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Radiation processing of EPDM/PP blends

Thermal effect of low dose irradiation

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Summary

The effect of ionizing radiation on thermal oxidation of ethylene-propylene copolymer/polypropylene (EPDM/PP) was evaluated over the range of total gamma doses up to 250 kGy. The influence of irradiation dose on oxidation induction periods was investigated by oxygen uptake and thermal analysis on polymer samples containing various concentrations of components (100/0, 80/20, 40/60, 60/40, 20/80 and 100/0 w/w). Drastic decrease in oxidation induction time was observed for low doses. The competition between crosslinking and scission has been examined on the basis of radical recombination on post-irradiation time. The influence of specimen formulations on oxidation induction time is discussed regarding to the contribution of antagonistic processes: crosslinking and oxidative degradation.

Introduction

The interest focused on radiation processing of polymers is found in carrying out several studies on mono and polycomponent systems [1-10]. The understanding of radiochemical phenomena requires not only endurance investigations when large irradiation doses are applied; short exposures must be selected for learning different effects of scission and crosslinking.

Complex description on the interaction between high energy radiation and polymers can be found elsewhere [11,12]. The formation of free radicals by several scissions of weaker bonds creates intermediates for subsequent processes namely recombination, disproportionation or oxidation. Conditions under polymeric materials have to be investigated regarding the influence of these reaction rates.

It is generally accepted that ethylene-propylene elastomers show significant resistance to the action of ionizing radiation [12,13]. Their radiochemical behavior is similar to polyethylene. On the opposite site irradiation of polypropylene in air induces oxidation because of great proportion of tertiary carbon atoms. In fact, radiochemical oxidation starts with reaction between free radicals and molecular oxygen that exists or penetrates material by diffusion process. The extension of oxidation depends on the lifetime of radicals, the time of exposure and the temperature of radiolysis. General mechanism of polyolefin oxidation was proposed by Bolland and Gee [14] for thermal degradation of these polymers but it is usually adopted for high energy irradiated polyolefins. The main reactions occurred under irradiation are gathered in figure 1.

Initiation

$RH \longrightarrow R^{\cdot} + H^{\cdot}$

Propagation

$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$

$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$

$ROOH \longrightarrow RO^{\cdot} + {}^{\cdot}OH$

$2\,ROOH \longrightarrow ROO^{\cdot} + RO^{\cdot} + H_2O$

Transfer

$RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot}$

$HO^{\cdot} + RH \longrightarrow H_2O + R^{\cdot}$

Termination

$2\,R^{\cdot} \longrightarrow R - R$

$ROO^{\cdot} + R^{\cdot} \longrightarrow ROOR$

$2\,ROO^{\cdot} \longrightarrow ROOOOR$

$ROOOOR \longrightarrow R'OH + R''R'''C{=}O + O_2$

Figure 1. Scheme on mechanism of radiation induced oxidation in polyolefins

Oxidative degradation can never be entirely eliminated because molecular oxygen is present in the majority of environmental conditions. Technological application of this class of polymers in the radiation processing field must take into account the consequences of oxygenated products accumulated during the start step of irradiation on material stability.

In the present paper the authors have intended to prove the importance of starting stage of irradiation on sample history by thermal assessment of low dose processing of EPDM/PP systems.

Experimental

Materials and sampling

Ethylene-propylene-diene terpolimer (EPDM, Terpit C®) and polypropylene (injection type, F 401®) were provided by ARPECHIM Piteşti (Romania). The main characteristics of elastomer were presented earlier [9]. It has to be mentioned that the elastomer contains 3.5 % ethylidene norbornene. Polypropylene has flow index 3.5 g/10 min [230^{0}C and 2.16 kg]). Plaques with various formulations (100/0, 80/20, 60/40, 40/60, 20/80 and 0/100 w/w) were pressed at 180^{0}C and 150 atm; small and uniform chops were cut from these specimens.

γ-Exposure was performed in air and room temperature in a GAMMACELL (USA) irradiation machinery by means of ^{137}Cs source at a dose rate of 0.54 kGy/h. Portions were taken off when certain doses were attained (6, 12, 30, 50, 105, 160, 250 kGy). The radiation processed specimens were investigated promptly after the end of γ-exposure.

Experimental procedures

Thermal stability of irradiated chops was assessed by two complementary procedures: thermal analysis and oxygen uptake. These methods can provide useful information on the kinetics of thermal oxidation of low dose effect on the subsequent resistance in relation with sample formulation and operation temperature range. The measurement errors for both methods were less than ± 1%.

Thermal analysis.

Thermal analysis curves (TG, DTG and DTA) on polymer samples were recorded with a Q-1500D (MOM, Budapest) Paulik-Paulik-Erdey derivatograph in static atmosphere on the temperature range 20 – 500^{0}C. The heating rate was 2.5 K.min^{-1}.

