

Spectroscopic study of poly (vinylidene fluoride)/ poly (methyl methacrylate) (PVDF/PMMA) blend

F. Z. Benabid ^{A,*}, F. Zouai ^B and A. Douibi ^A

^ALMPMP, Faculté de Technologie, Université Ferhat Abbas Sétif-1, Algérie

^BUnité de Recherche Matériaux Emergents, Université Ferhat Abbas Sétif-1, Algérie

* Corresponding author, e-mail address: fzbenabid@yahoo.fr

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Abstract

Poly (Poly (vinylidene fluoride)/poly (methyl methacrylate) blends casted in DMF could be used in the conservation of historic structures (monuments) exposed to atmospheric agents or as a coating to replace and maintain parts or missing pieces. This study deals with the effect of blending PVDF to PMMA to enhance their properties using FTIR and UV-visible spectroscopy. In FTIR spectra, it was found that PVDF/PMMA blend casted in the Dimethylformamide (DMF) showed the superposition of the spectra of all compositions, with the exclusion of any chemical reaction between two polymers or the presence of the double bonds characteristic of PVDF dehydrofluorination. The UV-visible spectroscopy before and after exposure to artificial weathering, showed that the PVDF is very stable (the invariant absorbance values at 200nm wavelength after the equivalent of two years of aging). In contrast, the absorbance of PMMA has changed at the same wavelength explaining its tendency of degradation.

Key words: Blend, PVDF, PMMA, Monuments.

Introduction

The conservation and protection of historic monuments or culturally significant structures have recently attracted much attention from material scientists [1]. A few years ago, various synthetic polymers have been widely used in the treatment of construction materials of historical monuments for consolidation and conservation of such structures [2]. Using polymeric coatings for this area has created serious challenges for the surface science and technology. Some of the challenges are as follows [3, 4]. Van Hees and Brocken [5] evaluated the salt growth in brick masonry specimens, coated with a water repellent, during a salt crystallization test. They demonstrated that the behavior of different salts on development of salt damages is completely different. However, it is demonstrated that the adsorption of dusts suspensions and water-soluble air pollutants decreases with increasing hydrophobicity of the surface of building materials [1]. The fluorine substitution of the hydrogen atoms present in a macromolecular chain improves the heat resistance and chemical resistance, delays or inhibits flame propagation, lowering the critical surface tension and exalts the dielectric characteristics [6]. Acrylic resins undergo deterioration face conditions under UV radiation and their climatic exposure causes degradation of their structure. However, their physical characteristics and low price always consider important research topics. Estevão Freire et al. [7] have studied the morphological, thermal and non-isothermal crystallization behavior of the PVDF and its blends

with the PMMA processed in low (LSM) and high (HSM) shear mixers using the differential scanning calorimetry (DSC). The addition of PMMA into PVDF increases of relative β phase content independent of the processing conditions. The validity of the modified Avrami and Kolmogorov-Johnson-Mehl-Avrami (KJMA) models for the non-isothermal crystallization of PVDF/PMMA blends were discussed. The results showed a shift in the PVDF crystallization/fusion peak to lower temperatures. The activation energies for crystallization of PVDF and its blends evaluated through the isoconversional method using Friedman's approximation were higher for samples processed in the LSM. Jing Sun et al. [8] have studied the modification on crystallization of PVDF by solvent extraction of PMMA in PVDF/PMMA blends. The mass crystallinity (χ_c) and further, the β -phase content (F_β) of PVDF, were studied for the blend films with different mass ratios.

DSC, FTIR and XRD measurements all indicated that χ_c , F_β and even the content of α -phase (F_α) decreased with the addition of PMMA and with the extraction of PMMA, both χ_c and F_β increased while F_α decreased. In this research work, the focus was on the development of films of PVDF and PMMA blends and their spectroscopic analysis (FTIR and UV-visible spectroscopy).

Materials and methods

PVDF (Hylar 5000), special coating as a white powder, manufactured by Ausimont, Italy [9] and PMMA (Vedril ® Spa-Resina Metacrilica) manufactured by Mont Edison, Italy were used [10].

