Original Article

Synthesis and structural-biological correlation of PVC\PVAc polymer blends

A.M. Abdelghany a,b,∗, M.S. Meikhalic, N. Asker d

a Spectroscopy Department, Physics Division, National Research Centre, 33 El Behouth St., 12311, Dokki, Giza, Egypt
b Basic Science Department, Horus University, International Coastal Rd, New Damietta, Kafr Saad, Damietta Governorate, Egypt
c Physics Department, Faculty of Science, Mansoura University, 355165, Mansoura, Egypt
d Basic Science Department, Faculty of Engineering, Horus University, International Coastal Rd, New Damietta, Kafr Saad, Damietta Governorate, Egypt

Article history:
Received 20 June 2019
Accepted 28 June 2019
Available online 22 July 2019

Keywords:
Polyvinyl chloride (PVC)
Polyvinyl acetate (PVAc)
FTIR
XRD
UV/vis Optical spectroscopy
Antibacterial

Abstract

PVC\PVAc polymer blend with different mass fraction concentration were prepared using traditional solvent casting technique. Fourier transform infrared FTIR used to identify various vibrational groups presented in associated with structural changes. X-ray diffraction data approve the amorphous nature of all samples despite their concentration while optical (UV\vis) spectra confirm the complexation behavior of blend system and their miscibility. Optical energy gap and Urbach energy were calculated for further data interpretation. The obtained energy gap data determine the direct transition which suggests that a prepared blend is a conductive material. However, Urbach energy shows no crystal lattice disorder change that ensures X-ray results. The Scanning electron microscope (SEM) reveals the smooth and homogenous nature of the surface morphology for all proportions. Prepared films showed good antibacterial characteristics against gram-positive pathogenic gram in contrast with gram-negative, fungal, and yeast.

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1. Introduction

Polymeric matrices have a considerable effect in the field of Biomedical, especially in cardiac surgery and dialysis treatment. The materials used in biomedical devices must have particular characteristics such as low cost, biocompatibility, resistance to kinking, service life, mechanical flexibility ability to sustain the procedure of sterilization [1].

Polymer blend has induced a lot of interest in each academic and industrial applications because blending process allows one to establish tailored properties in materials that are superior compared to that of each individual component polymer [2-4]. Such characteristics depend upon the miscibility between constituents of a polymer mixture [2,5] that arises from specific interactions including dipole–dipole forces and charge transfer complexes for homopolymer mixtures or segment–segment repulsion inside the blends [4].
The chemical structure of the virgin polymers and the preparation method play a great role in the physical properties of the resulting blend. These two aspects are related to the nature of the intermolecular interactions generated between the chains of polymers. It is reasonable to guess significant changes in the electrical, optical, morphological and antibacterial properties when two individual polymers are blended together. The ease of preparation with low cost and the simplicity of controlling the physical properties by using compositional changes were the main advantages in polymer blending [4].

Polyvinyl chloride (PVC) is the leading thermoplastic material that can be considered as a third widely produced polymeric material in the world that is formed by free radical polymerization of vinyl chloride [6,7]. This resin shows low thermal, thermoxidative and photostability and becomes colorless due to the genesis of a conjugated polyene series in a zipper-like technique [7]. In addition, PVC is assumed to be a relatively low-cost, it has huge industrial interests due to the ability to access the basic raw materials and its superior properties [8]; PVC owe a superior chemical stability, durability, non-toxicity, high biocompatibility, flexibility character and it has a good resistant for aggressive environments so it is a suitable candidate for manufacturing of wiring, cables, housing material and in many medical instruments due to their safety and transparency which makes it suitable to use as a resin and in blood bags [6].

PVC is used also in biomedical devices, it is the main participant in the use of catheters, endotracheal, blood bags and tubes oxygenators, surgical dressings, and circulation tubes [9]. PVC widely used in the blood derivatives storage because the effect of ascertained stabilizing that exerted on red blood cells by this material.

One of the most commonly used thermoplastic adhesives is polyvinyl acetate (PVAc). It is fabricated by polymerization the free radical of vinyl acetate. It is a synthetic resin polymer, which has a glass transition temperature: 70–210 °C and melting point 30 °C [10]. A possible application of this type of polymer is in the area of adhesives for porous materials, particularly for wood, paper, and cloth, bones and as a consolidating for porous building stone, in particular, sandstone [11].

