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Free Radicals in Plastic Food Containers

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Free radicals in polymers are produced during synthesis and interaction with catalysts, initiator of chemical reactions, fillers, stabilizers, and other substances which as chemically or physically active remain dissolved in condensed phase of final product. Also γ irradiation causes both immediate and time dependent changes which arise from the presence of long living free radicals. The free radicals can decay only *via* a convenient transport mechanism. The decay of free radicals can proceed only if two radical centers approach each other within an appropriate distance. Different preparations of polymers as: filler admixture, γ irradiation, annealing and ageing are discussed in term of free radical production, presence, transformation and decay.
Keywords: free radicals, EPR, polymer, γ irradiation.

1. INTRODUCTION

In the course of polymer fatigue, significant changes in the order of chains appear [1]. These changes influence the molecular dynamics of polymers. Because of free volume redistribution, some degrees of freedom of motion arise or disappear. The free radicals can decay only via a convenient transport mechanism. The decay of free radicals can proceed only if two radical centers approach each other within an appropriate distance. A great variety of molecular motions depending on temperature, pressure and chain order, are manifested in polymers. A small change in molecular dynamics may have a considerable influence on the kinetics of free radical decay.

The free radicals selectively generated by gamma radiation can thus serve as molecular labels for monitoring the changes in molecular motion due to the fatigue of a polymer [2]. The free radical decay of irradiated polymers is controlled by segmental movements of macromolecular chains. Therefore, the rate constant of free radical decay provides information about the molecular dynamics of the examined polymer system. Polymers filled with inorganic fillers show significant changes of mobility of molecular segments. Free radicals located on the polymeric chains can react with neighbouring segments only if the mobility state of chains is sufficient. Most physical methods for studing the properties of polymer composites give indirect information about the molecular dynamics of the system. Electron Paramagnetic Resonans (EPR) method to study free radical decay provides information about polymer – filler interactions unavailable by other methods. Irradiated polymer samples show a composite EPR spectrum. During the course of free radical decay the form of the EPR spectrum does not practically change.

Purpose of this article is to consider different preparations of polymers as: filler admixture, γ irradiation, annealing and ageing in term of free radical production, presence, transformation and decay.

2. MECHANISMS OF FREE RADICALS PRODUCTION AND DECAY

2.1. POLYMER FILLER

Addition of inorganic filler to the polymer slows down rate of the decay of free radicals. Rapid decrease is observed in the region of low filler concentration (up to 10 mass %). Adding inorganic filler to crosslinked polymer slows down rate of the decay much more. The polymer crosslinked itself results in a significant reduction of segmental movements of polymer chains and decrease of the decay rate of the macroradicals [3]. Migration and free radical decay take place in the amorphous phase. The movement of a radical centre has intermolecular character. The free radical centre is transferred to the neighbouring segments till it meets another radical centre and decays. In filled polymer an amorphous interphase is formed on the surface of the inorganic filler. In this layer of interphase the segmental movements are limited. The simultaneous action of two retarding factors results in a pronounced decrease of the rate constant of free radical decay in a modified structure of polymer because of the formation of both crosslinks in the amorphuos phase and a polymer interphase with reduced mobility of the chains.

The fact that free radical decay is controlled by segmental movements, is proved by high – pressure measurements. In the series of gamma – irradiated polymers it is observed the dependence of the rate constant of free radical decay on external pressure [4]. The applied high pressure leads to a free volume reduction in polymer, thus preventing the movements controlling the transport of macroradical centres. The kinetic study of the macroradical decay rate in filled or crosslinked – filled polymer shows that studies of free radical behaviour can provide partial information about molecular dynamics of polymer chains at the polymer – filler interface. The interphase properties depend on intermolecular polymer – filler interactions, as well as on the structural arrangement of the layer.

