groups of plasma polymers that have received increased attention are treated in detail in review [13].

A technology for generating craze-formation centers in polymers under the action of the electric discharge plasma and consider questions associated with a method for varying the geometrical sizes of crazes in the work [14]. The paper [15] presents a brief description of the plasma chemical method for synthesizing semiconducting polymers.

Low-pressure plasma co-polymerisation of binary gas mixtures of ethylene and ammonia was investigated in the work [16] in order to deposit N-rich plasma polymer coatings for biomedical applications. Authors of the work [17] used an atmospheric pressure apparatus to deposit novel

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families plasma polymers using mixtures of three different hydrocarbon precursors in nitrogen at varying respective gas flow ratios. The crystallization of “polymer–ferroelectric/piezoelectric ceramic” composites under the action of an electric discharge plasma and temperature is investigated in the work [18]. It is shown that this process results in strong oxidation of polymer chains.

The review article [19] presents various methods of plasma treatment of polymers. In particular, the dielectric barrier discharge method is described in detail. Plasma treatment serves mainly to modify the surface of polymers to increase adhesion.

The work is devoted to studying the effect of a gas discharge on high density polyethylene doped with particles of barium titanate by differential scanning calorimetric method.

2. MATERIALS AND METHODS

We used high density polyethylene (HDPE) as a matrix. Melting and softening points of polymer are 130-135˚C and 80-90˚C, correspondingly. The barium titanate particles with sizes of 600 nm (US, Research Nanomaterials, In.) were added into the fine powder of polyethylenewith different concentrations (5 vol. %, 10 vol. %, 20 vol.% and 30 vol.%). Then obtained mixture was shaken in a vortex mixer for 1 hour at room temperature, followed by sonication with dispergator Ultrasonic Cleaner NATO CD-4800 (China) for 4 hours. Disc-shaped samples of composites were obtained by hot pressing at temperature of 165˚C and pressure of 15 MPa. Pressing time after reaching the selected temperature is 15-20 minutes. The diameter and thickness of the obtained films were 4 cm and 100 μm, respectively.

The electric discharges were used as non-thermal non-equilibrium plasma, which is termed surface micro-discharges (SMD). The generation of SMDs at ambient pressure is obtained from the dielectric-barrier discharge (DBD) technology which is related to the corona discharge family. The DBD treatment carried out on the set up described earlier in the work [18]. In this case, the voltage of electric charge in the cells equals 8 kV.

The differential scanning calorimeter DSC 204 F1 (firm Netzsch, Germany) with the CC200 F1 cooling system regulating the flow of liquid nitrogen was used to determine thermophysical parameters. Argon was served to purge and to protect the cell at the pressure of 50 kPa. The DSC204F1 and Proteus Analysis software programmes were used to process the results. The rate of temperature change was 10 K/min in the temperature range between 20^0C and 150^0C. Exposure time was 30 min.

The critical temperature T_{cr}, at which the composite changes from one state to another, is determined by the local maximum of the heat flow while the change in enthalpy ΔH is determined by the expression

$$\Delta H = k \cdot \Delta A, \tag{1}$$

where the k-coefficient characteristic of this device, A - the area under the corresponding peak. The entropy change ΔS during transition is defined as

$$\Delta S = \frac{\Delta H}{T_{cr}}, \tag{2}$$

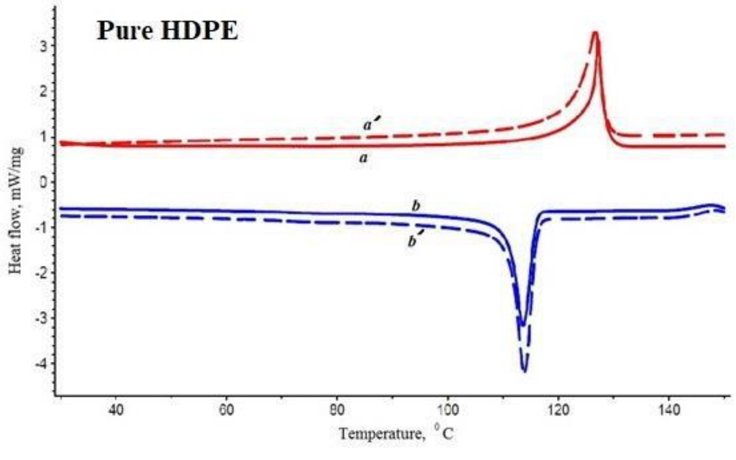
The degree of crystallinity K is found according to the expression:

