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Photochemical preparation of polymer-clay composites

RAPID COMMUNICATION

Summary — *In situ* photochemically initiated free radical polymerization was used to obtain an organophilic bentonite—polymer composite. The photoinitiation process of this polymerization could occur with the use of sunlight, but process is continued in dark, caused by the, so-called, dark reaction. The components of polymerizing formulation are: monomer — [2-(methacryloxy)ethyl]trimethylammonium chloride (I), electron donor — 2-(dimethylamine)ethyl methacrylate (II) and crosslinking monomer (III). Obtained composites are flexible and insoluble in water, but they do not exhibit good mechanical properties.

Key words: polymer—clay composites, bentonite, photopolymerization.

Smectite clays, such as montmorillonite or bentonite, are hydrophilic in nature, which hinders formation of homogenous dispersions in organic polymers. Ion exchange of the interlayer inorganic cations with organic cations may lead to transformation of hydrophilic clay surface into an organophilic one, thus, decreasing the surface energy responsible for the wetting characteristics of the clay with polymers and other organic materials.

Two idealized polymer-clay composites are possible: intercalated and exfoliated. Intercalation results from the penetration of polymer molecules into the interlayer space [1]. This type of clay modification is used for altering clayey subsoil properties [2, 3]. Exfoliation, by contrast, involves extensive polymer penetration and delamination of clay crystallites. In result, a composite built with the individual nanometer-thick silicate platelets randomly dispersed in the polymer matrix is received. Such composite displays significantly enhanced mechanical properties [4—6].

The above described composite materials are usually obtained by melt intercalation or by *in situ* polymerization. *In situ* polymerization involves monomer interca-

lation into the clay interlayer space followed by either free radical or by ring-opening polymerization. Usually, thermal activation is necessary to initiate the process.

The present study exploits the possibility of organophilic bentonite-polymer composite formation using photochemically initiated *in situ* free radical polymerization. This type of initiation may play an important role in dentistry materials as well as in on-site preparation of a foil material used for protection against leachates from agricultural lands, landfills, *etc.*

RESULTS AND DISCUSSION

Preparation of a highly inter-reactive clay-polymer composite with the use of light for polymerization initiation requires suitable monomers and a suitable photoinitiating system. Intercalation of a monomer, a cross-linking agent and a photoinitiating system into the host layers of the clay can efficiently occur from water solution of the polymerizing formulation. The process occurs *via* ion exchange between interlayer inorganic cations and organic cation of the monomer and the photoinitiating system forming the polymerizing composition. This requires all components of the polymerizing formulation to be water-soluble, and capable of penetrating into the interlayer space of clayey minerals. For the monomer, this prerequisite is fulfilled, as it is shown below, by [2-(methacryloxy)ethyl]trimethylammonium chloride (I) (Fig. 1).

To be practicable, sunlight should be capable of photoinitiating the free radical processes. Panchromatic sensitization of a vinyl polymerization process requires

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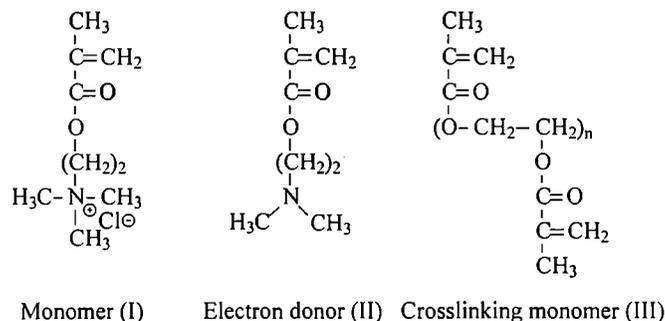
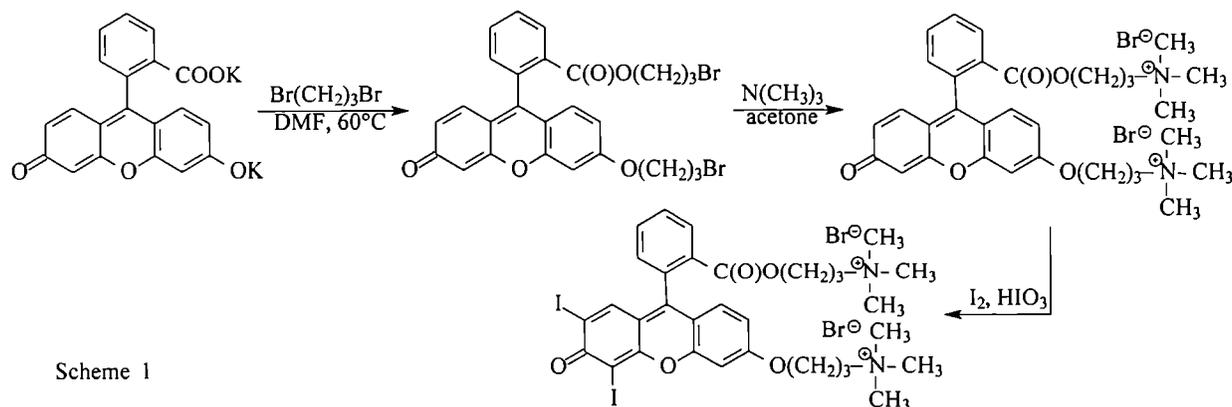


