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HIGH ENERGY RADIATION EFFECTS ON PET INSULATORS

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Abstract

The effects of high energy exposure of polyethylene terephtalate, the main electrical insulator for the conduction bars in alternative current generators, is presented. For comparison γ-irradiation was performed in distilled water and air at various doses, up to about 200 kGy. The dependencies of current on time for radiation processed PET sheets allow to depict the variation in the resistivity values as a measure of chemical changes in polyethylene terephtalate macromolecules. The comparison between the evolution of currents in irradiated specimens brings about a light on the accumulation or radiolysis product in PET matrix. The high energy exposure of PET in air causes an increase of final value of current, while similar experiments in water produces a contrary effect. Some considerations of degradation mechanism are presented.

1. INTRODUCTION

Polymer dielectrics are the most widespread materials used for manufacture of a large variety of electric and electronic devices and equipments. PET has gained various applications from parcel strapping and recording tapes to photographic, photoresist films for the manufacture of printed microcircuits and the manufacture of various electrical equipments. Other service areas include dielectrics in capacitors, motor and generator insulation, membrane touch switches, liquid crystal display laminations, and wire and cable insulation. In the field of polymer dielectrics a great attention has been focused on the most representative polyolefins (polyethylene [1-3], synthetic rubbers [4-6]) because they are preferred in the manufacture of electrical insulations of wires and cables. Polyethylene terephtalate received a special concern because its application area is still limited. There are few general papers that treat the behaviour of polyethylene terephtalate in high energy radiation fields [7-12].

Because polymer materials are extensively used as parts of safety systems of nuclear power plants or alternative current generators and it would be quite difficult and expensive to replace, the degradation process has to be understood in detail [13]. It will not be possible to evaluate the lifetime of any equipment where polymers are employed, if severe tests are not performed.

Mansour and Ikladious [14] studied depolymerization of PET under thermal conditions specifying the high resistance of this polyester to the sustained action of high energy agents (heat, radiation). The complexity of final composition demonstrates that the scission of polyethylene terephtalate generates several other polar compounds starting from initial structure (polyester configuration) or as the result of strong attack of oxidant environment.

Polymer coatings used in electrotechnics, like polyethylene terephtalate, must be studied under different operation conditions simulating emergency conditions, because the influence of service environment determines the level of structural modifications. On the range of radiation action, polyethylene terephtalate is not exhaustively qualified [15]. The understanding of modification sense for electrical behaviour depends on the operation parameters like temperature, electrical range, humidity, etc [16].

2. EXPERIMENTAL

Polyethylene terephtalate sheets (electrical grade) were cut into several circular specimens to present suitable shape for current measurement equipment. For each set of irradiation conditions there were investigated five samples. Each representative curve is the result of averaging the five dependencies of the same kind of processed set. The exposure of PET patterns to γ-rays was accomplished at room temperature in GAMMACELL irradiator provided with ^{137}Cs source. Two series of identical polyethylene terephtalate samples were processed in air and distilled water. Dose rate was 0.4 kGy/h. This dose rate is suitable for degradation of polymers, because the concentration of reactive intermediates is not sufficient high for placed them closed to each other avoiding electrical interaction. After the elapse of irradiation time, the specimens were subjected to electrical measurement, the dependence on current on investigation time. Keithley electrometer (United Kingdom), type 6517 at 500 V working tension coupled to a computer for automatic data acquisition was used for evaluation of current due to the movement of spatial charge in radiochemically modified PET.

3. RESULTS AND DISCUSSION

Due to their excellent electrical insulating and satisfactory physical and mechanical properties, polyethylene terephtalate (branded as Mylar or Melinex) offers a variety of applications. [17]. The light changes in initial characteristics of electrical insulator during continuous service recommends this material as a proper dielectric in the certain voltage range.

The presence of oxygen in the irradiation area accelerates the degradation of polymer substrate because the mobility of oxygen increases the reaction probability of free radical. Polyethylene terephtalate belongs to the radiation-degradable polymers and the effect of bond scissions may be assessed by current measurements. The polar products and the residual charge that remains in high energy irradiated material after strong trapping of electrons contribute to the electrical conduction of radiochemically degraded PET. Figure 1 presents the linear dependency of initial changes values for various polyethylene terephtalate samples irradiated in air. The differences between the four curves recorded for PET films exposed to various γ-doses consist of (a) the different initial value of current, (b) the rate of diminution in measured current, and (c) the different final current, which is attended at equilibrium (long period elapsed for total depletion of charge). These peculiarities illustrate the gradual degradation of polymeric material and the rapidity of recombination when the separation distances between opposite charge are shorter. A longer exposure to γ-rays would generate simultaneously charge and traps, which disappear faster after the application of driving tension. Electrical insulators will be damaged not only by shape and integrity modifications, but also by creation of localised charge on polar radiolysis products (in our paper, ketone structures).

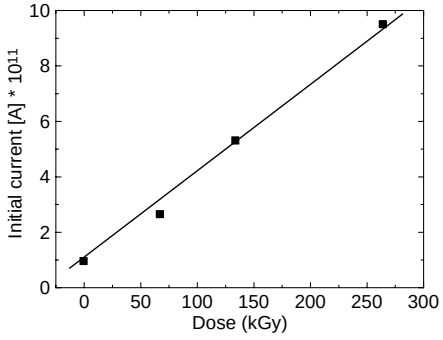

Fig. 1 Dose dependence of initial measured current for PET samples.