PVAc has also been applied in different medical application due to its biocompatibility. The presence of such functional group COOH in PVAc usually acquire it good biocompatibility when contact with body fluids, blood, tissues. Polyvinyl acetate is an inert polymer and it does not induce a deleterious reaction in living tissue. The previous study of the embolized rat kidney showed no detectable damage in the vessel wall and no recanalization for up to 6 months [12] In another paper, PVAc prevents the lysis of erythrocytes and adsorption of serotonin from platelet-free plasma [13].

PVCPVAc copolymer is one of the cheapest thermoplastic copolymers which possesses high oil resistance and lower softening temperature as well as reduced hardness and stiffness and needs less amount of plasticizer when compared with PVC [11].

Most of the previous studies were done on polyvinyl chloride (PVC) modified by a different type of polymers. Otherwise, limited papers on modification the characteristic of PVC by adding polyvinyl acetate (PVAc). So, this study is devoted to shedding light on the function of PVAc in the modification of wide range of characteristics of poly vinyl chloride (PVC).

The presented work aims to shade further insight about the new characteristics and applications of the prepared polymer blend, thus there is no survey in the use of both PVC/PVAc blend in the field of biomedical applications.

2. Materials and methods

2.1. Materials and sample preparation

Thin films of various mass fractions were prepared via traditional casting route using high molecular weight polyvinyl chloride (PVC) of chemical formula [−CH₂−CHCl−]ₙ and polyvinyl acetate (PVAc) of chemical formula (C₄H₇O₂)ₙ supplied by Sigma Aldrich company. Both polymers were dissolved in Tetrahydrofuran (THF) common solvent supplied by Fischer Co. Pre-calculated masses was dissolved separately using a magnetic stirrer at room temperature. Obtained viscous liquids stirred vigorously to about 3 h to ensure homogeneity and complexity of both polymers. Viscous liquids were then poured in a glass Petri-dishes at temperature 40 °C for 2 days until all solvent traces were evaporated. Obtained films were peeled from the petri-dishes and kept at dissector until use. Sample nomination and compositions were listed in Table 1.

2.2. Sample characterization and optimization

FTIR optical absorption spectra were recorded using a single beam Nicolet is10 spectrometer within the spectral range 4000–400 cm⁻¹ using absorption mode with 32 scans and resolution 2 cm⁻¹ to study the structural variations within the polymeric matrix. Electronic spectral data were recorded using the UV/vis spectrophotometer (V-570 UV/Vis–NIR, JASCO) in the wavelength region of 190–1100 nm at room temperature. Thin transparent films of about thickness (0.015–0.02 mm) were utilized with air as a reference substance. Amorphous nature of prepared samples were investigated using a (Philips PW1710 diffractometer) occupied with Cu ka as a source of X-ray, operating voltage 30 kV with (λ = 1.5406 Å) with a tube operating voltage of about 30 kV. The Bragg’s angle (2θ) in the range of (5–70°) at STP and the diameter of the incident beam can reach to 100 μm. The Diffraction pattern was indicated in reflection mode at scanning rate 0.6° /min. Scanning electron microscope type (JEOL JSM-6510LV. USA) was operated with 20 kV source to describe the surface morphology of the prepared samples. In order to minimize sample charging effect results from the incident electron beam prepared samples were coated with a thin layer of gold.

Traditional minimum inhibition zone (MIZ) method was used to investigate the antibacterial characteristic of the studied samples [10]. In this test, four different test microbes namely: Candida albicans (yeast), Staphylococcus aureus (G+ve), Escherichia coli (G–ve), and Aspergillus niger (fungus) were used. First, we have used plates of nutrient agar which were seeded regularly with 0.1 ml of 105–106 cells/ml in case of bacteria and yeast. After that gel cutter (Cork borer) was used in sterile
condition to make 1 cm diameter hole in media. In order to make base layer, we must pour only drop of the melted agar into the hole, then allowed it to solidify. Only (0.1 ml) of the tested sample was poured into this hole, then keep plates at a temperature about (4°C) for 2–4 h to allow maximum diffusion. For bacteria, plates were incubated then at 37°C for 24 h and at 30°C for 48 h in an upright position to allow maximum growth of the organisms.

The test was done more than once and the mean of the resulted reading was noted. Finally, we measured the diameter of zone of inhibition in (mm) in order to determine the antimicrobial activity of the tested samples, that tell us the largest the diameter of inhibition zone the more the ability of polymer blend to resist bacteria [14–16].