Oxygen uptake

The equipment used for thermal oxidation investigations is a laboratory made device presented in a previous paper [15]. Small pieces of irradiated samples were placed on round and thin aluminum plates. All oxygen uptake determinations were performed under isobaric (air at normal pressure) and isothermal (165^{0}C) conditions. These parameters were preferred to obtain accurately measured values of oxidation induction times for advanced irradiated samples.

Results and discussion

Different types of degradation processes involve reactions between organic free radicals and molecular oxygen. In the case of radiation exposure the competition between the generation of radicals and their depletion by oxidation plays an important role on the history of irradiated elastomer specimens. Radiation oxidation mechanism of ethylene-propylene rubbers presented in a previous paper [16] starts with the attack of molecular oxygen on radicals. On the beginning of irradiation the concentration of reactive intermediates is low but the amount of peroxy radicals becomes enough for sustaining propagation process.

Thermal analysis of present polymer blends consists of TG, DTG and DTA curves; for exemplification figure 2 depicts curves which were obtained for unirradiated sample containing 40 % EPDM. The DTA curve displays a first-order phase change at minimum point I characterized by the temperature T_m. At higher temperatures sample undergoes an exothermal change (peak II on the DTA curve) accompanied by a slight increase in weight. This process starts at temperature T_i. The exothermal peak corresponds to the thermo-oxidation of sample and some solid products, probably hydroperoxides are formed due to the attack of oxygen on the active carbon sites on macromolecular chains. Increased temperatures will promote progressive degradation accompanied by generation of volatile products [17]. Similar TG, DTG and DTA curves were obtained for unirradiated and γ-exposed EPDM/PP compositions. The unirradiated and γ-exposed EPDM samples exhibit the exothermal peak II, but it does not show the endothermal peak I.

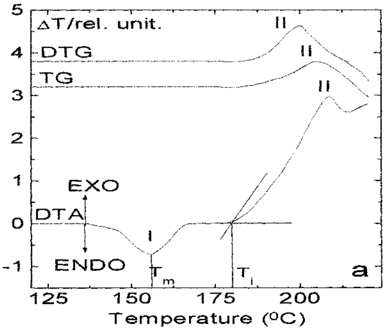

Figure 2. TG, DTG and DTA curves recorded for unirradiated polymer mixture EPDM:PP=40:60 (w/w)

Termo-oxidative degradation characterized by two kinds of oxidation processes, one accompanied by weight increase, and the other by release of volatile products was earlier reported in connection with investigation on polymeric materials [17-26]

Figure 3 shows the modification of characteristic temperatures for two randomly selected samples, namely EPDM 100% and EPDM/PP=20/80. The analysis of all thermograms recorded for samples reveals the sharp decrease in T_i and T_m values.

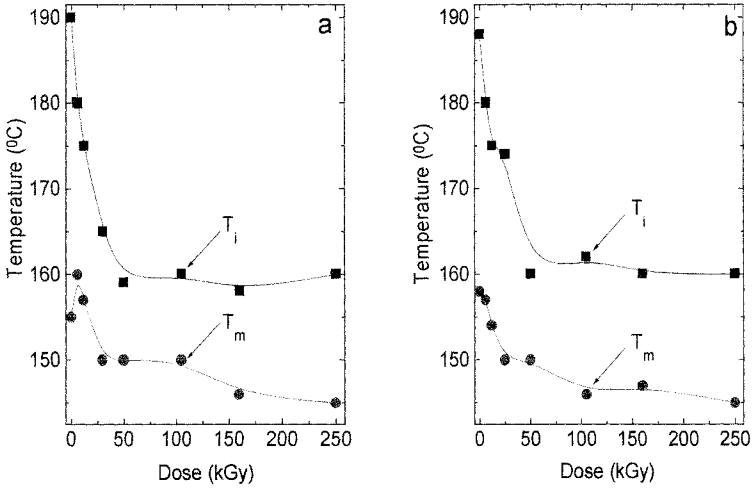

Figure 3. T_i and T_m values for (a) EPDM/PP=0/100 and (b) EPDM/PP=20/80 specimens vs irradiation doses.

Oxygen uptake determinations can illustrate the thermal stability of analyzed sample by accumulation of $RO_2^{\cdot}$ (figure 4).The first stage of curve (the horizontal potion) proves that the sample is thermally stable and sample does not consume any amount of oxygen. During this oxidation induction time peroxyl intermediates are formed in measureless quantity. The ascendant region of curve proves the propagation chain of oxidation. It is generally accepted that the intercept of tangent drawn to this portion of oxidation curve with Ox axis denotes oxidation induction time.

