

BASIC RADIATION PHYSICS AND CHEMISTRY OF COMPOSITES

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Until now, the radiation chemistry of composites, needed for effective radiation processing, has been not discussed. The survey of our research from that point of view is presented, starting with definition of a composite. Composites are more and more important in the applied and fundamental polymer science, and the participation of radiation processing of these systems will increase.

What is a composite? We have to answer the question before one can start the discussion of the radiation chemistry of the system. Polymeric composite is the combination of compositions that comprise two or more materials as separate phases, at least one of which is a polymer. On the other hand, polymeric compositions compounded with a plasticizer, stabilizer or very low proportions of pigments or processing aids are not ordinarily considered as composites. Typically, the goal of composites is to improve strength, stiffness or toughness, or dimensional stability by embedding particles or fibers in a matrix or binding phase. A second goal is to use inexpensive, readily available fillers to extend a more expensive or scarce resin. Such reason can be non-technical, like lowering the price of the product. In that sense the filler is categorized as a neutral additive to the polymer. However, in spite of to be composed for trivial reason, such material, when irradiated, it will behave like a composite.

The present attitude, especially nano-size oriented, treat composites as a hybrid material, which is a creation more or less different than the sum of constituents. The size, shape and chemical identity of the nanoparticle and interaction of the nanoparticles with the polymer matrix can affect significantly the final properties of a hybrid material. Radiation chemistry helps in fundamental understanding of hybrid materials containing inorganic nanoparticles embedded in an organic macromolecular matrix, in terms of the formation and intrinsic properties of the nanoparticles and the structure and properties inherent to the polymer. A composite from the point of view of radiation processing and radiation chemistry is any heterogeneous material in which the shortest size of a 3D, dispersed phase in the matrix is of the order of few nanometers. Shorter sizes do not qualify to the category of composites, because from the point of view of radiation chemistry they form homogeneous material. Such small sizes are comparable with sizes of spurs, in looking into radiation chemistry on the molecular level [1]. Upper limit of size of the dispersed phase is not defined. The proposed definition of composites from the point of view of radiation physics and chemistry does not define the state of aggregation of both components of composites. Although the most common combination is solid-solid, *e.g.* polymer/clay combination, possible are systems solid-gas, *e.g.* porous plastics (prepared in the Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology, as scaffolds for growing cells

[2]), polymers in the shape of pieces of medical devices with large volumes of air, *etc.* During radiation processing, the air gaps are also absorbing ionizing radiation, however with intensity by three orders of magnitude lower effect per volume.

Specific radiation chemistry of composites consists in:

- Different electron density of both substances results in different density of ionizations. This effect is not large, if both substances are chemical compounds of low Z number. However, the difference of electron density has to be taken into account.
- Different specific heat capacities of both phases, the dispersed and the main one, result in different temperatures reached in adiabatic irradiation, *i.e.* by electron beam.
- Large surface area of the interphase between two phases. It can reach enormous values with diminishing size of the dispersed phase. For instance, let us assume 1 kg of polymer composition with 30% content of dispersed phase (*e.g.* clay); the reduction of the diameter of particles from 1 μm , to 100 nm to 10 nm means an increase of the surface area respectively from 1800 m^2 , to 18 000 m^2 , to 180 000 m^2 (equivalent to 900 m x 200 m "lot"). These calculations are made for spheres, which show the smallest surface area for a given volume. Spheres occur in rather few composites, like latexes, and in most cases the shape of additional phase is far from the spherical. Therefore, any other shape means even higher surface area of the interface, with many consequences. In both phases independent radiation chemistries are running, with a variety of energy and material transfer in both directions. An important role is played by the quality of the interface. It is usually modified at the stage of preparation of a composite. Usually, the goal is to have the surface of dispersed phase as friendly to the host as possible, *e.g.* to make radiation-induced grafting possible, *i.e.* compatible. The consequences of enormous increase of the interphase, occurring with reduction of the size of dispersed phase, are well known in catalysis and adsorption, but are underestimated in radiation chemistry.

Any deviation from homogeneity, *i.e.* dealing with composites, introduces more or less disturbance into the depth dose curves. Keeping in mind the definition of the composite as the object with two or more bodies of different absorption characteristics towards interaction with radiation, one can start with a very common system of porous polymers, fibers, powders, *etc.* in which the second component of the system is air. Air is absorbing roughly by three orders of magnitude less per thickness than solid phase composed of low Z number. Therefore, the depth-dose curve shows a gap. The case of the same material, but divided into small particles gives the same basic curve for the same

polymer, but of apparent lower density. Gaps between particles are too small to be reflected in details in the curve, but the apparent bulk density is lowered. In that case, the depth-dose curve is simply extended and the object is behaving like the original polymer "diluted" by air, which does not contribute much to the absorption of energy (but can have enormous effect on the final results of radiation processing from other reasons, for instance due to oxidation of the surface of dispersed phase). Composites with air, in other words porous polymers, are very important in the preparation and application of scaffolds for growing cells [2].

More complicate situations, as concerns depth dose curves occur, if the second phase in the composite of higher density material, *e.g.* clay. The depth dose curve is squeezed in that case, because the dispersed phase absorbs more energy than the polymer per volume. What is more, the clay particles radiate degraded, low energy quanta back in the direction of incoming radiation and forwards into the polymer. Behind the particle, the dose absorbed by the polymer is lower in comparison to basic depth-dose curve. The distance of optimum thickness, *i.e.* when the entrance and exit dose are equal, is shortened. The consequences of the presence of two phases of different interactions with ionizing radiation are many, but the principal one is the unfavorable increase of DUR (dose uniformity ratio). In the case of homogenous polymeric material in liquid state or solid in a block shape or as homogeneous porous material, or medical device, the DUR will not exceed the value of 2 in most favorable cases. In the case of composites, reaching of such excellent value is usually not possible.

Second important aspect of radiation processing of composites is the different temperature of both phases during high dose rate irradiation. Electron beam creates such a condition during adiabatic supply of energy, without the possibility of rapid equilibration of temperature, otherwise possible in gamma irradiation. Specific heats capacities of both phases are always different. Details connected with the heating of irradiated objects are collected in monographic chapter [3]. However, they do not take into consideration composites and the present paper draws attention to that fact.

This energy balance applies to most cases of radiation processing of homogeneous and composite materials which involve radiation-induced crosslinking, grafting, oxidation, controlled degradation. Radiation yields expressed as described by the change of single molecules or effects (*e.g.* formation of one double bond) per 100 eV absorbed energy usually are up to 5. The situation changes if a chemical chain reaction occurs. That is the case when a monomer is added as one of the composite and ionizing radiation acts as an initiator of reaction. The radiation yield jumps to 1000 and more in the case of gamma radiation. In the case of electron beam radiation, the yield is not so high, according to $I^{0.5}$ law (where I is the intensity of radiation, or dose rate). Even in the case of electron beam the rate of reaction is usually so high that the thermal effect is much larger than the heat ef-

fect of absorbed radiation. The jump of temperature can be so high that the system boils and direction of reactions runs in unexpected directions.

The knowledge of specific heat capacity of materials is important in planning the procedure of radiation processing, especially if very different compounds are involved in particular composites. The data of specific heats can be found in the literature, but not always, because demand for that information is limited. Very often the need arises to forecast the temperature reached by constituent of composites and for that purpose the application of differential scanning calorimetry (DSC) technique to determine specific heat capacity of any material occurring in the composite is useful. It is often a mixture, like a bentonite, which contains montmorillonite (MMT), for that the data in the literature is not likely to be found. Specific heat capacity depends on the substrate temperature. Simple dividing the energy evolved by the specific heat to give the temperature rise is precise enough only if the dose is low and the specific heat is high. Otherwise, one has to analyze the changes in heat capacity as a function of temperature [3].

The phenomenon of different temperatures reached in adiabatic conditions by the main constituent and the composite phase is well pronounced if the latter has micrometer dimensions. With diminishing size of the second phase, the heat transport is more and more effective and eventually the thermal equilibration is comparable to the supply of ionizing energy. Calculations of the heat transport are complicated, but simplified estimations show that composites in which the second phase has indeed dimensions of single nanometers, can be treated as thermally homogeneous. Strictly speaking, the equilibration of the temperature proceeds as fast as the equilibration of temperature in multi-ionization spurs *vs.* the body of the system.