The PVDF/PMMA films were obtained by casting each polymer separately in with 1 % concentration of the polymer in the solvent (DMF) at temperature, 70°C (see table1).

Table 1: Different compositions in volume percentage proposed in this study

PVDF (%)	100	90	80	70	60	50	40	30	20	10	0
PMMA (%)	0	10	20	30	40	50	60	70	80	90	100

Moisture, temperature and ultraviolet radiation contribute to material degradation. Accelerated weathering test (Xeno Test) is the simulation of these conditions using special environmental chambers and instruments in order to speed up the weathering process and measure its effects on parts, components, products, and materials. On the other hand, the Salt spray testing is a test method for evaluating a product or a coating resistance to corrosion in the face of extended exposure to a saline, or salted, spray.

FTIR spectroscopy

Fourier-transform infrared spectroscopy (FTIR) spectra were recorded by means of a Perkin Elmer Spectrum 1000 spectrometer with a wavenumber resolution of 4 cm⁻¹ in the range from 450 to 4400 cm⁻¹, using attenuated total reflection. Each spectrum results from an average of 200 scans to detect any changes in the chemical structure of various compositions of PVDF/ PMMA blends before and after exposure to artificial weathering (Xeno Test and Salt Spray) according to ISO 11507:1997(F) and ISO 7253:1996(F) respectively.

UV-visible spectroscopy

The UV-visible spectroscopy was performed using a Unicam UV 300 spectrophotometer to determine the evolution of the absorbance of various compositions of PVDF/PMMA blends before and after exposure to artificial weathering (XENO Test and Salt Spray).

Results and discussion

FTIR spectroscopy

FTIR spectra of PVDF/PMMA blends showed the spectral superposition of all the compositions where the exclusion of any chemical reactions between the two polymers. The results of the FTIR of the PVDF/PMMA blend solutions in the DMF (Fig.1, 2 and 3) showed the appearance of a band at 3470 cm⁻¹ for the PVDF and at 3538 cm⁻¹ for the PMMA corresponding to the hydrogen bonds of the hydroxyl group initiated by the solvent. The DMF is also the source of the occurrence of the stretching vibration of C=O amide 1673 cm⁻¹ and for the PVDF to 1675 cm⁻¹ for the PMMA.

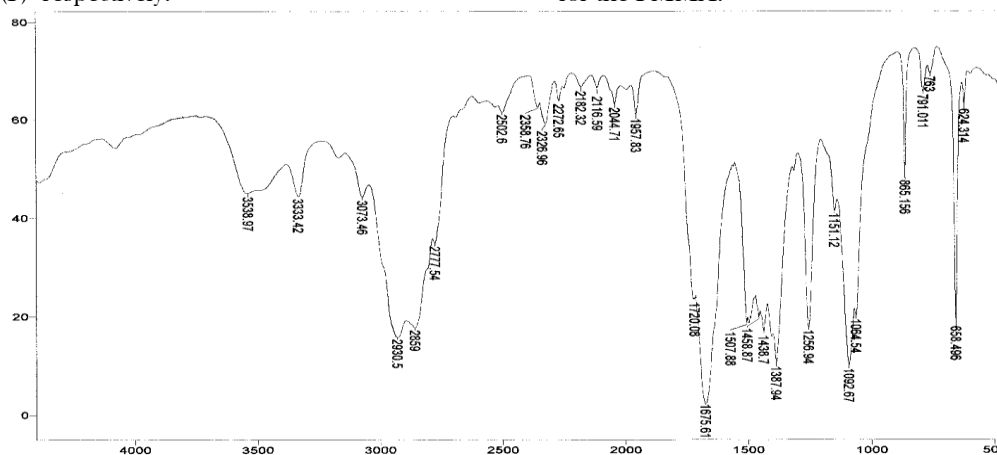


Fig. 1: Evolution of IR transmittance (%) of the PMMA casted in DMF as a function of the wave number (cm⁻¹)

In the films of PVDF/PMMA blend before and after exposure to artificial weathering and to the salt spray it is noted that the bands at 510, 839, 880 and 1406 cm⁻¹ are those of the β crystallinity phase of the PVDF [11, 12]. The α -phase is identified by the presence of peaks at 763 and 948 cm⁻¹ [13, 14]. It should be noted that according to the literature [15, 16], the increase in the

temperature reduces the presence of the crystallization of the β phase and it is clear that for a high proportion of this phase it must perform complete drying films at 75 ° C. The strong band at 1233 cm⁻¹ is due to CF₂ and while the CH bonds showed peaks at 2980 and 3022 cm⁻¹. The deformation of CH₂ bonds is located at 1429 cm⁻¹.

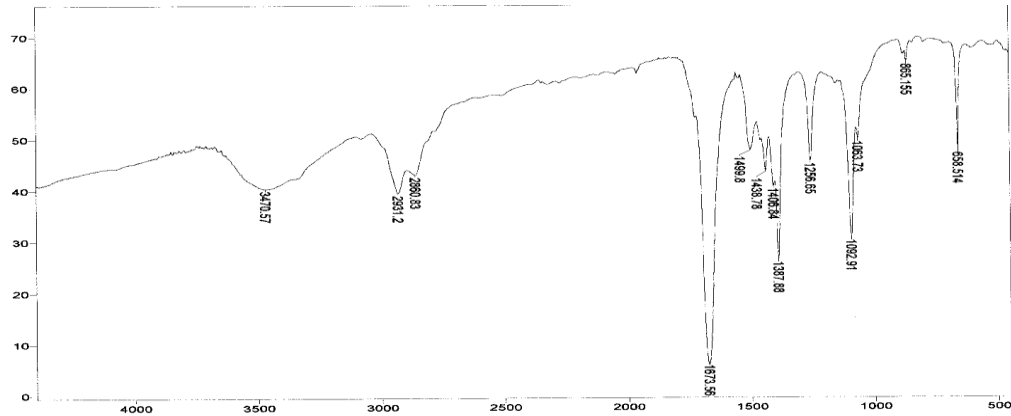


Fig. 2: Evolution of IR transmittance (%) of the PVDF casted in DMF as a function of the wave number (cm^{-1})

Concerning the PMMA, a strong peak at 750cm^{-1} present identifying the ρ (C-H) rocking; The C-O-C bond (ether ester) is indicated by the presence of peaks at 1151 and 1256cm^{-1} .

The peaks at 1438 and 1458cm^{-1} are characteristics of C-H bonds(bending) and the one at 1720cm^{-1} is due to presence of carbonyl group (C=O).

Peaks characterizing the vibration of symmetric and asymmetric -CH stretching are at 2859 and 2930cm^{-1} respectively.

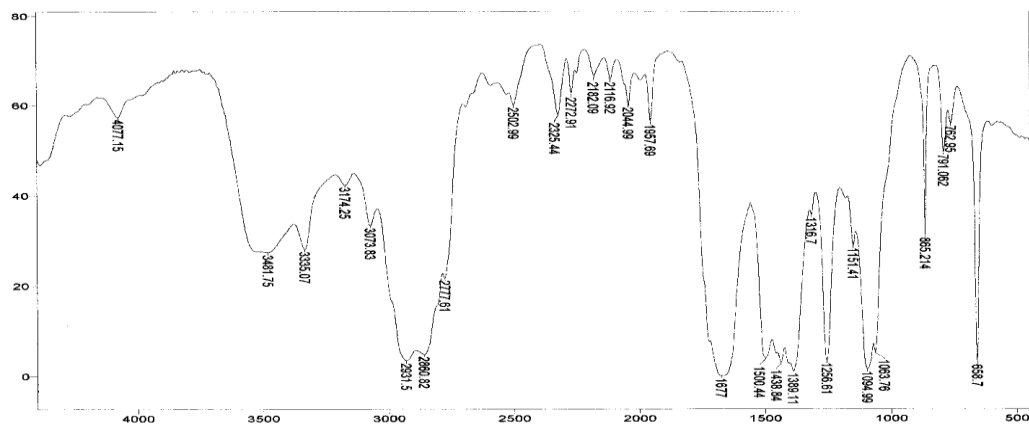


Fig. 3: Evolution of IR transmittance (%) of the different compositions of the PVDF/PMMA (50/50) casted in the DMF as a function of the wave number(cm^{-1})

UV-visible spectroscopy:

In table 2 and Fig.4 showing the absorbance variations as a function of the different compositions of the

PVDF/ PMMA blends in solution in DMF before and after exposure to artificial weathering and salt spray.

Table 2: Absorbance variation versus different compositions of PVDF/PMMA blends at before and after exposure to artificial weathering at wavelength of 200nm .

Absorbance	PVDF	PMMA
Before exposure	0,914	1,690
After exposure	0.927	0.565

Table 2 concerns films, before and after exposure to artificial weathering, it has been observed that for the PVDF, the absorbance value is the same compared to the reference film (before aging) (0,914) and that after exposure to artificial aging (0,927) which explains the

stability of PVDF even after the equivalent of two years of aging.

However, for the PMMA, the absorbance values changed compared to the reference film (before aging) (1,690), that after exposure to artificial aging (0.565) which explains the tendency of PMMA degradation.

Table 3: Absorbance variation versus different compositions of PVDF/PMMA blends at before and after exposure to salt spray a wavelength of 200 nm

Absorbance	PVDF	PMMA
Before exposure	0,914	1,690
After exposure	0,905	0,661

Table 3 concerns films, before and after exposure to salt spray, it has been observed that for the PVDF, the absorbance value is the same compared to the reference film (before exposure) (0,914) and that after exposure to salt spray (0,905) which explains the stability of PVDF .

However for the PMMA, the absorbance values changed compared to the reference film (before exposure) (1,690), that after exposure (0,661) which explains the tendency of PMMA degradation.

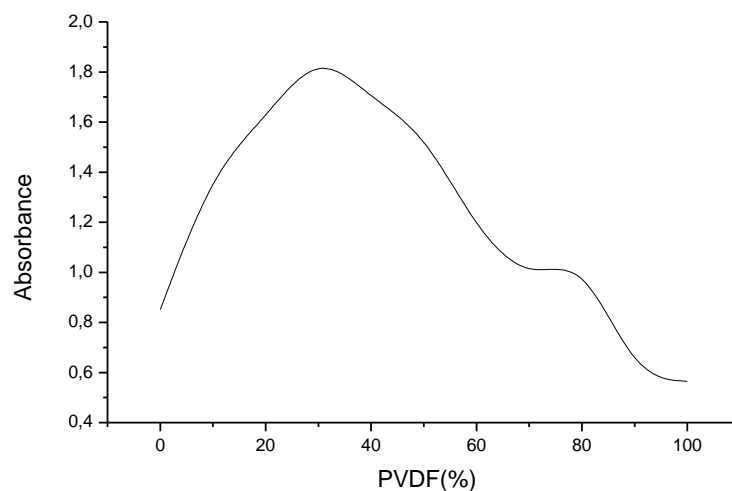


Fig.4: Absorbance Evolution as a function of the different compositions of PVDF/PMMA blend at a wavelength of 200 nm

The figure 4 which represents the absorbance variation as a function of the different compositions of the PVDF/PMMA blends dissolved in the DMF showed that there is a synergism with an optimum at 30/70.

Conclusion

From the different results obtained, it can be concluded that infrared spectroscopy (FTIR) of PVDF/PMMA blends casted in the DMF showed the superposition of the spectra of all compositions where the exclusion of any chemical reactions between two polymers or the presence of the double bonds characteristic of dehydrofluorination. On the other hand, the PVDF/PMMA studied blend showed the presence of two crystallinity phases α and β . UV visible spectroscopy showed that the PVDF is very stable (the invariant absorbance values at 200 nm wavelength) after the equivalent of two years of aging. In contrast, the absorbance of PMMA has changed at the same wavelength (200 nm), which explains its tendency to degradation. The UV-visible spectroscopy showed that for the various compositions of the PVDF / PMMA blends dissolved in the DMF, the absorbance increased and therefore the solubility of the blend.

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