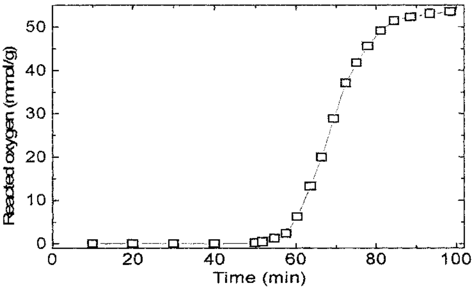

Figure 4. Dependence of consumed oxygen on degradation time for unirradiated EPDM @ normal air pressure and 195°C

The same drastic diminish in oxidation induction times was also pointed out by oxygen uptake on the dose range of 0 – 50 kGy. In addition first order dependence of oxidation induction time on sample composition is presented in figure 5. Similar feature was obtained by studying gel fraction modification [26].

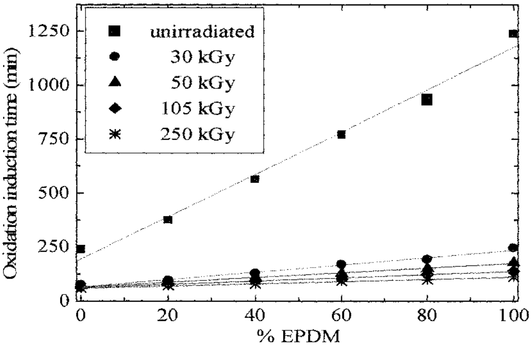

Figure 5. Changes in oxidation induction time for various compositions of EPDM/PP blends

As it was earlier reported in the case of unprocessed and irradiated ethylene-propylene terpolymer [24] the abrupt decrease in thermal parameter of degradation can be explain by the competition between crosslinking and scission, on one side, and crosslinking and oxidation on the other side. If unirradiated material provides free radicals at low rate and, consequently, the oxidative degradation of polymeric material takes place slowly, γ-exposed samples will be modified at significant higher rate because of greater volume concentration of radicals. The simultaneous occurrence of crosslinking and oxidation is proved by the similarity between the shift of starting oxidation temperature, T_i, and melting temperature, T_m, at increasing dose. The largest modification in oxidation induction period was detected over the low dose range (up to 50 kGy). If the irradiation doses exceed 50 kGy T_i remains practically constant in spite of the fact that melting temperature decreases with dose.

Physical modification of sample state by melting process followed by oxidation at moderate temperatures and expelling volatile products at higher temperature was studied extensively on polymer systems [21-25]. If samples are subjected to the action of high energy radiation these structural and physical alterations show different thermal characteristics. Short irradiation when samples receive doses of 6 and 12 kGy are favorable to crosslinking. In figure 6 it can be noticed that end induction temperature increases with elastomer content.

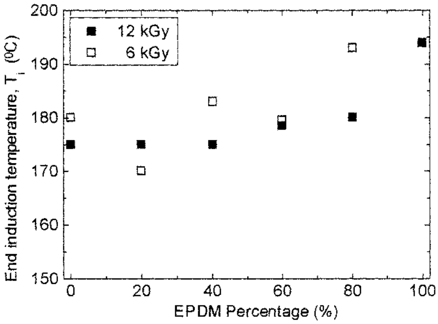

Figure 6. Modification of oxidation induction time with sample composition at two low irradiation doses.

The doses less 50 kGy, the gel dose for EPDM [13] does not stimulate the formation of insoluble fraction. It means that the low concentration of radicals will influence the low recombination probability. Reaction between free radicals and O_2 becomes predominant process. Because polypropylene is radiation-degraded polymer in air this component provides radicals more easy than ethylene-propylene terpolymer that behaves as radiation-crosslinked polymer [11]. As irradiation dose increases the amount of transferred energy is higher and the susceptibility of studied blends grows followed by relative stabilization. The asymptotic decrease in thermal parameters of oxidation time (for example, figure 3) provides larger contribution of crosslinking in the detriment of degradation. Polypropylene acts as the main radical source because it contains tertiary carbon atoms. Radical entities yielded from polypropylene are firstly depleted at low irradiation doses. At higher dose radicals are generated simultaneously by the both components of mixtures. Grafting various radicals on terpolymer backbone molecules will modify samples containing higher proportion of elastomer. The crosslinked portion of irradiated samples will reduce melting temperature while the oxidized radicals will promote degradation. The proportion between the recombined and degraded part of polymer will determine the post-irradiation history of material

Conclusions

Main modifications in the structure and thermal characteristics of high energy irradiated EPDM/PP blends happen at low doses. Melting temperature and end induction temperature are influenced either by exposure dose or by sample formulation. The competition between crosslinking and oxidation changes thermal behavior of materials. While a sharp decrease in oxidation induction time and melting or start oxidation temperatures can be remarked at low doses (less than 50 kGy, gel dose for EPDM), constant values of these properties will be revealed over higher dose range.

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