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Development of LDPE Crystallinity in LDPE/Cu Composites

Makki Abdelmouleh and Ilyes Jedidi

Abstract

This chapter summarizes the study of the filler (ie copper) effect on LDPE phasic composition in LDPE/Cu composites prepared in solution. During this research work, a particular effort is focused on the use of DSC under non-standard conditions. Therewith, the presence of copper microparticles has a great effect on the network phase than on the crystalline long-range-order phase of LDPE structure. Furthermore, LDPE phasic composition in absence and presence of copper microparticles is investigated by FTIR spectroscopy followed by a spectral simulation of the band that appeared at 720 cm^{-1} corresponding to the CH_2 . Anywise, the two-phase model confirmed that no variation is observed of LDPE phase composition for all copper contents into LDPE/Cu films. However, with the three-phase model the orthorhombic phase fraction was found to be constant compared to the fraction of amorphous and that of network phase were found to increase and decrease respectively with increase in the copper particle load in the film. Overall, the thermal and structural behavior of LDPE in presence of copper particles allows this type to be used as phase change materials (PCMs) by adding a paraffin fraction in the LDPE/Cu composite. An update of the most relevant work carried out in the field of phasic characterization of polyethylene is presented in this chapter.

Keywords: LDPE/Cu composite films, LDPE crystallinity, LDPE Network phase, thermal stability

1. Introduction

Inorganic fillers perform an important role in the production of polymeric composites. Several value-added properties other than low cost, are gained through the use of fillers. Fillers can improve the mechanical [1–3] and thermal [4–7] properties, as well as optical and electrical properties [8–12] of polymeric materials composites. The polyethylene (PE) as one of the most widely used thermoplastics resins possesses excellent biocompatibility with human body and usually used as implantable material [13]. The PE/Cu composites have been developed in a large range of applications. The physical properties depend on the percentage of filler in the composites materials. The crystallinity of a semi-crystalline polymer (in particular polyethylene) mostly decides its physical and some times chemical characteristics. Thereby, it is important to understand the effects of metallic fillers on the phase composition of a semi-crystalline polymer matrix.

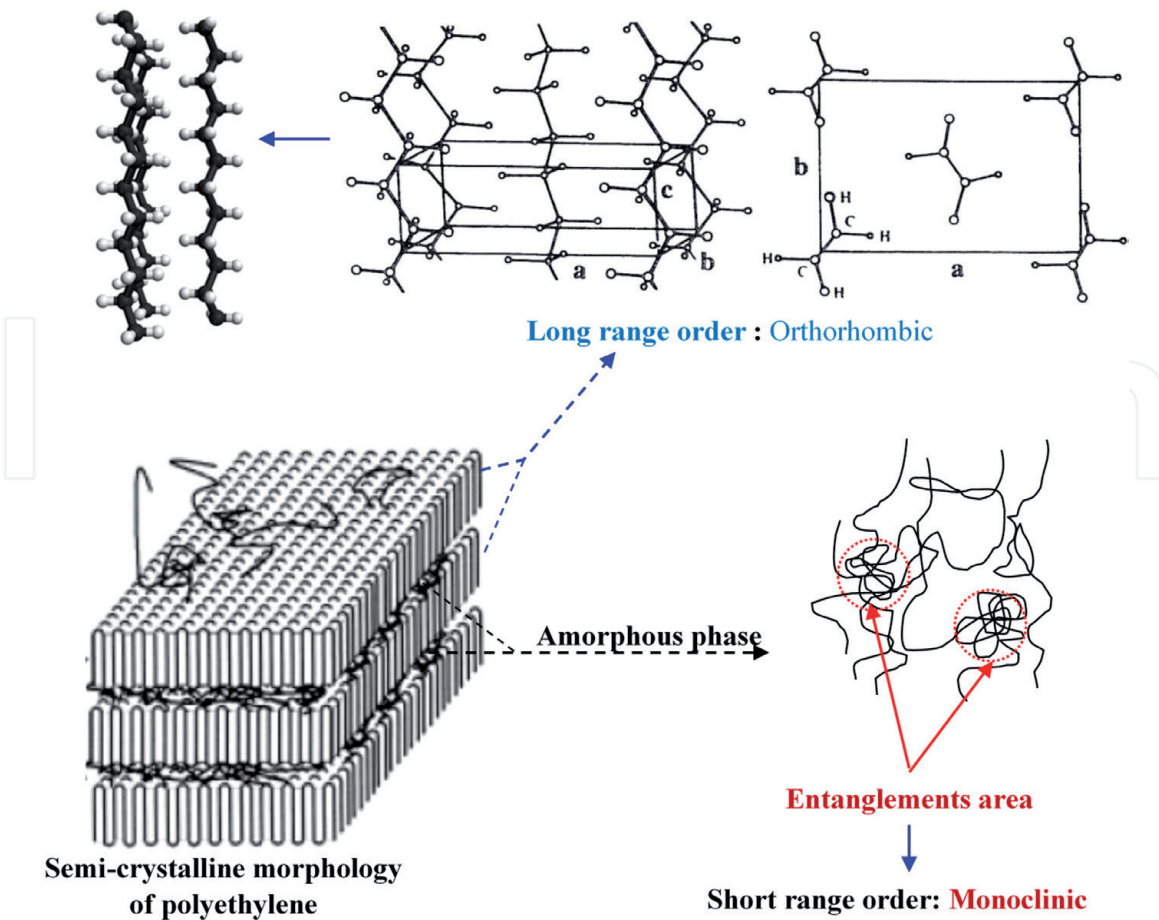


Figure 1.

Three-phase model. In areas of entanglement, a three-dimensional order at close range exists; this is the third phase.

The phase composition of polyethylene (PE) polymers has been described using a two phase or a three-phase model. In the two-phase model, the fraction of the long-range order phase is demonstrated by X-ray scattering and calorimetry but the other phase assumed to be liquid-like. Various techniques have been used to confirm the presence of a third-phase with mobility and order intermediate to that of the crystalline and amorphous phases for Polyethylene (PE). The name and the characteristics of this third phase depend on the type of crystal growth (bulk, solution, or fiber crystals) and on the technique used to analyze it. In NMR [14] and Raman [15–17] studies, the third phase in PE has been called interlamellar, inter-facial, or interzonal, in reference to its links to the crystalline and amorphous phases. The analysis of the melt is one of the techniques allowing suggesting the presence of more than two phases in a semi-crystalline polymer. Thus, ^{13}C NMR indicated the presence of two relaxation times [18, 19] relating to a heterogeneous fusion showing that the solid melts in a complex mode and incompletely.

