

EFFECT OF ELECTRIC DISCHARGE PLASMA ON THERMOPHYSICAL PROPERTIES OF HDPE-BN COMPOSITES

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The effect of dielectric barrier discharge plasma before and after modification on thermo-physical properties of composites based on high density polyethylene and boron nitride particles was studied. It has been established that with an increase in the volume fraction of the filler, the entropy and enthalpy decrease, except for 3vol.% and 7 vol.%. The entropy and enthalpy increase after the plasma while the critical temperature almost does not change. The degree of crystallinity decreases after plasma treatment.

Keywords: boron nitride, high density polyethylene, dielectric barrier discharge plasma; difference of enthalpy and entropy of composites, crystallinity.

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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 O₂ 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 O₂ 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]. 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 [6/8]. 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 [7] 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 [8], 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 [9,10-15]. The results of the study indicate that, with increasing filler volume fraction, the thermal conductivity of the samples also increased.

Hexagonal boron nitride (h-BN) has high thermal conductivity and chemical stability [16-17]. It is widely used in engineering and refractory industries. Its high chemical resistance, high thermal resistance, high electrical resistance, lubricity, lightness, and high thermal conductivity are the superior properties of the hexagonal boron nitride and the reason of broad application areas [18].

The goal of this work to study of the effect of dielectric barrier discharge plasma on thermophysical properties of high density polyethylene doped with BN particles.

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 hexagonal boron nitride particles with sizes of 2÷8 µm were added into the fine powder of polyethylene with different concentrations (3 vol. %, 5 vol. %, 7 vol. %, 10 vol. %, 15 vol.% and 20 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 [19-21]. In this case, the voltage of electric charge in the cells equals 8 kV. The plasma is created in an air layer of 2.5 mm. The exposure time of electric gas discharge plasma is taken to be 0.5 hours.

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 200C and 1500C. 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

$$\Delta H = k \cdot \Delta A, \quad (1)$$

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

$$\Delta S = \frac{\Delta H}{T_{cr}}, \quad (2)$$

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

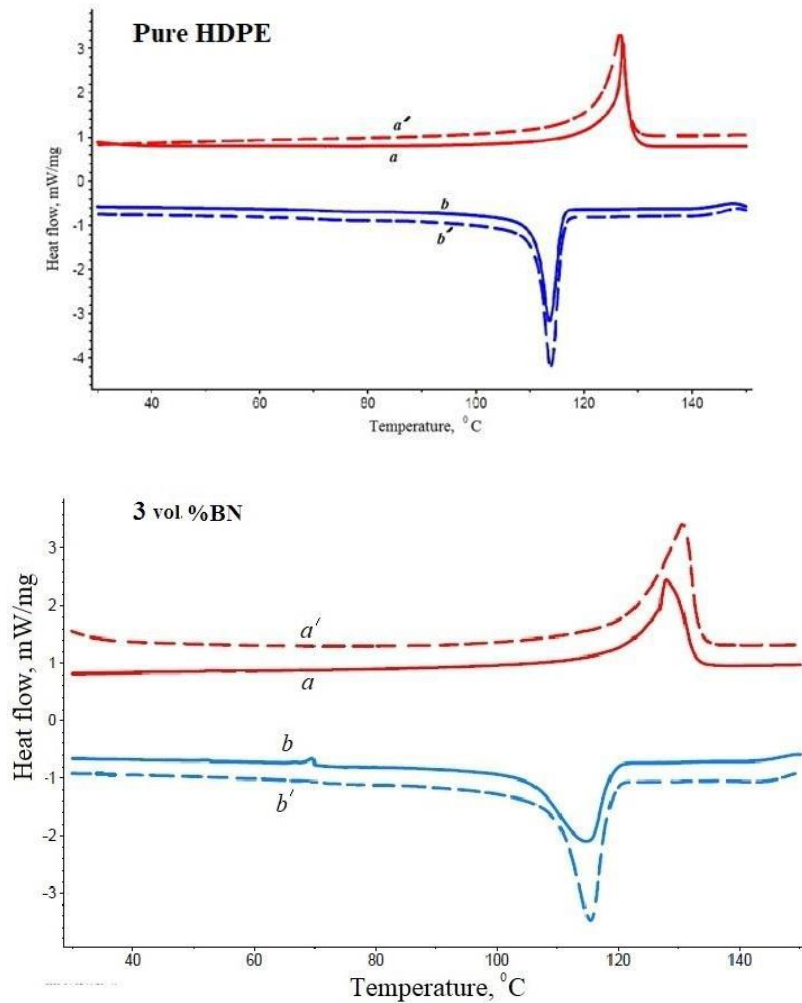
$$K = \frac{|\Delta H_h + \Delta H_c|}{\Delta H(100\% \text{cryst})} 100\% \quad (3)$$

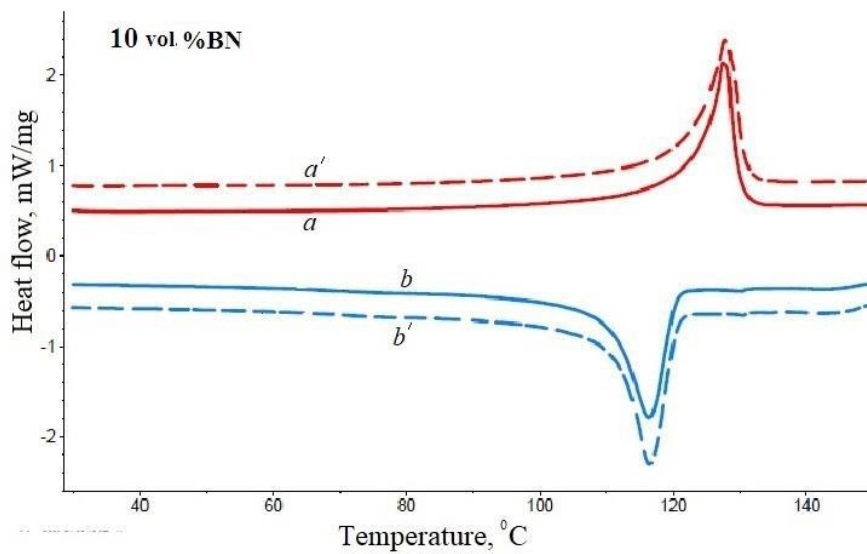
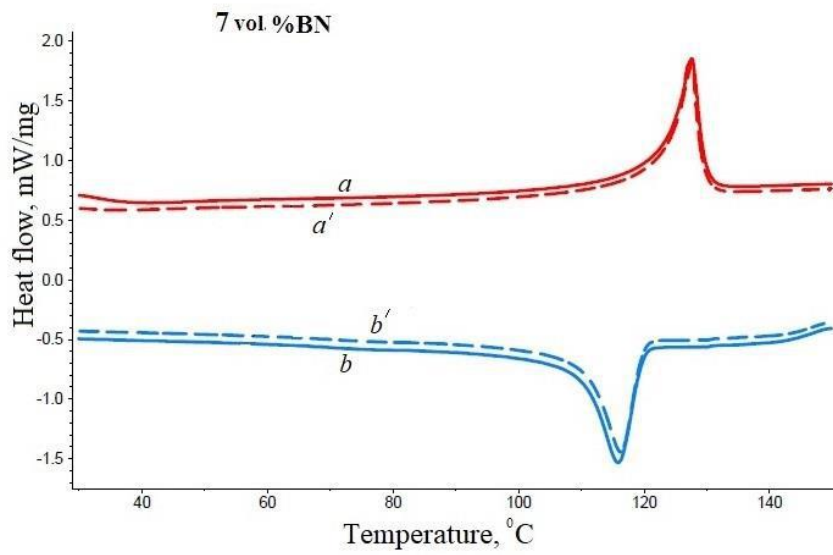
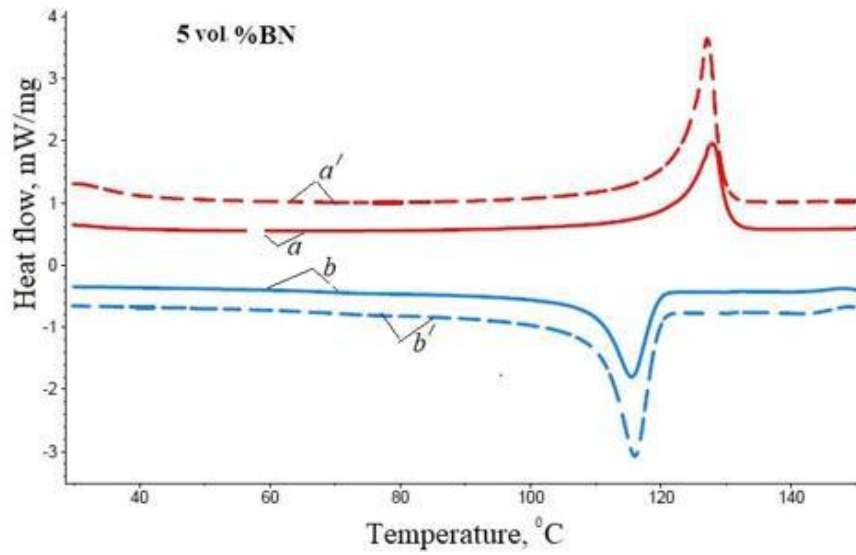
where ΔH_h and ΔH_c are changes of enthalpy at heating and cooling processes, correspondingly;

$\Delta H(100\% \text{cryst})$ 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.