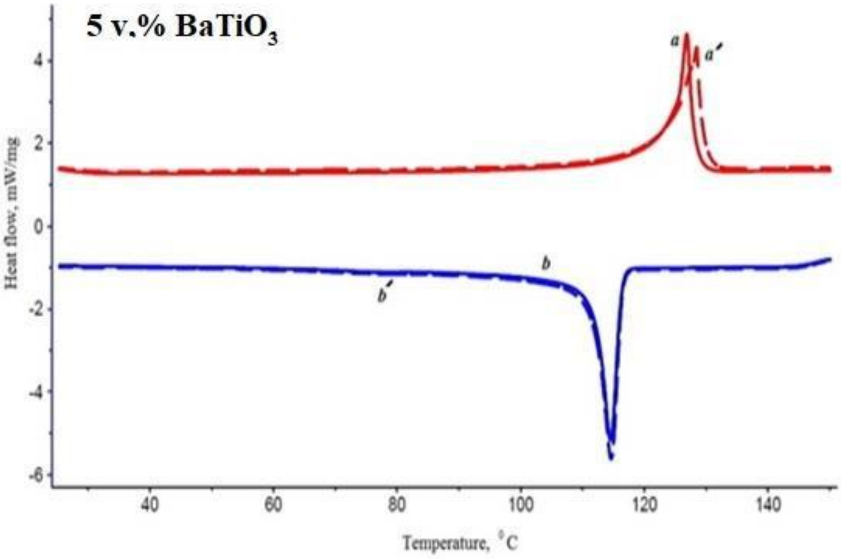
$$K = \frac{\left|\Delta H_h + \Delta H_c\right|}{\Delta H(100\% cryst)} 100\%, \tag{3}$$

where ΔH_h and ΔH_c are changes of enthalpy at heating and cooling processes, correspondingly;
ΔH (100 % cryst) is the change of enthalpy at 100% crystallites of matrix. For high-density polyethylene, the enthalpy change at 100% crystallization is taken to be equal to 293 J/g.

3. RESULTS AND DISCUSSION

Figure 1 shows DSC curves for both pure polymer and composites with different filler concentrations before and after discharge treatment.




5 v.% BaTiO$_3$
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Heat flow, mW/mg
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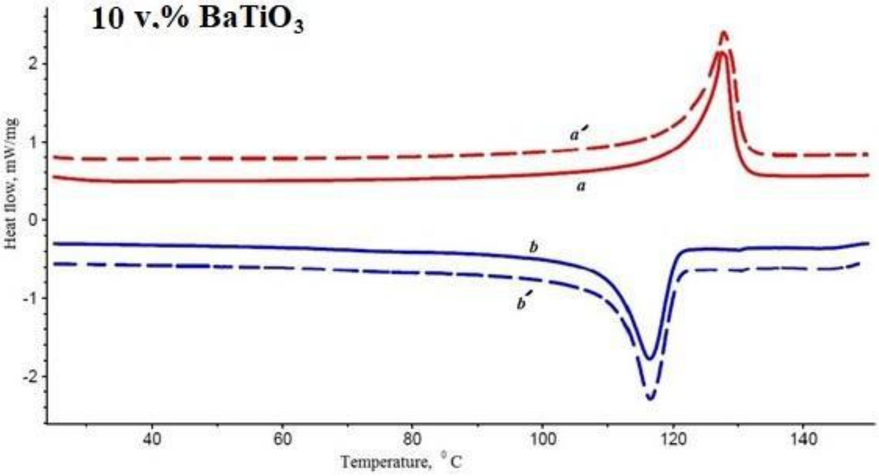
Temperature, °C


