Improvement of semiconducting and thermomechanical properties of polymer materials based on polypyrrole and polyvinylpyrrolidone

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Improvement of Semiconducting and Thermomechanical Properties of Polymer Materials Based on Polypyrrole and Polyvinylpyrrolidone

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Abstract

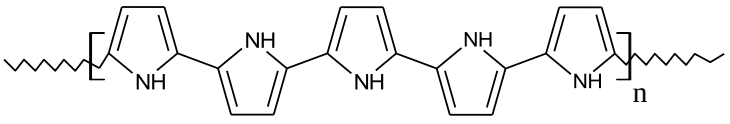
In this study, we investigate how the addition of polyvinylpyrrolidone (PVP), a thermoplastic polymer, contributes to enhance the processability, thermomechanical and semiconducting properties of a semiconducting polymer without side chains. Here, polypyrrole (PPy) is chosen as reference semiconducting polymer. Different blend ratio of PPy/PVP are prepared by in-situ polymerization in acidic solution. The pre-requisite for an effective gain in mechanical properties is to ensure an intimate mixing of both polymers. The miscibility of PPy with PVP is assessed preliminarily using thermodynamic approaches derived from the appropriate group contribution theory which is confirmed experimentally by thermal measurements using DSC and TGA, respectively. All PPy/PVP blend ratios exhibit a single glass transition temperature (Tg) characteristic of appropriate their miscibility in the solid-state. The morphology and thermal behavior of PPy/PVP mixtures is investigated by differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The potential specific interactions between PPy and PVP moieties are investigated both qualitatively and quantitatively using FTIR spectroscopy. The FTIR study reveal specific interactions mainly hydrogen bonding between antagonist groups of PPy and PVP. The TGA analysis showed an improved thermal stability. The optical gap of PPy in the mixture PPy/PVP (0.8- 0.5 eV) determined by UV-Visible spectrophotometry

is attributed to $\pi \rightarrow \pi^*$ transition, while the electric conductivity measured by the four-point method revealed their semiconducting behavior (57 - 3960 µS cm^{-1}). Electrochemical impedance spectroscopy (EIS) exhibits semicircles attributed to bulk material, whose diameter decreases with increasing temperature, thus confirming the semiconducting behavior of PPy; the data obey to an Arrhenius law with an activation energy of 0.1 eV and the conduction occurs by electrons delocalization though alternating double bonds.

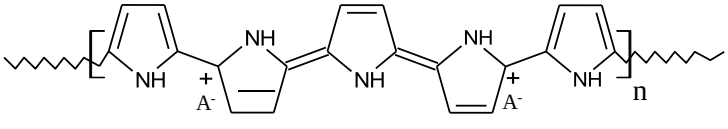
Keywords: Polypyrrole(PPy), Polyvinylpyrrolidone(PVP), thermal and semiconducting properties, heterogeneous system.

Introduction

The organic semiconductors are among the most and pertinent fields of research which continue to attract much attention to improve their physical and chemical properties. They are used in the solar energy conversion under various forms [1] and have many attractive properties like ease of synthesis, moderate electrical conductivity and thermal and chemical stability in their oxidized form. In this context, PPy is among the most extensively studied semiconducting polymers. Due to its intrinsic properties, it is a potential candidate as supercapacitors, batteries, biosensors and solar energy [2]. Structurally, PPy is more compact than polyaniline (PANI), and its linear structure contributes to its rigidity, which limits its applicability in various fields. Previous studies reported that PPy has a better thermal stability and electrical conductivity compared to doped (PANI). As shown in scheme 1, the presence of nitrogen in the polypyrrole structure allows specific interactions with a suitable thermoplastic matrix.



Benzenoid form (Neutral state)



(A^-: Countreion)

Quinoid form (Doped state)

Scheme 1. The neutral and doped forms of PPy.

It has been admitted that the nanostructured polypryrrole gives the obvious advantages over its bulk structured. Very recently, Y. Demei and co-workers have studied polypyrrole nanomaterials where they have focused mainly their interest on three aspects such as structure, properties and preparation of polypyrrole nanomaterials. They have concluded that controlling the size and morphology of PPy nanomaterials is still a major challenge in this field [3].

Previously, we have studied the semiconducting and photochemical properties of PPy [4]. and found that the conduction band is appropriately positioned with respect H_2O/H_2 level, yielding spontaneous hydrogen evolution reaction [5]. The doped polypyrrole can be obtained easily by chemical synthesis. However, the strong interchain interactions within the backbone of chain and the presence of conjugated double bonds make these conductive polymers infusible and insoluble in most organic solvents. Furthermore, due to this strong rigidity, these polymers exhibit poor mechanical properties, making the electrochemical characterization difficult to undertake.

To remedy this issue and enhance their properties, various methods have been proposed. One significant approach is blending of semiconducting polymers with suitable thermoplastic polymers, which represents a promising avenue for developing new organic semiconductors through in situ polymerization. This method is widely adopted and is regarded as both effective and cost-efficient. [6, 7].

Polyvinylpryrrolidone (PVP) is among the most studied thermoplastic polymer. It is an interesting linear polymer with a broad range of industrial applications. The presence of carbonyl groups in the structure of PVP is particularly interesting since it can be used to develop specific interactions with amine and imine groups of PPy. Thus, owing to advantageous characteristics, like its adhesiveness to various substrates, film formation property, and solubility in water, PVP can be applied in a variety of fields such as cosmetics, pharmaceutical and electronic [8,9].

In this contribution, we have firstly assessed thermodynamically the possibility to blend PPy with PVP using the group contribution model to calculate the solubility parameters of both polymers. Our main goal is to combine two types of polymers, conductor and insulator, in order to produce the semiconducting materials possessing improved properties with large scale applications. The binary system blend PPy/PVP are obtained by in-situ polymerization and studied by means of DMA and DSC analysis, FTIR spectroscopy and thermogravimetry (TGA). Their electrical conductivity and gap energy were measured by the four-point technique and

UV-Visible spectrophotometry respectively. The phase behavior and miscibility of these blends were examined according to their glass transition temperature (T_g). Moreover, the specific interactions, mainly hydrogen bonds, were studied qualitatively and quantitatively by FTIR spectroscopy. The X-ray diffraction (XRD), thermal stability and conductivity properties of these materials were also explored. The electrochemical properties of doped PPy were determined by EIS analysis.

Experimental

Materials

PVP with an average molecular weight of 40000 g/mol is purchased from Sigma Aldrich and used without any further purification. Doped PPy is obtained by chemical oxidation using molar ratios of HCl/pryrrole = 1.5 and $(NH_4)_2S_2O_8$/pyrrole = 1.15.

Pure PPy and PPy/PVP blend film fabrication

1 mL of pyrrole is added in the required amount of a HCl solution under stirring for 30 min. 3.79 g of $(NH_4)_2S_2O_8$ dissolved in distilled water is added dropwise to the solution. The polymerization was carried out under magnetic agitation at 273 K. The resulting dark green PPy powder is then filtrated and rinsed distilled water and ethanol to eliminate the traces of acid and oligomers. The obtained polypyrrole powders is dried under primary vacuum for several days.

Thus, PPy/PVP mixtures at different ratios were obtained by in-situ polymerization in the same conditions as mentioned above for pure PPy.

To prepare PPy/PVP films, different amounts of PVP are dissolved in methanol. An appropriate quantity of pyrrole and HCl (1 M) are added to the PVP solution. The resulting mixtures were stirred 1 h to ensure a better dispersion of pyrrole in the PVP polymer matrix. The polymerization is then initiated by a dropwise addition of the $(NH_4)_2S_2O_8$ solution. Blends of PPy/PVP are finally obtained by solution casting in a Teflon disk, dried in the open air for several days and in oven at 303 K for 48 h. The polymerization conditions of PPy and PPy/PVP are summarized in Table 1.

The glass temperature (T_g) of two polymers and of their binary blends was measured with a TA Instruments DSC 25 equipped with an intercooler and TA Instruments DMA DHR Series. The measurements were carried out at a heating rate of 20 ºC/min under N_2 flow and the Tg value was taken as the midpoint of the transition of the second scan.

FTIR measurement was carried out with a Nikolet iS10 FTIR spectrometer where 32 scans were collected with a spectral resolution of 2 cm^{-1} in ATR mode. The spectra of the PPy, PVP and their mixtures were obtained on the films prepared by casting in Teflon disks. All the samples were dried to constant weight under vacuum oven at 50 °C for several days to evaporate slowly the solvent.

DMA measurements were performed in a bending mode over the temperature range from -50 to 200 °C. Data acquisition and analysis of the storage modulus (E'), loss modulus (E''), and

loss factor (Tan δ) were recorded. The heating rate and frequency were fixed at 3 °C/min and 1 Hz, respectively.

TGA was carried out under N_2 atmosphere using a Mettler ToledoTGA2 with a heating rate of 10 °C/min.

X-ray diffraction was performed with a Malvern Panalytical diffractometer using a CuKα anti-cathode (λ = 0.154 nm) in the 2θ range (5 - 60°).

The UV-Visible spectrophotometry of solids was carried out with a Jasco V-650 over the λ-range (190 - 900 nm) with $BaSO_4$ as reference.

The electrical conductivity was measured under controlled atmosphere in a glove box using the four Point Probe Stand KSR-4. To avoid free humidity measurement, a primary pump allows the vacuum to be lowered down to ~ 0.1 mbar, then N_2 gas was introduced at 1 atm, this operation was performed 3 times and the same procedure was repeated for each measurement.

The impedance spectroscopy (IS) was performed using an Autolab 302N Potentiostat / Galvanostat coupled to a Microcell HC temperature controller between 25 and 95 °C. The compacted pellet was sandwiched between two stainless steel electrodes and the measurements during cooling, making the measurement more reliable; each point was stabilized within 30 min. The frequency range was set from 0.1 MHz to 0.1 Hz and 10 mV amplitude.

Composition of Pyrrole/PVP	Pyrrole (mL)	HCl 1M (mL)	$(NH_4)_2S_2O_8$ (g)	PVP (g)
1/0	1	21.68	3.79	-
1/1	0.5	10.84	1.90	0.61
1/2	0.5	10.84	1.90	1.21
1/5	0.5	10.84	1.90	3.03
1/10	0.5	10.84	1.90	6.06
1/20	0.2	4.33	0.76	4.84

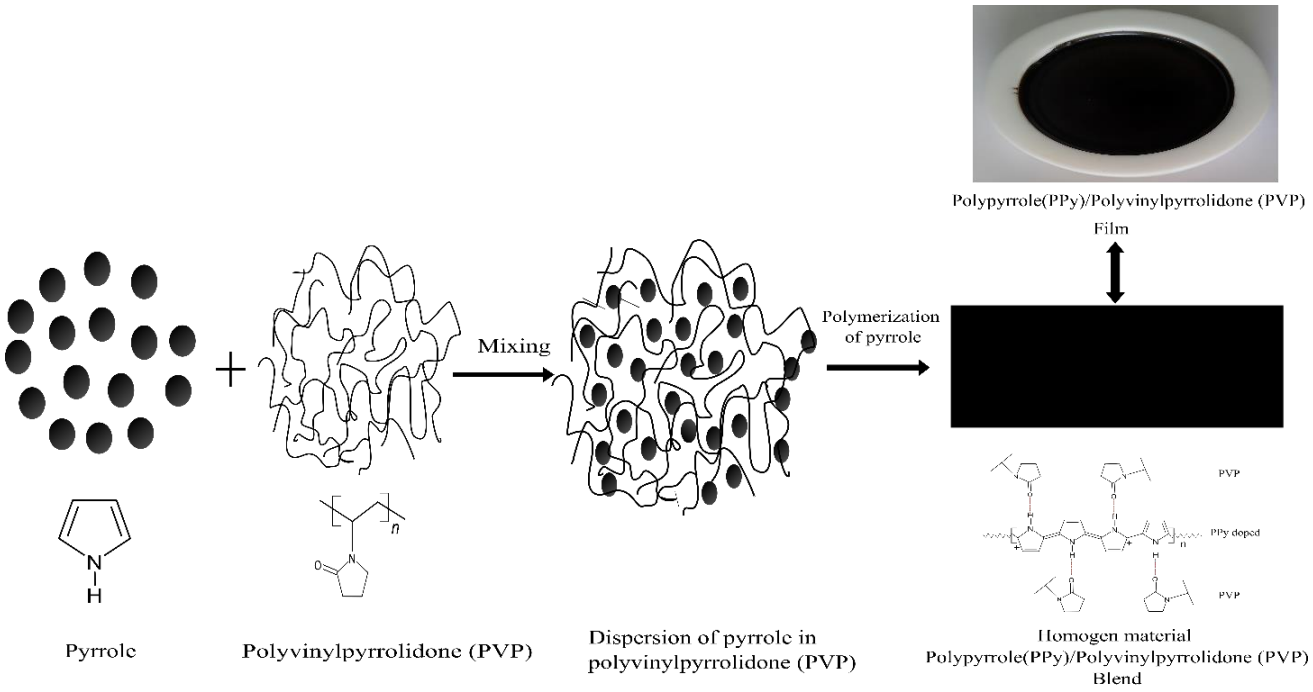
Table 1. Polymerization conditions of pure PPy and PPy/PVP blend at different ratios.

Results and discussion

1. Thermodynamic Study

As emphasized earlier, polymer blending is an attractive approach for obtaining new polymeric materials with desired properties. This process is an effective alternative for achieving enhanced material properties with improved processability and reduced costs. Thus, it is well-known that the miscibility of polymer blends primarily depends on the mixing enthalpy, as the contribution of mixing entropy is negligible. Consequently, the selection of polymer moieties is primarily assessed based on thermodynamic considerations. Generally, to achieve a miscible blend system, it is necessary to ensure the presence of favorable specific interactions between the components. In this context, various methodologies and strategies have been developed to enhance the thermomechanical properties of semiconducting polymer materials. Among these methods, the blending technique using the thermoplastic polymers as matrices, capable of incorporating semiconducting materials, has gained increasing importance and is regarded as one of the most economical approaches to achieve complete miscibility. However, it has been suggested that blending two polymers can be accomplished in different ways.

The first method involves mixing PPy with PVP in a common solvent, such as ethanol. However, this approach typically results in a heterogeneous system. Alternatively, the second method entails synthesizing PPy on a thermoplastic polymer matrix through an in-situ polymerization process. As shown in scheme 2, this approach is considered the most effective for producing homogeneous materials.



Scheme 2. In-situ polymerization of PPy in PVP matrix.

The solubility of the considered polymers depends on their chemical structures, it has been found that the miscibility of binary blends is not only influenced by their chemical structures but also by their physical state. Therefore, it is crucial to develop thermodynamic models that take into account these complexities.

Since their structures are linear and contain moderately attractive functional groups, we assume that PPy and PVP, are considered as a non-polar system. The free energy (ΔG^0) of mixing per segment, assuming the polymers are monodispersed, is given by equation of state [10]:

$$\frac{\Delta G_m}{RT} = \left(\frac{\Phi_A}{N_A} Ln\Phi_A + \frac{\Phi_B}{N_B} Ln\Phi_B\right) + \frac{V_r}{RT}\Phi_A \Phi_B (\delta_A - \delta_B)^2 \qquad (1)$$

where N_A, N_B, Φ_A and Φ_B are the chain length and volume fraction of two polymers A and B, respectively. δ_A and δ_B are the solubility parameters of both polymers.

As mentioned earlier, the enthalpic contribution is negligible, and the free energy of mixing is negative if the solubility parameters of the two polymers are close to each other. However, it should be noted that direct measurements of solubility parameters of polymers are relatively

limited, requiring the use of theoretical approaches. Therefore, group contribution theory is considered one of the most reliable methods for predicting these parameters.

The solubility parameter model has been successfully applied to polymer solutions, particularly when the liquid components are non or slightly polar, where their interactions are dominated by dispersion forces. Therefore, as the entropic contribution in polymer blends is usually negligible, it is generally accepted that two polymers are miscible if their solubility parameters are similar. This criterion is qualitatively used as a key factor to describe the miscibility of PPy with PVP.

Knowledge of the solubility parameters and/or surface tension parameters using group contributions can also be used to predict some physical properties of polymers and their blends. In this context, some approaches have been proposed to predict the solubility parameter of components (δ_i). Among them, the Hoftyzer and Van Krevelen method is the most reliable, especially when specific interactions are present within different species. For this purpose, δ_i is related to the of vaporization heat (ΔH_{vap}) and the molar volume of liquid (V_i) by [11]:

$$\delta_i = \left(\frac{E_{coh}}{V_i}\right)^{1/2} = \left(\frac{\Delta H_{vap} - RT}{V_i}\right)^{1/2} \qquad (2)$$

For a system involving specific interactions such as hydrogen bonding and/or ionic interactions, Hansen has considered that the total cohesive energy (E_{coh}) is the contribution of three types of interaction forces given by:

$$E_{coh} = E_d + E_p + E_h \qquad (3)$$

where E_d, E_p and E_h are the contribution of dispersion forces, polar forces and hydrogen bond, respectively.

Dividing the two sides of equation (3) by the molar volume gives the square of the total solubility parameter:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (4)$$

where δ_t as the sum of the squares of the dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) components.

According to Hoftyzer and Van Krevelen method, the total solubility parameter may be estimated from group contributions based on the following equations:

$$\delta_d = \frac{\sum F_d}{V}; \quad \delta_p = \frac{\sqrt{\sum F_p^2}}{V}; \quad \delta_h = \sqrt{\frac{\sum E_h}{V}} \qquad (5)$$

which F_d, F_p, and E_h are the contributions of the dispersion force, the polar forces, and the hydrogen bond force, respectively.

s

The predicted solubility parameters of PPy and PVP, using appropriate group contributions are given in Table 2. As observed, the solubility parameters of the two polymers calculated using the appropriate group contribution model, align with values reported in the literature [11].

The solubility parameter of PPy is very close to that of PVP, with a difference between them of ($\Delta\delta$_max) not exceeding 0.42. suggesting that the two polymers may be completely miscible. According to the mean field theory, this value indicates that the interactions between PVP and PPy groups are relatively moderate, consistent with the conclusions drawn by Coleman et al [12]. The presence of antagonistic groups, such as carbonyl, imine, and amine groups within the species, can be regarded as precursors for enhancing specific interactions.

Table 2 Predicted solubility parameters of PVP and PPy using group contributions theory

Polymers	δ_t	δ_d	δ_p	δ_h
PVP	21.24	15.50	11.70	08.60
PPy	21.66	19.50	04.60	08.24

Assuming the additivity rule of the solubility parameters of both polymers, one can calculate the solubility parameter of each ratio of the PPy/PVP blend across the entire composition range using the following expression [10]:

$$\delta_{PPy/PVP} = \Phi_{PPy}\delta_{PPy} + \Phi_{PVP}\delta_{PVP} \qquad (6)$$

where Φ_i and δ_i are the volume fraction and solubility parameter of each polymer, respectively.

The predicted solubility parameter of the mixture PVP/PPy plotted against the weight fraction of PPy is displayed in Fig. 1. The slight negative deviation from the additivity rule is observed with these blends, suggests the presence of specific interactions between PVP and PPy. Thus, it might be noted that the trend of this evolution generally indicates that the two polymers PPy and PVP are completely miscible over the entire range of composition where $\Delta\delta_{PPy/PVP}$ is less than or equal to 0.42.

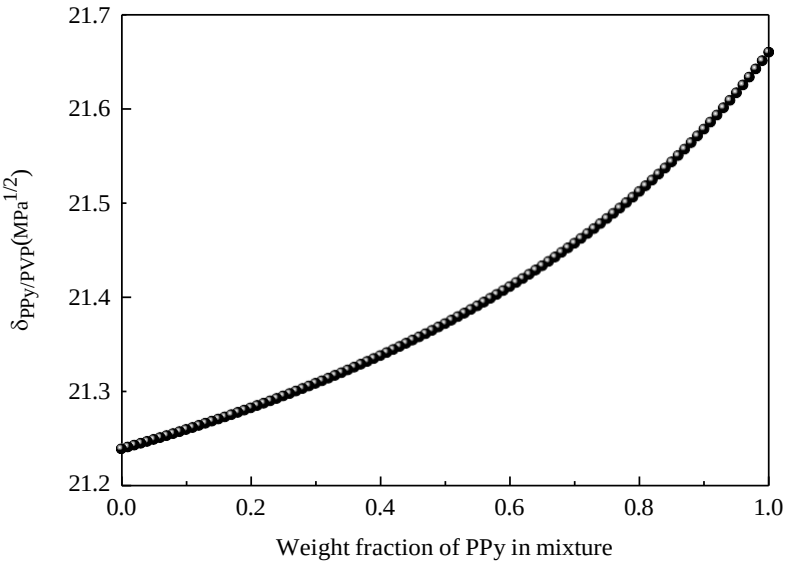


Fig. 1 Evolution of predicted solubility parameter versus PPy weight fraction in mixture PPy/PVP.

2. DSC Study

To further confirm this theoretical finding, the thermal measurements are conducted on pure PVP and the mixtures PPy/PVP. It is important to note that due to the compact structure of PPy, determining its glass transition temperature is challenging. Nevertheless, theoretical methods based on group contributions theory were employed to estimate it [11].

The transition phenomena observed in polymers serve as a fundamental criterion for studying the miscibility of polymer blends. In particular, glass transition phenomena provide valuable insights into the physical state and morphology of these blends. They reveal various relaxation processes and possible orientations occurring at the chain segment level during the transition.

Differential scanning calorimetry (DSC) is one of the most widely used techniques for studying these phenomena. It is a vital tool, providing rapid and reliable results for characterizing the physical state, morphology, and chain orientation of polymers.

In this study, we have employed DSC to investigate the PPy/PVP system. In this context, observing a single glass transition temperature (Tg) in such blends can indicate either an intermediate value between the Tg values of the two components or a significantly higher Tg compared to both polymers. The latter case is often associated with blends exhibiting strong specific interactions, such as hydrogen bonding or dipole-dipole interactions. The presence of a homogeneous phase in the binary blend can be considered a key criterion for assessing miscibility.On the other hand, the detection of two T_g corresponding to the pure constituents, with the observation of two or more phases is indicative of their immiscibility.

Poly(pyrrole) (PPy) is composed of conjugated motifs, making the determination of its glass transition temperature (Tg) rather challenging. Consequently, the group contributions method appears to be a reliable approach for estimating its Tg. In order to determine the glass transition temperature of PPy, we employed the Van Krevelen and Hoftyzer method, which is based on the additivity rule of structural groups as expressed in the following equation: [12]

$$Y_g = \sum Y_{gi} = T_g M \qquad (7)$$

where Y_{gi} is the specific contribution to a given structural group, and T_g M is called molar glass transition function. Using this approach, the calculated glass transition temperature of PPy was found to be 110 °C, which aligns well with those reported in the literature [13].

The DSC profiles of PPy/PVP blends (Fig. 2) revealed the presence of a single T_g specific to each composition. Although PPy does not exhibit a clear transition in this DSC analysis, probably because of its rigid structure, its combination with PVP in various ratios has resulted in transitions indicating that the structures of the developed materials have become flexible. Indeed, a single intermediate T_g indicates that the studied blends are miscible. Therefore, these results indicate that this miscibility is attributed to the presence of specific interactions such as hydrogen bonding that can occur between both two carbonyl groups of PPy and PVP, respectively.

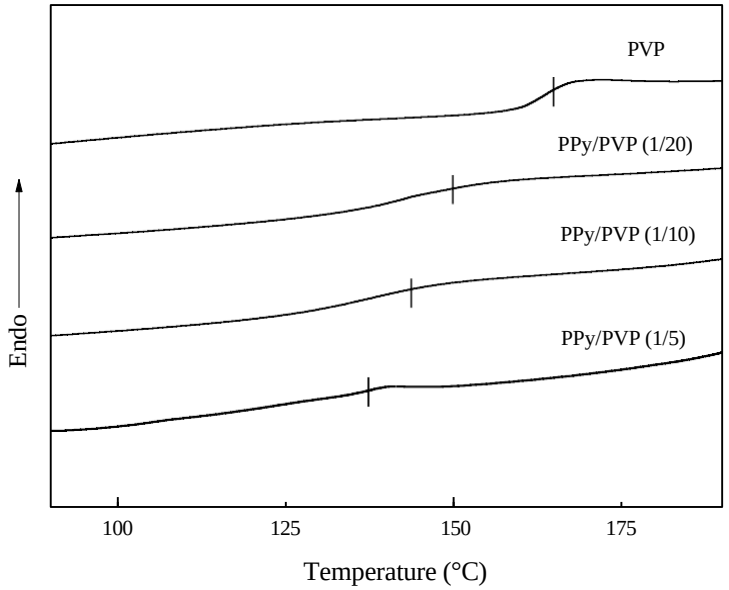


Fig. 2 DSC thermograms of PPy, PVP and their different mixtures.