The % activity index for the blend was obtained using the formula as:

\[
\% \text{Activity Index} = \frac{\text{The diameter of inhibition zone of test compound}}{\text{The diameter of inhibition zone of the standard}} \times 100
\]

3. Result and discussion

3.1. Fourier transform infrared analysis (FTIR)

Fig. 1 shows a FTIR optical absorption spectrum of virgin polyvinyl acetate (PVAc) sample. Obtained experimental data can be discussed and interpreted according to the studied regions that can be classified to functional group region (4000–1700 cm\(^{-1}\)) and fingerprint region (1700–500 cm\(^{-1}\)). The broad bands at about 3627, 3452 cm\(^{-1}\) are attributed to the vibrations of (OH) groups while the bands at 2966 cm\(^{-1}\) and 2928 cm\(^{-1}\) may be attributed for asymmetric and symmetric stretching vibration of (CH\(_2\)) respectively. The first pronounced peak observed in fingerprint region is at 1740 cm\(^{-1}\), is assigned to the vibration of the carboxyl group (C=O), a peak of medium intensity at 1434 cm\(^{-1}\) was pointed to \(\delta(\text{CH}_2)\) group, and the strong peak at 1372 cm\(^{-1}\) refers to \(\delta(\text{CH}_3)\). The peak around 1228 cm\(^{-1}\) for the (C-O) bond, while peak around 1121 cm\(^{-1}\) is the vibration of (C-C-C) and (C-C-O) bonds, also there is a strong intense peak at 1025 cm\(^{-1}\) which indicates vibrations of (C-C) group. The bands at 946, 797, 606 cm\(^{-1}\) were attributed to r (CH\(_3\)), r (CH\(_2\)), \(\delta(\text{CH}_3\text{COO})\) groups respectively [10]. All observed bands with their assignment can be tabulated as shown in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FTIR bands of constituent virgin polymer and their assignment.</th>
<th>Assignment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>3627–3452, 2966, 2868, 2928, 1740, 1434, 1372, 1121, 1025, 946, 797, 606</td>
<td>OH vibration, CH(_3) asymmetric stretching vibration, CH(_2) symmetric stretching vibration, C=O vibration, (\delta(\text{CH}_2)) vibration, (\delta(\text{CH}_3)) vibration, (C-C-C) and (C-C-O) vibration, C-C group vibration, r(CH(_3)) – r(CH(_2)) vibration, (\delta(\text{CH}_3\text{COO}))</td>
<td>[10]</td>
</tr>
<tr>
<td>PVC</td>
<td>2912–2970, 1427, 1333, 1254, 1100–1000, 962, 831, 692, 614</td>
<td>C=H stretching vibration, CH(_2)–Cl angular deformation, CH(_3) deformation group, CH–Cl out of plane angular deformation, C=Cl stretching bond vibration, C–H out of plane trans deformation, C–Cl stretching vibration</td>
<td>[8,17]</td>
</tr>
</tbody>
</table>
Fig. 2 - FTIR absorption spectra of pure PVC.

Fig. 3 - FTIR absorption spectra of several concentrations of polymeric blend PVC/PVAc.

Fig. 4 - X-ray diffraction patterns of (a) pure PVAc and (b) pure PVC.

Fig. 5 - XRD patterns of pure PVAc, PVC and different concentration of their blends.

Fig. 2 shows the characteristic absorption band of pure PVC. In function group region there are two peaks at 2912 cm\(^{-1}\) and 2970 cm\(^{-1}\) assigned to the C–H stretching bond, while the characteristic groups in the fingerprint region are: the angular deformation of CH\(_2\)-Cl at about 1426 cm\(^{-1}\), CH\(_2\) deformation group at 1333 cm\(^{-1}\), CH–Cl out of plane angular deformation at 1252 cm\(^{-1}\), and at about 1100–1000 cm\(^{-1}\) was the stretching bond vibration of C=C, C–H out of plane transformation at 962 cm\(^{-1}\), and C–Cl bond stretching at 831, 692, and 614 cm\(^{-1}\) [8,17]. All observed bands with their assignment can be tabulated as shown in Table 2.

FTIR would be important when complexation has occurred between crystalline and amorphous phase. The FTIR spectra of the addition of PVAc to PVC are shown in Fig. 3. The most dominant band to acetate groups was found at 1740 cm\(^{-1}\) which attributed to C=O, and its intensity increase obviously by increasing the concentration of PVAc. The second most intense peak was detected at 1254 cm\(^{-1}\) which became border with the addition of PVAc which suggest the acetate structure of PVAc.

