



# Electron beam induced modifications in crystalline structure of polyvinylidene fluoride/nanoclay composites



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## HIGHLIGHTS

- The crystallinity of PVDF varied with E-beam irradiation doses.
- Electron beam irradiation decreased the melting point of PVDF.
- The combined effect of nanoclay and E-beam on yield strength was synergistic.

## ARTICLE INFO

### Article history:

Received 7 April 2013

Received in revised form

23 August 2013

Accepted 21 October 2013

### Keywords:

Polyvinylidene fluoride

Electron beam

Nanoclay

Crystalline transformation

## ABSTRACT

PVDF/nanoclay nanocomposites were prepared via melt mixing method. The intercalated dispersion of the nanoclay in PVDF matrix was confirmed by XRD. According to FTIR, DSC and XRD results, the presence of nanoclay facilitated transition from  $\alpha$ -to- $\beta$  crystalline phase. Electron beam irradiation decreased the melting point of the nanocomposites. The decrease in melting point of the nanocomposites was about 11 °C at 500 kGy. The crystallinity of nanocomposites increased at an irradiation dose of 100 kGy and decreased at higher irradiation doses. The extent of crosslinking of the nanocomposites increased significantly with irradiation up to 300 kGy. The nanoclay intensified the increase in yield strength with irradiation doses up to 300 kGy. The combination of nanoclay and irradiation had a synergistic effect on the increase of yield strength.

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## 1. Introduction

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer and has various possible crystalline phases such as  $\alpha$ ,  $\beta$  and  $\gamma$  (Ma et al., 2008). The  $\beta$  phase has attracted more attention because of piezoelectric properties. Many investigations have been made to gain higher  $\beta$  phase in crystalline structure of PVDF.

Dillon et al. (2006) prepared PVDF/organoclay nanocomposites using montmorillonite-based clays Cloisite 15A and Cloisite 25A by two preparation methods of solution casting and co-precipitation and reported that the amount of  $\beta$  phase increased with increasing organoclay content. Buckley et al. (2006) reported that partially  $\beta$  phase formation in the PVDF nanocomposites with 0.025–0.5 wt% nanoclay content while, the nanocomposites with more than 0.5 wt% of organoclay showed complete  $\beta$  phase formation.

A number of investigations have been reported on the effect of irradiation on PVDF (Adem et al., 2004; Tiwari et al., 2009; Botelho et al., 2008).

Zhong et al. (1993) worked on the irradiation-induced changes in PVDF by XPS. They concluded that the main irradiation-induced structural changes in PVDF included both crosslinking of polymer chains and formation of unsaturated bonds.

Lim et al. (2006) investigated the effect of electron beam radiation on PVDF at melting temperature. They reported that the melting temperature decreased with increase in irradiation dose. Siddhartha et al. (2009) studied the effect of gamma irradiation on  $\alpha$ -phased PVDF and obtained  $\beta$  and  $\gamma$  phases.

Adem et al. (1999) studied the effect of electron beam (EB) radiation on PVDF. They observed crystalline phase changes by means of DSC and showed maximum about 50 percent crystallinity at a dose of 100 kGy.

In this work, PVDF/nanoclay nanocomposites using montmorillonite-based clay Cloisite 30B were prepared by melt mixing method. Some of the nanocomposites were exposed to electron beam irradiation at various doses. The simultaneous effect of irradiation and nanoclay on crystalline-phase transitions,

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crosslinking, thermal, and mechanical properties of PVDF were investigated by DSC, XRD, FTIR, gel content and mechanical properties.

## 2. Experimental

### 2.1. Materials

PVDF was Hylar 460 of Solvay Co. Belgium. Nanoclay was Cloisite 30B from Southern Clay Product Co. The solvent for gel content test was N-Dimethyl formamide (DMF) from Merck.

### 2.2. Sample preparation

First, the nanoclay was dried in a vacuum oven for 12 h at 60 °C in order to remove the absorbed water. Then PVDF and the nanoclay were mixed in a Brabender internal mixer at 175 °C and 60 rpm for 7 min. The nanocomposite films with thickness of 0.2 mm were produced using a Coolin P-200 compression molding machine first by preheating at 220 °C for 3 min and then pressing between the press plates at 220 °C and 200 bar followed by quenching in air. The percent of nanoclay was 1, 3, 5 and 7. Irradiation of the PVDF/nanoclay nanocomposites was carried out in the Yazd Radiation Processing Center using Rhodotron TT200 electron accelerator with energy of 5 MeV under various irradiation doses ranging from 100 kGy to 500 kGy in air atmosphere. The nanocomposite containing 5 wt% nanoclay was designated as NC5 and the irradiated NC5 at a dose of 100 kGy was designated as NC5-100.