The third phase, named the network phase, was identified following the characterization of the phase composition of different PE samples by slow Calorimetry, Calorimetry in non-standard conditions, FTIR and LCST technique [20–22]. This phase consists in a short range order located between the entanglements contained in the amorphous phase. In consequence, this network phase is heterogeneous with a range of order and tension (due to the entanglements) determined by the polymerization conditions [22], the sample history [21] and the charge load [23]. Taking this third phase into account, the phasic structure of polymers could be described as follows (**Figure 1**):

- Crystalline phase: the same as that described in the two-phase model, that is formed by sequences of ordered molecules in a crystal lattice forming a three-dimensional order at a long distance. The crystal unit cell is orthorhombic in the case of PE,
- Amorphous phase: disorderly and entangled chains,
- Network or interphase phase: formed by the entire network of entanglements contained in the amorphous phase. In these areas of entanglement, a certain three-dimensional crystallinity exists due to the organization of short sequences of chains in a short-distance crystal lattice. In the case of PE, the lattice of crystals of the small distance order would be of the orthorhombic and monoclinic type [24].

Using a three phase system (crystalline, network and amorphous) instead of a two phase system (crystalline and amorphous) to study the effect of filler particles on the crystallinity of LDPE can be more appropriate. This due to the existence of a third phase having a morphology intermediate between that associated with long-range order and that consisting of disordered chains. For a thin film of PE melted on a substrate composed by the zinc selenide (ZnSe) microparticles or the titanium dioxide (TiO₂) nanoparticles, Bernazzani and Sanchez [24] found a relationship between the amorphous phase (of a two-phase system) and the T_m variation. With these results, they confirmed that the crystalline phase (long distance order) was not affected by the nature of the substrate or the particle size.

In the present chapter, we investigate the effect of the filler (ie copper) on LDPE phasic composition in LDPE/Cu composites prepared in solution. The main objective of this work is to highlight the effect of the presence of copper microparticles on the network phase and on the long and the short-range order crystalline phase of the LDPE structure. To determine the effect of the copper microparticles addition on the LDPE matrix crystallinity we used different physico-chemical characterization techniques have been used such as FTIR spectroscopy and Differential scanning calorimetry (DSC) at standard and non standard conditions (**Figure 2**).

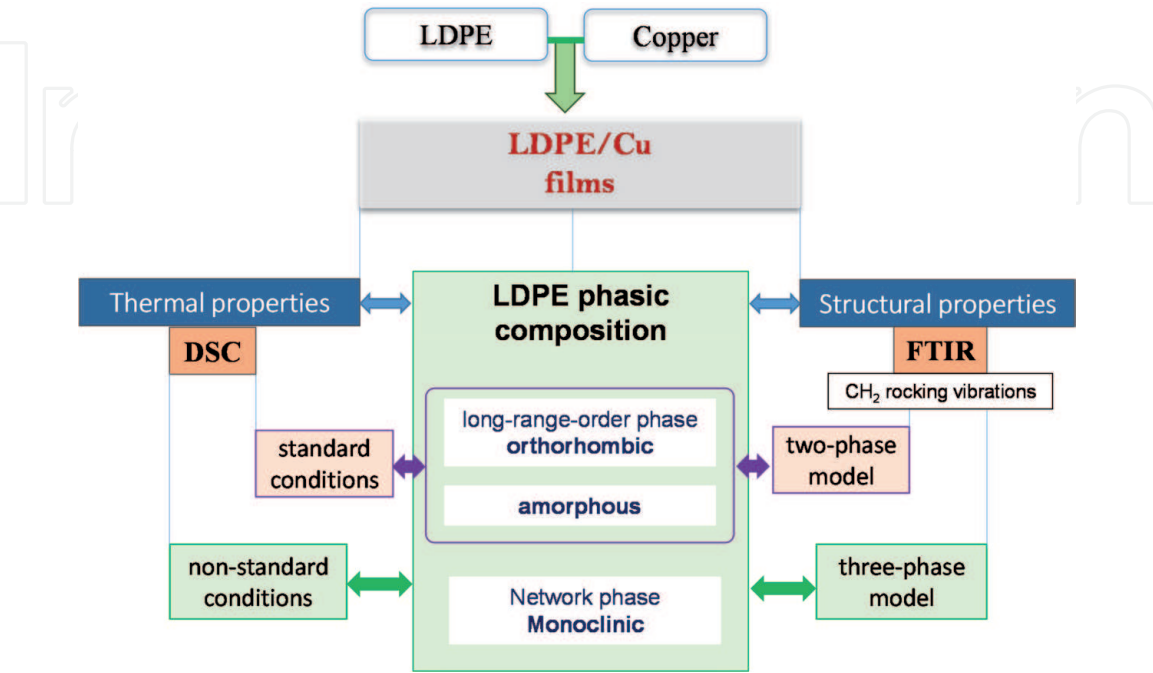


Figure 2.
Schematic representation of the thematic analysis of the chapter.

2. Preparation of the Cu/LDPE composite films

The low density polyethylene (LDPE) in pellets used in this work has a melting temperature of 107°C, a crystallinity around 40% (as determined by differential scanning calorimetry (DSC) with a heating rate of 10°C/min) and a density at room temperature of 0.9 g/cm³. The particles sizes were < 38 µm and were supplied by Sigma-Aldrich. High purity toluene (99%) supplied by Sigma-Aldrich was used as solvent for the preparation of the solution made films. Different solutions of LDPE-toluene at 1% in the absence and in the presence of copper microparticles were prepared at 80° C. and cooled to room temperature. After total evaporation of the solvent in a Teflon mold, thin films (50 to 60 µm thick) were obtained [25].

3. Characterization of the Cu/LDPE composite films

3.1 Microscopy observation

Optical microscopy was used to investigate the distribution of the Cu microparticles in LDPE. The polarized optical microscopy photos of different LDPE/Cu composites were exposed in **Figure 3**. The copper particles distribution in the composite films are relatively uniform at both low (8%) and high (16%) copper contents.