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2.2. LONG TERM STABILITY OF THE POLYMER AFTER γ IRRADIATION

Food irradiation treatment is highly efficient in avoiding undesirable phenomena such as sprouting and contamination by poisoning bacteria. With the aim of decreasing the occurence of food disease and delaying the growth and ripening of fruits and vegetables, radiation is used to kill cells and to alter the enzyme activities in food. Depending on the desired effect, the dose of food irradiation is associated with a typical range: from few kGy (sprout inhibition) up to tens of kGy (sterilization) [5]. Most foods are subjected to irradiation treatment after they have been packaged. Hence, in order to reveal possible interactions between the packaging, the food and the radiation, it becomes crucial to study the effects of radiation on both the food and the packaging.

Also interest in the effects of γ irradiation on polymers has been provoked by concern about the consequences of the sterilizing procedures employed when the material is used in medical implants. γ irradiation causes both immediate and time dependent changes in the mechanical properties and there is considerable experimental evidence that the time dependent effects arise from the presence of long lived free radicals. Chain scission processes occur both during and after irradiation, leading to release of inter – lamellar tie chain material which then causes an increase in crystallinity. Mechanical changes can be closely related to the crystallinity increase and are of considerable importance in property critical applications such as medical prostheses.

In addition to the medical device concerns there is also continuing general interest in the consequences of high energy radiation on the long term stability of polymers. Whether the species responsible for the scission processes in irradiated polymer are the primary products of irradiation, or are products which arise as a result of further reaction remains uncertain but details of their identity are of importance to attempts to produce more stable grades of irradiated polymer.

Analysis of polyethylene by EPR has established, with reasonable confidence, the identity of the types of carbon radicals formed by absorption of high – energy radiation:

– the alkyl free radical, $\sim CH_2–\dot{C}H–CH_2\sim$;

– the allyl radical, $\sim CH_2–\dot{C}H–CH=CH–CH_2\sim$;

– the polyenyl radical, $\sim CH_2–\dot{C}H–(CH=CH–)_n–CH_2\sim$.

Seguchi and Tamura [6] reported that when polyethylene is irradiated in air at room temperature the spectra recorded could be attributed to alkyl radicals with a contribution from peroxy radicals and they presumed that allyl radicals were not observed because they react rapidly with air at the temperature of their experiments.

Matsuo and Dole [7] proposed the following reaction sequence for the oxidation of alkyl radicals.

$$\sim CH_2–\dot{C}H–CH_2\sim + O_2 \xrightarrow{(1)} \sim CH_2–\underset{\displaystyle O–O^{\cdot}}{\underset{|}{CH}}–CH_2\sim$$

$$\sim CH_2–\underset{\displaystyle O–O^{\cdot}}{\underset{|}{CH}}–CH_2\sim + \sim CH_2–CH_2–CH_2\sim \xrightarrow{(2)}$$

$$\sim CH_2–\underset{\displaystyle OOH}{\underset{|}{CH}}–CH_2\sim + \sim CH_2–\dot{C}H–CH_2\sim$$

$$\sim CH_2–\underset{\displaystyle OOH}{\underset{|}{CH}}–CH_2\sim \xrightarrow{(3)} \sim CH_2–\underset{\displaystyle O}{\underset{\|}{CH}}–CH_2\sim + H_2O.$$

In the raction (2) free alkyl radical is regenerated to that reaction (1) and (2) occur as chain reactions. This reaction sequence fits the observations in the presence of oxygen if the rate at which peroxy radicals are produced from alkyl radicals is very high and if reaction (3) is the slow step in the production of carbonyl groups. The growth in carbonyl concentration, consequent on reaction (3), is readily observed using FTIR [8] and it might be considered likely that the reaction scheme given above describes the ageing process.

2.3. ANNEALING OF THE POLYMER

Annealing of the polymer does reduce the concentration of radicals. The type and concentration of remaining radicals depends on the duration and conditions of annealing. Following 24 h annealing in air at 360 K (87 °C) only a small amount of peroxy radicals remained within the sample and these had almost completely disappeared after 1-week annealing. Effectively the material is stabilised. In contrast, following 24 h of annealing in vacuum at 360 K about 10 % carbon radicals remain in the sample. A small concentration of peroxy radicals is present, probably as a result of the reaction of oxygen incorporated in the polymer during processing, although reaction with residual oxygen in the vacuum oven may contribute too. Some peroxy radicals are still present in the material following 1-week of vacuum annealing, but by this stage all of the carbon radicals have disappeared.

