

Spectroscopic analysis of PMMA/PVC blends containing CoCl₂



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ABSTRACT

Composites of polymethyl methacrylate (PMMA) and polyvinyl chloride (PVC) polymer blend containing different concentrations (≤ 10 wt.) of cobalt chloride (CoCl₂) were prepared by casting techniques. The changes of the structural, spectroscopic, optical and thermal parameters of the samples are studied using different tools. FT-IR spectroscopy confirmed the complexation between the blends and Co²⁺-ions. The decrease or increase of IR band intensity with some shifts of other bands suggests an interaction and compatibility between PMMA/PVC blends with CoCl₂ take place. The Ultra violet and visible (UV/Vis) spectra indicated that the presence of band gap energy depends on increasing of CoCl₂ contents. The absorption intensity of the samples doped with CoCl₂ becomes faint lower than the pure blend. The values of energy gap for direct and indirect transition decreases with the increase of CoCl₂ due to the presence of charge transfer between PMMA/PVC and CoCl₂. The thermogravimetric analysis (TGA) curves for all the samples have the same behavior and more steps of decomposition were observed. The reduction of mass loss for samples containing CoCl₂ compared to the pure blend was observed and it was attributed to crosslink formation between the blend and CoCl₂.

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Introduction

Polymers have a large molecular weight and are composed of a higher numbers of repeating units. Polymer synthesis takes place on a very wide scale and polymers have a large range of properties to use in different applications [1,2].

Polymer materials have particular usefulness when in combination with appropriate metals, they give composites which are beneficial for the evolution of advanced high energy electronic devices, e.g., batteries, fuel cells, display devices and photo cells with easiness of fabrication as thin films of eligible sizes and shape. Fillers are additives to polymers and/or for diversity of reasons like: low cost, amended processing, density control, optical effect, thermal conductivity, control of thermal expansion, electrical properties, magnetic properties and hardness [3,4].

Blending between one or more polymers is an experimental way for the development and evolution of novel polymeric composites [5]. On adding polymethyl methacrylate (PMMA) with polyvinyl chloride (PVC) it would be possible to expand the properties and characteristics of the two polymers to obtain mechanical properties as well. PMMA is commonly modified by introducing polyvinyl chloride to produce flexible materials with enhanced mechanical, structural, and thermal stability [6–8].

Polymethyl methacrylate (PMMA) has good chemical resistance and high optical transparency. PMMA is a largely used as transparent covers for many purposes like special devices for electronic industries. However, its poor heat resistance, brittleness and stress cracking in most organic solvents limit its application. PMMA has wide applications in productive fields and several technologies take advantages of the unique combination of excellent optical properties with chemical inertness, good spectroscopic properties, thermal stability, electrical properties and easy forming and shaping [9,10].

Polyvinyl chloride (PVC) has wide applications in several industries. Polyvinyl chloride has disadvantages such as poor thermal stability, low impact strength and large melt viscosity. So, there have been several studies on the modification of polyvinyl chloride [11]. The methods by which modifications of Polyvinyl chloride are done are classified into: (i) grafting copolymerization of chemical modification, and (ii) blending physical modification; these mainly concentrate on modifications of plasticizers and elastomers [12,13].

Cobalt chloride (CoCl₂) as a filler will attach onto the polymeric chains at both the amorphous or crystalline regions and disperse through the disordered regions (amorphous regions) forming charge transfer complexes or aggregates between the polymeric chains [14]. Several studies [15–17] considered the CoCl₂ filler as an efficient electron acceptor and this was attributed to the presence of Co²⁺. Many investigations of our group revealed that the

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metal halide modifies the structural and physical properties of the polymers [18].

One of the main objectives in polymer research is to develop polymeric systems with high ionic conductivity. This is due to their potential application as an electrolyte and as a separator in solid state batteries. Various types of polymers have been employed as hosts such as PEO, PVA, PVDF, PVC and PMMA.

In this work, polymethyl methacrylate (PMMA) and polyvinyl acetate (PVC) have been chosen as polymer hosts and investigate the effect of the changes and verifications of the chemical structure of segments of PMMA on the miscibility and compatibility with PVC and the structure property relationships in these polymer blends before and after adding of CoCl_2 .

Experimental details

Materials used

Basic materials used are polymethyl methacrylate (PMMA) [$(\text{C}_5\text{H}_8\text{O}_2)_n$; density: 1.18 g/cm^3] of molecular weight 120,000 and polyvinyl chloride (PVC) [$(\text{C}_2\text{H}_3\text{Cl})_n$; density: 1.39 g/cm^3] supplied by Merck, Germany. Cobalt chloride (CoCl_2) (purity: 99%, Hayashi pure chemical industries, Ltd. Japan) was provided in a fine powder state and used without any purification.

Preparation of PMMA/PVC blend films

Composites of PMMA/PVC/ CoCl_2 were prepared using the casting method as: Amount of PMMA and PVC were dried before use in a vacuum oven at 55°C about 1 h to remove the moisture content in the polymers. Weight ratio of PMMA and PVC (70: 30 wt.%), respectively was dissolved in double distilled water as a solvent with stirring about 6 h at 60°C until a homogenous viscous liquid solution was formed. Cobalt chloride powder were dissolved in double distilled water and the solution of CoCl_2 was added to the blend solution (drop by drop) with weight percents of 0, 5.0, 7.5 and 10. The resulting homogeneous solutions (PMMA/PVC/ Co^{2+}) were casted onto glass Petri dishes and these dishes were kept in air to dry. After drying, the films were peeled from Petri dishes and kept in vacuum desiccators until use. Calculated weight of PMMA/PVC blend and CoCl_2 mass fractions were prepared according to:

$$W\% = \frac{w_{\text{Co}}}{w_{\text{Co}} + w_{\text{blend}}} \times 100 \quad (1)$$

where w_{Co} and w_{blend} represent the weights of cobalt chloride and the polymer blend, respectively. The films were cut into suitable pieces for measurements. The thickness of the prepared films is in the range around $40 \mu\text{m}$.

Measurement techniques

The functional groups of PMMA, PVC and PMMA/PVC blends containing CoCl_2 films were examined using different techniques. The X-ray diffraction scans were obtained using PANalytical X'Pert PRO XRD system using $\text{CuK}\alpha$ radiation (where, $\lambda = 1.540 \text{ \AA}$, the tube operated at 30 kV, the Bragg's angle (2θ) in the range of $5\text{--}80^\circ$). The UV-Vis absorption spectra were measured in the wavelength region of 200–900 nm using a spectrophotometer (V-570 UV/VIS/NIR, JASCO, Japan) to study the change in structures of the samples prepared and their optical properties. The FT-IR spectrophotometer (Nicolet iS10, USA) was recorded at room temperature. IR spectra were collected between the wavenumber of 4000 and 400 cm^{-1} at a resolution of 2 cm^{-1} . Differential scanning calorimetry of the prepared films was carried out using an equipment type (SETARAM labsys TG-DSC 16) from room temperature to 500°C with a heating

rate of $10^\circ\text{C min}^{-1}$. Shimadzu TGA-50H was used for the thermogravimetric analysis of the samples. A small amount of the sample was taken for the analysis and the samples were heated from room temperature to 550°C at a rate of $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere on a platinum cell.

Results and discussion

X-ray diffraction

Fig. 1 depicts the X-ray diffraction (XRD) of PMMA/PVC polymer blend and the blend with different concentrations (0.0, 5.0, 7.5 and 10 wt.%) of CoCl_2 . As seen in Fig. 1, the spectra of X-ray exhibit a semi crystalline nature and there are two halos observed at $2\theta = 17.73$ and 24.52° . X-ray spectra reveal a decrease in the intensity of the two halos without any change in the halo position with increase in the content of CoCl_2 . This result indicates that the addition of CoCl_2 can cause a variation of the structure in the polymeric matrices [19]. However, no significant difference between the PMMA/PVC blend and the blend doped CoCl_2 was observed which may be attributed to good dispersion without the aggregation of CoCl_2 in the polymeric matrices.

The degree of crystallinity for PMMA/PVC blend and the blend doped CoCl_2 can be measured by calculating the area under the peaks (A) of the two halos at $2\theta = 17.73$ and 24.52° . The estimated values of crystallinity (χ) were recorded in Table 1. It is clear that the values of the area (A) decreases as CoCl_2 increases which indicates that CoCl_2 may be the effect of the degree of crystallinity and produce more defects in the polymeric matrices (increase in amorphous regions) [20].

Uv-visible analysis (UV-Vis)

Fig. 2 shows the UV-Vis absorption spectra of PMMA/PVC incorporated with various concentrations of CoCl_2 in the range around 200–1100 nm at room temperature. A sharp peak at 216 nm for pure PMMA/PVC which was attributed to $\pi \rightarrow \pi^*$ transitions was observed [21,22]. This peak comes from unsaturated bonds ($\text{C}=\text{O}$) which were observed in FT-IR at about 1724 cm^{-1} . This peak was shifted from 216 nm to 244 nm after adding CoCl_2 . It was seen from the spectra that there was most absorption edge for all curves. A shift in band edges toward the higher wavelengths with different absorption intensities for doped between PMMA/PVC and CoCl_2 may be also attributed to the change in crystallinity due to adding of the filler. In other words, the absorption band at about

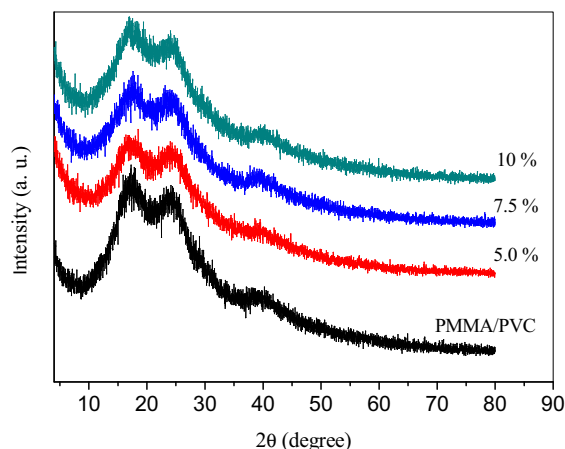


Fig. 1. The X-ray diffraction scan of the PMMA/PVC blend with 0.0, 5.0, 7.5 and 10 wt.% of CoCl_2 .

Table 1

The estimated values of the area under the peaks and variations of direct and forbidden band gap energy of the PMMA/PVC blend with 0.0, 5.0, 7.5 and 10 wt.% of CoCl_2 .

Samples	Area (cm^2)	Energy band gap		The activation energies (J/mole)
		Indirect E_{indirect} (eV)	Forbidden $E_{\text{Forbidden}}$ (eV)	
PMMA/PVC	3.42	5.01	5.08	126.45
5.0% CoCl_2	2.81	4.62	4.73	103.27
7.5% CoCl_2	2.22	4.17	4.48	78.23
10% CoCl_2	2.03	3.92	4.19	64.34

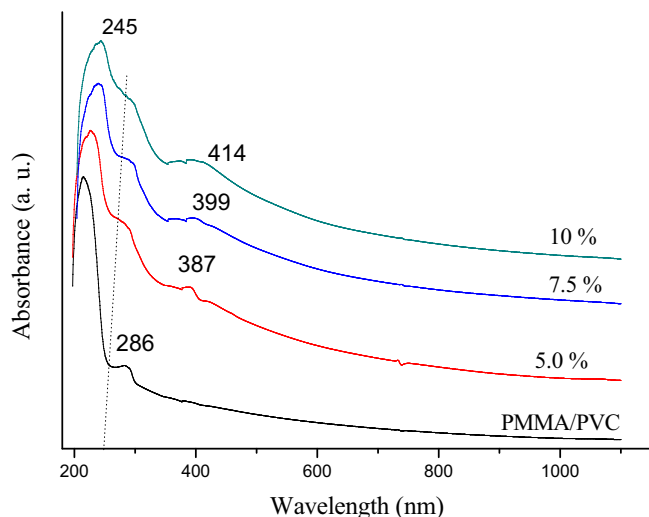


Fig. 2. The UV-Vis absorption spectra of PMMA/PVC incorporated with various concentrations of CoCl_2 .

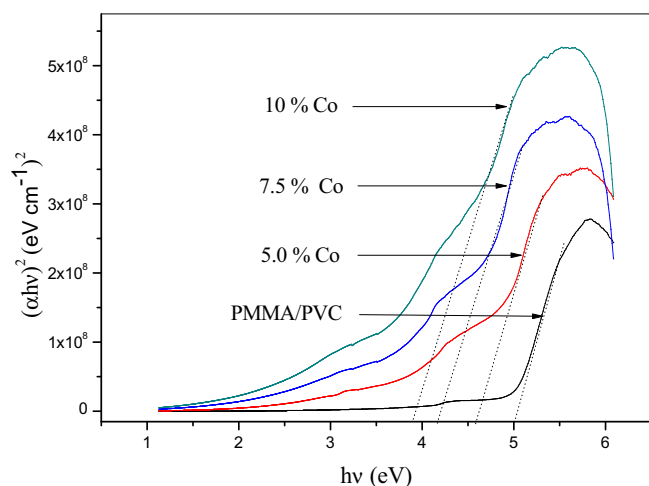


Fig. 3. The relation between $(\alpha hv)^2$ various photon energy (hv) of PMMA/PVC incorporated with various concentrations of CoCl_2 .

287 nm in the spectrum of PMMA/PVC blend was observed which was attributed to the spin tetrahedral structure of $3d^7$ configuration of Co^{2+} . This band is also ascribed to the optical transmission due to spin orbit coupling effects. This absorption band was increased and shifts with an increase of CoCl_2 content due to the presence of metal-ions indicating a complexation between the PMMA/PVC blend and Co^{+2} .

Determination of optical energy gap (E_g)

The optical energy gap (E_g) for indirect and forbidden transitions can be determined. Figs. 3 and 4 show Tacu's plot of the $(\alpha hv)^2$ and $(\alpha hv)^{3/2}$ as a function of photon energy (hv), where (α)

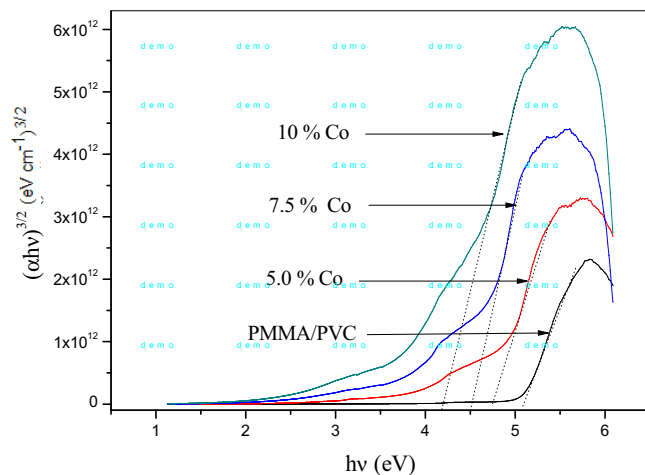


Fig. 4. The relation between $(\alpha hv)^{3/2}$ and photon energy (hv) of PMMA/PVC incorporated with various concentrations of CoCl_2 .

is the absorption coefficient. The intercept on the photon energy axis on extrapolating the linear portion of the curves may be interpreted as the value of the band gap. The plots can be used to calculate the optical energy gap. The obtained values of (E_g) are listed in Table 1.

From the figures, the values of both direct band gap and forbidden band gap decreases with an increase in the CoCl_2 concentrations. This decrease indicates that charge transfer complexes arose between the polymer blend and Co^{2+} and these may be attributed to the formation of defects in the polymeric matrices. These defects produce the localized states in the optical band gap. These overlaps are responsible for decreasing energy band gap when CoCl_2 concentrations are increased in the polymer matrix. Moreover, the decrease in the optical gap values causes an increase in the degree of disorder (amorphous nature of the prepared films) or due to invoking the occurrence of local cross linking within the amorphous phase of the blend. These results are supported by XRD studies.

FT-IR analysis

Fourier transform infrared (FT-IR) absorption spectra of pure PMMA, PVC and their blend are shown in Fig. 5. Pure PMMA showed an IR absorption band at 1434 cm^{-1} due to asymmetric bending vibration (CH_3) of methyl group. The band at 1195 cm^{-1} was due to $-\text{OCH}_3$ stretching. A sharp band located at 1723 cm^{-1} was ascribed to the carbonyl group. The band located at 1148 cm^{-1} was attributed to the C-O group. The band at about 1059 cm^{-1} was assigned to the stretching vibration of the C-O-C group. The bands at 3446 cm^{-1} and 3622 cm^{-1} were attributed to the OH group. The bands at 2947 cm^{-1} and 2986 cm^{-1} were assigned to $-\text{CH}$ stretching. While the absorption spectrum of pure PVC showed characteristic absorption bands at 2981 cm^{-1} attribu-

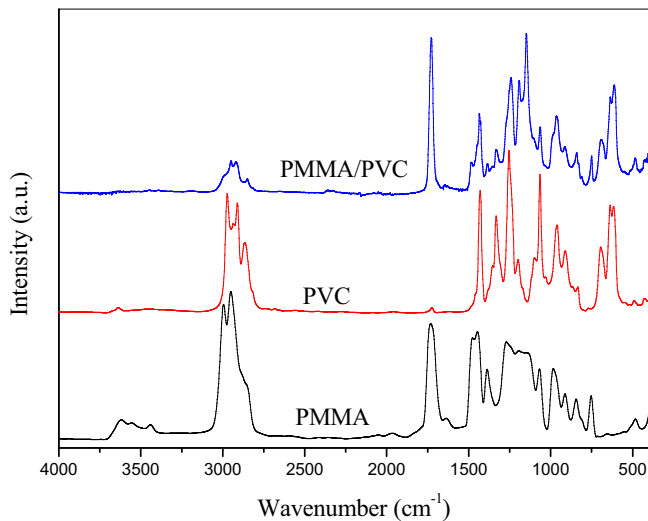


Fig. 5. The FT-IR absorption spectra of pure PMMA, PVC and PMMA/PVC blend.

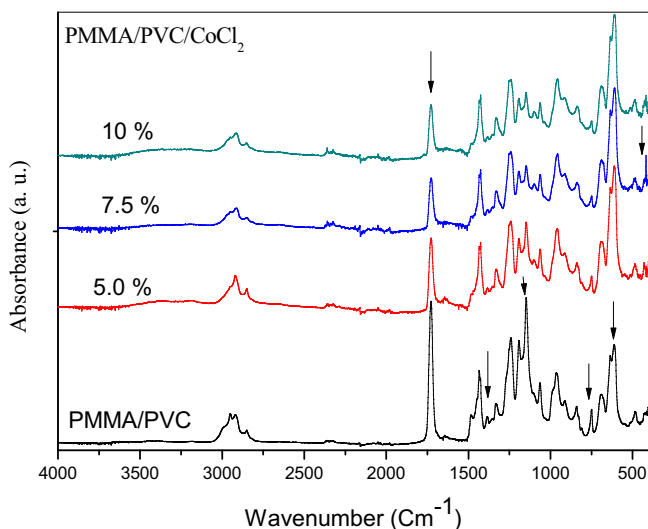


Fig. 6. The FT-IR absorption spectra of pure PMMA/PVC blend and the blend with various contents of CoCl_2 .

ted to $-\text{CH}$ stretching, 2911 cm^{-1} and 2822 cm^{-1} were assigned to CH_2 asymmetric stretching. The bands at 1426 cm^{-1} due to $-\text{CH}$ bending vibration mode, at 1340 cm^{-1} were assigned to $-\text{CH}_2$ deformation, at 1251 cm^{-1} for CH rocking mode, at 970 cm^{-1} attributed to trans CH wagging mode and the band at 612 cm^{-1} due to $-\text{CH}$ cis wagging mode [23,24]. Blending of PMMA and PVC showed characteristic absorption bands for both PMMA and PVC. This may imply that an interaction between PMMA and PVC occurs.

Fig. 6 shows the FT-IR absorption spectra of the PMMA/PVC blend and the blend with different concentrations of CoCl_2 . The following was observed: The small band at 1470 cm^{-1} disappeared and sharp bands at 1723 cm^{-1} , 1148 cm^{-1} and 747 cm^{-1} decreased, while the sharp band at 611 cm^{-1} increased. This may be due to the link between the functional group inside the blend and Co^{+2} ions.

Thermogravimetric analysis (TGA)

Fig. 7 depicts the TGA thermographs of the PMMA/PVC blend doped with different contents of CoCl_2 from room temperature to

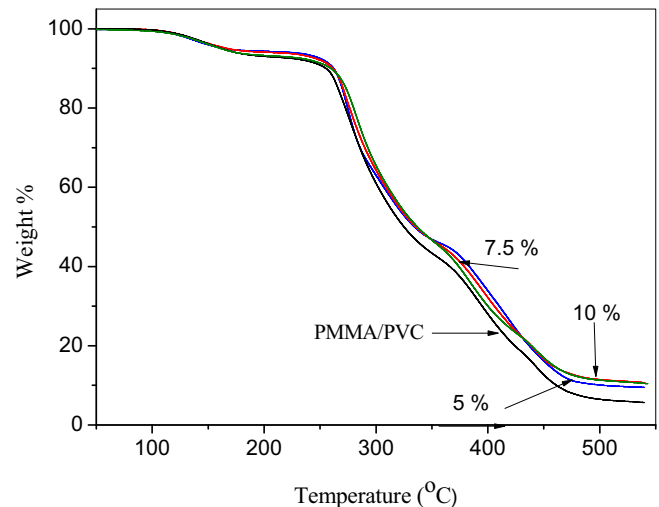


Fig. 7. TGA thermographs of PMMA/PVC blend doped with different contents of CoCl_2 from room temperature to $550\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

$700\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. All curves show three regions of weight loss for the prepared samples. These regions are classified as: (i) The first region due to the evaporation of physically weak, chemically strongly bound H_2O and evaporation of CO and CO_2 gases from polymers with weight percent of 7, (ii) The second transition region from $255\text{ }^\circ\text{C}$ upto $485\text{ }^\circ\text{C}$ is attributed to the main decomposition temperature (degradation temperature) of the blend having a weight loss of about 9–92 wt.%. The transition peak of the third stage after $500\text{ }^\circ\text{C}$ is due to the cleavage backbone of the polymer. The degradation peaks of the cross-linked polymers are less intense and shifted to higher temperatures with adding of CoCl_2 .

It is clear that the degradation temperature gradually increases with increasing of CoCl_2 contents and the thermal decomposition of all samples shifts slightly toward higher temperature ranges than in the pure polymer blend indicating the enhancement of the thermal stability of the samples. Furthermore, the final weight losses of the pure blend is less than that of the samples doped with CoCl_2 that may be due to the chemical reaction between CoCl_2 and the blend, then the addition of CoCl_2 to PMMA/PVC films enhances their thermal stability.

Calculation of activation energy

The determination of activation energy from the thermal decomposition for TGA measurements of the prepared films depending on the residual weight, can be determined using the Coats and Redfern equation [25]:

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2} \right] = \log \frac{R}{\Delta E} \left[1 - \frac{2RT}{E} \right] - \frac{1}{2.303} \frac{E}{RT} \quad (1)$$

where T is the absolute temperature, E is the activation energy in J/mol , R is the universal gas constant (8.3136 J/mol K), n is the order of reaction and α is the fractional weight loss at that particular temperature calculated as:

$$\alpha = \frac{w_i - w_t}{w_i - w_f} \quad (2)$$

where w_i is the initial weight, w_t is the weight at given temperature and w_f is the final weight of the sample.

For $n \neq 1$, Eq. (2) reduces to:

$$\log \left[\frac{-\log(1 - \alpha)}{T^2} \right] = \log \frac{R}{\Delta E} \left[1 - \frac{2RT}{E} \right] - \frac{1}{2.303} \frac{E}{RT} \quad (3)$$

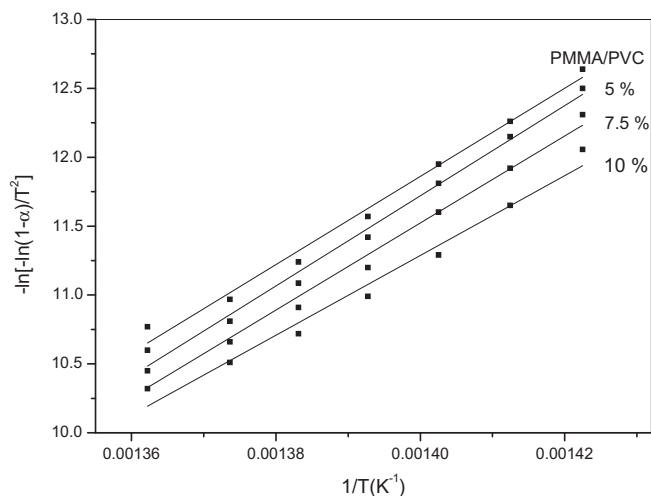


Fig. 8. The plot between $-\log \left[\frac{-\log(1-\alpha)}{T^2} \right]$ against $1/T$ for PMMA/PVC blend with different concentrations of CoCl_2 .