3.2 Thermogravimetric analysis: TGA

The thermal stability of the composites was investigated by the Thermo Gravimetric Analysis (TGA). An amount of 5–10 mg of each sample were analyzed by Perkin-Elmer TGA7 Instrument from 35–600°C with a heating rate 20°C/min under nitrogen (N₂) atmosphere.

The TGA curves for LDPE and its copper composites are shown in **Figure 4**. Neat LDPE showed a one-step decomposition process starting at 464°C due to the degradation of saturated carbon atoms in polyethylene that is displayed by peak on the curve DTG (**Figure 5**). The increase in the thermal stability of LDPE with increasing copper content showed in the composite films may be explained by the higher heat capacity (0.39 J/(Kg), compared to 0.18 J/(Kg) for PE) and thermal conductivity of Cu. This will result in the onset of the degradation of PE chains at higher temperatures. After the loss of this degradation, the level of mass loss are in good agreement with the amount of copper originally mixed into the samples.

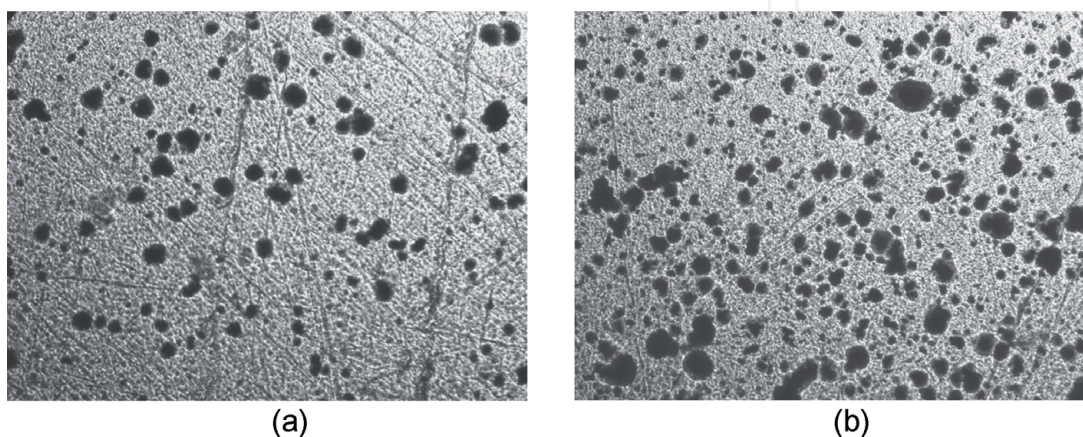


Figure 3.
Polarized optical microscopy photo of LDPE/Cu composites [100× magnification]: (a) 8%Cu; (b) 16% Cu.

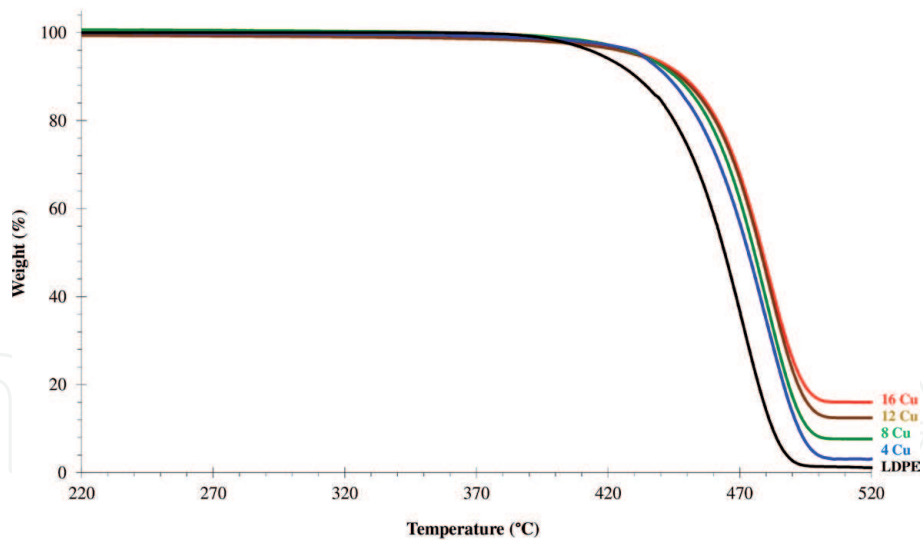


Figure 4.
TGA curves of LDPE and LDPE/Cu composites with different content of copper microparticles.

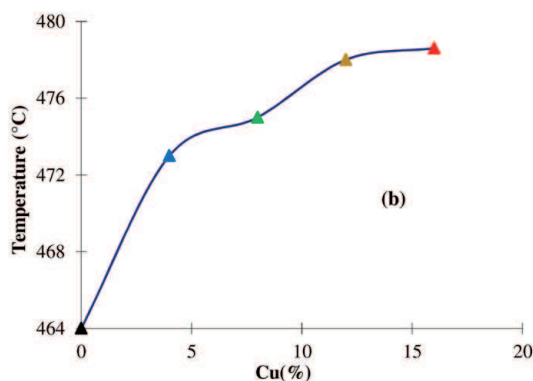
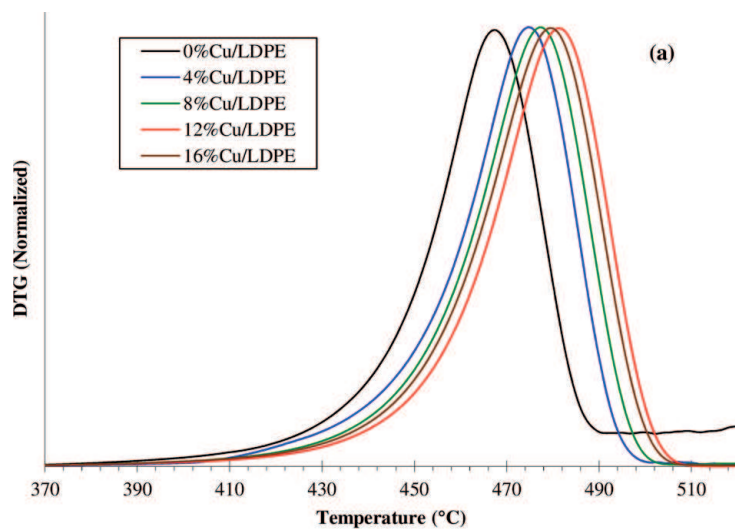


Figure 5.
(a) DTG for composite films at varying levels of copper. (b) Evolution of thermal decomposition temperature vs. Cu microparticles content.

