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Radiation effects in polyisobutylene succinic anhydride modified with silica and magnetite nanoparticles

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HIGHLIGHTS

- The oxidation is initiated by the scission of double bonds and the bonds of tertiary carbons.
- PIBSA presents a single oxidation peak in nonisothermal CL spectra.
- PIBSA systems modified with Fe_3O_4 or SiO_2 exhibit two oxidation peaks.
- The oxidation occurred at higher temperatures used by radiolysis radicals.
- The rates of oxidative degradation in PIBSA/Fe_3O_4 are higher as filler concentration increases.

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ABSTRACT

Polyisobutylene succinic anhydride (PIBSA) was modified with nanoparticles of magnetite and silica for the appraising the modification in the thermal stability of organic component after gamma irradiation. Pristine anhydride was loaded with different amounts of nanofiller (1, 2 and 5 wt% of each oxide). Gamma exposure was performed in air at several doses: 10, 20, 50 and 100 kGy. The stability determinations were carried out by nonisothermal chemiluminescence in stationary air atmosphere. The presence of these oxides induces an increase in the oxidation level corresponding to their chemical availability as the filler amounts and exposure doses are enhanced. The oxidation takes essentially place on quaternary carbon atoms and double bonds, which was demonstrated by the presence of two chemiluminescence intensity peaks. The comparative analysis on the radiation oxidation of PIBSA modified with Fe_3O_4 and SiO_2 is presented.

1. Introduction

Polyisobutylene succinic anhydride (PIBSA) is versatile raw compound that adds functionalities, particularly dispersion, to hydrocarbon products (in engine oils, gasoline and greases) used in a wide range of applications (Pucci et al., 2005; Bubálik et al., 2009; Mena-Cervantes et al., 2013). Its capacity of particle coverage allows the preparation of long term colloidal suspensions (Park et al., 2001). The stability of colloidal systems involving surfactants depends on the structural integrity of outer layer, which is affected by the action of external factors like heat and ionizing radiation. The resistance of the thin pellicle formed around volume distributed particles determines the stability of colloidal and the efficiency of particle covering (Vékás, 2004; Reynolds et al., 2010). PIBSA is one of the efficient surfactants used in the preparation of magnetic liquids. However, the nuclear application must take into consideration the double bonds contained in PIBSA molecules (Fig. 1) as sensitive sites to oxidation, when temperature and irradiation dose are growing up.

Magnetic fluids (ferrofluids) belong to the category of smart fluids. They are ultrastable suspensions of nanosize magnetic dipolar particles in appropriate carrier liquids, with which can actually be driven and controlled the particular adjuster devices in pipeline circuits, including pressured cooling fluids in nuclear power plants.

The susceptibility to degradation must be investigated for the qualification of magnetic liquid system behavior during the operation in the field of ionizing radiation. The use of magnetic nanofluids in the sealing of pressured fluid circuits of nuclear power stations requires detailed investigations on the radiochemical strength of surfactants, on which the operation warranty depends on. The accomplishment of improved stability of colloidal magnetite systems

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can be attained by the treatment of solid nanoparticles with polar compounds. They provide an advanced stability by Van der Waals bonds (Vékás et al., 2009).

There are no references on the radiation stability of surfactants for magnetic liquids, namely polyisobutylene succinic anhydride (PIBSA). This paper analyses the radiation stability of PIBSA/Fe_3O_4 and, for comparison, PIBSA/SiO_2 systems, which were investigated in the similar irradiation conditions of low and medium doses.

2. Experimental

Polyisobutylene succinic anhydride (PIBSA, Fig. 1) was provided by Ganesh Benzoplast Ltd., India. Surface coated magnetite nanoparticles were synthesized by chemical coprecipitation according to the procedure described earlier (Vékás et al., 2009). Average particle diameter was 20 nm. Silica nanoparticle powder were delivered by Degussa, as fumed silica, Aerosil 380 with specific surface 380 $m^2\,g^{-1}$, particle diameter range 3–15 nm. They were used as received. Mixtures consisting of PIBSA and 1, 2 and 5 wt% magnetite were obtained by intimate shaking of suspensions. γ-Exposure was accomplished in an irradiation machine (Gammator M 38, USA) provided with ^{137}Cs source in air at room temperature. Dose rate was 0.4 $kGy\,h^{-1}$. This dose is sufficient low for the simulation of accident conditions. The stability measurements were performed on LUMIPOL 3 (Slovakia) by nonisothermal chemiluminescence (CL) procedure on the range of 25–250 °C according with the procedure earlier reported (Rychlý et al., 2009) in stationary air atmosphere. Aliquots of about 2 mg were places on aluminum round trays and dried at room temperature. Heating rate was established at 2 $°C\,min^{-1}$. Because of the proportionality between the CL emission intensities (the emitted photon is the result of falling down of bonded oxygen atoms from excited level onto fundamental level in oxygenated intermediates) the oxidation process can be watched effectively as a process is in progress. The error in temperature measurements is ± 0.2 °C. All samples were measured immediately after the end of irradiation for avoiding any change in the concentrations of oxygenated intermediates with short lifetime.

