# OPTICAL PROPERTIES OF PVDF/ZNO NANOCOMPOSITES

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***Abstract*— : Polymeric materials that are used in photonic devices gain a strong interest by scientific researchers. To improve their optical properties, there is a need to focus on polymeric nanocomposites. In the present work, pure PVDF and PVDF/ZnO nanocomposite films have been prepared by using a casting method. Acetone is used as the solvent for the polymer. PVDF/ZnO nanocomposites are prepared by mixing ZnO nanoparticles with polyvinylidene fluoride (PVDF) as the polymer matrix. Different contents of ZnO nanoparticles are used as the filler.Analysis of FTIR spectra confirmed the formation α and β phases. The transmittance, absorbance and reflectance spectra are tested. They showed a very low transmittance and a high absorbance in the UV region. The linear absorption and extension coefficients are calculated. They depended on the concentration of ZnO nanoparticles in the nanocomposites. Evaluation of the refractive index is also carried out. SEM and FESEM images of the samples showed that their surfaces are rough.**

*Index Terms*— **: Nanocomposites, PVDF/ZnO, Optical properties, ZnO nanoparticles**

## I. INTRODUCTION

In the last decade, a new research area had opened up and received strong attention on the use of polymeric nanocomposites.The synthesis of polymer nanocomposites, which include the nanometric inorganic materials is considered as an integral aspect of polymer nanotechnology. Depending on the presence of the inorganic materials, these nanocomposites have improved and offered particular properties in variety compared to pure polymers.

Nowadays, PVDF has been in the center of scientific interest. It is a semi crystalline polymer which has a special feature that distinguishes it from other polymers its uncommon polymorphism.It shows five crystalline phases named α, β, γ, δ and ε [1]. During the crystallization, the α form,which is representing the most stable polymorph of PVDF [2], can be obtained easily from the melt. Whereas β phase can be produced by mechanically deformation, which has the greatest attention technologically due to its better piezoelectric properties. [1] During the preparation of a PVDF sample, more than one phase were usually produced depending on the different parameters. These parameters include temperature,the type of solvent, ambient conditions, solution concentration and crystallization rate, which in turn depend on the rate of solvent evaporation. Although a fine control is still lacking, researchers are focusing on the evaporation rate. Formation of β phase occurred during low evaporation rates of solvent, while high evaporation rates resulted mostly the α phase [3]. The properties of PVDF afford a wide range of scientific and technological applications such as optical switches, optical waveguides, light emitting diodes, lenses and nonlinear optical devices [4].

By successfully joining materials of different characteristics to prepare nanocompositeas a single material, novel properties can be obtained. Optical properties of nanocomposite have gotten much attention because they are different from the individual polymers. In addition, they offer unexpected properties which greatly differ from that of conventional materials [5]. The film of pure inorganic material has loose film stress and reduces its compatibility with the substrate.Whereas, film of nanocomposite polymer-inorganic material owns good film form and mechanical properties. They lead to improving the film stress and its compatibility with the substrate[6].Promising applications encouraged the study of the optical properties of nanocomposites. Important changes in optical properties can be detected when they contain nanoparticle materials.

Zinc oxide is one of the most attractive semiconductors due to the unique combination of electrical and optical properties. Besides that, ZnO can be synthesized in a wide range of particle sizes and shapes [7]. Our earlier report [ 8 ] revealed that adding inorganic nanoparticles,such as ZnO into an organic polymer,such as PMMA and PVDF, can enhance their optical properties due to an interfacial interaction between them.