DTG thermograms (**Figure 5**), thermal stability was clearly observed in LDPE/Cu composite films compared to unfilled LDPE film. This stability is reflected by a shift, towards high temperatures, of the decomposition peak of the composite films following the incorporation of copper microparticles into the LDPE. The curves of the thermal decomposition temperature versus the amount of copper particles are

presented in **Figure 5a**. This figure shows that the thermal decomposition temperatures of the LDPE/Cu are also higher than that of the pure LDPE, the tendency of the thermal decomposition temperature of the microcomposites increases with the increasing of the copper microparticles. They also show that the thermal decomposition temperature of the microcomposites reaches its peak as the amount of the copper microparticles is about 12 wt%, and then keeps on this scale when the amount of the copper microparticles is more than 12% wt in this experiment.

3.3 Differential scanning calorimetry: DSC

The DSC calorimeter is a Perkin-Elmer DSC7 with 20 mL/min flow of N₂. DSC in Standard Conditions ($m = 2\text{--}3\text{ mg}$ and $v = 10^\circ\text{C/min}$). The crystallization exothermic and endothermic curves of the neat LDPE and its composites with various copper micro-particles contents are illustrated in **Figure 6**. **Table 1** shows the T_m , T_c , the melting enthalpies ΔH_m , the crystallization enthalpies ΔH_c and the total crystallinity X_c values obtained for the neat LDPE film and the different LDPE/Cu composite films. The crystallinity X_c was determined as follows:

$$X_c = \frac{\Delta H_m}{W_m \Delta H_m^0} \quad (1)$$

Where $\Delta H_m^0 = 285\text{ J.g}^{-1}$ is the heat of fusion for 100% crystalline PE and w_m is the weight fraction of polymeric matrix material in the composite [38].

Figure 6 show that both the melting temperatures range and the crystallization temperatures range decrease with increasing of copper micro-particles content. Data in **Table 1** indicate a slight decrease of the melting temperatures T_m but a slight increase of the crystallization temperatures T_c with the increasing of copper micro-particles content. ΔH_m and ΔH_c decreases with the percentage of copper which is normal due to the decrease of the LDPE content in the composite film. The crystallinity X_c shows a slight decrease with the increase of the Cu content in the material showing

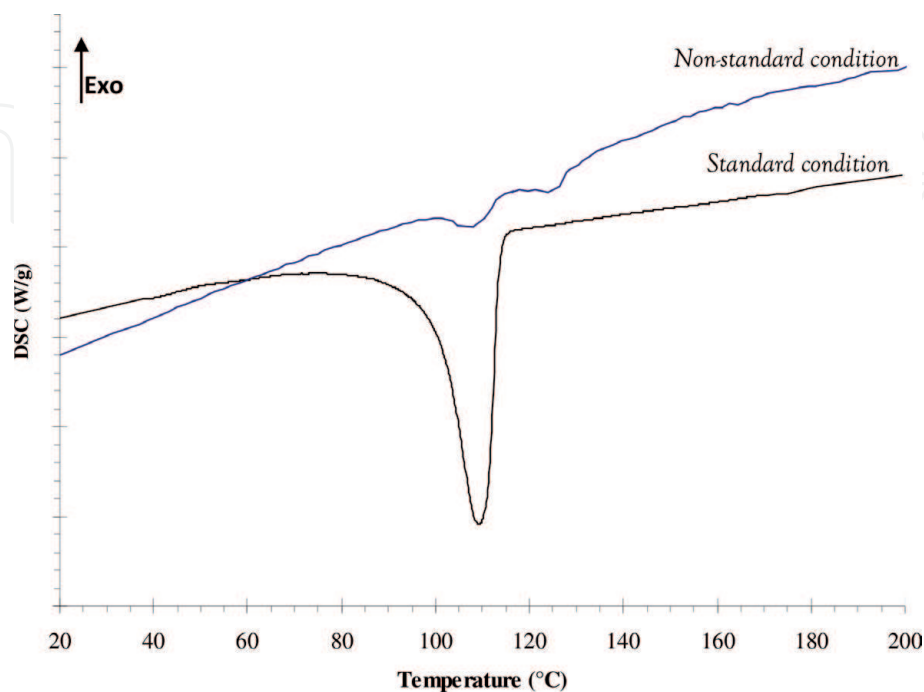


Figure 6. Complete DSC in standard-condition heating and cooling scan of pure LDPE and LDPE/Cu composites.

LDPE/Cu (%)	100/0	96/4	92/8	88/12	84/16
ΔH_m (J/g)	112,3	108,9	94,4	95,4	89,8
T_m (°C)	110,7	109,3	110,1	109,6	109,7
X_c (%)	39,4	39,8	36,1	38,0	37,5

Table 1.
Thermal characteristics (T_m , T_C , ΔH_m , ΔH_C) and degree of crystallinity (X_c) of LDPE/Cu composites.

that the copper particles get a very limited effect on the orthorhombic long range order phase. This is confirmed by the fact that T_m does not did not suffer any noticeable variation. With DSC in standard conditions the strain created in the crystalline fraction particularly at T_m leaves an ordered fraction (network phase) un-melted [22].

DSC in non-standard conditions ($m = 0.2\text{--}0.3$ mg and $v = 0.5^\circ\text{C}/\text{min}$): Due to the low values of mass and heating rate the sample (PE) will undergo a maximum heat flow [21]. The trace obtained for a neat LDPE film at the non-standard conditions (**Figure 7**) represents the endotherm of fusion of the orthorhombic crystals at 107.7°C (witch is the same T_m than that obtained by a fast T-ramp). On the other hand, at high temperatures the second endotherm obtained characterizes the melting of the strained short-range order crystals (network phase) [21, 22]. DSC in non-standard conditions ($m = 0.2\text{--}0.3$ mg and $v = 0.5^\circ\text{C}/\text{min}$): Due to the low values of mass and heating rate the sample (PE) will undergo a maximum heat flow [21]. The trace obtained for a neat LDPE film at the non-standard conditions (**Figure 7**) represents the endotherm of fusion of the orthorhombic crystals at 107.7°C (witch is the same T_m than that obtained by a fast T-ramp). On the other hand, at high temperatures the second endotherm obtained characterizes the melting of the strained short-range order crystals (network phase) [21, 22].