3. DMA Study

The presence of phenyl groups along the PPy chain significantly affects its elasticity, making the detection of the glass transition temperature using DSC more diffuclt. For this reason, we have additionally used DMA measurements to provide supplementary information about the homogeneity of the structure of PPy/PVP materials and to verify the possible relaxations occurring at the segment level during the transition. In this context, DMA analysis is more sensitive than any other thermal analysis technique, particularly for determining T_g and detecting transitions of polymers. Fig. 3 illustrates the loss factor (tan δ) of PPy, PVP, and their blends in different ratios. As can be seen, the relaxation behaviors of the samples are observed, reflecting the mode of chains motion in the amorphous region. This corresponds to the maximum of tan δ, attributed to the glass transition temperature (T_g), which increases with increasing the PVP content in the mixture. Thus, it should be noted that all mixtures revealed one Tg between those of the pure constituents PPy and PVP. Also, the obtained T_g values using DMA measurements are very close to those obtained by DSC study. The small level of tan δ observed with doped PPy may be due to low relaxation reflecting its higher crystallinity and, therefore, its rigidity.

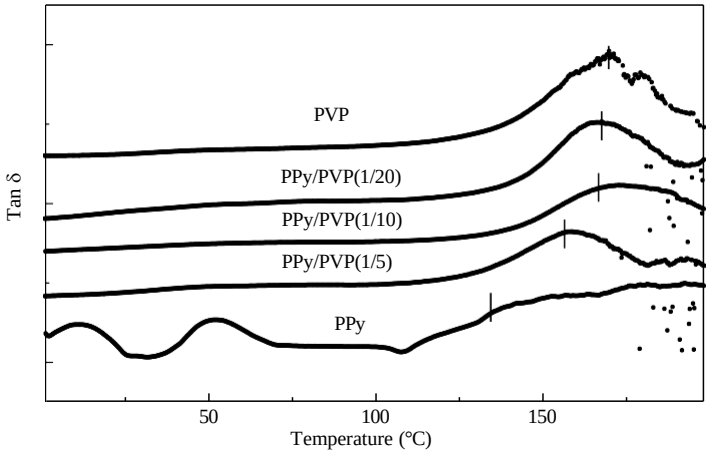


Fig. 3 Loss factor vs temperature of mixtures PPy/PVP in different ratios

4. FTIR Study:

The presence of different chemical groups in polymer blends often leads to various types of repulsive and/or attractive interactions. For this reason, FTIR spectroscopy commonly used to explore such interactions, was undertaken. It is a powerful technique for studying specific interactions, particularly for detecting hydrogen bond. However, it has been suggested that hydrogen bonds significantly affect covalent bonds on interactive species, which a frequency shift. The FTIR carbonyl-carbonyl stretching range is sensitive to the formation of hydrogen bonds. It should be noted that this region is particularly important because PVP absorbs and not PPy.

Firstly, we focused on the FTIR analysis of the two polymers and their blends. The primary objective is to identify the characteristic bands related to the functional groups present within the basic structures, and subsequently, detect any potential change and/or shift in these characteristic bands when the two polymers are blended. Additionally, the specific hydrogen bonds interactions may occur between the carbonyl groups of PVP and those of PPy, and then on their quantification as a function of PVP composition in the blend.

As mentioned above, the first step is devoted to the qualitative study of the overall spectra of PVP and PPy, in order to assign the bands related to the functional groups. Indeed, the regions of interest that could serve as references in this spectroscopic study are the regions...

Fig. 4 displays the global FTIR spectra of PVP and PPy. Although PPy does not absorb in the carbonyl and hydroxyl regions, it presents characteristic bands in the phenyl and amine/imine regions. Examination of the overall spectrum of PPy reveals several bands that can serve as references in our spectroscopic study.

The spectrum of PPy shows two bands centered at 1553 and 1459 cm^{-1}, corresponding to the stretching vibration of the double bond C=C and C-N of pyrrole cycle respectively, which depends directly on the degree of electron π delocalization and doping of PPy [13]. Additionally, the two bands observed at 1292 and 915 cm^{-1} are attributed to the deformation vibration of =C-H, in perfect agreement with the literature [14].

The spectrum of PVP has two principal bands localized in C=O and O-H regions, characterizing the different groups existing in this polymer. The broad band at 3400 cm^{-1} is assigned to the elongation of the associated OH…O mainly due to the existence of hydrogen bonding between the PVP carbonyls and H_2O, confirming the high hygroscopy of PVP. The intense band at 1652 cm^{-1} is attributed to the stretching vibrations of the free carbonyl groups of PVP.

On the other hand, several bands are also observed in the region (1245-1520 cm^{-1}). The band appeared at 1443 cm^{-1} is due to the stretching of -(N-C)=O while the band at 1292 cm^{-1}, is attributed to the stretching vibration of -(C-N)-C.

It should be noted that the doped PPy does not absorb in carbonyl and in hydroxyl regions but has rather characteristic bands in the phenyl and amine / imine region. In addition, the global spectrum of PPy shows several bands that can serve as reference in this spectroscopic study.

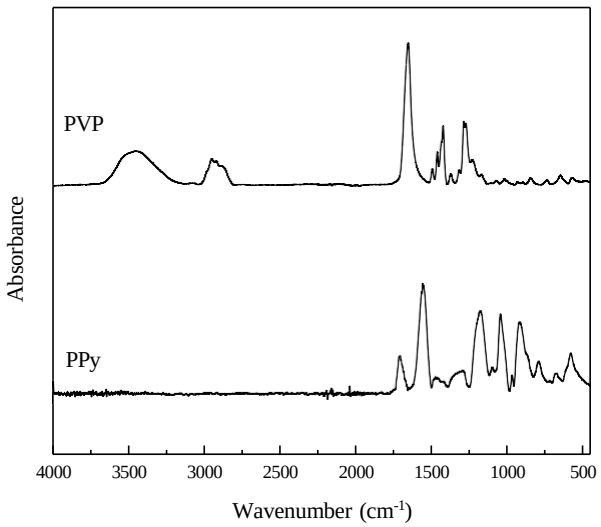
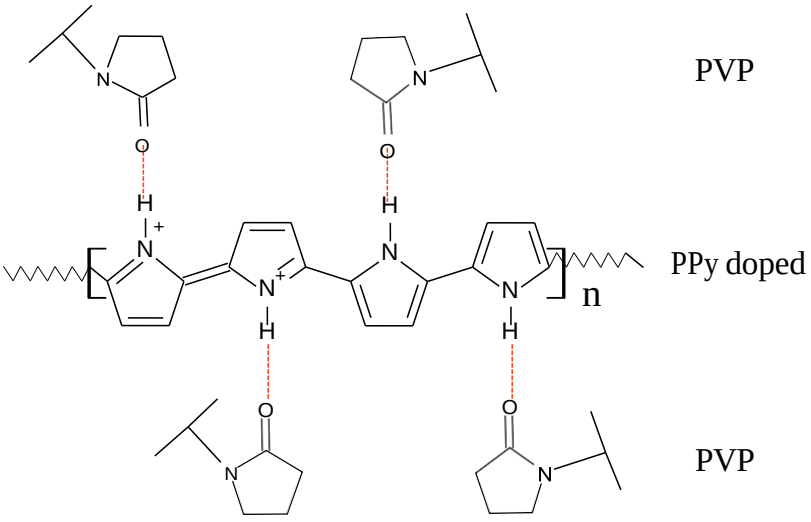


Fig. 4 FT-IR spectra of PVP and PPy in the 400–4000 cm^{-1} region.

As mentioned above, due to its high sensitivity, the FTIR spectroscopy is particularly suitable for the elucidation of specific interactions, in particular the hydrogen bond. In general, the presence of groups of different chemical nature within the polymer mixtures often induces several types of repulsive and attractive interactions.

In this part, we have firstly focused our interest on the demonstration of the specific interactions hydrogen bond type that take place between the C=O groups of PVP and the amine / imine groups of the doped PPy, and their quantification depends on the composition of PVP in the mixture.

The first step is devoted to the qualitative study of the specific interactions of the hydrogen bond present in the different PPy / PVP binary mixtures in the fields of interest. The effectiveness of this technique has been proven in the polymer mixtures, particularly when one of the constituents is absorbed and the other is not. As can be seen, PVP absorbs in the stretching carbonyl region unlike PPy, which is a further advantage to spectroscopic study in this region. Although PPy does not absorb in hydroxyl region ranging from (3100 - 3500 cm^{-1}), which is relatively complex since PVP is considered among the potential hygroscopic polymers. According to the chemical structures PPy and PVP, the expected specific interactions within the PPy/PVP systems are illustrated in scheme 3.



Scheme 3: Potential specific interactions involved on PPy/PVP systems

For this purpose, two regions of interest were selected for the characterization of the different carbonyl-amine and carbonyl-imine interactions. On the other hand, the C=O stretching region (1600-1780 cm^{-1}) is important because the doped PPy is transparent and show no absorptivity

in the C=O region, whereas PVP has one characteristic band observed at 1652 cm^{-1} corresponding to free carbonyl. It is important to note that when the amount of PVP is progressively added to the doped PPy in the mixture, the characteristic band shifts progressively to a lower frequency stretching mode up 1633 cm-1(Fig. 5). This important shift may be attributed to the increased rigidity of the PVP rings, serving as evidence of hydrogen bonding between PVP and PPy. Besides, we observe the apparition of the second band localized at 1620 cm^{-1} assigned to the hydrogen bond in the mixture. Therefore, as two type of specific interactions carbonyl-amine and carbonyl-imine have approximately the same forces and consequently their characteristic bands could overlap [15, 16]. It must be noted that these interactions are more pronounced in the composition with the ratio (1/2).

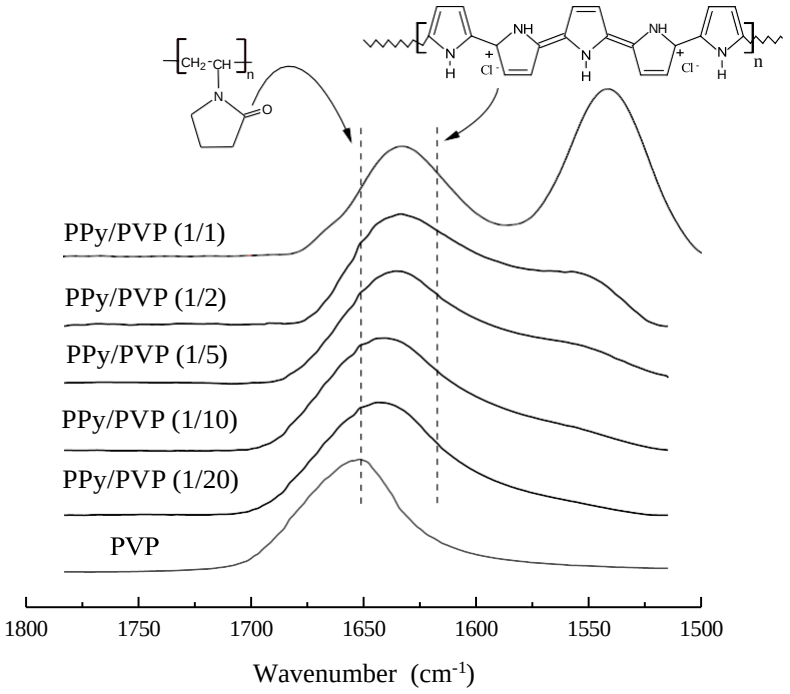


Fig. 5 FTIR spectra of PVP and PPy in the 1500–1800 cm^{-1} region.

Our results agree with those obtained previously with blends of polyaniline with polyvinylpyrrolidone [17], poly (4-vinylphenol) and polyvinylmethylketone blends, and those reported by Belabed et al [18]. Similar observations have been also made by Kuo and coworkers in their study of blends of poly (vinylphenol-co-methyl methacrylate) with poly (ethylene oxide) [19]. Although the qualitative study is relatively difficult in this region due to the overlapping between the characteristic bands, we have attempted to study quantitatively using an appropriate curve fitting procedure.