In recent years, many studies have focused on the crystalline structure and the crystalline phases that were produced during the preparation of the PVDF film. Most of those studies are interested in the formation [1] of β phase, and sometimes γ phase, because they are very important to be used as piezoelectric material due to its high piezoelectric activity. In addition, they used DMF, HMPA, DMSO and mixed DMF - acetone as solvent. Despite of a few studies which are looking for the optical properties of PVDF, there is a clear lack of details of those studies. Cardoso et al (2011)[9] have prepared PVDF thin films by spin coating. They used DMF as the solvent. They studied the effect of temperature annealing on the transmittance spectra and FTIR of the samples. Abdelrazek and Holze (2011) [10] have studied the optical properties of PVDF and LiBr/$MnCl_2$ as fillers. They studied the absorption spectra of the samples and determined the energy gap between them. Different concentrations of ZnO nanoparticles were used as filler into polyvinylidene fluoride (PVDF) by Indolia and Gaur (2013) [4].They used DMF as solvent. Those studies on the optical properties found that increasing the ZnO nanoparticles in nanocomposite had increased the absorption of UV light.The absorption coefficient and optical band gap of nanocomposites were calculated.Bhatti et all (2013) [11] have prepared PVDF film by using casting method. They used acetone as solvent. They confirmed the production of both α and β phases, and then investigated the optical properties of the samples and studied the effect of annealing. Zhang et all (2013) [6] have prepared and characterized PVDF/ $ZrO_2$-$TiO_2$ film .They showed the transmittance spectra of the films and calculated their energy gap and refractive index. Ahmed et all (2013) [1] have studied the effect of Gamma radiation on the absorption spectra and the energy gap of PVDF sheets.

In the present work, pure PVDF and PVDF/ZnO nanocomposites as films are prepared by casting method. Acetone was used as a solvent for the polymer. The linear optical properties of pure polymer and nanocomposites are investigated. To the best of our knowledge, there is no report published to describe the details of linear optical properties of pure PVDF and PVDF/ZnO nanocomposites by using acetone as solvent. There is only one research [11] for pure PVDF.

## I. METHOD

Preparation of PVDF/ZnO nanocomposites was done as follows: Firstly; PVDF solution was prepared by adding a suitable solvent such as acetone. To prepare 2 wt % of PVDF /Acetone, 8 mg of polyvinylidene fluoride(PVDF), which was purchased from Sigma-Aldrich,was dissolved in 0.492 ml acetone. A magnetic stirrer at an angular velocity (400 RPM), temperature (60 $^{Oz}$) and time (30 minutes)was put into the PVDF/Acetone solution to help them dissolve. Secondly, to prepare nanocomposite PVDF/ZnO with different concentrations of ZnO (1 %, 3 %, 5 %,8 % and 10 %), ZnO with particle sizes (50 < size < 100 nm),which was purchased from Sigma-Aldrich, were added to the mixture of PVDF/ Acetone.Then, using a sonicator for 15 minutes, nanoparticles in the solution were dispersed.After that, the solution was stirred at room temperature, time 1hour and angular velocity 400 rpm by a magnetic stirrer to obtain homogeneous solution. Deposition of the solution was done by a casting method which was used to prepare pure PVDF and PVDF/ZnO films by pouring the prepared solution onto a quartz substrate. The solvent was then allowed to evaporate inside the lab at room temperature, until dried samples of pure PVDF and nanocomposites (PVDF/ZnO) of different concentrations were obtained.

The transmittance, absorbance and reflectance spectra values of the present samples were measured using UV-Vis spectrophotometer (PerkinElmer instruments-Lambda 900 UV/VIS Spectrometer).The samples were checked by FT-IR spectroscopy, Brand: Perkin Elmer, Range : 4000 $cm^{-1}$ – 650 $cm^{-1}$ , Resolution: 4 $cm^{-1}$.

## II. RESULT AND DISCUSSION

### *A. FTIR Analysis*

Samples of pure PVDF and PVDF/ZnO nanocomposites were examined by FT-IR spectroscopy, brand: Perkin Elmer, range: 4000 $cm^{-1}$-650$cm^{-1}$ , resolution: 4 $cm^{-1}$. FTIR spectra, as the transmittance mode, of PVDF films in the range 650– 4000 $cm^{-1}$ are shown in Fig.1. According to previous works, the peaks at 766, 795, 974, 1402, $cm^{-1}$ identify the α phase, while peaks at 840$cm^{-1}$ and 1275–1279 $cm^{-1}$ are the identification of β phase[12,13]. Also, the peak at 3021$cm^{-1}$ corresponds to β phase[7] . IR vibration modes due to the γ-phase are at 833, 1171 and