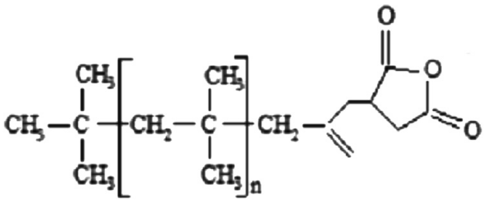

Fig. 1. Structure of polyisobutylene succinic anhydride.

3. Results and discussion

The exposure of organic compounds to the action of ionizing radiation produces radicals by the bond scission of different atoms on susceptible sites, double bonds and quaternary carbon atoms. Their reactions with molecular oxygen lead to peroxyl intermediates, which are emitters of chemiluminescence photons (Zaharescu and Jipa, 2013). The strength of bonds determines the place where molecules are fragmented. In the molecules of polyisobutylene succinic anhydride are two sensible places, where the scission and oxidation may be occurred. The dissociation of PIBSA molecules would be possible in the inner part of isobutylene units, because the bond energy of C–C is low (344 $kJ\,mol^{-1}$) (Pauling, 1972). However, the double bond can be also affected, because π bond is split easier. Similar degradation route was found for the radiation degradation of polyethylene and ethylene–propylene–diene terpolymer (Zaharescu et al., 2013).

The CL spectra recorded on unirradiated PIBSA/Fe_3O_4 and PIBSA/SiO_2 are illustrated in Fig. 2. The two peaks placed about at the same temperatures, 110 and 180–200 °C. These CL intensity maxima are associated with the splitting of PIBSA molecules are broken on two sites according with the energetic conditions. They may be quaternary carbon atoms and unsaturation. This assessment is an extension of the results published earlier concerning the radiolysis mechanism reported on polypropylene (Bernstein et al., 2007). According with the thermal degradation mechanism of polyisobutylene (Sawaguchi and Seno, 1996), primary and tertiary terminal radicals are generated as *t*-butyl and *i*-propyl intermediates. In pristine polyisobutylene they are decayed to polymeric structures, terminal trisubstituted double bond or terminal vinylidene double bond compounds and polymer. In the presence of nanoparticles, radical intermediates are adsorbed being released at higher temperatures.

There are some differences between these two types of mixtures:

- The emission intensities recorded for the PIBSA/SiO_2 samples are higher than the corresponding figures for PIBSA/Fe_3O_4. Silica particles form O–Si–O bonds, being jointed to the oxygen atoms belonging to product carbonyls (Tanaka, 2005) with an effect on slight compound stability. Magnetite behavior proves the interaction between iron atoms from filler and oxygen atoms from PIBSA.
- The increase in the concentration of filler brings about a larger differences between thermal stability of nonirradiated formulations (Fig. 2). They contain magnetite which may be depicted as more aggregated systems relative to the formulations consisting of PIBSA and silica nanoparticles. The dissimilar behavior noticed in the concentration effect of inorganic fillers is revealed not only in the different emission intensities corresponding to similar

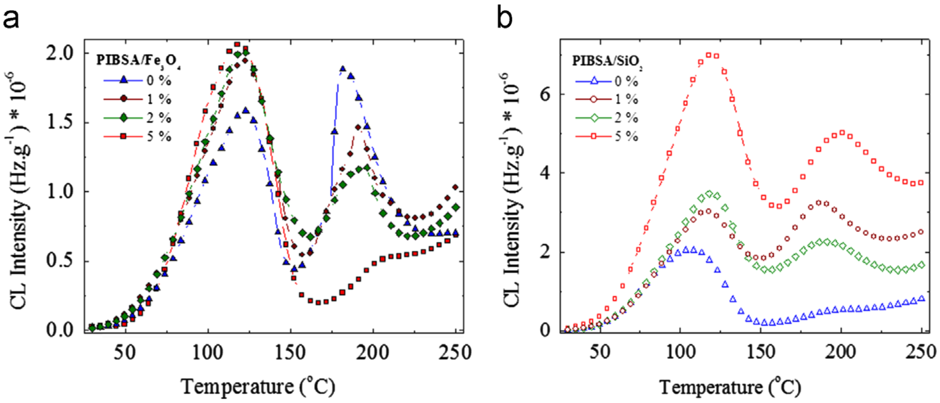

Fig. 2. Nonisothermal CL spectra recorded on unirradiated PIBSA loaded with Fe_3O_4 and SiO_2.