The second step of this contribution is devoted to the quantification these interactions using the deconvolution methods in the range (1780-1630 cm^{-1}). The free and associated carbonyl fractions are also calculated by the following equation using an adequate curve fitting [20]:

$$f_{free}^{C=O} = \frac{A_{free}^{C=O}}{A_{free}^{C=O} + \alpha A_{fAsso}^{C=O}} \qquad (8)$$

where *A* is the peak areas corresponding to free and associated carbonyls and the absorptivity ratio (*a*) is assumed equal to 1.5. Table 3 summarizes the free and associated carbonyl fractions for the system PPy/PVP system. The careful examination of these fraction values indicates that the fraction of carbonyl bound associated to hydrogen decreases intimately with increasing the PVP content in the mixture, while that of free carbonyls remains almost constant. This is in good agreement with others works previously published [19]. Thus, we suggest that the hydrogen bond interactions occurring between the amine /imine groups of PPy and the oxygen atom of PVP could be formed by breaking the hydrogen bond initially between PVP and water molecules. However, the carbonyl stretching may certainly be affected by the presence of eventual hydrogen bond. In the other hand, we believe that the hydrogen bonded interactions occurred between PPy and PVP is more pronounced with the mixture in composition 1/1.

Table 3 Curve fitting data from infrared spectra of PPy/PVP mixtures in the 1550-1750 cm^{-1} region.

Blend composition	Free C=O			Hydrogen bonded C=O		
	Frequency	Width	Fraction	Frequency	Width	Fraction
PPy/PVP	$\nu(cm^{-1})$	$w_{1/2}(cm^{-1})$	f_{free}	$\nu(cm^{-1})$	$w_{1/2}(cm^{-1})$	f_{Asso}
1/1	1650	18	0.641	1635	26	0.359
1/2	1651	20	0.523	1634	27	0.477
1/5	1648	21	0.427	1633	26	0.573
1/10	1651	22	0.278	1634	29	0.722
1/20	1650	19	0.259	1635	28	0.741

The FTIR spectra of PVP, PPy and their mixtures in the hydroxyl region are shown in Fig. 6. The spectrum of PVP exhibits three characteristic peaks at 3500, 3400 and 3260 cm^{-1}, assigned to stretching vibrations of free and associated hydroxyls, as well as to tertiary amine, respectively [17]. This phenomenon could be attributed to the hygroscopic nature of PVP, where the

nitrogen atom is adjacent to the carbonyl group in the PVP species, and which the water molecules can be easily adsorbed by forming a hydrogen bridge.

Fig. 6 illustrates that as the PVP content in the thermoplastic matrix increases, the intensity of the characteristic bands corresponding to the free hydroxyl groups of PVP, observed at 3453 cm^{-1}, progressively decreases and shifts to lower frequencies. This shift is likely attributed to the disruption of self-association interactions.

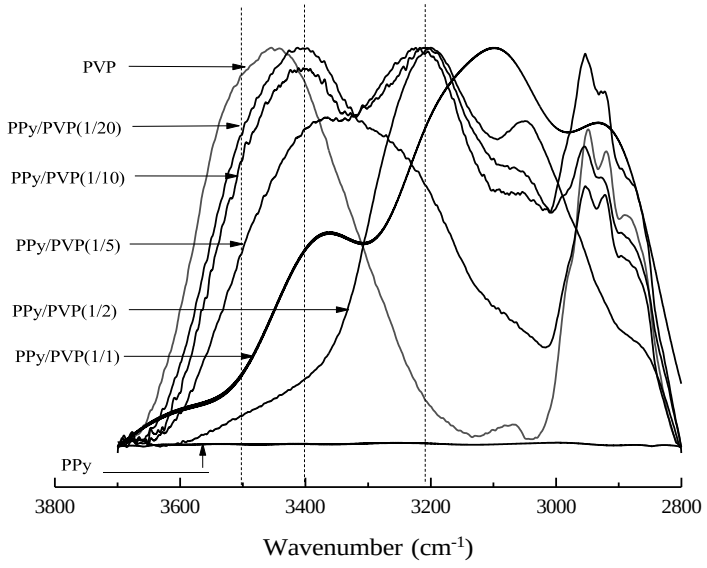


Fig. 6 FTIR spectra of PVP, PPy and their blends in the 2800–3800 cm^{-1} region

On the other way, a new band is detected at lower frequency (3220 cm^{-1}) confirming the presence of strong hydrogen bond between amine / imine groups with the carbonyl groups present within PVP.

5. TGA Study

The thermal stability of polymers is a crucial property that defines their potential applications and usage limits. During processing, polymeric materials are often exposed to relatively high temperatures and pressures. Consequently, the study of the thermal behavior of synthesized polymers and their blends continues to generate significant interest, as reflected in the numerous studies published regularly [21, 22].

In order to determine the upper temperature limit of the processing and utilization these materials, the thermogravimetric analysis is widely used for the kinetic of the thermal degradation and the possibility to form cross-linked structures. For these purposes, the TGA study is carried out to get preliminary insights on the thermal stability of PPy combined with the thermoplastic matrix of PVP. Fig. 7 displays the thermogravimetric curves for PPy, PVP and their mixture

obtained by in situ polymerization. It is seen that PPy shows a thermal stability up to 170 °C above which the polymer degrades in two main stages of which the first, in the temperature region (80-120 °C) consists of one minor step. The main loss in this region is assigned to the elimination of water adsorbed by the hydrophilic groups. The second stage observed above 200 °C, is mainly attributed to the decomposition of the main chain by random scissions.

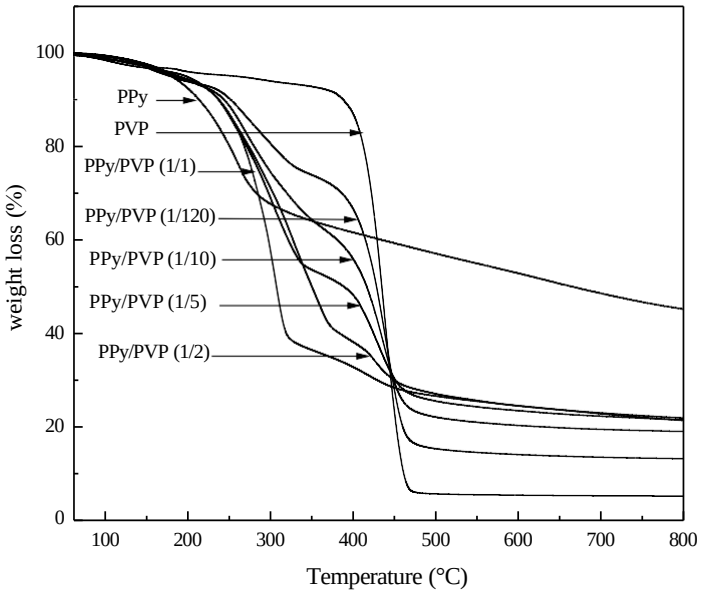


Fig. 7. TGA thermograms of PPy, PVP and their different ratios

However, despite the prolonged drying of this polymer under vacuum at 50 ºC for several days, traces of moisture still remain. Indeed, the weight loss varying from 2 to 20%, observed with this polymer, in the range (90-150 ºC), is attributed to the water molecules retained and possibly to the traces of monomers or solvent trapped within the polymer chains. Overall, this polymer exhibits significantly a better thermal stability compared to that of PPy. The onset of main degradation is observed from 380 °C.

The addition of PVP within PPy substantially increases its thermal stability. It should be noted that the mass losses recorded in the considered temperature range is notably decreases notably with increasing of PVP composition in the mixture. This could be due, in part, to the formation of specific hydrogen bond between the two polymers, as confirmed previously by FTIR, the same thermal behaviour was observed in the polyaniline/polyvinypyrrolidone mixture [17]

6. X-RD analysis

Fig. 8 shows the diffractograms of doped PPy powder, PVP films and their mixture (PPy/PVP: 1/10). The former has a broad band centred at 25.6° characteristic of the amorphous nature of PPy [24]. On the other side, the amorphous morphology of PVP is illustrated by the presence of two broad bands centred at 11.6 and 21.2°, respectively.

A comparison of the patterns shows that PPy has no peaks up to 15°. We can therefore use the peak 11.6° of PVP to study the miscibility of PPy/PVP and this band is slightly shifted towards lower 2θ angles indicating greater inter-reticular distances. This is due, partially, to the specific interactions by 'hydrogen bond' between the two polymers. Similar results were found recently for the ternary system "PPy/polyvinyl alcohol/chitosan blend" [25].

The XRD peaks (28.9°, 38,9°, 42.74°, 47°,48.1°) belong to inorganic salts resulting from the synthesis of PPy using the persulfate $S_2O_8^{2-}$ which is reduced to SO_4^{2-} (Fig. 8). It is useful to emphasize that the elimination of these salts requires several washes with distilled water for a time not exceeding 1 h, otherwise swelling occurs due to the hygroscopic nature of the PVP matrix.

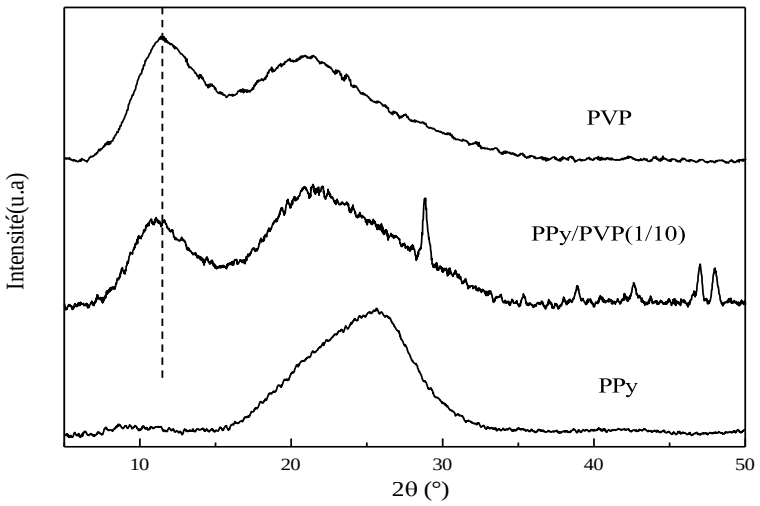


Fig. 8 X-ray diffraction patterns of PPy, PVP and PPy/PVP (1/10) blend.

7. Electrical conductivity and optical gap

The intrinsic conductivity of PPy is attractive in photoelectrochemistry [3] and has already been explored since its discovery. It is due to alternating bonds ($\pi \rightarrow \pi^*$) of the benzenoid leading to electronic delocalization with moderate carrier density [26].

All samples have a conductivity between 57 and 3960 μS cm^{-1}, a range belonging to the semiconducting materials as expected, σ decreases with the film thickness and diminishes with

increasing the PVP amount in the mixture PPy/PVP, to reach its minimal value of 235 µS cm^{-1} for a ratio (PPy/PVP=1/20).

The PPy based materials are used in the solar energy conversion [3], and the knowledge of the gap (E_g) is crucial and is determined from the variation of the optical absorption coefficient (α_λ) with the photon energy (hν) using the well-known relation:

$$(\alpha h\nu)^n = K \times (h\nu - Eg) \qquad (9)$$

K is a specific constant of the semiconductor and the exponent ***n*** indicates the nature of the optical transition, indirect (= 0.5) or direct (= 2). The values (Fig. 9) are obtained by extrapolating the lines $(\alpha h\nu)^2$ to the energy-axis and the transition is directly allowed.

The gap E_g and conductivity (σ) (Table 4) are correlated to each other. As we can see, the higher the conduction, the lower the gap, a predictable result. In addition, σ increases and E_g decreases with increasing the PPy percentage in the mixture PPy/PVP. This is due to a homogeneous dispersion of PPy on the PVP film with an increased active surface area; such property is attractive in photocatalysis [4] and similar results were obtained with the system PANI/PVP [17].

Table 4 The Electrical conductivity and energy gap of different samples.

