The results obtained for polypropylene modified by amines show that crystallization temperature decreases by about 6-10°C upon exposure to ionizing radiation. Thus, upon irradiation the additives loss partly the nucleating properties, probably due to chemical changes of HALS stabilizers during the Denisov cycle that leads to decrease of crystallization temperature. It was found by Ahmed and Basfar that polypropylene in presence of nucleating agent is less resistant towards irradiation than without such admixture [7]. Therefore, considering the interaction of HALS with polypropylene one must take into account that amines, prompting formation of nuclei, increase imperfection of crystals, what results in easier and stronger stabilization of unpaired electrons in the crystal defects. In this way, amines strongly influence the radiosensitivity of crystalline phase, whereas their role as radical terminators in this phase is limited, contrary to the amorphous one as was confirmed earlier by EPR study.

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MODIFICATION OF MONTMORILLONITE FILLERS BY IONIZING RADIATION

Zbigniew Zimek, Grażyna Przybytniak, Andrzej Nowicki, Krzysztof Mirkowski

Nanofillers are a new class of particles that are applied to polymeric composites and other materials to improve some of their properties [1]. Elements, oxides, carbides, simple and composite salts, and other compounds can be used as the nanofillers. Manufacturing and investigation of properties of the composites have recently focused attention of many laboratories in polymer science.

The main problem in preparing composites from polymers and fillers is the incompatibility of components. Disperse phase is usually inorganic, hydrophilic compounds or minerals, while the main types of polymeric matrices are hydrophobic. For good mixing, the fillers should be modified to obtain hydrophobic layer on their surface. The modification is possible in many ways; the most popular is the impregnation of fillers with bifunctional molecules, containing in one molecule hydrophobic (*e.g.* long alkyl) and hydrophilic (*e.g.* ionic or polar) groups. Typical is the impregnation with ammonium salts having long alkyl chains. Such modified bentonites were mixed with commercially available polyolefines, *e.g.* polypropylene and polyethylene in molten state. For modification of the filler surface, other methods also are used, *e.g.* grafting of organophilic units on mineral particles.

As we reported earlier [2], the mineral fillers can be modified by using unsaturated compounds: styrene, methacrylic acid and maleic anhydride (MA), following by irradiation with high energy electron beam. Recently, we have used this method for compatibilization of montmorillonite (MMT) [3]. We selected maleic anhydride as a modifying agent because it does not undergo homopolymerization, is cheap and forms homogeneous mixtures with many polymers, for example, polypropylene. Now, we have used this method to change properties of bentonite "Specjal", containing about 70% of pure montmorillonite.

Acetone, maleic and phthalic anhydrides were obtained from P.O.Ch (Poland) while succinic anhydride was purchased from Fluka.

The samples were prepared by boiling bentonite with an acetone solution of suitable anhydride (10% w/w) for half an hour. The precipitate was filtered, dried at 30°C under low pressure, grinded and sieved to obtain a powder of particles below 70 μm. The concentration of adsorbed anhydride was about 5 to 8% w/w.

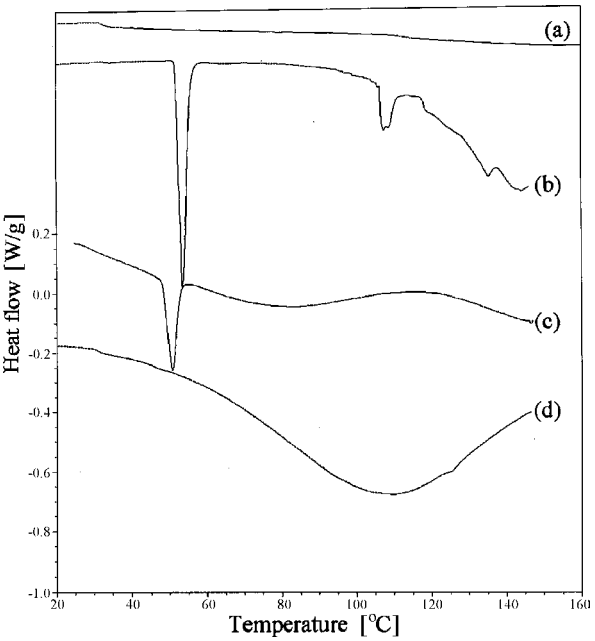

Fig.1. DSC results for bentonite "Specjal" (a), maleic anhydride (b), physical mixture of MMT/MA (c) and MMT/MA obtained *via* absorption from solution (d).

The samples were irradiated in an "Elektronika" accelerator using electron beam of energy 9 MeV and cumulative doses of 26, 52, 78 and 104 kGy.