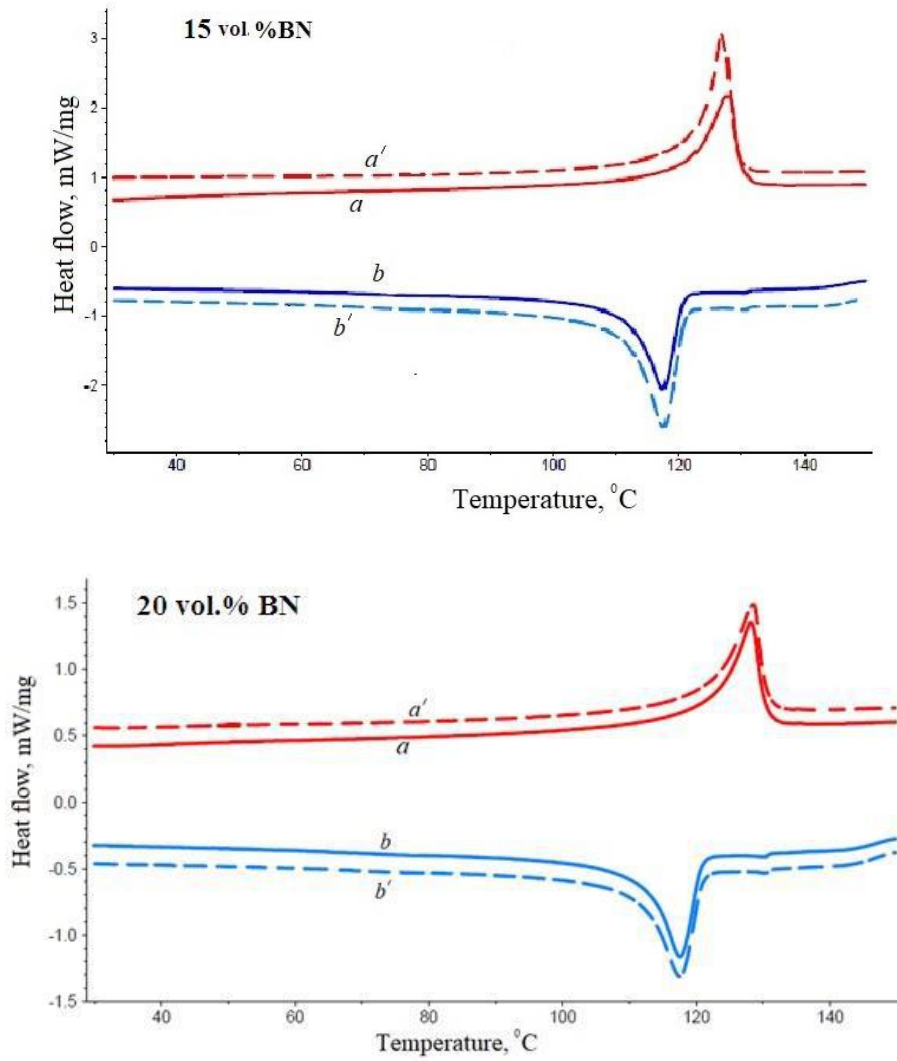


Fig. 1. Heat flow versus temperature for composites at various filler concentrations: (a) untreated sample at heating regime, (a') plasma treated sample at heating regime, (b) untreated sample at cooling regime, (b') plasma treated sample at cooling regime.

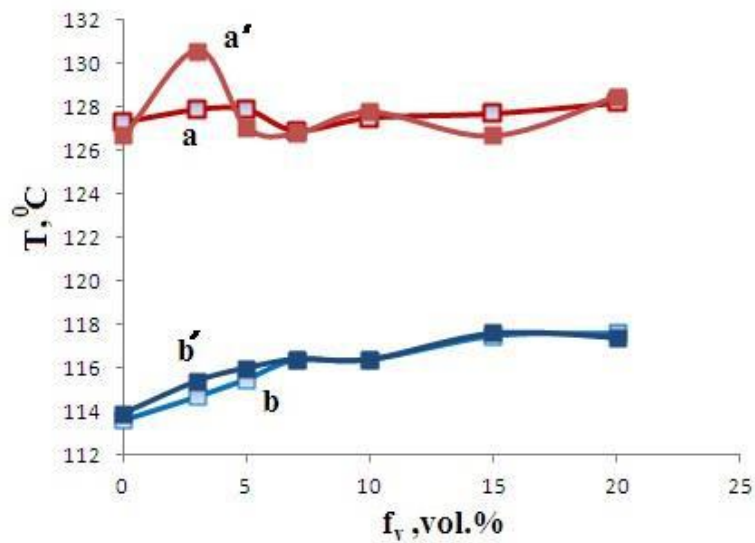


Fig. 2. Dependence of critical temperature on filler concentration: (a) untreated sample at heating regime, (a') plasma-treated sample at heating regime, (b) untreated sample at cooling regime, (b') plasma-treated sample at cooling regime.