In addition to that, by cross-linking PVC with PVAc, the intensity of CH\(_2\) asymmetric stretching vibration peak (\(\nu = 2971\) cm\(^{-1}\)) was decreased rapidly with the first addition of

PVAc when compared to pure PVC. When PVAc is blended with PVC a small shoulder appears in the spectrum at the lower wavenumber (\(\nu = 1025\) cm\(^{-1}\)). It has found a great increase and decreases in intensity with increasing PVAc content at wavenumbers 1025 and 599 m\(^{-1}\), respectively.

3.2. X-ray diffraction analysis (XRD)

XRD is a very important tool for the investigation of the internal structural arrangement of solid materials [18]. In the present study, the amorphous structure of varying weight fractions PVAc/PVC were determined via XRD patterns and to correlate their internal structure with other physical and chemical properties [19].

Fig. 4 reveals XRD spectra of both polyvinyl acetate (PVAc) and polyvinyl chloride (PVC) virgin polymers. Spectral data of PV sample shows at least three halos at about 17.7 °, 24.7 ° and 40.6 ° as reported previously by Abdelghany et al. [8,20], while the diffractogram of PVAc sample exhibit two broad halos at 2θ = 15.07° and 22.71° reflecting the amorphous nature of the studied virgin polymers [21].
3.3.2. UV/vis absorption spectroscopy

UV/vis spectroscopy is used as a powerful technique to investigate the optical properties of an organic compound. Optical absorption and the optical absorption edge play an important role in getting information about optically induced transitions and study the energy gap and band structure of a non-crystalline material [22].

3.3.1. Analysis of UV/vis spectrum of the blending system

Fig. 6 shows UV/vis spectra of both pristine polymers in combination with their varying mass fraction blend (PVC/PVAc). All samples showed only two UV absorption peaks at about λ = 233 and 280 nm without any other peaks till the end of measurements this may be attributed to the transparent nature of both PVC and PVAc [23]. Previously published data attributed the absorption band at about 280 nm to π−π* electronic transition and the increased absorbance at wavelengths 233 nm is identified as C–Cl bond. The intensity of two absorption peaks at 233 nm and at 280 nm are slightly increased with increasing the concentration of PVAc which indicates an increase in the size of conjugated structures and unsaturated group concentration.

3.3.2. Calculation of optical energy gap

Electrical properties of materials (insulator–semiconductor–conductor) are classified into 2 types: (a) direct band gap where the top of the valence band is corresponds to the bottom of the conduction band, (b) indirect band gap in which the transition from valence band always associated with a phonon of the right magnitude of crystal momentum due to the bottom of the conduction band does not correspond to valence band [19].

The determination of polymer blend electrical behavior, values of direct and indirect energy gaps of all concentration are figured and calculated. The resulting values are then compared to Tauc’s values of the prepared samples which calculated using the following formula after extrapolating the maximum absorption peak to zero value (λc):

\[
E_{\text{gap}} = \frac{hc}{\lambda_c}
\]  

where \( h \) is Planck constant which equals to 6.62607004 \( \times 10^{-34} \) m\(^2\) kg/s.

As shown in Fig. 7, the determination of direct band gap and the indirect one occur by plotting a relation between \((ah) (ah)^{1/2} \) vs \( h \), respectively, then extrapolating the linear portion of the curves to zero absorption [24].

The relationship between absorption coefficients with photon energy has been proposed by Mott and Davis to calculate direct and indirect transition occurred in the band gap [18]:

\[
(ah)^n = k(h - E_{\text{opt}})
\]  

where \( h \) in eV is the incident photon energy \( (h = \frac{hc}{\lambda}) \), \( k \) is an energy independent constant is called band tailing parameter. Values of \( n \) are 2 for direct transition and 1/2 for indirect transition, \( a \) is the absorption coefficient [22].

The obtained values of \( E_d \), \( E_u \) and \( E_{\text{Urbach}} \) of different mass fractions PVC/PVAc samples estimated from Tauc plots Fig. 7 and tabulated in Table 3. Obtained data suggests that direct transition is the most prominent route that can be used to illustrate optical transition within the studied samples.

3.3.3. Determination of Urbach energy

The width of band tails \( E_U \) for localized states within the forbidden band gap that is related to the amorphous nature of the materials can be calculated via Urbach equation [21]:

\[
\ln(a) = \ln(a_0) + \frac{h \nu}{E_U}
\]

where \( a_0 \) is a constant, \( E_U \) is the Urbach energy, \( h \nu \) is the incident photon energy.