Irradiation in aqueous environment PET is subjected to hydrolysis produced by radiolysis product of water. They attack polymer macromolecules is performed by $HO_2^{\cdot}$ and atomic hydrogen. The transformations of dimethylene unit into an unsaturated structure or ketonic group in alcoholic moiety by abstraction of hydrogen are the specific steps of degradation that do not occur in the irradiation in air. Consequently, the behaviour of polyethylene terephtalate differs in function on the surroundings of polymer during irradiation.

Figure 2 presents the modifications induced during γ-exposure of polyethylene terephtalate in water relative to control. It may be noticed that the measured current decreases with about one order of magnitude. The comparison between the decrease in current values for control and irradiated samples it may be learn that water induces less prominent effects than air. In fact, the reaction between two hydroxyl functions diminishes the availability of protons for conduction. Thus, the growth in PET resistivity involves the consumption of more polar moieties. The unsaturated fragment that is formed by abstraction of hydrogen due to reactive intermediates of water may react with alcoholic unit. This pathway is an alternative source of ketones, less polar than alcohols.

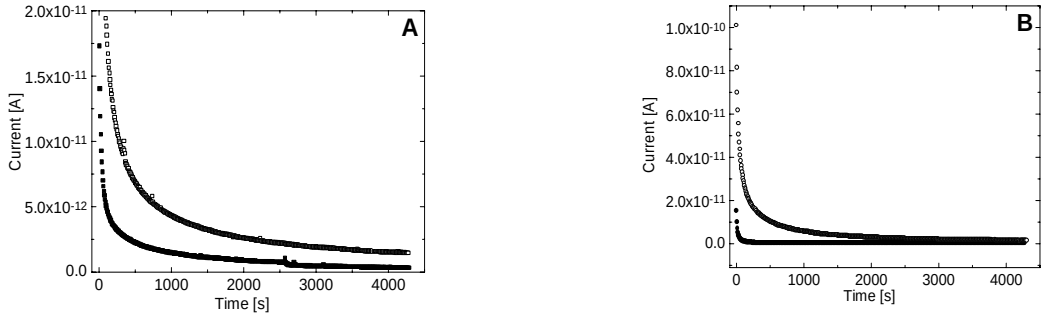

Fig. 2 Dependencies of current values on measuring time for PET samples irradiated in water. Hollow marks: unirradiated samples; solid marks. (A) 67 kGy; (B) 210 kGy.

The spectral investigation on polyethylene terephtalate irradiated in water and air over the region 3800-3200 cm^{-1} revealed the faster accumulation of carbonyl units in comparison with the buildup of alcohols. The maximum absorbance placed at 3400 cm^{-1} remains practically constant in spite of the generation of alcoholic groups during radiolysis. It seams to be appropriate the assumption on the equivalency between the rate of formation and of decay for alcohol units. Similar hypothesis on carbonyls can not be launched, because the progress of radiochemical degradation of PET takes place by the conversion of a part of hydroxyl function into carbonyl part of polymer molecule.

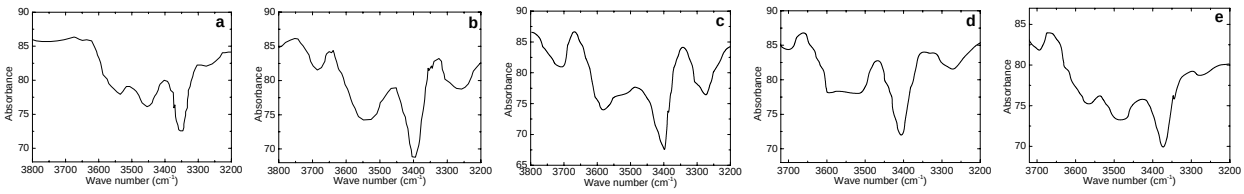

Fig. 3 IR spectral records for various PET specimens: (a) unirradiated, (b) irradiated in air at 70kGy, (c) irradiated in air at 140 kGy, (d) irradiated in water at 70 kGy, (e) irradiated in water at 140 kGy.

Similar results were reported on poly(vinyl alcohol)/poly(vinyl acetate) system which was irradiated in water [18]. The pulse radiolysis performed by von Sonntag et al [19] has

emphasised the significance of radiochemical conversion of polar group, namely the accumulation of carbonyl groups in the detriment of hydroxyl funtions.

4. CONCLUSION

This study illustrates the general concern on dielectric properties of PET proper selection of electrical insulators. The accelerated degradation demonstrates the capability of polyethylene terephtalate to exhibit higher resistance in aqueous environment than in air. However, there is a real possibility to avoid advanced degradation by adding an appropriate additive, which would be able to react with hydroxyl groups. The improvement in electrical resistance represents the main condition for longer period work under severe stress. It would be achieved either by addition of an efficient radical scavenger, or by limiting radiation effects due to the action of stabilisers. The intermediate reactions indicate the route on which material is degraded, and the restrictions imposed to dielectrics must be connected by the presumable accidents.

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