1233 $cm^{-1}$.Vibrational bands at 766 are $CF_2$ bending and skeletal bending mode and 795 $cm^{-1}$ $CH_2$ rocking mode, the peaks at 840 $cm^{-1}$ is $CH_2$ rocking mode [2,14]. The 840 $cm^{-1}$ band is common to the β and γ phases; a sharp and well-resolved band indicates the β phase, whereas a broadband indicates the γ phase. The broad band is due to imbrication, in which the 833 $cm^{-1}$ band often appears as a shoulder [13,15]. The 1404 $cm^{-1}$ represents a typical vibrational band which corresponds to the deformed vibration of the $CH_2$ group[16] . Besides that, literatures indicated that ZnO nanoparticles have stretching and bending bands. But they appeared to be suppressed, one of them revealed that the peaks are between 360cm $^{-1}$ and 420$cm^{-1}$ [ 17 ] or near 420 $cm^{-1}$ [18], or at 468$cm^{-1}$ and 480 $cm^{-1}$ [19 ],or near 438$cm^{-1}$ [20 ]
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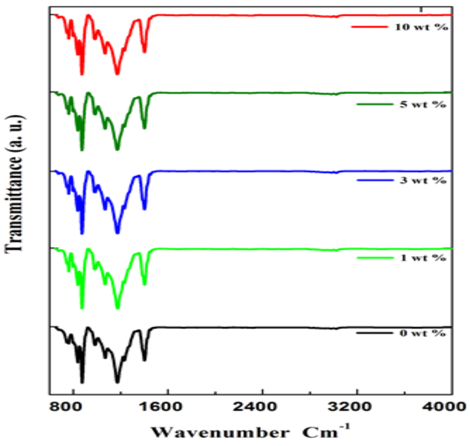


**Figure1. FTIR spectra of pure PVDF and PVDF/ZnO nanocomposites films.**

*B. UV- Visible Spectra*

**1. Transmittance spectra**

Figure 2 demonstrates the transmittance of pure PVDF and PVDF/ZnO nanocomposites. The transmittance of pure PVDF is higher than PVDF/ZnO nanocomposites. The transmittance of pure polymer and nanocomposites shows more decrement in the UV region than in the visible region. The effect of adding ZnO nanoparticles is clear; they have a very low transmittance in the UV region that decreased with increasing content of ZnO in nanocomposite.These results correspond to the study by Indolia and Gaur [4].

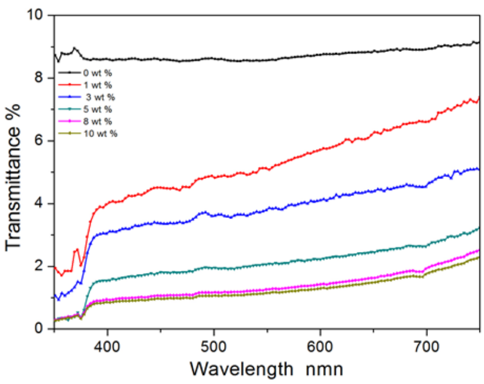


Figure 2. Transmittance of pure PVDF and PVDF/ZnO nanocomposites .

*C. Absorption spectra*

Figure 3 demonstrates the UV-visible absorption spectra of pure PVDF and PVDF/ZnO nanocomposites .The absorption spectrum of pure PVDF is limited in the UV region, but it is enhanced when ZnO nanoparticles were added, which had a high energy gap .[10] .

The curves of nanocomposites of high ZnO concentration showed a clear peak in the UV region and less absorption in the visible region. The peak of high absorption at around 375nm is observed. That is due to the absorption of ZnO nanoparticles, which was corresponding to the results that was obtained by Indolia and Gaur [4]. In addition, the lower absorption in the UV and visible regions is due to the roughness of the surfaces that increased with increasing of concentration ZnO, thus caused the scattering and then losing to incident intensity. [21]