Fig. 1. Components of polymerizing formulation

the presence of a suitable dye as the light absorber. In such a case, photo-physical energy transfer between the dye excited state and another chromophore, which yields free radicals, is generally disfavored. Thus, an alternative processes allowing to avoid typical energy restrictions should be considered, e.g. photo-induced intermolecular electron transfer, being a non-classical, endothermic energy transfer process. This process involves the use of light to initiate electron transfer from a donor to an acceptor molecule. The basic requirements for the electron donor are fulfilled by 2-(dimethylamino)ethyl methacrylate (II), a typical tertiary amine, of the type commonly used as the electron donors in photo-induced electron transfer reactions [7] (Fig. 1).

The structure of the dye, being the electron acceptor in the tested system, has to be more complex because of the intercalation process requirements, whereby presence of an organic cation in the molecule is needed to allow penetration of the dye into the interlayer space of clay *via* the cation exchange reaction. Fluoresceine was the initial substrate and the photoinitiating dye (based on the chemistry of xanthene dyes clarified by Neckers [8–10]) was prepared by a sequence of reactions described in Scheme 1.



$^1\text{H-NMR}$ and IR spectroscopy were used to confirm desired structure of the final product.

Initially, the polymer-clay composite components, *i.e.* monomer (I, ~10 g), electron-donor monomer (II, ~0.5 g), cross-linking monomer (III, ~0.5 g), photo-initiating dye (IV, 0.0015 g) and clayey mineral [Pliocene clay from Ce-

ramic Plant in Bydgoszcz (~10 g) or bentonite (~5.0 g)] are vigorously mixed for 30 minutes. Next, the mixture was exposed to the sunlight or tested using an argon-ion laser as a light source. Figure 2 shows kinetics recorded during the laser photoinitiated polymerization of tested formulations. Kinetics was recorded using a method developed previously by these authors [11, 12].

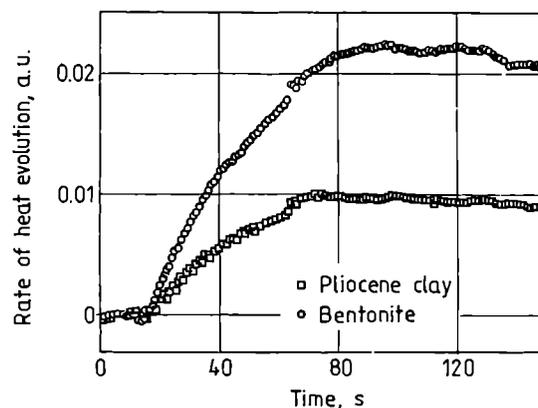
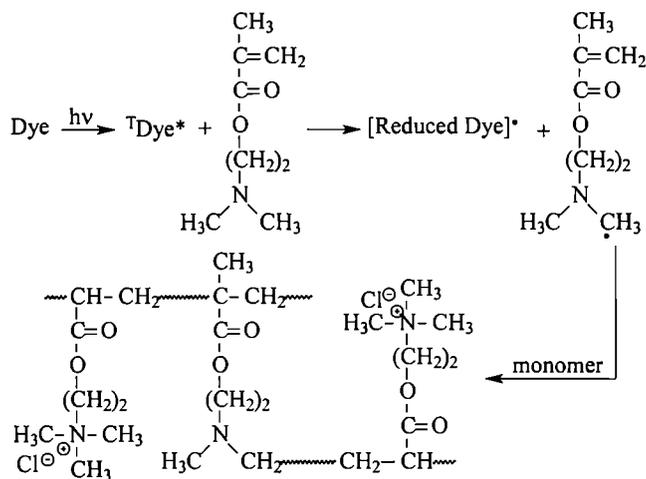


Fig. 2. Kinetic curves recorded during laser photoinitiated polymerization of formulations containing clayey minerals as fillers; laser intensity 100 mW/0.78 cm², layer thickness 2.0 mm

Data obtained from argon-ion laser sensitization (Fig. 2) show exothermal nature of the process. Polymerization continues for several minutes, even in the dark (so-called, dark reaction [13]). The formulation is also capable of polymerizing under sunlight passing through laboratory windows. The process ends 1–4 hours after exposure.

Light absorption during photopolymerization discolors the dye. The final product is insoluble in water, obviously due to presence of a cross-linking monomer

(III) in the initial mixture. However, absence of the cross-linking monomer (III) also leads to a product insoluble in water. In the latter case, water insolubility is caused by mechanism of the photoreaction taking place during polymerization [7] (Scheme 2).



The thick foils (2–3 mm), formed during sunlight exposure are flexible and insoluble in water. The clay is not rinsed out from the composite even after hundreds of hours of water treatment. However, the obtained composites do not exhibit good mechanical properties and their improvement requires more research.

ACKNOWLEDGMENT

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