Sample	σ (S cm^{-1}) ×10^5	E_g (eV)
PPy	5.70	0.80
PPy/PVP (1/2)	396	0.49
PPy/PVP (1/5)	212	0.50
PPy/PVP (1/10)	72.4	0.74
PPy/PVP (1/20)	23.5	0.77

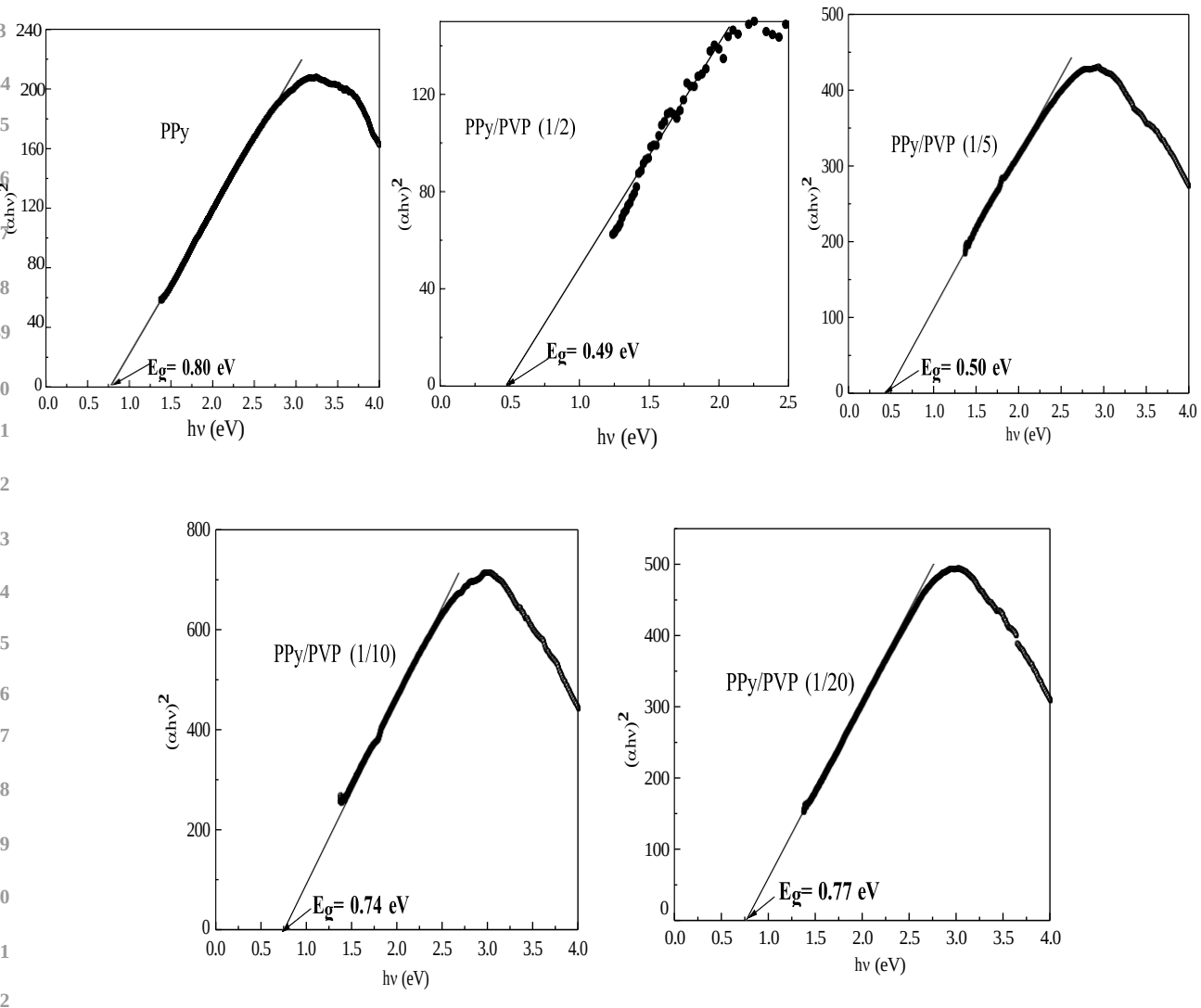


Fig. 9 Band gap transition of doped PPy and PPy/PVP mixtures at different ratios.

8. Electrical impedance

The impedance plots of doped PPy show large semicircles related to the bulk contribution whose diameter decreases with increasing temperature., thus supporting the semi conductivity (Fig. 10). The real axis gives the resistance of the sample and the non-existence right-hand semicircle indicates a weak contribution of grain boundaries. An equivalent electric circuit is suggested, consisting of the bulk resistance (R_b) in parallel with the capacity (C_b), the latter can be evaluated from the Bauerle' relation {= 1/ $R_b\omega_p$) ω_p is the frequency at the top of the semi-circle. The thermal variation of the electrical conductivity (σ) follows an exponential law Fig. 11.

$$\sigma = e\mu N_A \qquad (9)$$

where μ is the mobility of holes and N_A their density. The activation energy of doped PPy

(0.10 eV) determined from the slope ($d\log\sigma/dT^{-1}$), is close to that reported elsewhere (0.12 eV) [27]. This value is larger than the thermal energy kT (26 meV at 300 K) and this implies that both the mobility (μ) and density (N_A) are thermally activated at room temperature.

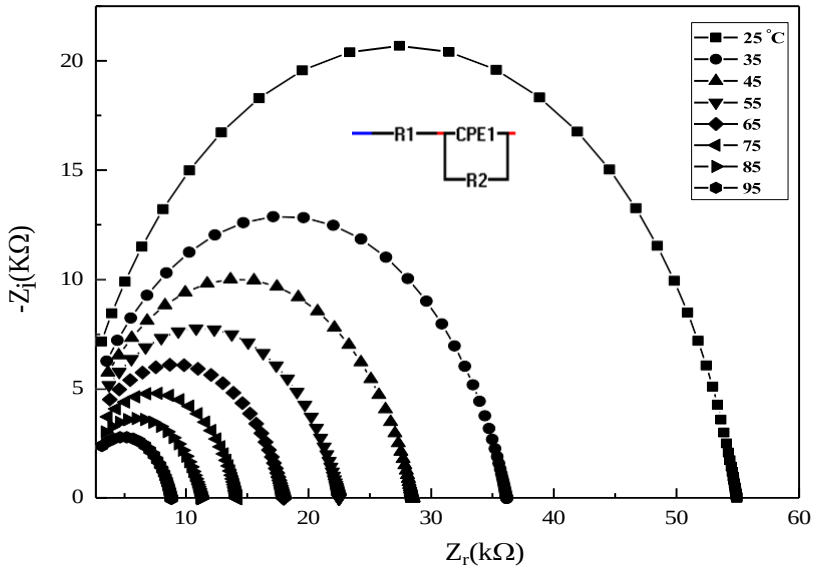


Fig. 10 The EIS representation of doped PPy in the temperature range (25 - 95 °C). Inset: the equivalent electrical circuit.

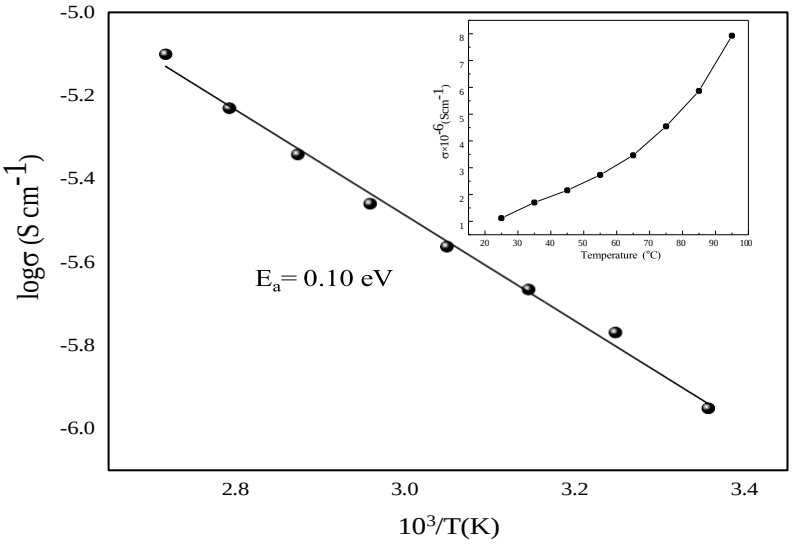


Fig. 11 Variation of the electrical conductivity (σ) of doped PPy versus 1/T (K)

Conclusions

In this study, we developed a series of semiconductor materials using in-situ polymerization, based on polypyrrole (PPy) and polyvinylpyrrolidone (PVP). Initially, we optimized the conditions for synthesizing pure PPy. These conditions were then applied to synthesize the PPy/PVP heterosystem.

In this context, we assessed the optimal conditions to ensure their total miscibility using thermodynamic considerations based on the group contributions method. By applying this method, we calculate the solubility parameters of the two considered polymers. The results indicate that complete miscibility occurs when the solubility parameters of the two polymers are very closely.

The DSC and DMA analyses confirmed the miscibility of all PPy/PVP mixtures through the observation of a single glass transition temperature (Tg).

The FTIR study shows the presence of specific intercations of the hydrogen bond between the unlike groups present towards the two polymers; amine and imine in PPy and carbonyl in PVP. These interactions are evidenced by a shift of the free carbonyl band centered at 1652 cm^{-1} towards lower wavelengths with increasing the PVP composition in the mixture, and the observation of a new band at 1622 cm^{-1}, characteristic at the associated carbonyl.

The presence of hydrogen bond in different mixtures is also highlighted by quantitative analysis in which the fraction of free and associated carbonyl in the corresponding regions was estimated.

The XRD study of the PPy/PVP mixture shows that the peak 11.6° characteristic of PVP shifts slightly toward lower 2θ angles indicating a greater inter-reticular distance. This is due, partially, to the specific interactions that occurred between unlike species of two polymers.

The thermogravimetric analysis (TGA) of the various PPy/PVP materials demonstrated enhanced thermal stability. The incorporation of PVP into PPy not only increases its thermal stability but also alters the degradation process. This improvement can be attributed to the excellent dispersion of PPy within the PVP matrix and the strong intermolecular interactions formed between the two polymers.

Additionally, the thermal stability of the synthesized materials was significantly enhanced.

The optical gap of PPy in the mixture PPy/PVP determined by UV-Visible spectrophotometry is attributed to $\pi \rightarrow \pi^*$ transition while, the electric conductivity, measured by the four-point method reveal a semiconducting behaviour.

Electrochemical impedance spectroscopy (EIS) exhibits semicircles attributed to bulk material, whose diameter decreases with increasing temperature, thus confirming the semiconducting behavior of PPy; The data obey to an Arrhenius law with an activation energy of 0.1 eV and the conduction occurs by electrons delocalization though alternating double bonds.

Acknowledgements

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Conflict of interest: The authors declare that they have no conflict of interest.

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Figure 1

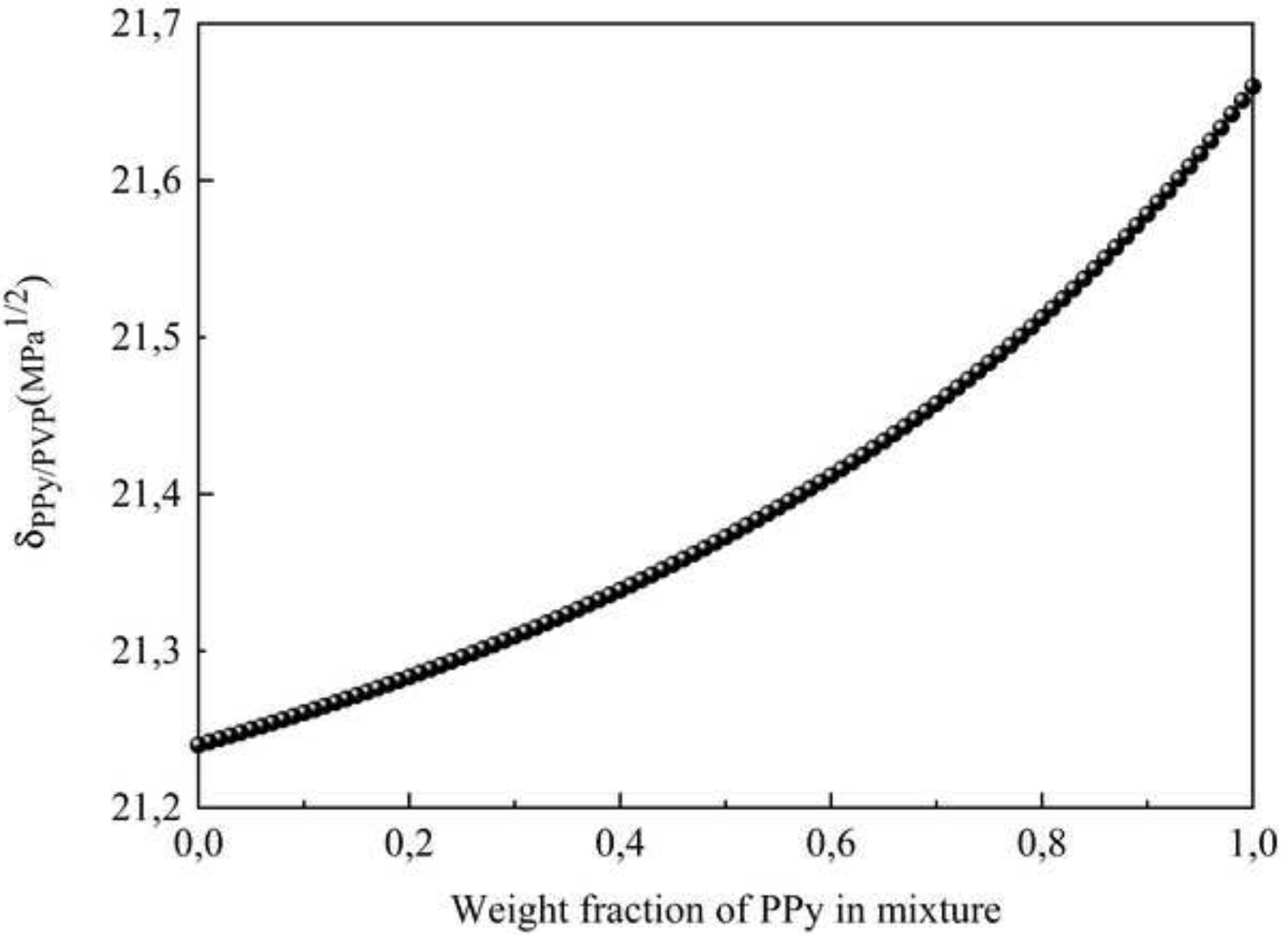


Figure 2

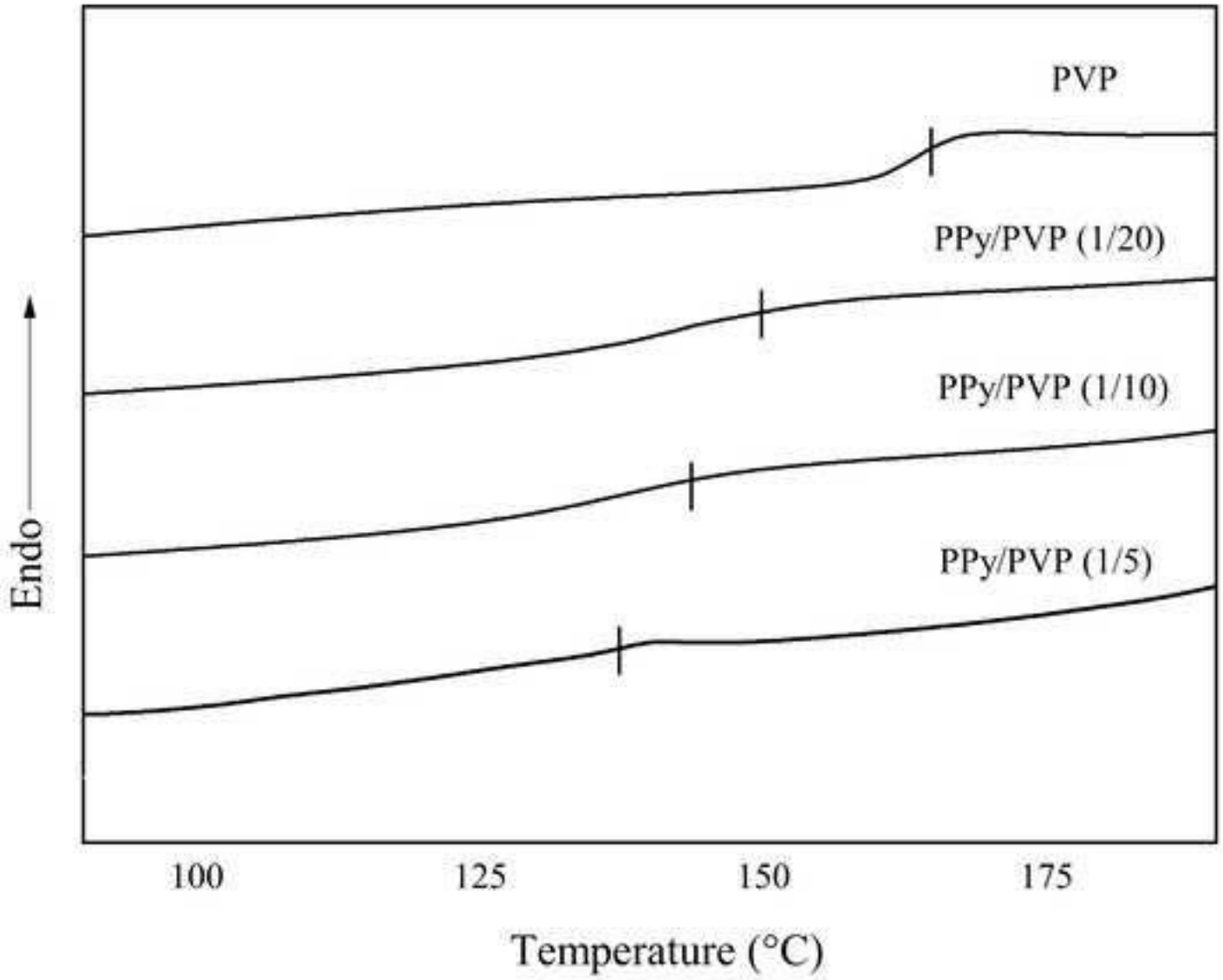


Figure 3

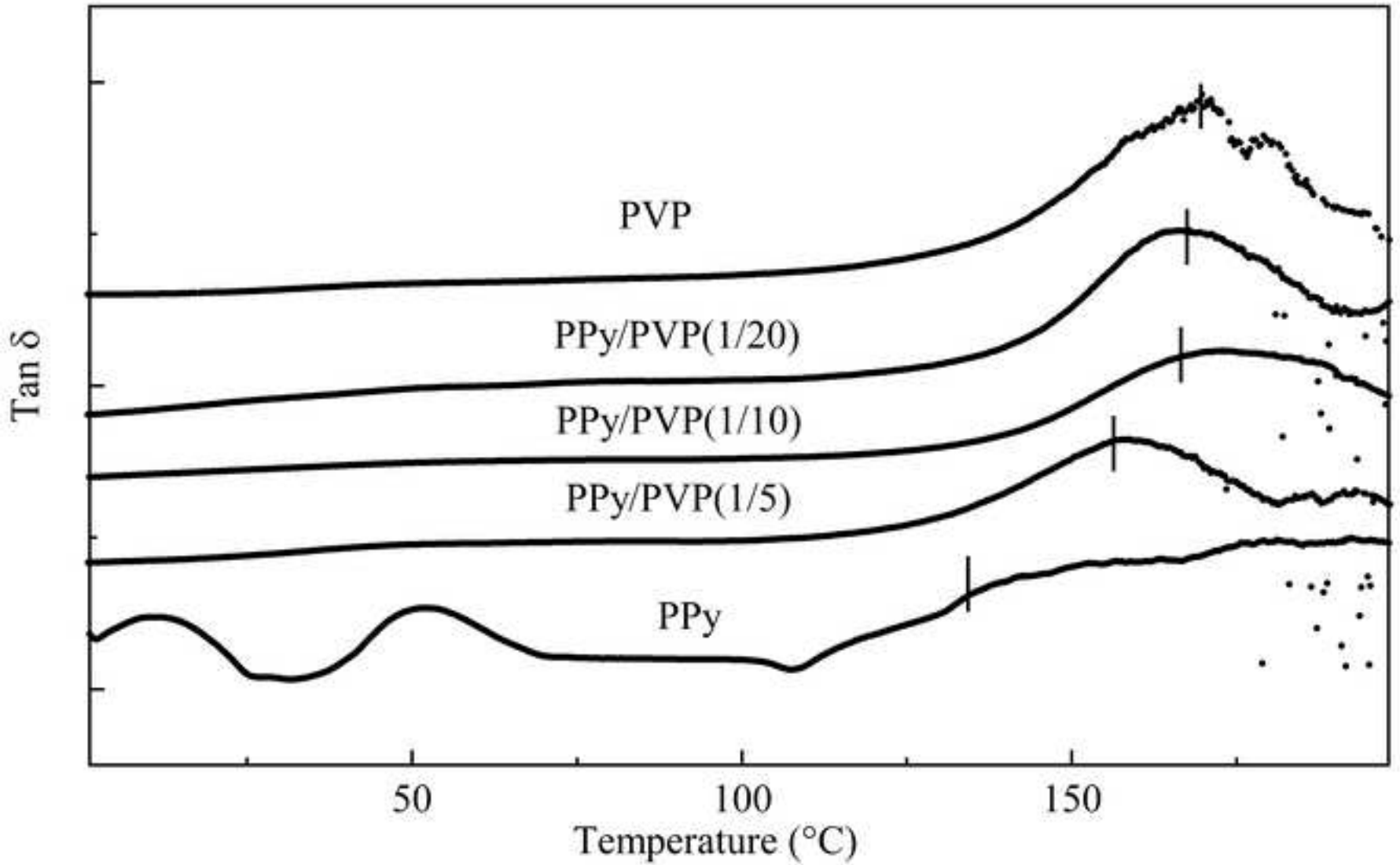
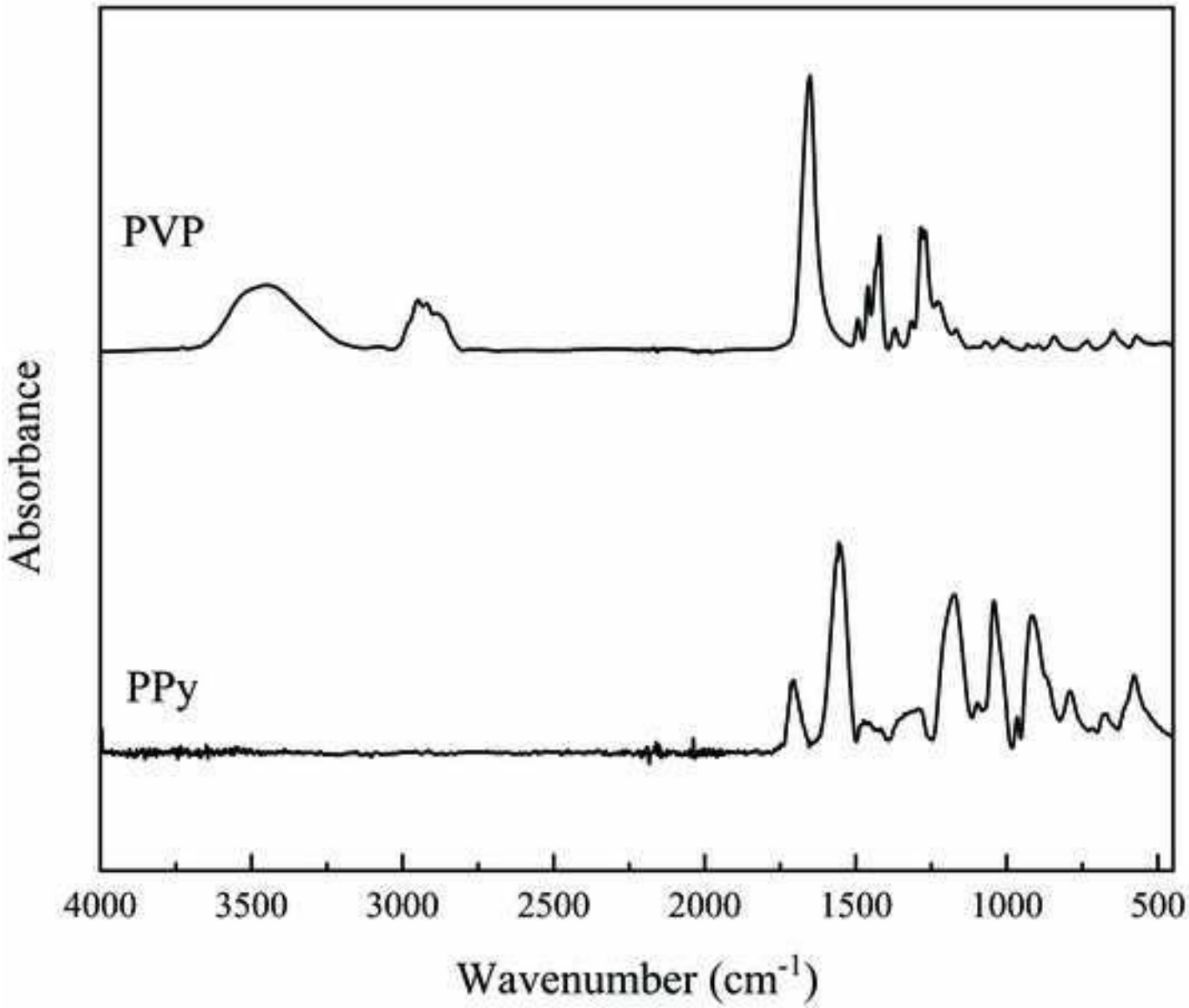