Endotherms in non-standard conditions of neat LDPE and LDPE/Cu (84/16) composite (**Figure 7**) does not present any variation in the T_m value with the addition of copper particles. Never the less, the shape of the network melting endotherm of the different LDPE/Cu composite films looks very different when comparing it with that obtained for the neat LDPE film. In fact, in the traces of all the LDPE/Cu films, a more obvious separation between the Orthorhombic and the network

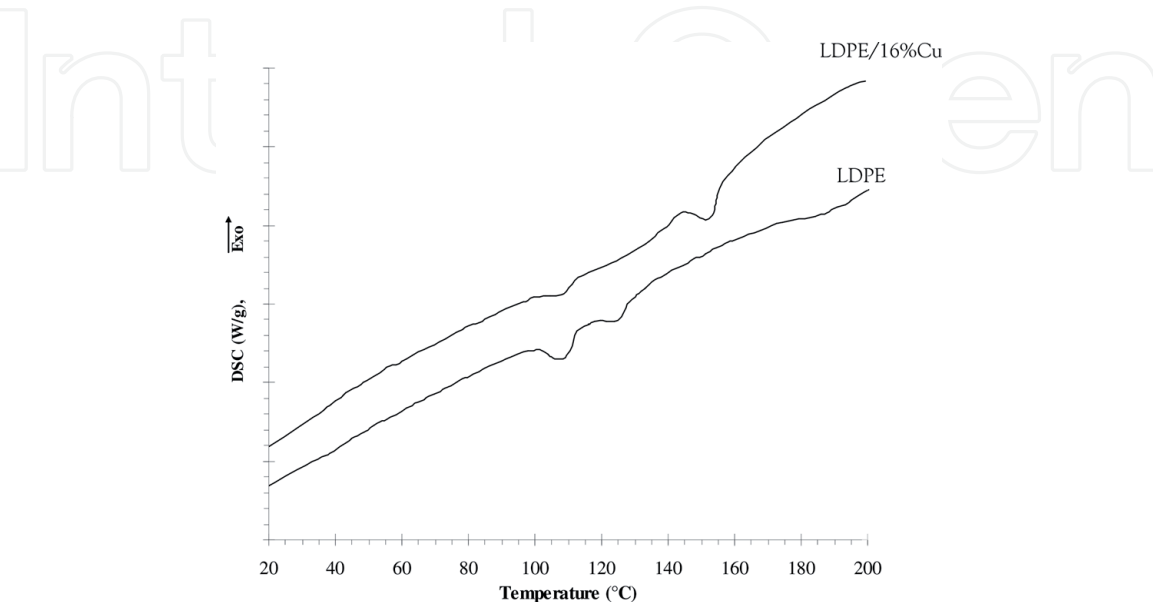


Figure 7.
Endotherm of neat LDPE at standard conditions (blue line) and endotherms in non-standard conditions of neat LDPE and LDPE/Cu(16%) composite (black line).

endotherms is observed. Also, more events happened in the melt expressed by the different melting/crystallization/melting observed in comparison to the more flat endotherm of the network melting endotherm of the neat LDPE film. These observations suggest that the presence of the micro-particles copper have more effect on the network phase than that can be observed on the crystalline long-range order phase. It is then more consistent to study the effect of the copper particles by analyzing the changes occurring on the network phase. The expansion during the temperature ramp operates a strain on the sample and the network phase is deformed. Over the melting of this phase showed by a succession of melting/crystallization/melting a complex phenomenon can be observed [21]. In fact, the copper micro-particles participate in the strain applied on the sample which explains the higher melting temperatures and the larger endotherms obtained for the network phase melting.

3.4 Infrared spectroscopy

The FTIR spectra of the studied films were obtained with a Perkin–Elmer Paragon 1000 FT-IR spectrometer used in transmission mode. The spectra were treated using BOMEM GRAMS software for the determination of the study of the different phases of the LDPE.

3.4.1 Pure polyethylene thin films

The IR spectrum provided by the LDPE (**Figure 8**) shows absorption bands characteristic of different vibration modes of methylene group. The main vibrations obtained on the spectrum are grouped together in **Table 2**. The elongation vibration, also called vibration of valence or “stretching”, concerns the variation of the interatomic distance. When the molecule has symmetries, we can distinguish symmetrical or antisymmetrical modes of elongation, which can be easily seen in the case of a methylene CH_2 group of LDPE (2919 cm^{-1} and 2845 cm^{-1}). In addition to stretching, the angles between the adjacent bonds of the CH_2 can vary, we then speak of deformation modes, which can be symmetric or asymmetric, and occur in the plane or out of the plane (1472 cm^{-1} , 1460 cm^{-1} , 720 cm^{-1} and 730 cm^{-1}). The presence of $(-\text{CH}_3)$ is rarely desired when manufacturing a polymer. Indeed,