Urbach energy is the degree of crystalline lattice disordering caused by structural peculiarities that induced by external factors [25] and imperfection in the polymeric structure. The values of Urbach energy is obtained by plotting relation between photon energy \( (h \nu) \) against \( \ln(a) \) as shown in Fig. 8 and extrapolating the straight line of the curves to zero, then calculate the inverse slope of these lines in each curve.

From Table 3, it is concluded that Urbach energy of different concentration never show an obvious change with increasing the concentration of PVAc which indicate that the degree of crystal lattice disorder remains in the same range.

3.4. Scanning electron microscopy (SEM)

The miscibility of the PVC and PVAc was tested using SEM. Fig. 9 shows the surface morphology for selected samples (PVC–PVAc20–PVAc 50–PVAc 70–PVAc80–PVAc) with magnification 1500×. Firstly PVC makes pores in PVAc 20 in order to
start mixing and be miscible with polyvinyl acetate. Then it gradually increases with the concentration of PVAc, thus it is found increasing in the distribution of PVC inside PVAc. Finally, it is shown that there was a uniform distribution of PVC with PVAc which ensure the miscibility, homogeneity and the amorphous nature of the blend and support the validity of the method of preparation for the blend system.

3.5. Antibacterial activity

The antibacterial activity of the different concentration of polymer blend was tested against a panel of four microbes namely: (a) Staphylococcus aureus (Gram +ve), (b) Escherichia coli (Gram –ve), (c) Candida albicans (yeast) (d) Aspergillus niger (fungus).

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**Table 3 – Values of optical energy gap calculated by Tauc ($E_{\text{Tauc}}$), direct ($E_d$), indirect ($E_{\text{id}}$) and Urbach energies of studied samples.**

<table>
<thead>
<tr>
<th>PVAC conc. (%)</th>
<th>0.0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_d$ (eV)</td>
<td>5.09</td>
<td>5.14</td>
<td>4.95</td>
<td>5.04</td>
<td>4.98</td>
<td>5.09</td>
<td>5.12</td>
<td>5.03</td>
<td>4.76</td>
<td>5.16</td>
<td>5.09</td>
</tr>
<tr>
<td>$E_{\text{id}}$ (eV)</td>
<td>4.79</td>
<td>4.77</td>
<td>4.47</td>
<td>4.71</td>
<td>4.56</td>
<td>4.68</td>
<td>4.72</td>
<td>4.61</td>
<td>4.35</td>
<td>4.87</td>
<td>4.78</td>
</tr>
<tr>
<td>$E_{\text{Tauc}}$ (eV)</td>
<td>5.06</td>
<td>4.93</td>
<td>4.74</td>
<td>4.93</td>
<td>4.67</td>
<td>4.93</td>
<td>4.90</td>
<td>4.86</td>
<td>4.87</td>
<td>5.00</td>
<td>4.96</td>
</tr>
<tr>
<td>Urbach energy $E_U$</td>
<td>0.19</td>
<td>0.29</td>
<td>0.46</td>
<td>0.28</td>
<td>0.33</td>
<td>0.24</td>
<td>0.22</td>
<td>0.25</td>
<td>0.52</td>
<td>0.17</td>
<td>0.23</td>
</tr>
</tbody>
</table>
The important factors affecting on the antibacterial activity are the concentration, thickness of bacteria, the diameter of the clear inhibition zone and the quantity of an antibacterial agent that existing in the blend [26]. The data resulted in Fig. 10 shows that the zone of clear inhibition (diameter) in the case of gram-positive bacteria (Staphylococcus aureus) increase with increasing of the concentration of PVAc that means that the blend owes good results combined with such microbe. While the cases of gram negative bacteria (Escherichia coli), yeast (Candida albicans) and fungus (Aspergillus niger) demonstrated their poor effectiveness with different concentration of blend this conclusion as a result of a very small diameter of the inhibition zone even if increasing the concentration of PVAc. Finally, it is obvious that PAVc:PVC blend does not have broad-spectrum antibacterial activity.
4. Conclusion

Pristine samples of poly (vinyl chloride), poly (vinyl acetate) in combination with their variable mass fraction blends were successfully prepared using traditional solvent casting route. Prepared samples were examined for their structural changes using different spectroscopic techniques. FTIR spectral data reveal the presence of prominent characteristic bands attributed to the vibrational building units of both PVC and PVAc pristine partner. XRD pattern reveal the amorphous nature and homogeneity of all synthesized samples. Prepared films showed good antibacterial characteristics against gram-positive pathogenic gram in contrast with gram-negative, fungal and yeast.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES