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Chemiluminescence study on the endurance of ethylene-vinylacetate (EVA) under radiation and thermal degradation

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Ethylene vinylacetate copolymer is largely used as electrical insulation material in nuclear applications. Synergistic effects of radiation and heat on the degradation of EVA was investigated. The chemiluminescence procedure at three temperatures exceeding 200^{0}C for kinetic characterization of oxidative degradation was applied. The co-operative factors for radiation and thermal degradation were calculated for polymer samples after energy transfer by irradiation with accelerated electrons and heating. The modifications occurred in the thermal resistance were discussed on the free radical formation. The subsequent thermal treatment will carry on the stimulated oxidation between radical intermediates. The cumulative doses induce fast degradation as the result of high concentration of reactive intermediates.

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1. Introduction

The use of polymer material in nuclear applications requires a detailed approach on the radiochemical modifications induced during their service [1-3]. The degradation of such components is therefore of considerable interest, generating a large number of studies worldwide. In the radiation field, polymer items are subjected to various degradation agents, namely ionizing radiation, heat, mechanical charge, which are always accompanied by the chemical action of oxygen.

The prediction of long period behaviour has to be based on the evaluation of material stability, which determines the safety considerations on the nuclear equipment. The life of cables, seals, gaskets, diaphragms, coatings depends strongly on the intensity of radiation, the duration of exposure and the environmental conditions. Many reports on the radiation effects on nuclear-interesting polymers has been published [4-10], because unlike materials and working conditions can be involved.

The exposure of polymers to ionizing radiation modifies the thermal resistance of material, because some weaker bonds are split and, subsequently, reactive radicals are formed. They are involved in different further reactions, which change the operation life. The presence of oxygen worsens the material confidence under their complex functional duty in radiation field. Oxygen restricts the crosslinking of irradiated polymer by the reaction with free radicals through a chain process [11].

Chattopadhyay et al [12] investigated the modification in mechanical properties of ethylene-vinylacetate copolymer and they found that EVA can be crosslinked with various vinyl compounds which prevent degradation during electron beam processing. Other method for avoiding the alteration of oxidation stability is the addition of suitable antioxidant, which blocks free radicals to promote oxidation [13].

In this paper, we present the synergistic effect of radiation and heat on the thermal stability of ethylene vinylacetate copolymer.

2. Experimental

This study was performed on ethylene vinylacetate based compound (FRANGOM P/1) provided by SACOM Parma (Italy). Its main characteristics (density 1.5 g.cm^{-3}, flow index 21 g/10 min @ 21.8kg and 190 ^{o}C) allowed to prepare plaques by pressing of material for 10 min at 180 ^{o}C and 150 atm.

EVA specimens were irradiated with 2 MeV electron beam provided by ILU 6M (Russia) accelerator. The irradiation doses were 12, 30, 60 and 90 kGy. Heart treatment was accomplished in an air-circulating oven at 120^{0}C for 72 and 125 h.

Chemiluminescence measurements were carried out under isothermal procedure at 200, 210 and 220^{0}C with oxyluminograph OL 94 (ICPE Romania). The details on equipment, procedure and the determination of kinetic parameters for material oxidation have been previously reported [14].

3. Results and discussion

The dependencies of the degradation level on time for three temperatures reveal the progress in the thermal resistance of irradiated ethylene-vinylacetate copolymer. Fig. 1 is an example for all irradiation doses, at which EVA samples were subjected. The decay of long-life radicals that remained after irradiation may be noted on the first step of measurements, namely on the first 35 minutes. Because of higher instability at elevated temperatures, the oxidation induction time becomes shorter as the temperature increases. The material durability, which is depicted by the values of oxidation induction time decreases either due to the higher amount

of oxidation initiators (peroxyl radicals), or due to the light modification in the material structure. The severity of material ageing is in a tight connection to the received dose, to the applied pre-treatment or to the dose rate [15]. For EVA copolymer, the applied irradiation causes an advanced degradation by the macromolecular breakdown.

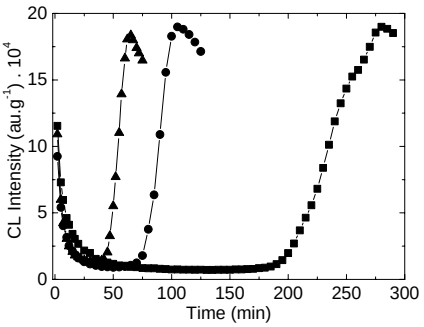

Fig. 1. The time dependency of CL intensity for irradiated EVA copolymer at 12 kGy. Measurement temperatures: (■) 200 °C; (●) 210 °C; (▲) 220 °C.

The variation in the values of temporal kinetic parameters for irradiated and heated EVA specimens points out the synergistic effect of the two types of energetic treatments. The differences between the thermal behaviour of EVA samples irradiated at the same doses, but heated for longer time at the same temperature (Figs. 2 and 3) emphasize the contribution of heating to the acceleration of degradation. The most significant effect of this pair of treatment would be obtained, if the simultaneous actions (irradiation and heating) will be done.