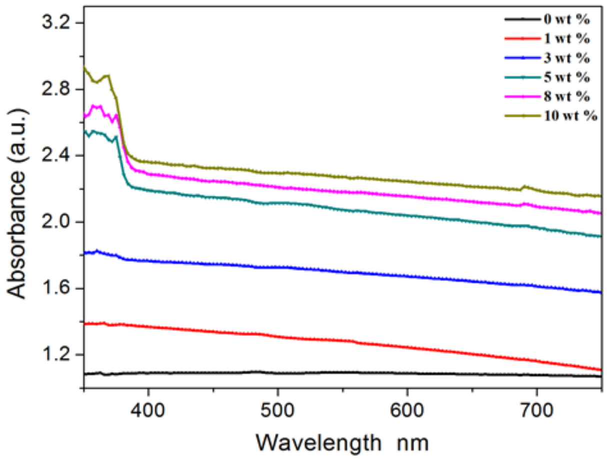


**Figure 3 The Absorbance of PVDF pure and PVDF/ZnO nanocomposites**

**3. Reflectance spectra**

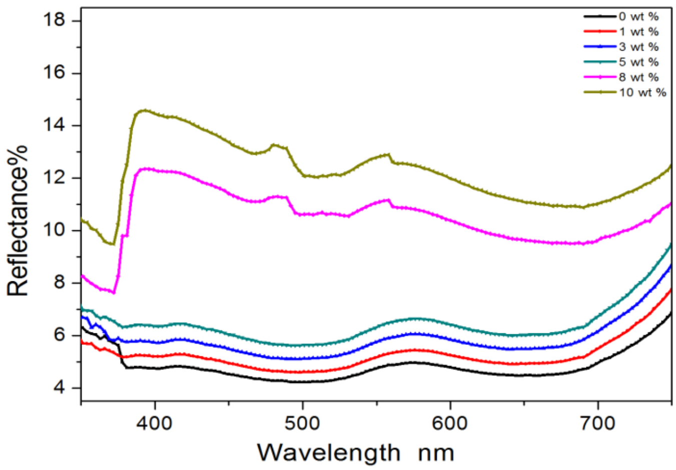


**Figure 4. The reflectance of pure PVDF and PVDF/ZnO nanocomposites .**

Figure 4 shows the reflectance of pure PVDF and PVDF/ZnO nanocomposites. The reflectance of the PVDF film is lower than the nanocomposites. It increased with increasing concentration of ZnO nanoparticles in nanocomposites. The reflectance in the UV region decreased sharply at around 375nm, which represents the peak absorption of ZnO nanoparticles, then increased until around 400 nm .That is clear in the high concentration of ZnO nanoparticles in nanocomposites .The increment of reflectance in the visible region, especially in samples which contained a high percentage of ZnO, is due to the roughness of the surfaces that were observed in SEM and FESEM images.

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*D. 4. Calculation of linear absorption coefficient ( α ):*

The linear absorption coefficient (α) for the samples were calculated from [22]:

$$\alpha = \frac{1}{d}\ ln\ \frac{(1-R)}{T} \qquad (1)$$

Where d is the thickness of the sample , T is the transmittance and R the reflectance.

The thickness of the film was measured by FESEM cross section; it was 9.5-9.9 µm. The values of transmittance and reflectance were obtained from the data of UV-Vis. Fig. 5 demonstrates the absorption coefficient α as a function of wavelength for pure polymer and PVDF/ZnO nanocomposites of different weight %. It is clear that α depends on the wavelength of light that is actually being absorbed. Pure PVDF sample has a lower value of α than nanocomposites samples,due the effect of ZnO nanoparticles.The absorption coefficient increased with increased concentration of ZnO nanoparticles.Since ZnO nanoparticles have low transmittance and high absorbance in the UV region, tnanocomposites samples show higher value of α in the UV region compared with its value in the visible region.