After irradiation, the fraction of particles below 70 μm was selected.

The thermal properties of modified bentonite were tested using a differential scanning calorimeter MDSC2920CE in standard mode.

We used differential scanning calorimetry (DSC) measurements to determine the type of binding of maleic anhydride to bentonite. In Figure 1, are presented thermographs for: bentonite "Specjal" (a), maleic anhydride (b), physical mixture of bentonite "Specjal" with maleic anhydride (c) and sample of bentonite after absorption of maleic anhydride from acetone solution (d).

The thermograph (a) of unmodified bentonite does not confirm any exo- or endothermic process between 20 and 160°C. The diagram (b) indicates the melting point of maleic anhydride at 55°C and, additionally, at about 110°C peak belonging to the melting transition of maleic acid that could be present as an impurity. The physical mixture of bentonite with maleic anhydride shows the super-

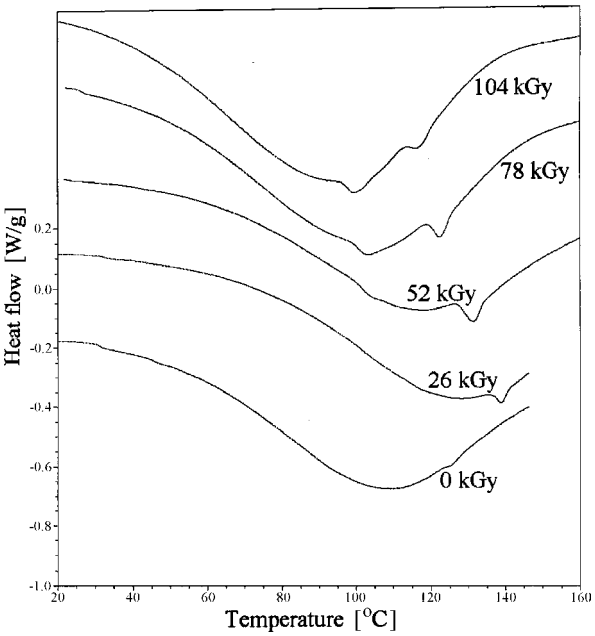

Fig.2. DSC thermographs for montmorillonite modified by maleic anhydride upon irradiation with electron beam with different doses.

position of components, however the melting point of maleic anhydride is shifted slightly towards lower temperatures. The lowest thermograph (d) recorded for bentonite with the absorbed layer of anhydride reveals a different relationship. Lack of the signal at 55°C strongly suggest that the chemical reaction between maleic anhydride and active groups of bentonite takes place, leading to salt-type compounds that are responsible for the broad endotherm of minimum above 100°C. Additionally, it was confirmed that analogous DSC curves were obtained in the case of modification of bentonite with succinic or phthalic anhydrides (data not shown).

Figure 2 shows the DSC results obtained for bentonite "Specjal" modified with maleic anhydride (MMT/MA) after ionizing radiation with the different doses. In comparison with previous results shown in Fig.1 new endothermic peaks appear what suggests that during irradiation a new phase of transition in the range 120-140°C is formed. The signal is strongly dose-dependent, the higher dose the greater is the shift towards lower temperatures. Futhermore, for doses above 50 kGy, a second low intensity peak is formed. It was also found that bentonites modified with succinic or phthalic anhydride upon irradiation do not reveal these additional DSC signals. The investigations indicate that the changes induced in the MMT/MA system by electron beam involve probably coupling between both components utilizing double bond of maleic anhydride.

Conclusion:

- Modification of the domestic bentonite "Specjal" by absorption of maleic anhydride, followed by irradiation with electron beam to the overall dose in the range 26-104 kGy, shows that the particles obtained in this process can be good fillers for the production of composites.
- Maleic anhydride reacts *via* anhydride group with active ionic sites of bentonite, forming a salt-like compound. Irradiation with electron beam leads to the breakage of double bond in maleic anhydride and to the production of new organic phases.

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STUDY OF THE PROPERTIES OF POLY(ESTER URETHANES) FOLLOWING IONIZING IRRADIATION

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Copolymers of polyurethanes and polyesters were found unsuitable for long-term implants because of fast hydrolysis of the ester soft segments. On the other hand, such properties make them valuable, gradually degradable biomaterial that might be used as scaffolds for tissue engineering [1-3]. The elastomeric polyurethanes are known to be radiation stable materials in sterilizing dose. Nevertheless, if additional components appear in the system, *e.g.* segments of polyesters, then the influence