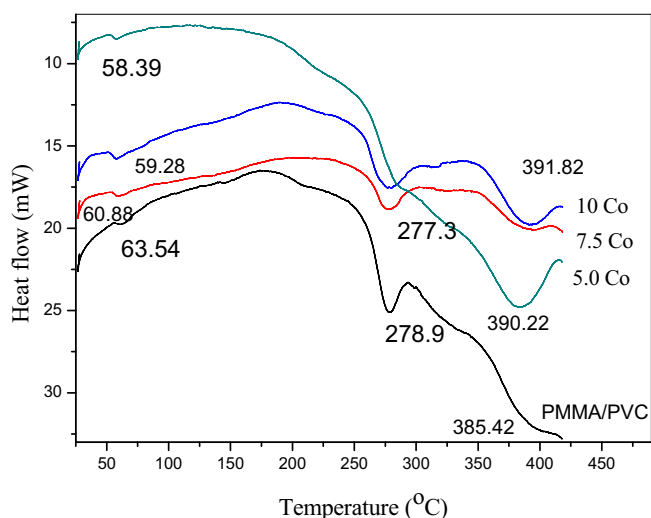


Fig. 9. DSC thermographs of the PMMA/PVC blend with different concentrations of CoCl_2 in the temperature range of 30–500 °C.

By plotting $-\log \left[\frac{-\log(1-\alpha)}{T^2} \right]$ against $1/T$ for each sample, we obtain a straight line as shown in Fig. 8. The value of activation energy (E) was calculated from the slope of the plot as:

$$E = 2.303R \times \text{slope} \quad (4)$$

The calculated activation energies of the samples are shown in Table 1, where it is clear that the values of the activation energy are decreased from 126.45 to 64.34 KJ/mole with an increase of CoCl_2 concentrations indicating that CoCl_2 intensively affects the blend.

DSC studies

Fig. 9 shows differential scanning calorimetry (DSC) curves of PMMA/PVC as a host material with different concentrations of CoCl_2 in the temperature range of 30–500 °C. As we see, all DSC curves of the prepared films in the figure exhibited endothermic peaks. The thermographs are characterized by three main endothermic peaks: Small peak (T_g) in the range of 63.5–58.3 °C which can be assigned to the glass–rubber transition due to the micro-brownian motion of main chain segments of the polymer

and/or assigned to the glass transition of the β -microphase formed in the α -phase [26], another endothermic peak at about 278.9 °C is attributed to melting temperature (T_m) of the composites and the last sharp peak (main peak) at about 385.4 °C is attributed to the decomposition temperature of composites. Generally, the DSC curve of the pure blend shows a single T_g also with one melting peak, due to that component blend molecules would interact with each other. This interaction effects of the crystallization and glass transition temperature of the blend. The presence of one single glass temperature (T_g) indicates miscibility of the pure blend.

The values of the glass transition temperatures of T_g is decreased with increasing the content of the CoCl_2 filler. This suggests that the segmental mobility of the amorphous polymer increases due to the addition of CoCl_2 and becomes less rigid segments. The change in the position of T_g might mainly have been due to the effect of filling on the orientation of crystals, crystallinity and micro-structure of the films [27]. The thermal degradation temperature. The values of decomposition temperature (T_d) are also decreased with increasing the concentration of CoCl_2 indicating that the addition of the filler to the blend films decreases the thermal stability; therefore, the CoCl_2 powders affected the blend structure which also confirms the TGA results. Also, these results suggest the influence of the intercalation treatment of the polymeric matrices.

Conclusions

Neat PMMA/PVC blend and the blend embedded with different contents of CoCl_2 were prepared and studied using XRD, UV-Vis, FT-IR, TGA and DSC techniques. The degree of crystallinity of the prepared samples was measured using area under the peaks. Values of the area decrease as CoCl_2 increases, indicating that CoCl_2 may influence crystallinity and produce more defects in the polymeric matrices. In the UV-Vis spectra, the absorption band at about 287 nm was attributed to the spin tetrahedral structure of $3d^7$ configuration of Co^{2+} . This band was ascribed to the optical transmission due to spin orbit coupling effects. The absorption band was increased and shifts with an increase of CoCl_2 content due to the presence of metal-ions indicating that the complexation between PMMA/PVC blend and Co^{2+} occurs. The decrease in optical gap energy indicates that a charge transfer complex arose between the polymer blend and Co^{2+} and was due to the formation of defects in the polymeric matrices. These defects produce the localized states in the optical band gap. IR analysis show characteristic absorption bands for both PMMA and PVC. This may imply that there is an interaction between PMMA and PVC. Some shift of IR bands indicates that an interaction occurred between the PMMA/PVC and CoCl_2 . TGA thermographs for all samples have the same behavior with three steps of decomposition of samples being observed. It can be concluded that increasing the addition of CoCl_2 to the blend shows high order, low thermal motion and more thermal stability compared to the pure blend due to random scission of the macromolecule chain in the polymeric matrices predominating and a lower activation energy.

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