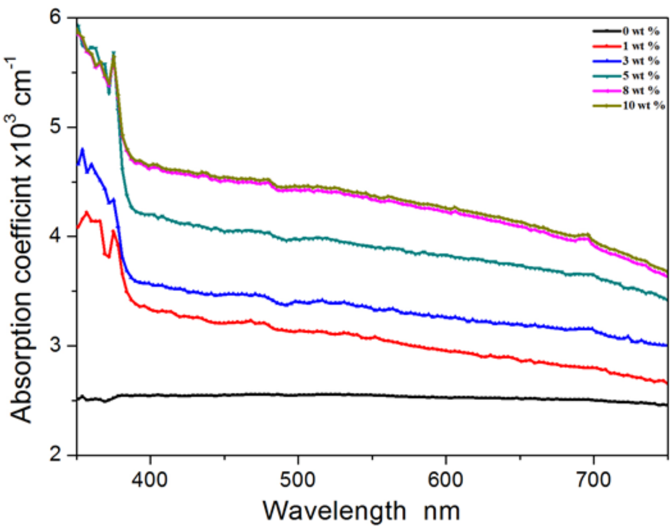



**Figure 5. Absorption coefficient α for PVDF/ZnO nanocomposites .**

*E. Calculation of extinction coefficient (K):*

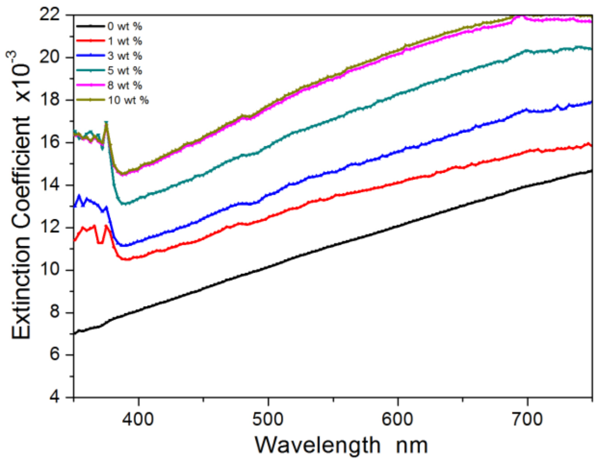



**Figure 6. Extinction coefficient (K) for pure PVDF and PVDF/ZnO .**

The extinction coefficient (K) was calculated from[23,24]:

$$K = \frac{\alpha\lambda}{4\pi} \qquad (2)$$

Where α is the linear absorption coefficient and λ is the wavelength

From Fig. 6 the curve of pure polymer shows a gradual increment in the UV and visible regions. The curves of nanocomposites show increment in the UV region until the absorption peak of ZnO at 375nm,and then they decreased. They increased gradually in the visible region until the end of the region to near IR, 700-750 nm, when they appeared to be decreased.

*F. Calculation of Refractive index (n) :*

The refractive index (n) was calculated from[23, 25] :

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \qquad (3)$$

Where R: Reflectance, n: linear refractive index, K: extinction coefficient.

When $K^2 << (n-1)^2$, so

$$R = \frac{(n-1)^2}{(n+1)^2} \qquad (4)$$

$$n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \qquad (5)$$

Figures 7 describes the change in refractive index (n) for pure PVDF and PVDF/ZnO nanocomposites as a function of wavelength. The refractive index of pure PVDF film has the value of around 1.5.In nanocompasites samples, refractive index increased with the increment of ZnO nanoparticles.These results corresponded to the results which were obtained from [4]

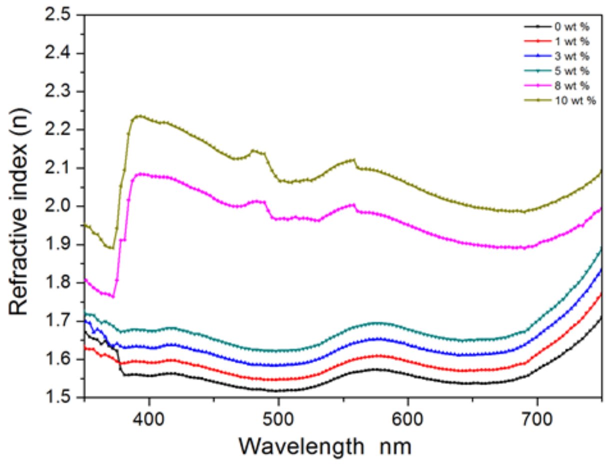
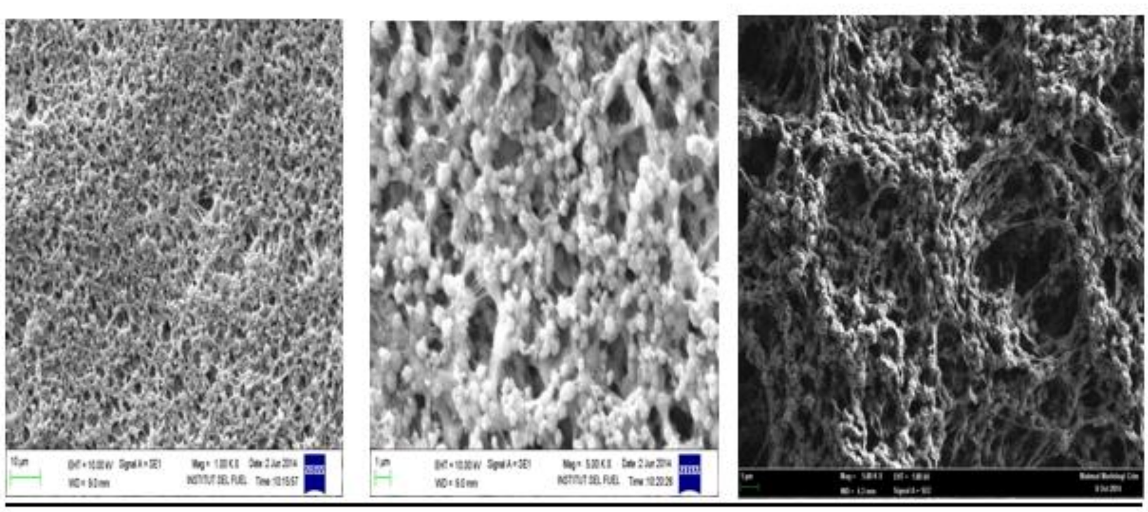



