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Effects of gamma irradiation on poly(vinyl chloride)/polystyrene blends: Investigation of radiolytic stabilization and miscibility of the mixture

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ABSTRACT

Commercial polystyrene (PS) has been studied as a modifier for commercial poly(vinyl chloride) (PVC) when it was submitted to gamma irradiation. PVC/PS blends were prepared with 100/0, 95/05 and 90/10 compositions. Results for gamma-irradiated (^{60}Co) blends are reported and changes in viscosity-average molar mass (M_v) were analyzed. The study showed that the addition of PS into PVC decreased by 73% (95/05) and 79% (90/10) the number of scissions/100 eV in the dose range of 25–100 kGy. Viscosity analyses by the Pan et al. criterion and analyses of FT-IR spectra in the C–Cl vibration region showed negligible intermolecular interactions between the components of PVC/PS blends. However when the films of blends were irradiated to 50 kGy, certain intermolecular interactions were observed by the viscosity method. The addition of PS to PVC and the main scission effect induced by gamma irradiation decreased crosslink density of blends causing changes in the elongation of break and Young's modulus.

1. Introduction

The poor stability of poly(vinyl chloride), PVC, against heat and some kinds of radiation is attributed to structural defects formed during polymerization. These defects are mainly allylic and tertiary chlorine atoms, known as labile chlorine atoms. These labile atoms are extremely unstable and easily detached by effect of heat or even sunlight to evolve HCl gas, leading to the formation of polyenes and hence to high degree of discolouration [1].

PVC is a polymer widely used for radio-sterilisable food packaging and medical devices. However when the polymer systems are submitted to sterilisation by gamma radiation (25 kGy dose), their molecular structures undergo modification mainly as a result of main chain scission and crosslinking effects [2]. For PVC both processes coexist and either may be predominant depending not only upon the chemical structure of the polymer, but also upon the conditions (temperature, environment, dose rate, etc.) under which irradiation is performed. The crosslinking and main scissions that take place during irradiation may lead to sharp changes in physical properties of the PVC [3,4]. Vinhas et al. [5] reported radioprotective action of a common photo-oxidative stabilizer, HALS (Hindered Amine Light Stabilizer), in PVC films plasticized with DEHP (di-2-ethylhexyl phthalate). The HALS additive is believed to interrupt oxidative propagation reaction by scavenging of chlorine radical formed in PVC radiolysis.

On the other hand polymer blends are an attractive route to formation of a novel material. Polystyrene, PS, contains aromatic groups which increase radiation resistance and stabilise the excited species formed by irradiation [6]. The presence of PS in PVC/PS blends could be an interesting route to PVC radiolytic stabilisation. However, most polymers are immiscible and form discrete phases often with high interfacial tension which results in a sharp interface between the two phases and leads to poor mechanical properties of the blend [7]. The viscosity method reveals important information regarding polymer–polymer miscibility in polymer blends and has been frequently employed in miscibility characterization [8–10]. Based on a simple cluster theory recently proposed for the viscosity of polymer dilute solution, a new viscometry criterion was suggested by Pan et al. [11] to probe the interaction between unlike polymers. In addition frequency shifts in infrared spectra by Fourier Transform Infrared Spectroscopy (FT-IR) are considered to be evidence of intermolecular interactions in polymer blends and suggest miscibility between the polymer pair [12].

Thus the aim of the present work was to evaluate the performance of PS as a stabiliser in the radiation-induced degradation of PVC. For this purpose 95/05 and 90/10 PVC/PS blends were exposed to gamma irradiation. The comparison of the miscibility of non-irradiated and irradiated PVC/PS blend in these compositions by both viscosity method using Pan et al. [11] criterion and analyses of FT-IR spectra was performed.

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2. Experimental

2.1. Materials and preparation of films

PVC and PS used in this study were supplied by Tiletron S.A. and Compahia Brasileira de Estireno S.A. (Brazilian manufacturer), respectively. The PVC, PS and PVC/PS blend films ($\approx$0.1 mm) were prepared by solvent-casting from methyl ethyl ketone (MEK) solvent by slow evaporation in air at room temperature. Any remaining MEK was removed by drying of the films in desiccators for 24 h. The blends were prepared at ratios of 95/05 and 90/10.

2.2. Irradiation of films

The PVC/PS films were exposed to gamma radiation from a ^{60}Co source (rate of 7.5 kGy/h) at doses of 15, 25 (sterilisation dose), 50 and 100 kGy in the presence of air and at room temperature.

2.3. Viscosity analyses

The viscosity of the samples was calculated from the relative viscosity ($\eta_{rel} = \nu/\nu_0 \approx t/t_0$), where ν and ν_0 are the kinematic viscosities of the polymer solution and the solvent, respectively. The t and t_0 are the solution and solvent tetrahydrofuran (THF) flow times, respectively, which result from the kinematic viscosity measurement. These measurements were carried out using an Ostwald-type capillary viscometer maintained at 25.0 ± 0.1 °C. After obtaining the relative viscosity, the specific viscosity ($\eta_{sp} = \eta_{rel} - 1$) and the reduced viscosity ($\eta_{red} = \eta_{rel}/C$), where C is the concentration of the solutions (0.1 g/dL), were calculated. The intrinsic viscosity was determined by the Solomon–Ciuta equation [13]:

$$[\eta] = \left(2^{1/2}/C\right)\left(\eta_{sp} - \ln \eta_{rel}\right)^{1/2} \quad (1)$$

Then the viscosity-average molecular weight, M_v, of PVC was obtained by means of the Mark–Houwink relation [13]:

$$[\eta] = K(M_v)^a \quad (2)$$

where the constants K and a are 15×10^{-5} (dL/g) and 0.77, respectively, for THF–PVC at 25 °C [14]. For THF–PS (25 °C), the constants K and a are 13.63×10^{-5} (dL/g) and 0.714, respectively [14]. Due to the additive properties of polymers in blend systems, Eq. (3) is valid to calculate the intrinsic viscosity of the blend $[\eta]_b$. The viscosity-average molecular weights of blends (M_{vb}) were obtained by Eq. (4), which is valid for PVC/PS systems in THF at 25 °C.

$$[\eta]_b = [\eta]_{PVC} w_{PVC} + [\eta]_{PS} w_{PS} \quad (3)$$

where $[\eta]_{PVC}$ and $[\eta]_{PS}$ are the intrinsic viscosities of PVC and PS, respectively. The w_{PS} and w_{PVC} are the mass fraction of PS and PVC in the blend, respectively.

$$[\eta]_b = (13.63 - 1.37 \times w_{PVC}) \times 10^{-5} M_{vb}^{0.74} \quad (4)$$

The 0.74 value is the arithmetic average of the a, constants of PVC and PS polymers.

The ionizing radiation effect on the polymer is expressed as a function of the G value (number of events/100 eV absorbed energy). The relationship between M_v, G and dose (in kGy) was obtained by Araújo et al. [15] and for PVC the expression is:

$$10^6/M_v = 10^6/M_{vo} \pm 0.0549GD \quad (5)$$

where M_v and M_{vo} are the viscosity-average molecular weights before and after irradiation, respectively, and D is the dose in kGy. The relationship is linear and provides the G value from the slope of the straight line obtained from a plot of $10^6/M_v$ vs D. The linear relation guarantees that the radiolytic events are random and only under this condition can Eq. (5) be used. From G values is possible to calculate the protective factor (P) (Eq. (6)) which indicates the reduction in yield of events in PVC formulations containing PS.

$$P = (G_{PVC} - G_b)/G_{PVC} \quad (6)$$

G_{PVC} and G_b are the G value calculated for PVC and blend, respectively. Any radio-stabilising action of PS on PVC can be assessed by comparison of degradation index (DI) parameter ($DI = M_{vo}/M_v - 1$) for a determined irradiation dose. The DI is obtained from viscosity analysis and reflects the number of main chain scissions per original molecule after irradiation.

The Pan et al. [11] criterion was used to study the miscibility of PVC/PS blends at 95/05 and 90/10 compositions. Films of these composition irradiated at 50 kGy also were analysed by Pan et al [11] criterion. On the base of this cluster theory, an ideal mixed polymer solution should be defined as one in which there does not exist net attractive interaction between unlike polymers. For PVC and PS ideal mixed solution the experimental apparent association constant of the polymers in the mixture, K_m^{exp}, was calculated using Eq. (7) [11].

$$K_m^{exp} = b_b/6[\eta]_b \quad (7)$$

where b_b is the viscosity parameter of the blends that was taken from the slope of the straight line obtained from a plot of reduced viscosity as a function of the concentration. The 0.1, 0.3, 0.4, 0.5 and 0.7 g/dL solution concentrations were used. $[\eta]_b$ is the intrinsic viscosity determined by the usual method of extrapolation using the reduced viscosity [2]. Regarding the polymer blend as a single solute, the viscosity of ideal polymer solution can always be treated in same form and Eq. (8) was used to calculated the apparent association constant of an ideal polymer solution mixture, $\langle K_m \rangle^{id}$ [11].

$$\langle K_m \rangle^{id} = \left(b_{PVC} w_{PVC}^2 + b_{PS} w_{PS}^2\right) \Big/ 6([\eta]_{PVC} w_{PVC} + [\eta]_{PS} w_{PS}) \quad (8)$$

where b_{PVC} and b_{PS} are the viscosity parameter of the PVC and PS, respectively. Therefore, for mixed polymer, any deviation of its experimental overall apparent association constant from its ideal value $\langle K_m \rangle^{id}$ due to Eq. (8) can be regarded as an indication of an attractive interaction between unlike polymers.

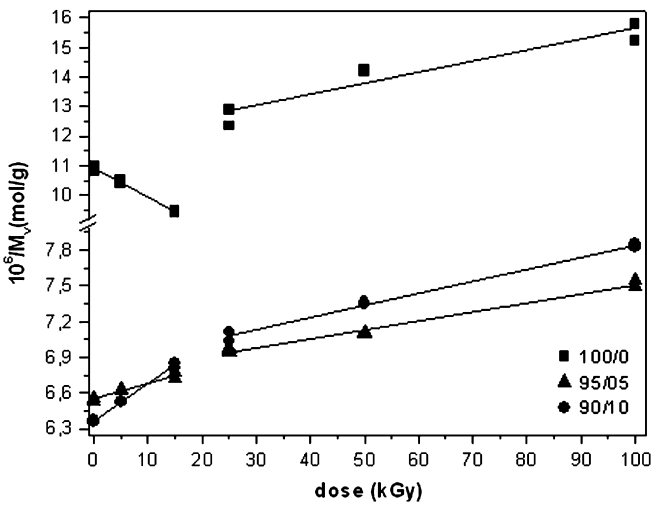

Fig. 1. Reciprocal of M_v as a function of the irradiation dose of PVC and PVC/PS blends.