Limited volume of the report allows discussion of one type of composite only, used in the Department. It belongs to the group dealing with incorporation of inorganics into polymeric base. The polymer phase of our composite is polypropylene, the second one is exfoliated silicate sheet minerals (montmorillonite). Earlier, we were using also polyolefine matrix composites with low molecular weight organics *e.g.* crystalline alanine in polyethylene matrix for spectrophotometric and electron paramagnetic resonance (EPR) dosimetry [4]. Polymer-clay composites attract considerable scientific and industrial interests, because they exhibit significant improvements in physical and mechanical properties over virgin polymers. From the applied perspective, determining the rheological properties of nanocomposites is vital to optimize processing during the manufacture and resulting properties. From the scientific research point of view, nanocomposites provide a nanoscale space to study confined polymers and examine the effect of nanoclays on the rheology of nanocomposites. Since nanoclays significantly affect the rheological properties of nanocomposites, the network formation would be related to the microstructure of nanocomposites

and interaction between nano-clays and polymer matrix. Introduction of spectroscopic methods is improving the knowledge of the chemistry of montmorillonite/polymer. The intercalated polymer chains lie flat between the layers. There is not always a need to use clay of high montmorillonite content. In many cases the bentonite is sufficient. That composite is used in the Przybytniak group [5] in the paper on thermal stability of nanocomposites based on polypropylene and bentonite. A polycationic bentonite clay was modified with a quaternary organic salt and added to isotactic polypropylene. Compression moulded films were exposed to a thermal environment at 110°C to evaluate the thermal stability of polypropylene matrix after chemical modification of bentonite. Polypropylene with a modified clay has a higher thermal stability than with the natural clay. Work on radiation chemistry of composites was helped by experience gained on the investigation of blends with the help of electron beam [6,7].

There are many approaches to preparation of clays before combining with the polymer. There can be oligomerically modified clays for successful creation of a composite with styrenic, polyethylene and polypropylene matrix with sodium montmorillonite. The preparation of a nanocomposite is critical, if full advantages of the material have to be achieved. All clays are rather hydrophilic and combination with most hydrophobic popular polymers used as matrix, listed above is difficult, considering enormous surface area of contact of both phases, mentioned above. One can use organo-clay modified by organophilic surfactant. Going down to nanodimensions, the exfoliated nanocomposite shows a greatly improved modulus, higher glass transition temperature and better thermal stability compared to the neat polyethylene and the intercalated polypropylene/montmorillonite composites.

Already at the beginning of application of montmorillonite as the key constituent of clay/polymer composites, the observation was made that these materials show better properties when grafted with maleic anhydride as compatibilising agent. Considerable number of papers on composites with montmorillonite has created the base for radiation processing. The Laboratory of Radiation Modification of Polymers is working along that line, es-

pecially on radiation chemistry of polypropylene/montmorillonite composites.

In conclusion, although at present main experimental effort is directed towards the development of composites as such, and investigation of their specific properties, mechanical, physicochemical and physical, the radiation processing will enter the field on the wider scale, especially as concerns specialized plastics. It will happen under the acceptance of high cost of ionizing radiation. In medical applications any expenses are acceptable.

For the first time, in the field of radiation chemistry of polymers, at the initiative of the International Atomic Energy Agency (IAEA), there was a consultants meeting held at Sao Paulo, Brazil, August 2005, discussing specifics of radiation chemistry of composites [8,9].

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ABSTRACTION OF HYDROGEN FROM ORGANIC MATTER, CAUSED BY IONIZING RADIATION IN OUTER SPACE

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In the continuation of research on radiation-induced dehydrogenation, work has been concentrated on simulation of radiolysis of live species transported presumably from the Cosmos to Earth (panspermia). The idea of panspermia started a century ago, when Svante Arrhenius, the chemist, faced the question of origin of life on Earth and has found difficulties to find an answer. As the best solution, he has invented the concept of extrater-

restrial origin of life and of transportation to Earth from outer space, including even galaxies. The idea has attracted many followers and was a subject of extended interpretations. For instance, some preachers of panspermia have assumed the idea that life was always and everywhere present, from the beginning of the World, easily formed, and it was the transportation between different places only, which mattered. As there are still no plausible