**Figure 7 . Refractive index (n) for pure PVDF and PVDF/ZnO nanocomposites**

## SEM AND FESEM



(a) (b) (c)

**Figure 8. demonstrates the micrograph of the PVDF film, (a) and (b) SEM images of PVDF and (c) FESEM image of PVDF/ZnO.**

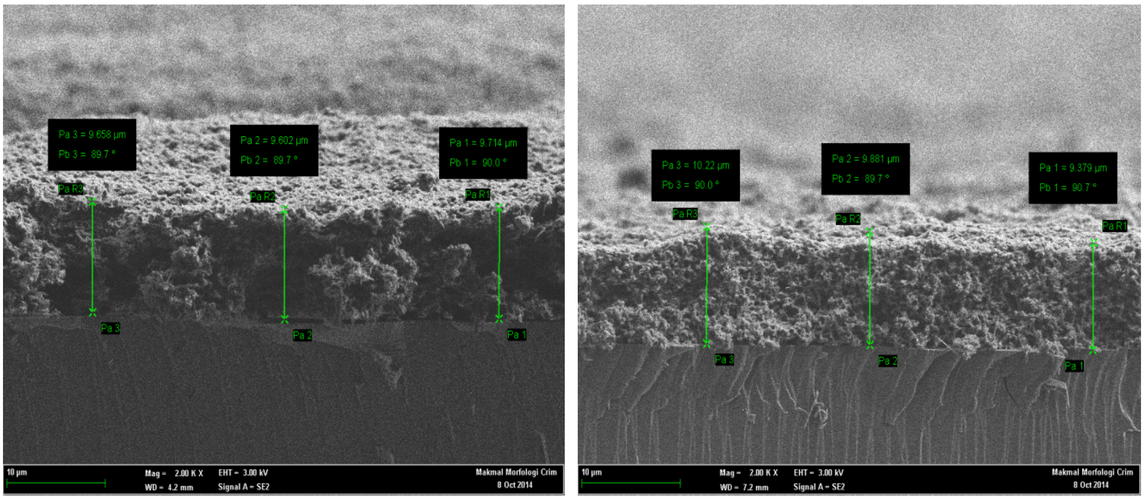



**Figure 9 The FESEM cross section of the PVDF/ZnO film.**

Figure 8 shows the SEM and FESEM micrographs of PVDF films. It is clearly seen that the surfaces of all samples appeared rough, porous and contained inhomogenously distributed spherulites (nearly spherical shape) with different sizes. Random distributions of pores at spherulite boundaries were also observed. Fig. 9 shows the cross-section of the PVDF/ZnO films. The thicknesses of the films were approximately 9.6-9.9µm. It is noted that the shape of the top and bottom surfaces is irregular and contained a non-homogeneous distribution of spherulites.

## III. Conclusion

Films of pure PVDF and PVDF/ZnO nanocomposites with different concentrations of ZnO nanoparticles are prepared successfully by the casting method. The formation of α and β phases was confirmed through the analysis of FTIR spectra.Nanocomposites samples showed low transmittance and high absorbance in the UV region depending on the content of ZnO. The reflectance of samples showed a lower value at 375nm, which represents a peak absorption of ZnO nanoparticles.An increment of the refractive index was observed with increasing ZnO concentration.SEM and FESEM images of samples demonstrated that the surfaces of the samples appeared rough.

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