10 v.% BaTiO$_3$
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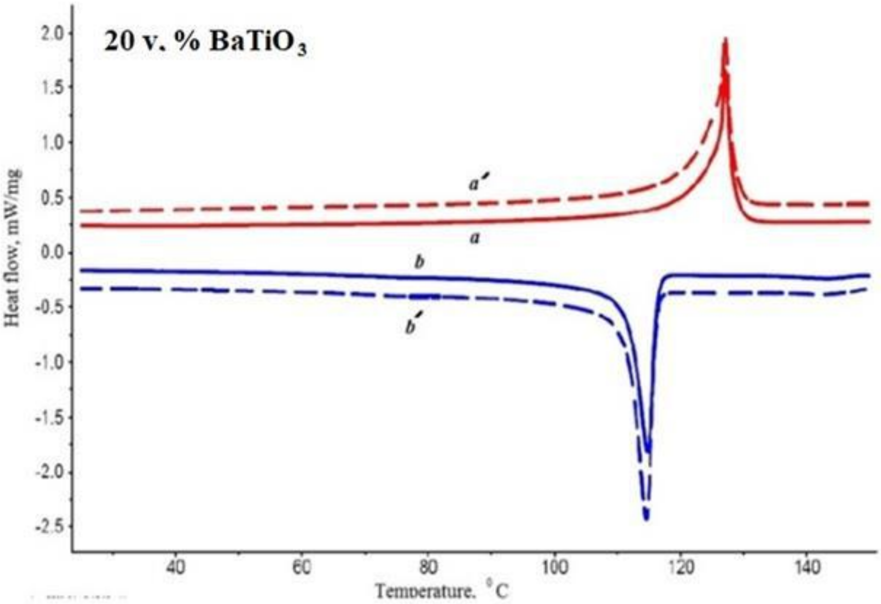
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Heat flow, mW/mg
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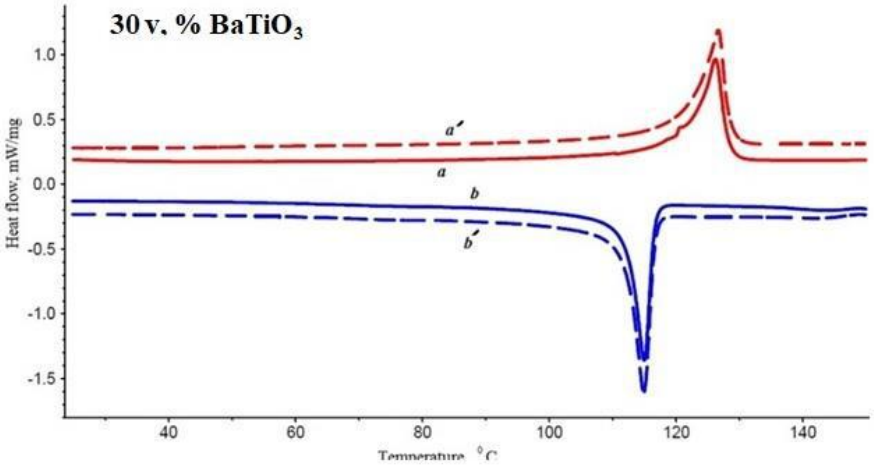

Fig. 1. Heat flow versus temperature for composites at various filler concentrations: (a) untreated sample at heating regime, (a′) plasma treated sample at heating regime, (b) untreated sample at cooling regime, (b′) plasma treated sample at cooling regime.

As can be seen, the peaks of the curves corresponding to cooling regime, shifts to low temperatures. This indicates that the transition to the solid state of the composite occurs at lower temperatures. To more clearly determine the change for different filler concentrations, we plot the dependence of the critical temperature T_{cr} on the filler concentration and scanning regime. The corresponding graph is shown in Figure 2.

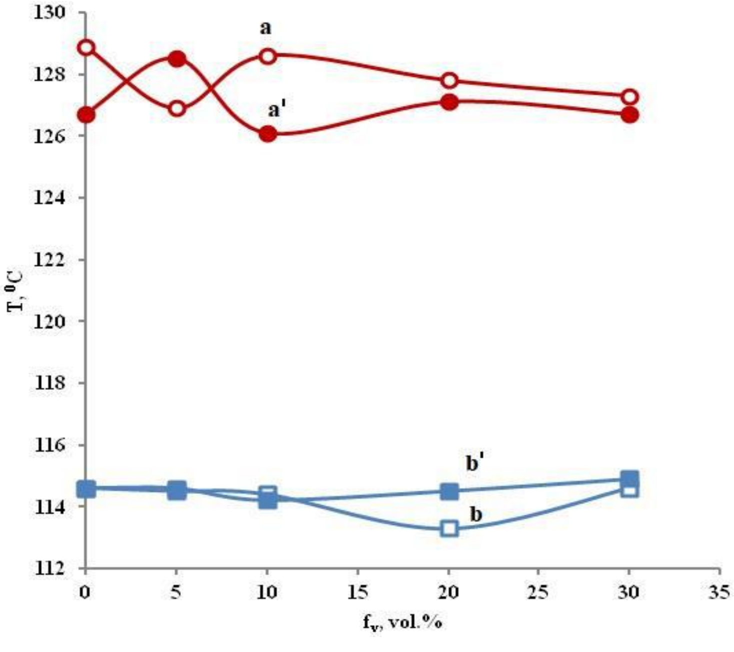

Fig. 2. Dependence of critical temperature on filler concentration: (a) untreated sample at heating regime, (a′) plasma-treated sample at heating regime, (b) untreated sample at cooling regime, (b′) plasma-treated sample at cooling regime.

