

# Polymerization of vinyl acetate in bulk and emulsion by gamma irradiation

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## Abstract

The vinyl acetate polymerization to produce poly(vinyl acetate) was carried out in bulk and emulsion using a  $^{60}\text{Co}$  gamma irradiator Gammacell-220 type. The irradiation was carried out in a dose rate of 5.25 and 5.30 kGy/h, respectively. The polymers obtained were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimeter (DSC) and gel permeation chromatography (GPC). Tests of density, hardness and Vicat softening temperature were carried out.

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## 1. Introduction

One of the applications of chemical radiation in the field of polymers is vinyl monomer polymerization by exposure to gamma radiation (Chapiro, 1962). Many works have been published on the induced polymerization for irradiation of some monomers in bulk (Yigit and Güven, 1989; Sheikh and Taromi, 1995) and emulsion (Panarin et al., 1994).

When a pure substance undergoes ionizing radiation, the produced effects are ionization and excitation of molecules. However, when the same substance is irradiated in solution, the produced effect can have direct and indirect actions.

In the polymerization for free radicals induced by radiation, the formation of primary radicals does not depend on the temperature, but only on the radiation intensity. This allows that the polymerization is initiated in low temperatures, viscous way or even in solid phase (Chapiro, 1979; Bhattacharya, 2000).

In the polymerizations initiated by radiation, the main advantages of the traditional methods are: free from impurities such as chemical residues from initiators, a temperature control on the chemical propagation step which does not interfere with the initiation, and an immense choice of conditions of initiation (intensity, physical state and temperature) (Charlesby, 1991).

The aim of this work is the synthesis and characterization of the poly(vinyl acetate)—(PVAc) using ionizing radiation.

## 2. Experimental

Irradiations were carried out with gamma rays coming from a  $^{60}\text{Co}$  irradiator, Gammacell-220 of Atomic Energy of Canada Limited, with a dose rate of 5.25 and 5.30 kGy/h. For the irradiation of samples a polymerization reactor was used. This reactor has two paths (inlet and outlet), for the circulation of the monomer solution, located at the center of a tube for the introduction of the thermocouple that is used to control the temperature of the polymerization reaction.

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The irradiation system used to carry out this work was the same as that presented in Mesquita et al. (2002).

Bulk polymerization was carried out with the pure monomer, which was irradiated for 1 h and 45 min corresponding to a radiation dose of 9.18 kGy. After irradiation the polymer obtained was precipitated with distilled water. The precipitate was washed three times with distilled hot water, for the elimination of residual monomer. After that, the sample was dried in stove at 140°C for 2 h until constant weight was reached.

In emulsion polymerization, monomers and the sodium lauryl sulfate surfactant were used, which were irradiated for 34 min corresponding to a radiation dose of 3.00 kGy. After the irradiation the polymer obtained was precipitated with ethanol and the excess ethanol was removed. The precipitate was washed three times with distilled hot water, for the elimination of residual monomer. After that, the sample was dried in stove at 140°C for 2 h, until consistent weight was reached.

The conversion percentage was calculated by the weight ratio of polymer to monomer.

The polymers obtained were characterized by Fourier transform infrared spectroscopy (FTIR), using a Great Nicolet—IR 550 equipment. The samples were placed in crystals of KBr and analyzed directly.

The molecular weights of PVAc obtained in bulk and emulsion polymerizations were determined, using a Waters 244 GPC chromatograph equipped with Ultrastaygel columns and THF as the eluting solvent. The flow rate was kept at 1 ml/min in both cases.

The calorimetric measurements were performed using a Shimadzu DSC 50 at 10°C/min heating rate, temperature range from –50°C to 70°C, nitrogen gas flow rate of 30 ml/min and sample mass around 8 mg.

Table 1  
The PVAc conversion percentage obtained in bulk and emulsion polymerizations and respective radiation doses

| Polymerization | Irradiation time | Radiation dose (kGy) | Conversion (%) |
|----------------|------------------|----------------------|----------------|
| Bulk           | 1 h 45 min       | 9.18                 | 20.12          |
| Emulsion       | 34 min           | 3.00                 | 79.17          |

Table 2  
Molecular weight, glass transition temperature, density, hardness and Vicat softening temperature of PVAc obtained in bulk and emulsion polymerizations

| Polymerization | Molecular weight (g/mol) | Glass transition temperature (°C) | Density (g/cm <sup>3</sup> ) | Hardness (Shore D) | Vicat softening temperature (°C) |
|----------------|--------------------------|-----------------------------------|------------------------------|--------------------|----------------------------------|
| Bulk           | 240 000                  | 37.80                             | 1.10                         | 64                 | 71.7                             |
| Emulsion       | 600 000                  | 40.74                             | 0.89                         | 64                 | 41.8                             |

The glass transition temperature ( $T_g$ ) was determined by differential scanning calorimeter, using a Shimadzu—50 equipment, under a pure nitrogen gas flow rate of 30 ml/min, 10°C/min heating rate and sample mass around 8 mg.

The test of hardness was carried out using a Shore D, Zwick-7203 equipment.

The Vicat softening temperature was carried out using a Ceast-6505 equipment at 50°C/h heating rate.

The density of the polymers was also calculated by the ratio of mass to volume.

### 3. Results and discussion

The PVAc conversion percentage results obtained in bulk, emulsion, and their respective radiation doses are shown in Table 1.

The conversion percentage result of PVAc in emulsion is four times higher than in bulk, approximately.