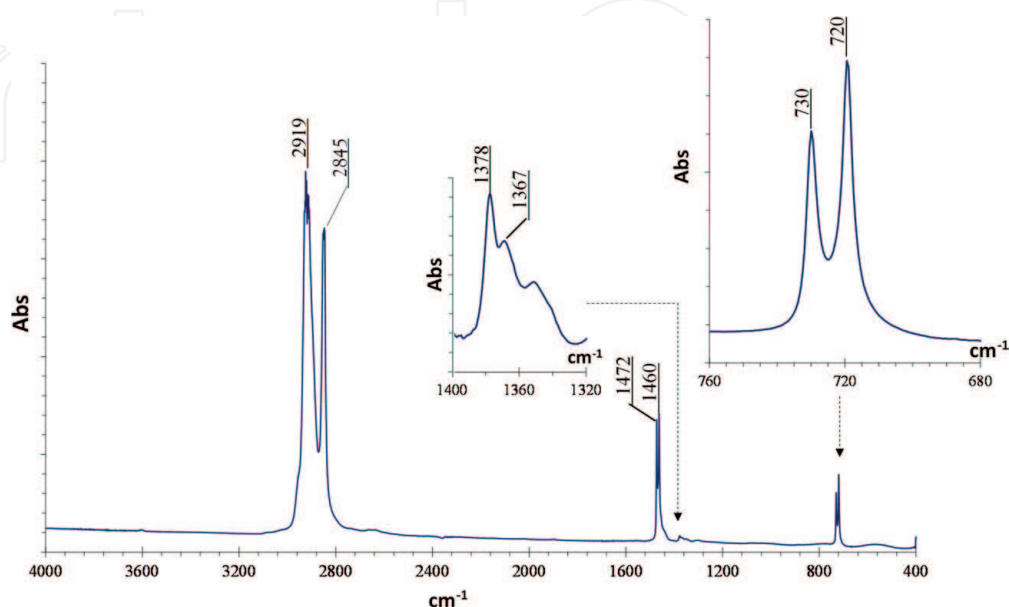


Figure 8.
FTIR spectra of LDPE film prepared from a solution.




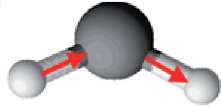
Absorbance (cm ⁻¹)	Nature of vibrations		
720	γ C-H (amorphous phase)	Rocking CH ₂	
730	γ C-H (crystalline phase)		
1460	δ C-H (amorphous phase)	Scissoring CH ₂	
1472	δ C-H (crystalline phase)		
2845	ν CH ₂ (s)	Symmetric stretching CH	
2919	ν CH ₂ (as)	Asymmetric stretching CH	

Table 2.
Different absorption bands of LDPE.

a methyl group will decrease the density of the polymer by limiting the superposition of the layers, then making it of poorer quality. There is therefore an IR analysis method for determining the concentration of methyl group in a polymer as a function of the absorbance with two closely spaced bands (1378 cm^{-1} and 1368 cm^{-1}). These two bands visualized on the spectrum of the polyethylene used during this work (**Figure 8**) confirms the low density character of the polyethylene polymer and indicates its low rate of crystallinity by the existence of CH_3 groups in the polyethylene structure.

A series of standard infrared spectra as a function of temperature was first performed for pure LDPE thin film in order to understand the effect of interactions on the melting transition of LDPE. **Figure 9** shows the typical evolution of the infrared spectra of pure LDPE in the CH_2 rocking region as a function of temperature. The CH_2 rocking region is of particular interest. It shows a doublet attributed to the CH_2 rocking vibration. This doublet, caused by a field splitting, occurs only when the chains are in the orthorhombic crystalline phase. If the sample is not in the crystalline phase then only a broad peak around 725 cm^{-1} is observed. As the temperature approaches the melting temperature, the absorbance decreases until melting occurs and, as the polymer flows, the amount of sample effectively detected is reduced significantly leading to a sharp decrease in absorbance. The changes observed concern the relative intensity of the bands and their position.

3.4.2 Phase content by IR analysis: spectral simulations

An extensive research in the past have as objective the elucidation of the molecular structure of PE by IR. The assignment of the trans-trans and gauche conformations has led to the identification of ordered and less ordered regions. The ordered phases in the orthorhombic regions give a doublet in the rocking vibration at $730\text{--}720\text{ cm}^{-1}$ and bending vibration at $1500\text{--}1400\text{ cm}^{-1}$ due to the interaction between two chains in the unit cell. The analyzing the spectrum of molten PE and liquid, linear and cyclic alkanes gave mores information on mite less ordered region of a semi-crystalline polymer [26]. The amorphous regions have been associated with peaks at $725, 720, 1078$ and $1300\text{--}1368\text{ cm}^{-1}$ [23].