When sample are annealed in both atmospheres at 360 K for 24 h and allowed to age 2 month following annealing it is found that, during the ageing period, little change occure in the small number of peroxy radicals. During ageing of the vacuum annealed sample, most of the alkyl radicals which had survived the 24 h annealing process, have been oxidized and an enhanced peroxy radical spectrum resulted.

Annealing is effective in decreasing the number of radicals by two means. Firstly, the relationship between the reaction temperature and the reaction rates for the various processes may be expected to follow an Arrhenius equation:

$$K = A \times \exp(\Delta H / kT),$$

where K is the reaction rate constant, A is a constant, ΔH the activation energy of the reaction and T, the absolute temperature. Secondly, the increase in temperature relaxes the polymer chains and increases the extent of chain motion so increasing the possibility of cross-linking reaction.

Vacuum annealing should cause free radicals to form cross-links without oxidation, but EPR spectra indicate that some oxidation still occurs, either through leakage of air into the apparatus or subsequent to the annealing process. As the rate of crosslink formation is slower than the rate of

oxidation (or more specifically the rate of peroxy radical formation rather than rate of oxidation) annealing carried out in vacuum requires a longer period of heat treatment for complete elimination of the radicals present.

3. CONCLUSIONS

If the molecular mobility of the polymer chains is low, because the sample is at room temperature, and oxygen is absent, as in the centre of a thick specimen, then radicals persist for many years. With time various radical combination processes take place and these can be accelerated by appropriate thermal treatment. However the quickest way of reducing the free radical concentration is by heating material in air, increase in crystallinity indicates that this leads to tie chain scission processes with adverse change in mechanical properties. It also explains why close to the surface the carbonyl concentration is high and the free radical concentration low. The principal oxidation sequence which takes place is the conversion of alkyl radical to peroxy radical and then futher reaction to give a carbonyl group, and the scheme of Matsuo and Dole seems an appropriate description.

Important problems remain regarding location of the long lived radicals. These could be in the core of the crystals, on the surface of the crystals or in the amorphous regions. Presumably the interfacial zone is one of greatly restricted mobility and so it is possible that here radical concentrations could remain high for long periods of time. Experiments with materials of varying crystallite size and content may be able to cast some light on this.

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REFERENCES

1. **Kausch, H. H.** Polymer Fracture. Springer – Verlag, Berlin, 1978.
2. **Pentimalli, M., Capitani, D., Ferrando, A., Ferri, D., Ragni, P., Segre, A. L.** Gamma Irradiation of Food Packaging Materials: an NMR Study *Polymer* 41 2000: p. 2871.
3. **Szőcs, F., Klimova, M., Bartos, J.** An ESP Study of the Influence of Fatigue on the Decay of Free Radicals in Gamma Irradiated Polycarbonate *Polymer Degrade and Stab.* 55 1997: p. 233.
4. **Szőcs, F., Klimova, M., Chodak, I., Chorvath, I.** EPR Study of Free Radical Decay in Low Density Polyethylene Filled with Silica *Eur. Polym. J.* 32 1996: p. 401.
5. **Burg, K. J. L., Shalaby, S. W.** Advances in Food Irradiation Research. In: Clough R. L., Shalaby S. W. Editors, Irradiation of Polymers, Vol. 620. Washington D. C.; *Am. Chem. Soc.* 1996: pp. 254 – 262.
6. **Seguchi, T., Tamura, N.** Mechanism of Decay of Alkyl Radicals in Irradiated Polyethylene on Exposure to Air as Studied by Electron Spin Resonance *J. Phys. Chem.* 77 1973: p. 10.
7. **Matsuo, H., Dole, M.** Irradiation of Polyethylene IV. Oxidation Effects *J. Chem. Phys.* 63 1959: p. 837.
8. **O'Neill, P., Birkinshaw, C., Leshy, J. J., Ashida, T.** Distribution of Oxidation Products in Irradiated Ultra High Molecular Weight Polyethylene *Polymer Degrad. and Stab.* 49 1995: p. 239.

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