The results of investigation of molecular weight, glass transition temperature ( $T_g$ ), density, hardness and Vicat softening temperature of PVAc obtained in bulk and emulsion are shown in Table 2.

It should be noted that molecular weight of polymer obtained in emulsion is higher than polymer obtained in bulk.

In relation to the glass transition temperature ( $T_g$ ) it is observed that the value of polymer obtained in bulk is less than the one obtained in emulsion, therefore the  $T_g$  decreases with the increase of the dose. The  $T_g$  also decreases with the decrease of the molecular weight.

The density of the PVAc obtained in emulsion, presents a lower value, and probably had formation of ramifications in the chain.

The values found in hardness demonstrate that although the present value was equal, it had been smaller than the one presented in literature (Gowariker et al., 1986), whose value range from 80 to 85. We can confirm that the polymer obtained by radiation is less resistant to penetration and risk.

Figs. 1 and 2 present the absorption spectra in the infrared area of the poly(vinyl acetate) obtained by gamma radiation in bulk and emulsion. These spectra

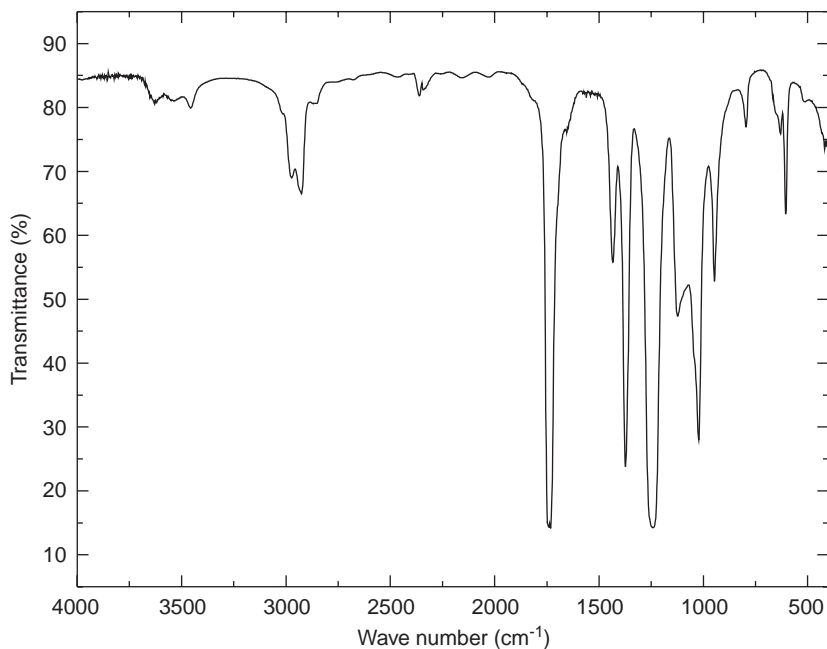


Fig. 1. PVAc spectrum obtained in bulk polymerization.

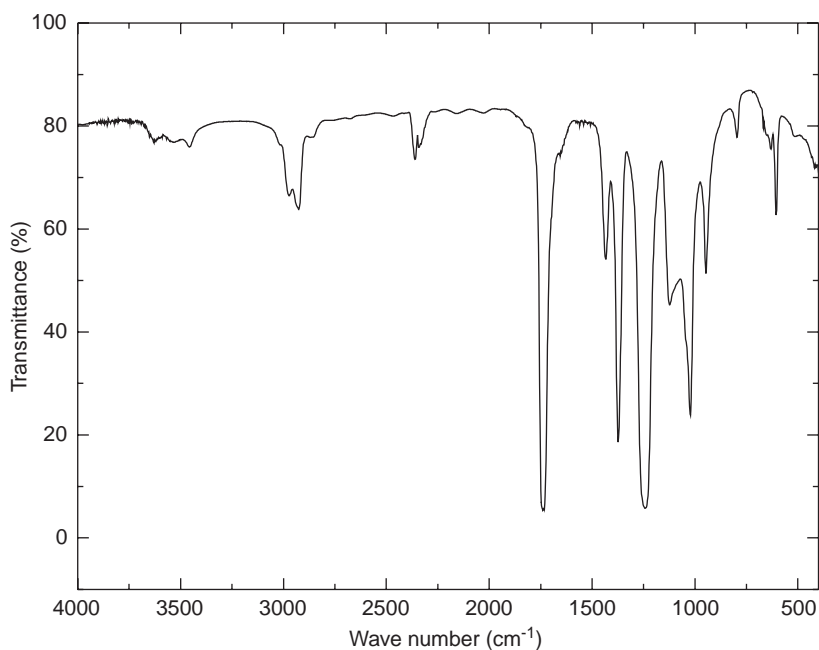


Fig. 2. PVAc spectrum obtained in emulsion polymerization.

showed characteristic absorption bands in  $1735\text{cm}^{-1}$ , corresponding to the axial deformation  $\text{C}=\text{O}$ , and in  $1244\text{cm}^{-1}$ , corresponding to the axial deformation  $\text{C}-\text{O}$ , and characterizing the presence of an acetate.

Comparing the spectra obtained from those of the Library “Hummel Polymer and Additives”, it can be

affirmed that both samples analyzed correspond to a PVAc due to the peaks presented in Figs. 1 and 2.

In accordance with the analysis of absorption spectra in the infrared area it can be affirmed that the polymers obtained in bulk and emulsion really correspond to the PVAc.

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