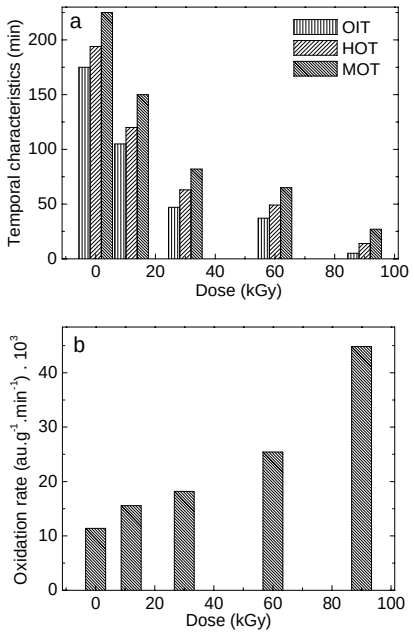

Fig. 2. (a) Temporal parameters and (b) rate of oxidation calculated for irradiated EVA samples and subsequently heated at 120 °C for 120 h. Testing temperature: 200 °C OIT = oxidation induction time; HOT = half-oxidation period; MOT = maximum oxidation time.

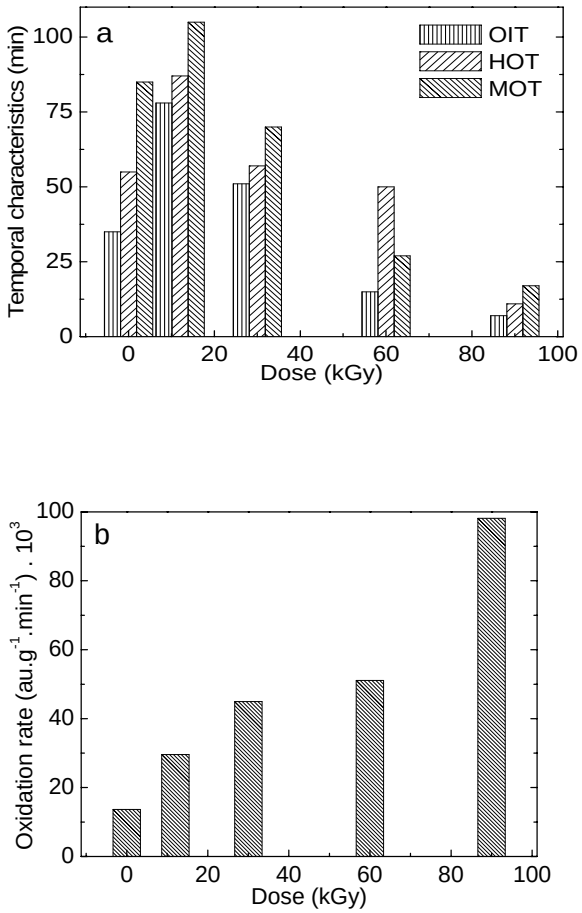

Fig. 3. (a) Temporal parameters and (b) rate of oxidation calculated for irradiated EVA samples and subsequently heated at 120 °C for 120 h. Testing temperature: 210 °C Temporal parameters have the same meanings as in Fig. 2.

The comparison between the kinetic parameters, which depict the ageing of EVA by radiation and by double treatment (radiation and heating), points out the progress in the material degradation under multistress processing. The formation of reactive intermediates due to the energy transfer on the polymer macromolecules, followed by backbone scission is the reason for accelerated oxidation during thermal ageing. Along the propagation step, when free radicals are consumed, the co-operative factors decrease as the process advances (table). In addition, for the low dose irradiation that provides lower amount of free radicals than happens for other higher doses, the thermal treatment of irradiated ethylene vinylacetate samples confers a somewhat higher stability, because the intermediates are preferentially recombined to each other. However, EVA is practically suitable for the equipment components that are not subjected to high irradiation doses.

Table. Co-operative factors for the synergistic effect of radiation and thermal ageing.

Dose (kGy)	Co-operative factors*			
	Treatment: 72h @120^{0}C		Treatment: 125h @120 ^{o}C	
	from oxidation rate	from maximum intensity	from oxidation rate	from maximum intensity
12	1.21	0.32	1.51	0.99
30	1.68	0.69	1.63	1.04
60	2.51	1.29	1.84	1.10

*the ratio between the kinetic parameter for simultaneous action of stressors and the sum of the same parameter obtained for individual treatment

The synergistic effect of radiation and heat that is happened during long term irradiation in nuclear reactors is the consequence of the competition between the generation and the consumption of free radicals. The greater contribution of thermal degradation is explained by the larger possibility of movement due to the higher kinetic energy of free radicals and, consequently, the higher probability of collision with oxygen molecules. The influence of experimental conditions plays an important role on the operation conditions and on the material durability [16].

However, at low irradiation doses like the values we had selected, the material degradation would occur at lower rates, if the environment temperature is significantly decreased. The temperature of 120 ^{o}C does not meet in minor accidents, so that the present information is useful for the usage of EVA for electrical cables in the areas with light exposure conditions.

4. Conclusions

EVA copolymer may operate satisfactorily under low dose irradiation, even though heat is involved in the material degradation. The superposition of radiochemical and thermal ageing accelerates the oxidative degradation, if elevated temperatures are applied. The environmental qualification of polymer materials for their use in nuclear power plant must to take into account the synergistic effect of the two main stressors: radiation and heat.

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