As can be seen, the critical transition temperature of pure polyethylene and composites decreases after gas discharge treatment at the heating regime, except for the composite with concentration of 5 vol. %. A similar result, namely, an increase in the critical temperature at low filler concentrations, was obtained in the processing of low density polyethylene film by low pressure O_2 plasma treatment [4]. Probably, the increase in the critical temperature at concentration of 5 vol. % is associated with a more uniform distribution of particles in the polymer matrix. At cooling regime, a higher concentration of filler induces the transition to solid state at higher temperatures.

Figure 3 shows the dependence of the change in enthalpy on the concentration of the filler during melting and solidification of the samples.

As can be seen, the change in enthalpy during melting and solidification decreases with increasing filler concentration. At the same time, it is sharper at low concentrations while it is slower at high concentrations.

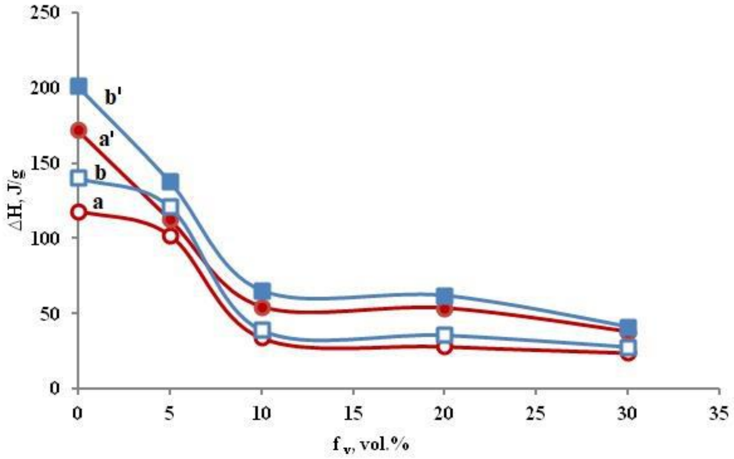

Fig. 3. The dependence of the change in enthalpy on the volume concentration of the filler during melting and solidification of the samples: (a) untreated sample at heating regime, (a′) plasma-treated sample at heating regime, (b) untreated sample at cooling regime, (b′) plasma-treated sample at cooling regime.

The values of the enthalpy change during the solidification process at the same filler concentrations are less than during the melting process. In addition, gas discharge treatment of the samples increases the enthalpy change.

It is known that the enthalpy of fusion (melting) of a substance is the energy that is absorbed as heat from the body when it changes from solid state to liquid state (an exothermic process) and it occurs without raising the temperature for crystalline substances. It serves to disorganize the intermolecular bonds that hold molecules together. During curing, the reverse process (endothermic) occurs in which heat is removed from the substance. In this case, intermolecular bonds are restored, and the temperature does not change. For crystalline substances, the change in enthalpy during melting and solidification has the same value. The degree of crystallinity of polymers is small, so the above regularities do not apply to them. Enthalpy is an extensive quantity, that is, for a composite system; it is equal to the sum of the enthalpies of its independent parts. Likewise, the enthalpy change of the composite is also the sum of the matrix and filler changes. The total change in the enthalpy of barium titanate particles is small, associated with a change in the symmetry group near the same temperature. But the volume fraction of the matrix, which has a sharp change in enthalpy, decreases. Therefore, the overall enthalpy change of the composite is reduced. These conclusions are in good agreement with the experimental curves of the change in enthalpy as a function of concentration.

The used technique of the barrier discharge plasma modifies the composite not only on the surface, but also in the bulk. This type of discharge is accompanied by the formation of accelerated electrons and ions, recombination radiation, active gas products and the appearance of surface electron-ion effects. The process occurs as a consequence of some breaks on the polymer chain; this situation allows the occurrence of some phenomena such as cross-linking, free radical formation, etc., with dramatic effects on the final performance of polymeric materials. The surface of composites could be oxidized when it is exposed to oxygen environment.