Figure 4



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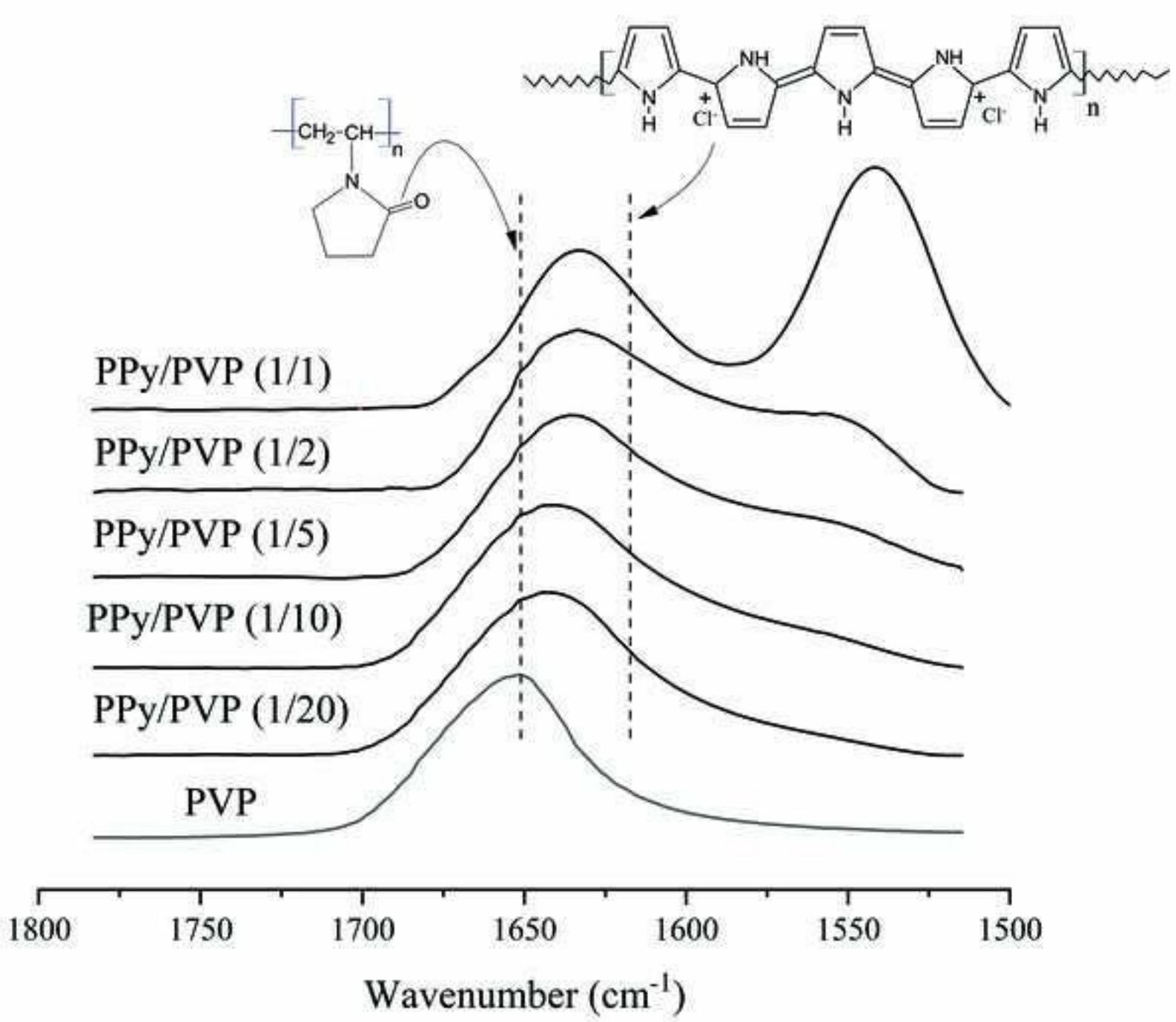

Figure 6

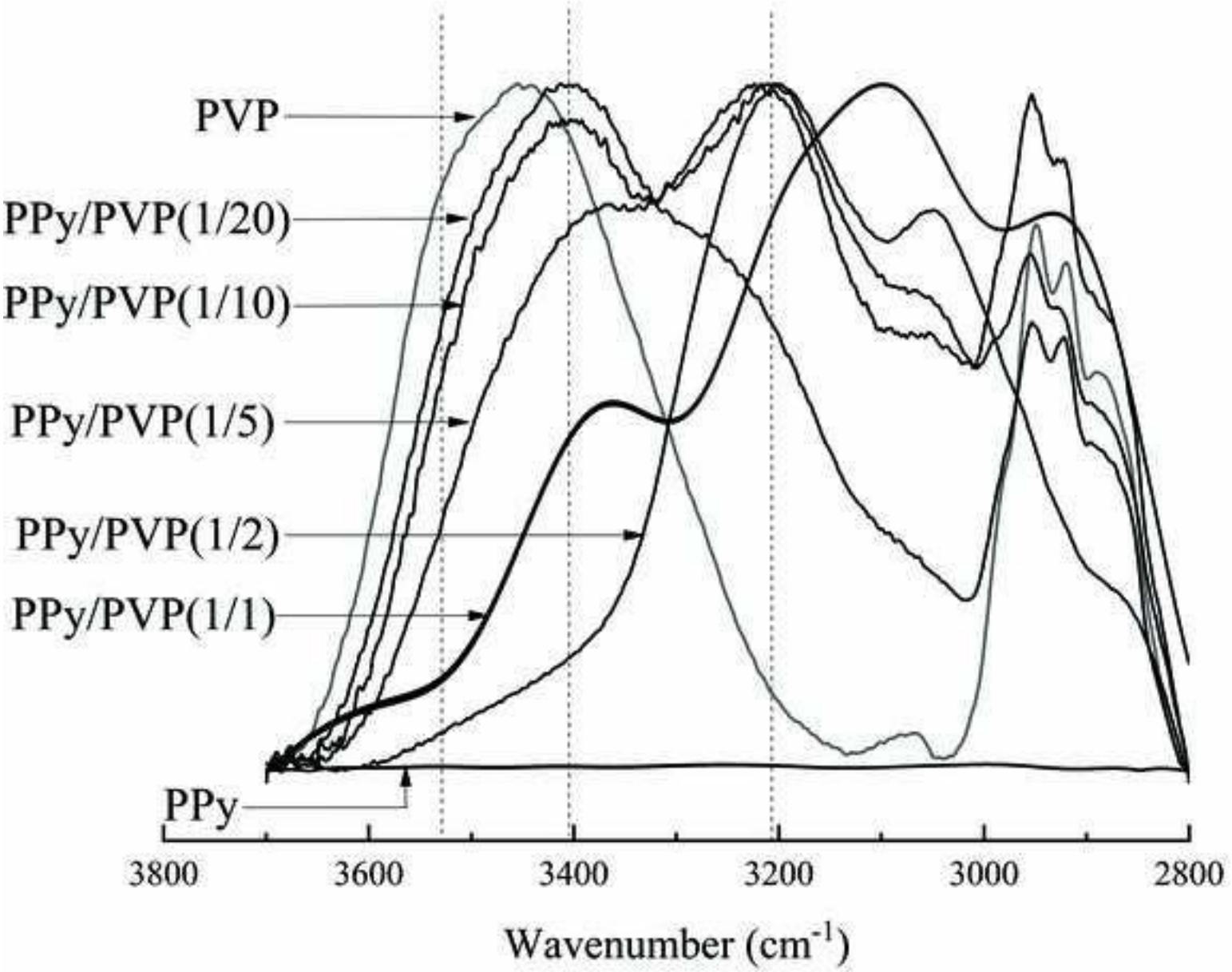

Figure 7

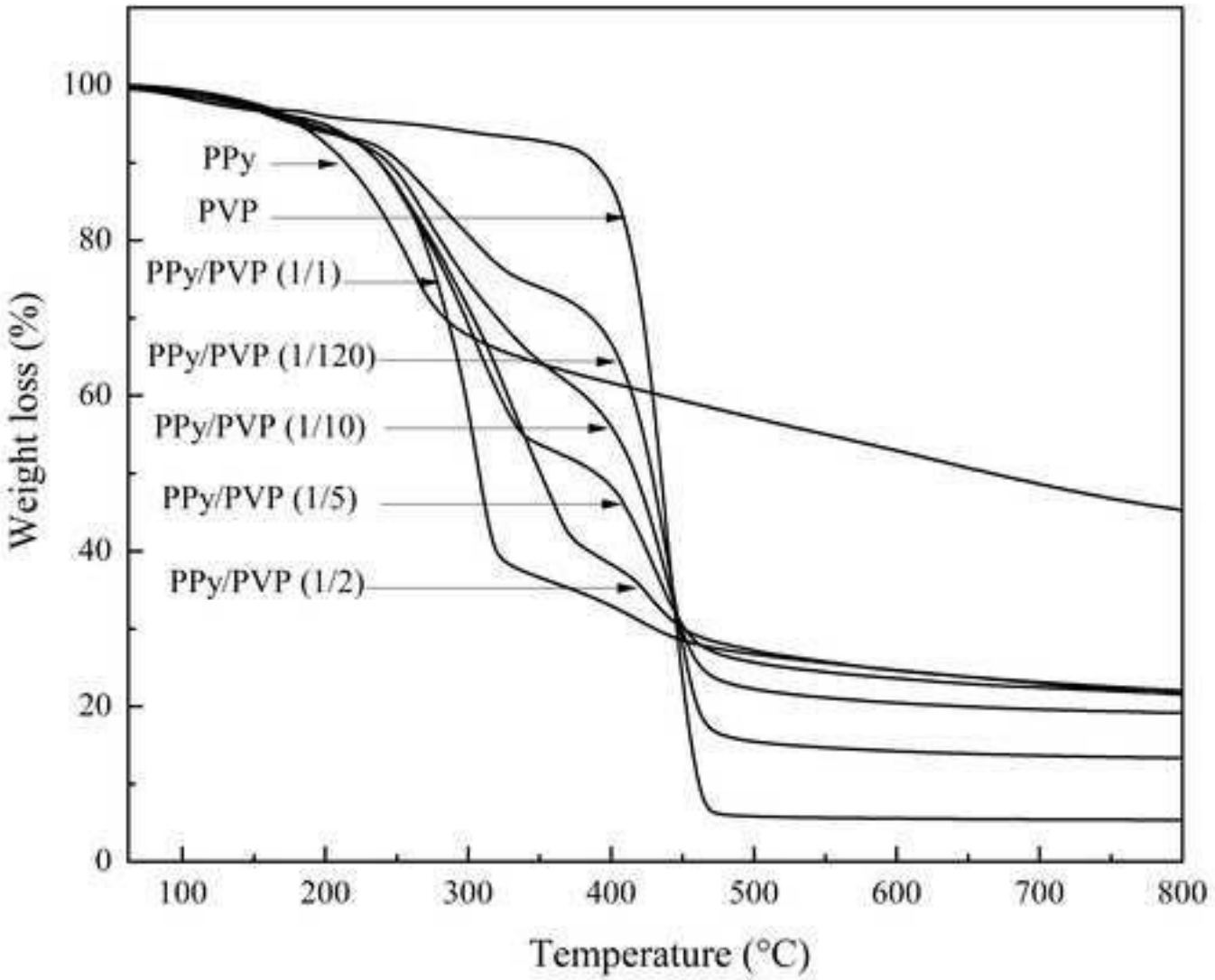

Figure 8

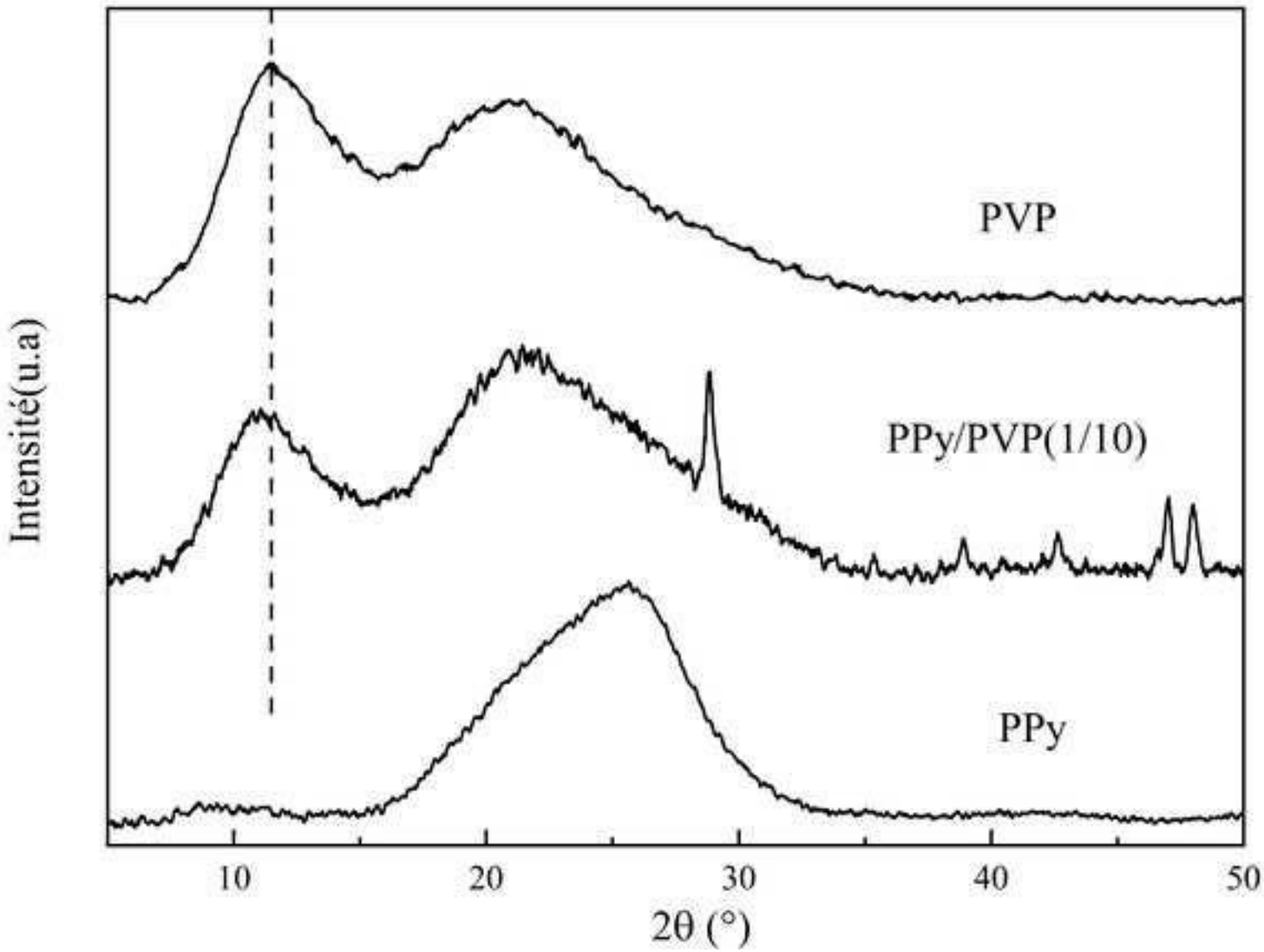

Figure 9

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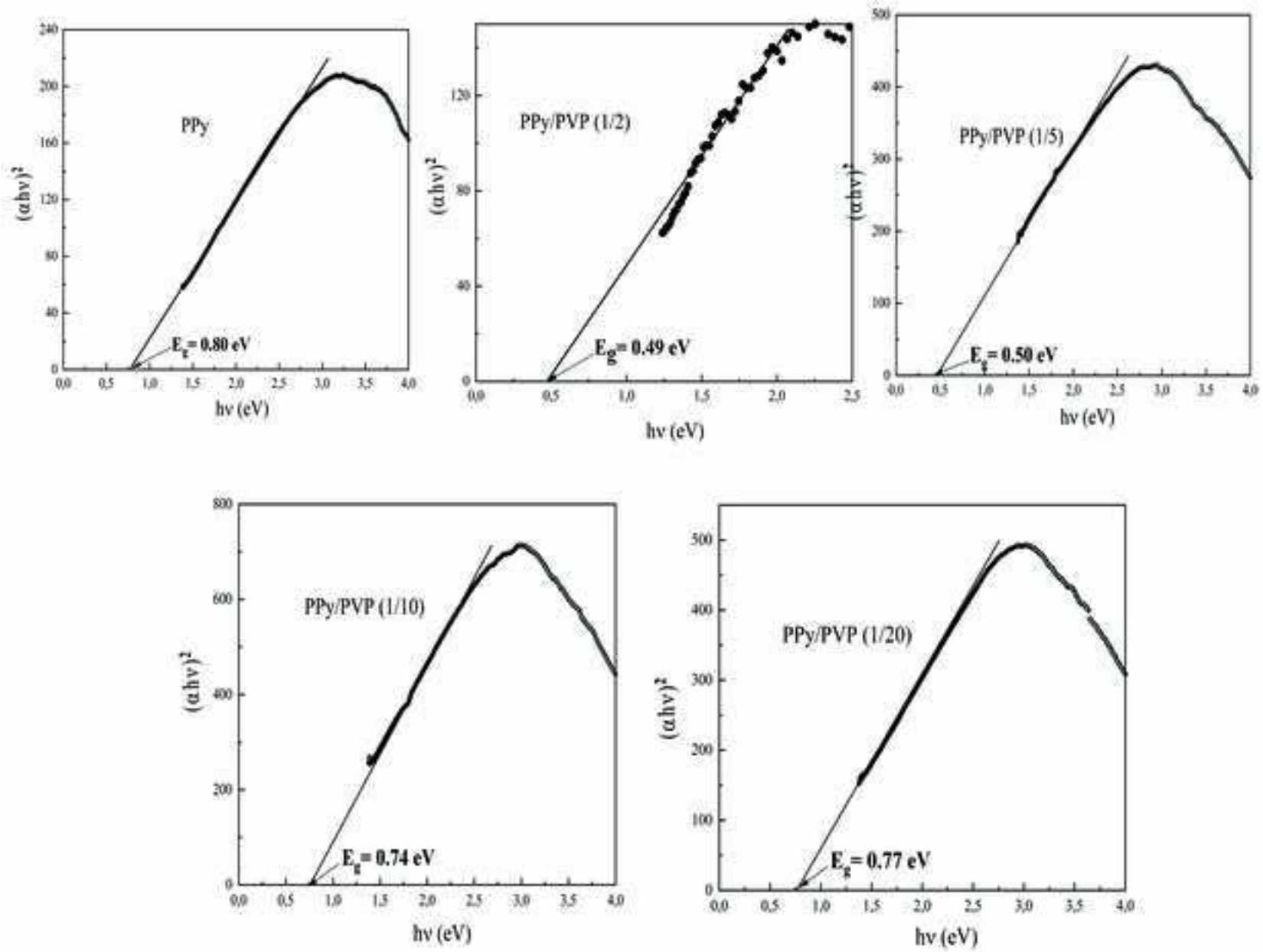

Figure 10

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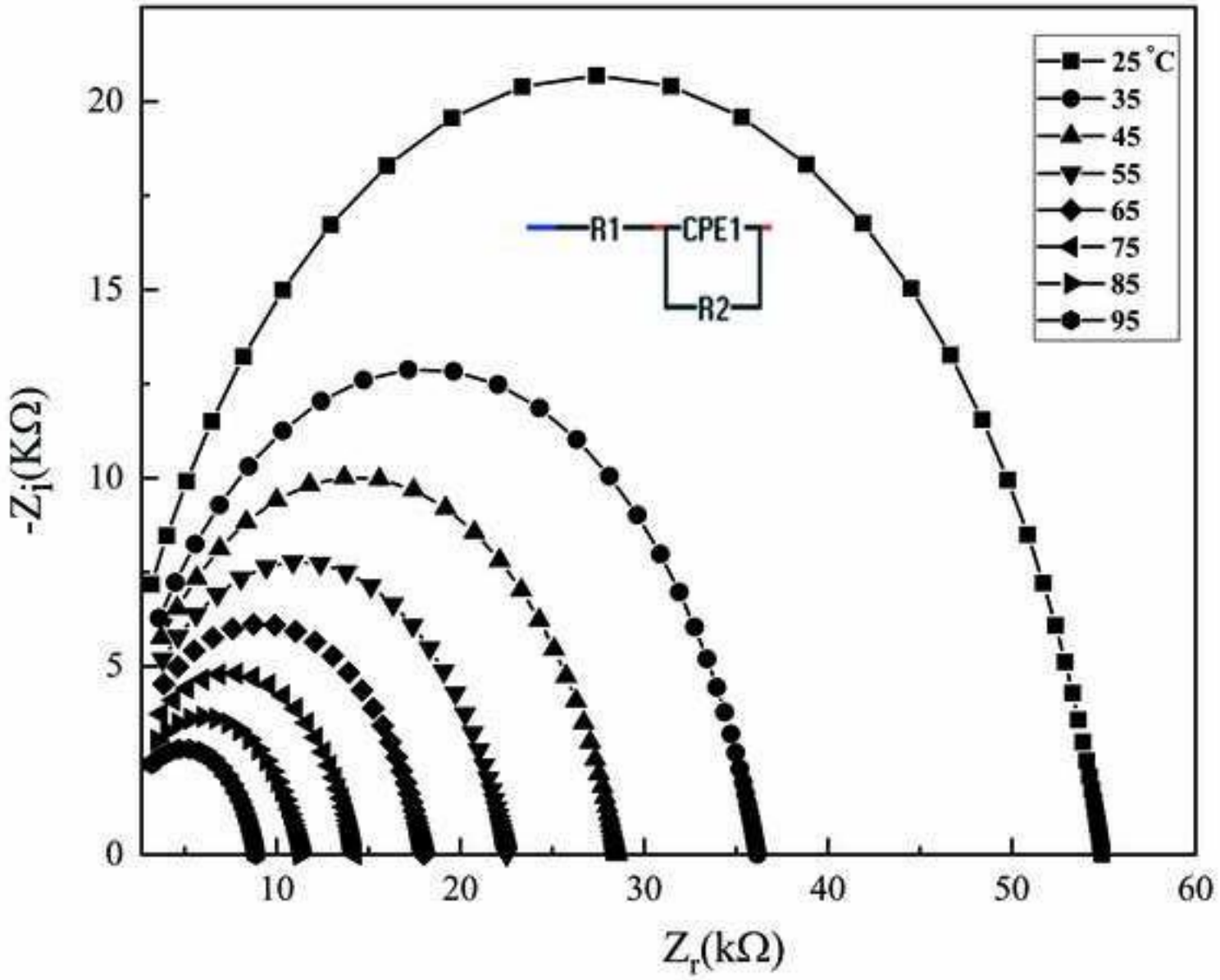

Table 1. Polymerization conditions of pure PPy and PPy/PVP blend at different ratios.

Composition of Pyrrole/PVP	Pyrrole (mL)	HCl 1M (mL)	$(NH_4)_2S_2O_8$ (g)	PVP (g)
1/0	1	21.68	3.79	-
1/1	0.5	10.84	1.90	0.61
1/2	0.5	10.84	1.90	1.21
1/5	0.5	10.84	1.90	3.03
1/10	0.5	10.84	1.90	6.06
1/20	0.2	4.33	0.76	4.84

Table 2 Predicted solubility parameters of PVP and PPy using group contributions theory

Polymers	δ_t	δ_d	δ_p	δ_h
PVP	21.24	15.50	11.70	08.60
PPy	21.66	19.50	04.60	08.24

Table 3 Curve fitting data from infrared spectra of PPy/PVP mixtures in the 1550-1750 cm^{-1} region.

Blend composition	Free C=O			Hydrogen bonded C=O		
	Frequency	Width	Fraction	Frequency	Width	Fraction
PPy/PVP	$\nu(cm^{-1})$	$w_{1/2}(cm^{-1})$	f_{free}	$\nu(cm^{-1})$	$w_{1/2}(cm^{-1})$	f_{Asso}
1/1	1650	18	0.641	1635	26	0.359
1/2	1651	20	0.523	1634	27	0.477
1/5	1648	21	0.427	1633	26	0.573
1/10	1651	22	0.278	1634	29	0.722
1/20	1650	19	0.259	1635	28	0.741

Scheme 1

Table 4 The electrical conductivity and energy gap of different samples.

Sample	σ (S cm^{-1}) $\times 10^5$	E_g (eV)
PPy	5.70	0.80
PPy/PVP (1/2)	396	0.49
PPy/PVP (1/5)	212	0.50
PPy/PVP (1/10)	72.4	0.74
PPy/PVP (1/20)	23.5	0.77