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Properties of irradiated PVC plasticized with non-endocrine disruptor

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Abstract

Polyvinylchloride (PVC) is under heavy attack from environmentalist groups due to the use of plasticizers and its recycling difficulties. Chloro-organics and phtalates are considered now as ubiquitous global contaminants due to their potential as weak endocrine disruptor and huge consumption. In order to make PVC acceptable for the irradiation processing industry in the long term, non-toxic plasticizers should be used. PVC was added with dioctyl phtalate (DOP) and epoxy soybean oil (ESO) and irradiated up to 50 kGy. Mechanical properties, optical properties and viscosity were measured and compared. The elongation and mechanical strength were under the usual range and they didn't show any significant change in the studied range of irradiation dose. All the samples showed a weak yellowing effect after irradiation and the molecular weight measured by viscosimetry showed only negligible changes. In conclusion, DOP and ESO were shown to be effective in stabilizing the radiolytic abstraction of HCl from PVC. Both plasticizers imparted good color stability and overall properties to the products.

1. Introduction

Chloro-organics are one of the most persistent chemicals in the environment ever produced. They remain undegraded and their attraction to fat allows them to bioaccumulate in living organisms. From a perspective of human health there is strong evidence of hormone disruption action, as those compounds resemble their chemical structure.

PVC is present in every day life in a ubiquitous way. PVC is used from short-life consumer products as packaging, toys and others to long-life goods such as furniture, windows frames, tubes, wire and cable and so on. Environmentalist groups like Greenpeace believe that PVC is the most dangerous plastic due to its high chlorine content and the highest amount of additives impairing its recyclability. PVC under recycling processes can generate dioxin, an extremely hazardous pollutant. There are many examples of public reaction to PVC, the most representative and opportune is that PVC was banned from the Sydney Olympic Games facilities.

The use of additives is mandatory in plastic processing and PVC formulation contains almost all kinds, like lubricants, plasticizers, UV-stabilizers, flame retardants, anti-statics, heat stabilizers, light stabilizers, impact modifiers and so on. Phtalates are the most common plasticizers for PVC, paints, inks and ad-

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hesives. A large number of phtalate esters were screened for estrogenic activity (Harris et al., 1997) and it was found that they are weakly estrogenic, in vitro. It has been suggested (Jobling et al., 1995) that they may be etiological agents in several human diseases, including disorders of the male reproductive tract, breast and testicular cancer.

On the other hand, radiation in all its forms has been one of the preferred targets of the environmentalists groups. The three together (PVC, phtalates, radiation) make up a melting pot for environmentalists and the industries involved in this area.

The aim of this study is to show that it is possible to develop a formulation for processing PVC by radiation able to cope with degradation and discoloration and, at the same time, friendly to the environment, or at least, less polluting.

2. Materials

A primary plasticizer, which contains an aromatic ring in its structure able to act as a quencher, was used. The aromatic groups absorb the excitation energy acting as traps and converting this energy into other non-reacting forms. The additive chosen was dioctyl phtalate (DOP), a common plasticizer which is approved by the FDA for use in food packaging and medical supplies (Kojima et al., 1981). As a secondary plasticizer epoxy soybean oil was used due to its capability of acting synergistically with metallic stabilizers. Zn and Ca are the recommended additives to react with the HCl from PVC decomposition and are also approved by the FDA as additives for radiation sterilization (Saxena et al., 1987).

The PVC samples were kindly supplied by Kompor Industries with different plasticizer concentrations using a proprietary formulation. Tubes and films were supplied depending on the final purpose. The sample N was provided as an extruded tube. Sample A was 0.6 mm width and B, C and E were films with 1 mm thickness. Samples A, B, C and E have more plasticizer than sample N and they have the secondary plasticizer ESO. Samples A and E have zinc and calcium in the proportion 3:1. Samples A and C contain bleacher.

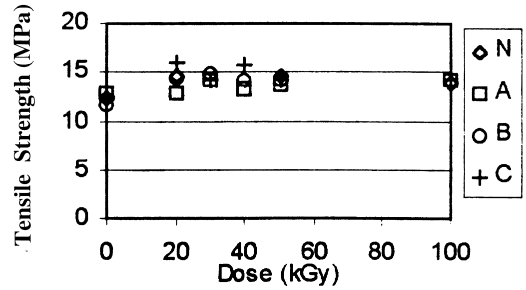

Fig. 2. Tensile strength versus dose for different formulations.

All the samples were irradiated at EMBRARAD in a Co-60 industrial irradiator, at a dose rate of 3 kGy/h and total dose from 0 to 100 kGy. Mechanical properties, tensile strength and elongation, were measured in a universal testing machine INSTRON model 5567, according to NBR 6421. Optical tests, transmittance as a function of dose, were conducted with a spectrophotometer Pharmacia, model Novaspecil, according to ASTM D-1746-92. Color determination was performed in a photocolorimeter Datacolor, spectraflash 500. Viscosity measurements were done in a Ubellohde 1 following ASTM D-1243-79. Each point is the average value of five assays.

3. Results

The results of elongation at break versus irradiation dose are shown in Fig. 1. Samples with various width and shape were tested and the results showed this intrinsic difference. The samples with higher width showed higher elongation but they all showed the same behavior in respect to dose variation (Fig. 1).

The results of tensile strength as a function of irradiation dose are shown in Fig. 2. Minor variations were observed for different formulations and shapes.

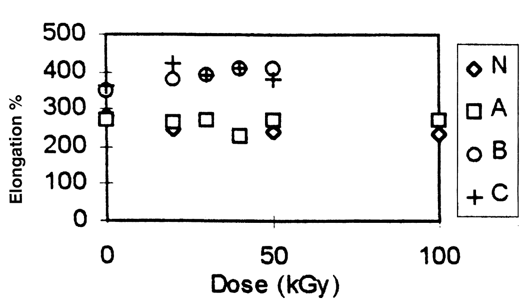

Fig. 1. Elongation versus dose for different formulations.

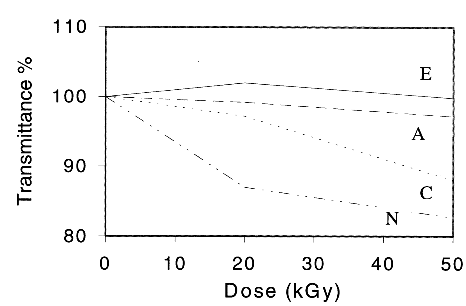

Fig. 3. Transmittance versus dose for different formulations.

Table 1
Visualization of the irradiated samples

Sample	Before irradiation	After irradiation
N	Transparent	Transparent and strongly yellowed
A	Transparent and bluish	Transparent, lightly yellowed with blue
C	Transparent and bluish	Transparent, yellowed with blue
E	Transparent	Transparent with some yellowing

Again, the differences were not significant due to the intrinsic dispersion of this assay (Fig. 2).

PVC is well known as a degrading type polymer under radiation, with HCl release upon irradiation. The viscosity provides a measure of the polymer molecular weight. However, PVC was heavily loaded with additives, so the viscosity was only partially related to the degradation of the polymer. In order to check the consistency of the viscosity data, χ^2 was used with 5% significance to validate the results. The inclination of the regression line was a measurement of the degradation behavior. This angle was 0.06 for N, 0.007 for A and 0.023 radian for C formulation. It was easy to see that N was by far more degraded than the others were, even though the degradation is small.

As a beam of light goes through matter, the emerging radiation will be less intense as a result of its absorption in the matter. This effect can be selective, i.e., more intense for specific wavelengths. The visible color is the complement of the absorbed one. For instance; the color violet is complementary of green–yellow, blue is complementary of yellow and blue with yellowing is complementary of red with yellowing. The selective absorption in organic molecules was related to the lack of electrons in the molecule (saturated compounds do not show selective absorption). Absorption at higher wavelengths was characteristic of conjugated double bonds in a proportional intensity, i.e., the more intense the system of conjugated double bonds resulted in longer wavelengths or more intense color. The polyenes are well known as the center of color for PVC, which is the primary reason for the strong dose-related effect of yellowing, observed in irradiated PVC.

Table 1 shows the main color effects by direct observation. All the samples showed a yellowing effect after irradiation seen by direct observation.

Fig. 3 shows the transmittance results of the irradiated samples. The results are compatible with the results of direct observation. The decrease in transmittance is related to color induction. It was quite evident that good results were obtained with samples A and E, as compared with the commercial one N. Table 2 showed the results of color analysis.

The values of b mean color change from blue (−) to yellow (+) and L value mean changes from light (−) to dark (+). The different behaviors come out clearly in this analysis. A and E showed much better results, validating the previous observations. The lighter appearance of sample A was a result of the addition of a clarifier.

4. Conclusions

The elongation and mechanical strength of PVC with environmentally friendly additives (DOP, ESO) were under the usual range and they didn't show any significant change in the studied range of irradiation dose. All the samples showed a weak yellowing effect after irradiation and the molecular weight measured by viscosimetry showed negligible changes. In conclusion,

Table 2
Color analysis

	A		C		E		N	
Dose (kGy)	Δb[a]	•L[b]	Δb	•L	Δb	•L	Δb	•L
20	+2.2	+0.2	+6.5	+0.3	+2.8	+1.2	+8.5	+2.1
50	+4.7	−0.7	+9.5	−1.1	+4.3	+1.4	+12	+4.3

[a] b: blue (−); yellow (+).
[b] L: light (−); dark (+).

DOP and ESO are effective in stabilizing the radiolytic abstraction of HCl from PVC. Both plasticizers imparted good color stability and overall properties to the products. Nevertheless, as there is a concern regarding the possibility of leaching of additives, its estrogenic effects after irradiation should be tested in the future.

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