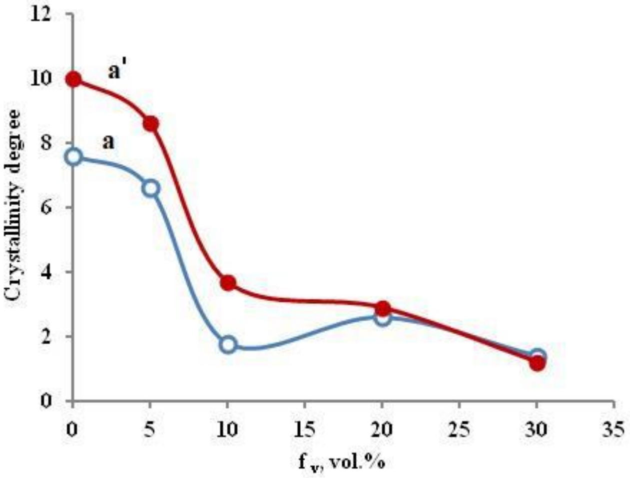

Fig. 4. Dependence of the degree of crystallinity on the volume concentration of the filler before (a) and after (a′) action of the gas discharge.

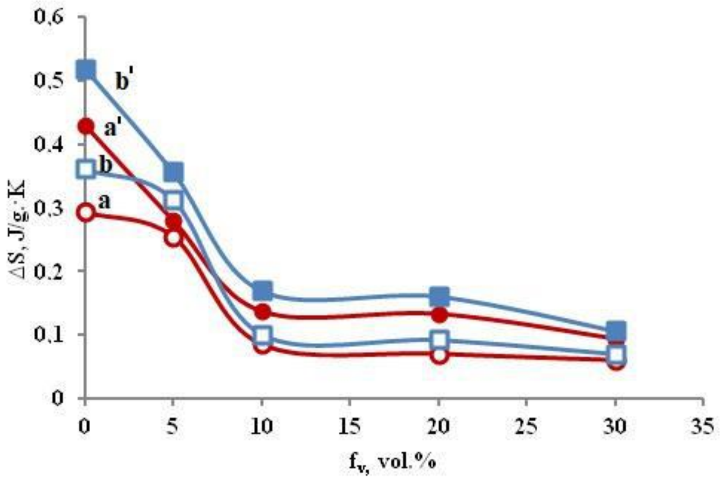

Fig. 5. The dependence of the change in entropy on the volume concentration of the filler during melting and solidification of the samples: (a) untreated sample at heating regime, (a′) plasma-treated sample at heating regime, (b) untreated sample at cooling regime, (b′) plasma-treated sample at cooling regime.

According to [4, 18, 19], additional oxidized species appear and oxygen atomic concentration increases. In particularly, ketone [−(C=O)−] and acetal [−(O−C−O)−] carbons are formed while the latter represents carboxyl [−(C−O)−O−] carbon. The formation of new connections contributes to the increase in the crystallinity of the composite. This corresponds to the experimental curves of crystallinity depending on the concentration (Fig. 4). At the same time, the decrease in the degree of crystallinity before and after processing is associated with a decrease in the volume fraction of polyethylene with an increase in the volume concentration of the filler.

Figure 5 shows the dependences of the enthalpy change during the transition from one aggregate state to another before and after the action of the gas discharge.

The entropy of melting and solidification is a measure of the disorder of the substance accompanying the melting or solidification, not only in the sense of changing the arrangement of atoms and their configuration, but also in the sense of changing the nature of the chemical bonds. The greater importance of the entropy of solidification compared to the entropy of melting is explained by the more ordered state of the composite in the solid phase during cooling. This is also consistent with the lower temperature transition. As it was said above, the total change in enthalpy, similar to the entropy of the filler, is small. But the volume fraction of the matrix, which has a sharp change in entropy, decreases with an increase in the concentration of the filler. Therefore, the overall change in entropy of the composite also decreases. Since the degree of crystallinity increases after exposure to a gas discharge, the degree of ordering or disordering increases accordingly, that is, the enthalpy of solidification and melting.

4. CONCLUSIONS

It is shown that the critical temperature after the action of a gas discharge decreases during the heating process and increases during the cooling one, except for the volume concentration of barium titanate particles of 5 vol. % which is associated with a more uniform distribution of particles in the polymer matrix. With an increase in the concentration of the filler, the volume fraction of the matrix decreases leading to a decrease in entropy and entropy, and degree of crystallinity. In addition, the change in entropy and enthalpy during discharge processing increases as well as the degree of crystallinity owing to the increase of oxygen atomic concentration and formation of novel bonds.

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