### 2.3. XRD

X-ray diffraction (XRD) tests were performed with Cu-K $\alpha$  X-ray source which operated at 40 kV and 30 mA at irradiation wavelength of 0.154 nm and step size of 0.02°/s ranging from 1 to 10 and 10–45 degrees at ambient conditions for characterizing the nanoclay and the crystalline structure of nanocomposites respectively. The d-spacing of (001) peak of the nanoclay and the crystal size of PVDF were obtained with the following Bragg-law equation:

$$n\lambda = 2d\sin(\theta)$$

where  $n$  is an integer,  $\lambda$  is the wavelength of incident X-ray (0.154 nm)  $d$  is the spacing between the planes in the lattice and  $\theta$  is the diffraction angle.

### 2.4. DSC

Differential Scanning Calorimetry was carried out according to ASTM D-3418 using Perkin-Elmer DSC Pyris-1 purged with

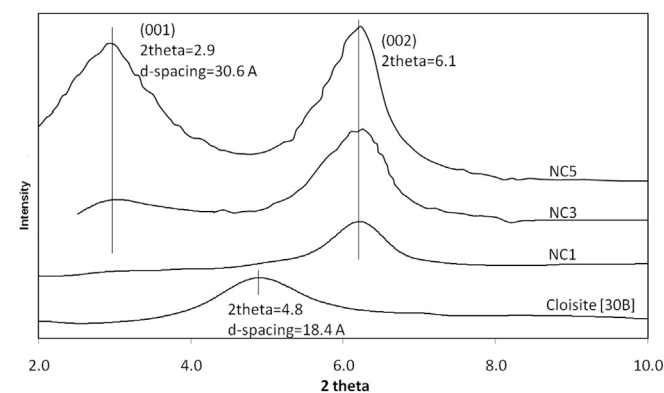


Fig. 1. XRD of the nanoclay and nanocomposites at low  $2\theta$ s.

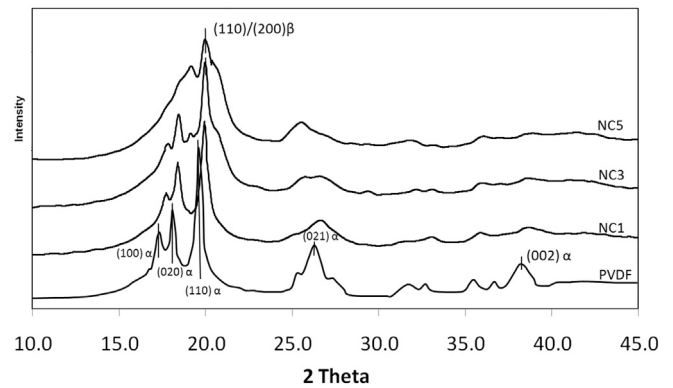


Fig. 2. XRD patterns of PVDF and the nanocomposites.

nitrogen at 15 mL/min and calibrated with indium to ensure the accuracy of the calorimetric scale. Melting and crystallization temperatures and the percent of crystallinity of the nanocomposites were determined. The first scan was performed from 50 °C up to 200 °C at a scan rate of 10 °C/min, holding at 200 °C for 5 min to remove all the thermal history of the polymer and cooling back to 100 °C at a scan rate of 10 °C/min. The second heating was carried out from 100 to 200 °C at a scan rate of 10 °C/min under N<sub>2</sub> atmosphere. The percent of crystallinity  $D$  was calculated from the following relation:

$$D = 100H_f / (W \cdot H_{f0})$$

where  $H_f$  is the enthalpy of melting of the sample and  $W$  is the weight fraction of PVDF in the nanocomposite. A value of 102.5 J/g was used for  $H_{f0}$ , the melting enthalpy of the 100% crystalline PVDF obtained from reference 12.

### 2.5. FTIR

FTIR was used to investigate the crystalline structure by a Bruker vertex 80 spectrophotometer.

### 2.6. Gel content

Gel content of the electron beam irradiated samples was determined to measure the percent of crosslinking using solvent extraction method according to ASTM D-2765. The extraction was carried out with N,N-Dimethyl formamide at 90 °C for 3 days. The percent of gel content of the nanocomposites was calculated from the following relation:

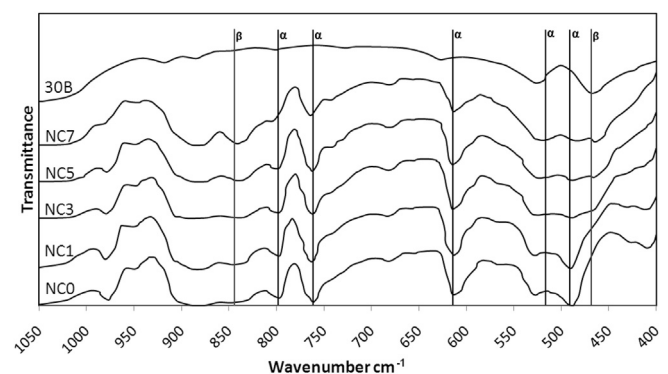


Fig. 3. FTIR spectra of the un-irradiated PVDF (NC0), the nanoclay (30B) and the nanocomposites (NC1, NC3, NC5, NC7).

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