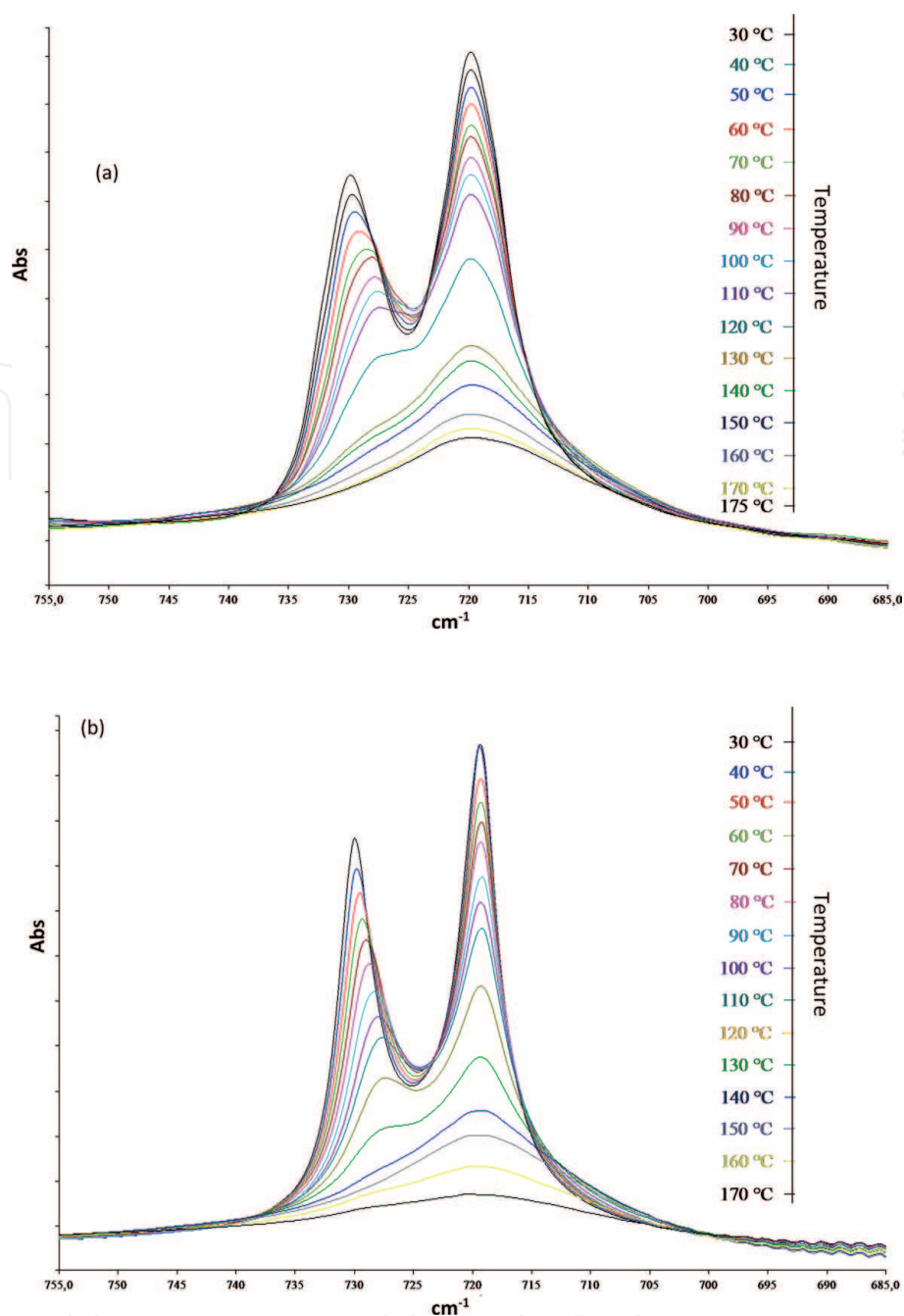


Figure 9. Typical evolution of the CH_2 rocking region of the IR spectrum of a pure LDPE film (a) and LDPE/16%Cu, (b) composite film as a function of temperature.

The bands associations with a monoclinic-like organization have been studied on fibers and modified samples where the orthorhombic crystals had been deformed by shaking or drawing [27–34]. Thereby, the singlet at $715\text{--}718\text{ cm}^{-1}$ was replaces the doublet in the spectrum of these samples [35–37]. Using the spectral subtraction, these bands were also be detected in solution-grown crystals and on annealed melt-crystallized samples [35].

The superposition of the spectral region $670\text{--}770\text{ cm}^{-1}$ (**Figure 10a**) of LDPE and LDPE/Cu (84/16) shows a slight decrease in the peak around 730 cm^{-1} compared to that at 720 cm^{-1} in presence of micro-particles copper. Thus, to develop the crystallinity study of a LDPE/Cu composite film grown in solution, spectral simulation of the rocking CH_2 vibrations region for the different samples have been performed. Spectral simulations of the $770\text{--}670\text{ cm}^{-1}$ regions in the IR spectra were then performed by software BGRAMS/386 using a Gauss + Lorentz band shape with

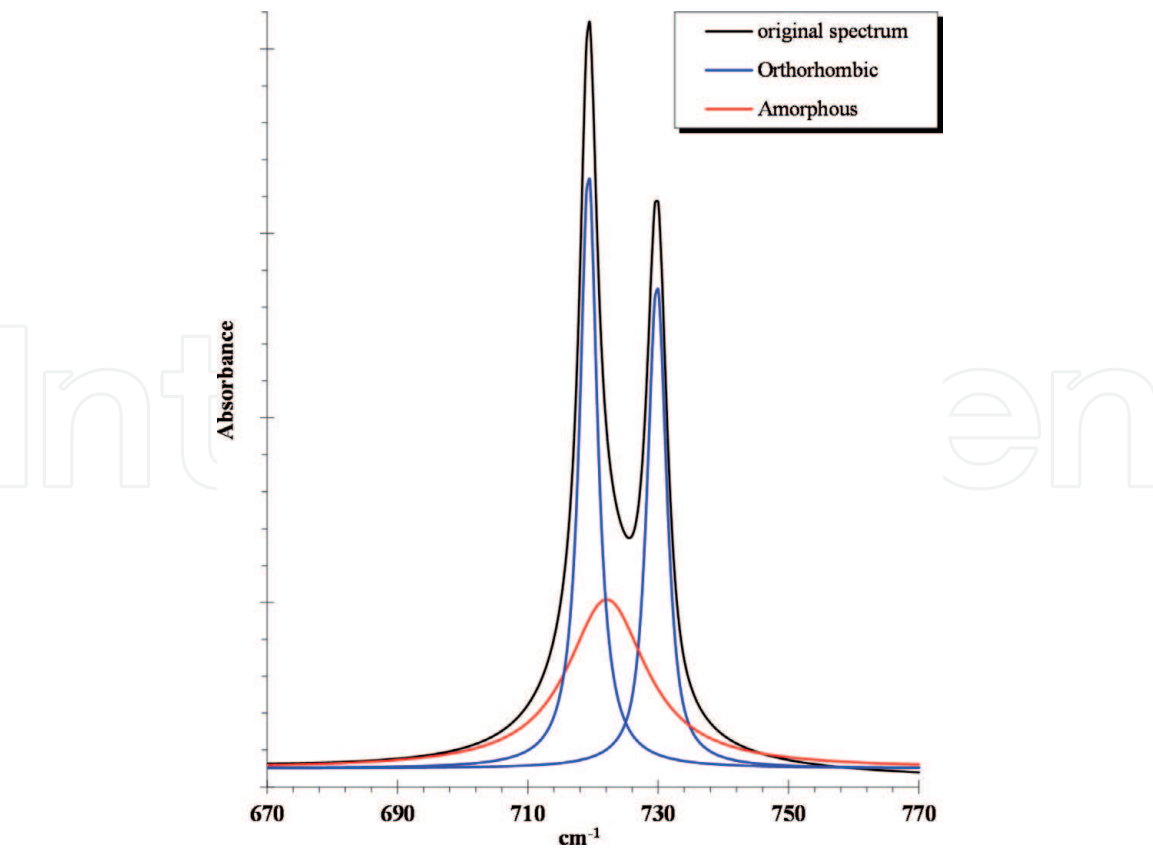


Figure 10.
(a) FTIR spectrum in the rocking region of LDPE and LDPE/Cu (84/16). (b) two-phase deconvolution of FTIR rocking region of LDPE and LDPE/Cu (84/16).

a band width at half-height of 3.5 cm^{-1} for the orthorhombic peaks, $10\text{--}16\text{ cm}^{-1}$ for the single-chain band or amorphous regions (725 cm^{-1}), and $15\text{--}19\text{ cm}^{-1}$ for the monoclinic-like peak (717 cm^{-1}) [25]. The phase fractions were calculated from the simulated spectra using the equation:

$$\alpha_{\text{phase}(i)} = \frac{\text{Integrated area}_{\text{phase}(i)}}{\text{Integrated area}_{\text{all the phases}}} \quad (2)$$

The integrated absorbance of each band was rationed against the total area of the $770\text{--}670\text{ cm}^{-1}$ regions. The integrated absorbance of the two peaks at 730 and 720 cm^{-1} , both representing the orthorhombic fraction, were summed.