As can be seen from the DSC thermogram curves, the glass transition does not observe for pure polymer as well as composites. There are only peaks corresponding to transition from solid state to liquid one and vice versa. 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 curves are shown in Figure 2.

As can be seen, melting temperature as well as solidification one almost do not change except for the composite with concentration of 3 vol.% after plasma modification. Probably, the increase in the critical temperature at concentration of 3 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 filler concentration during melting and solidification of the samples.

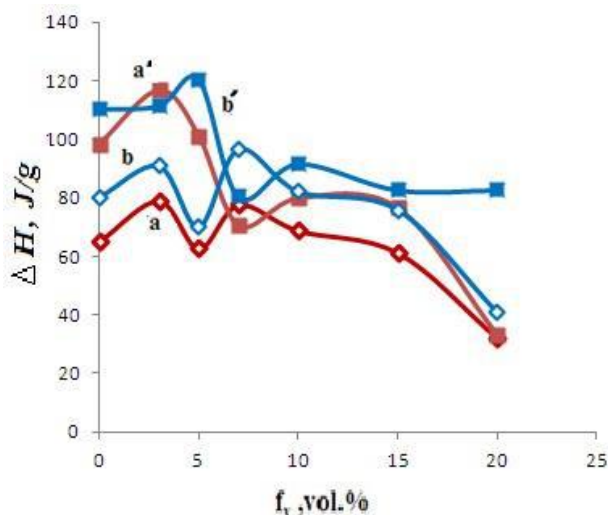


Fig. 3. The dependence of the change in enthalpy on the volume concentration of the filler during melting and solidification of the samples: (a) untreated sample at heating regime, (a') plasma-treated sample at heating regime, (b) untreated sample at cooling regime, (b') plasma-treated sample at cooling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

The enthalpy of the exothermic transition corresponding to melting according to the given volume fractions increases after the plasma modification. This is observed by the increase in the areas of the peaks shown in the figure. This is explained by the fact that more energy is required to activate the limited segmental movements of polymer chains after plasma modification.

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. 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 [22]. 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. According to [6, 21, 23], additional oxidized species appear and oxygen atomic concentration increases. In particular, 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.

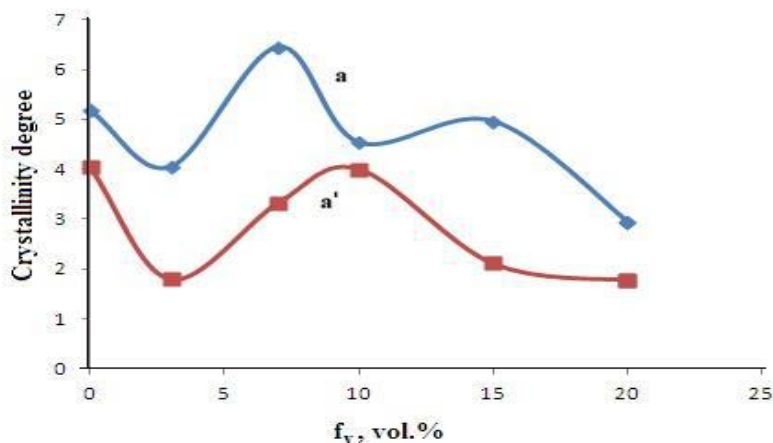


Fig. 4. Dependence of the degree of crystallinity on the volume concentration of the filler before (a) and after (a') action of the gas discharge.

The results obtained show that the degree of crystallization decreases after plasma modification leading to an increase in the degree of amorphous. An increase in the degree of amorphous leads to the formation of stronger coordination bonds between the polymer and BN due to the breaking of the polymer chain during the plasma modification. The impact of electrical discharge plasma on BN also causes the destruction of its crystal lattice. Here, due to the influence of oxygen-containing groups, BN is split and its crystal structure is destroyed. As a result, B₂O₃ with an amorphous structure is formed. It can be seen from the graph obtained that the degree of crystallization decreases after plasma modification [24]. It can be explained by the formation of a new group with an amorphous structure in the composite.

4. CONCLUSIONS

It is shown that the critical temperature practically does not change during heating and cooling except for 3 vol.% after plasma modification. With an increase in the filler concentration, the volume fraction of the matrix decreases, which causes a change in the entropy and degree of crystallinity. In addition, there is an increase in entropy and enthalpy during plasma modification, as well as a decrease in the degree of crystallinity due to the formation of new bonds due to the influence of oxygen-containing groups. The particles decrease the degree of crystallinity developed within the matrix due to the constriction in the mobility of the polymer chains.

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