Using two phases model, the spectral simulation of transmission spectra of LDPE/Cu films with different copper content in the spectral range between 670 and 770 cm^{-1} , shows the presence of only three bands (**Figure 10b**):

- 725 cm^{-1} for amorphous phase
- 720 cm^{-1} and 730 cm^{-1} characteristic of the orthorhombic crystalline phase

Such deconvolution does not show any variation in the phase composition of the LDPE matrix for all copper contents (**Figure 11**). In fact, the fractions of orthorhombic and amorphous phases (respectively about 62% and 38%) are the same values obtained for the neat LDPE. Thus, copper does not have any noticeable effect on the structure of LDPE in the model of two phases [25].

Using three phases model, **Figures 12 and 13** shows four-band deconvolution for neat LDPE film (0% Cu) and a 16% copper loaded LDPE/Cu composite film. The orthorhombic peaks at 730 and 720 cm^{-1} appeared to be unchanged for all copper content witch comforts the thesis that such phase is not affected by the copper particles presence. Nevertheless, the peaks assigned to the amorphous phase (725 cm^{-1}) and to the network phase (717–715 cm^{-1}) had their integrated area respectively increased and decreased with the copper percentage in the film (**Figure 14**). This observation means that when three phases were introduced, the amount of the orthorhombic phase was found to be constant. However, starting at 4% copper content, the amount of the amorphous and that of the network phase were found to respectively increase and decrease with the increase of copper particles load in the film. This result are in agreement with the non-standard DSC observations mentioned

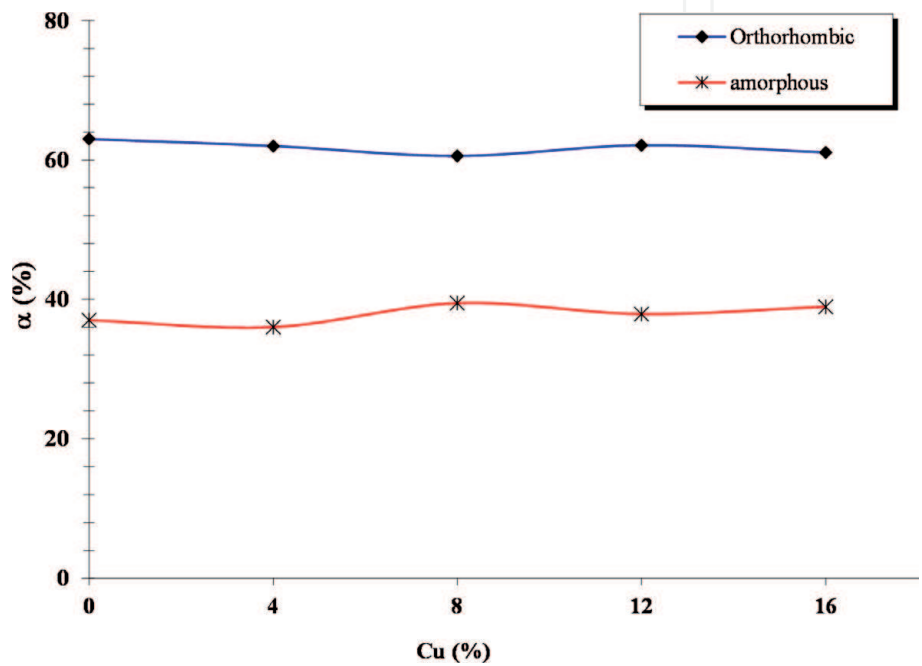


Figure 11. Fractions of crystalline and amorphous phases of LDPE as functions of copper particle content in LDPE determined by FTIR using two-phase model simulation.

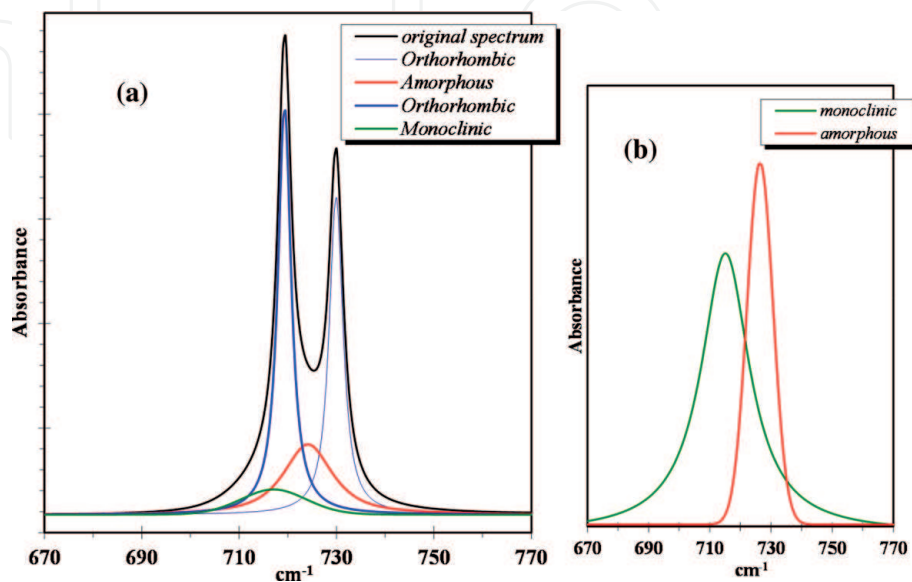


Figure 12. FTIR spectrum in the rocking region showing three phases (orthorhombic, monoclinic, amorphous) of pure LDPE (a) Monoclinic and amorphous band evolution (b).

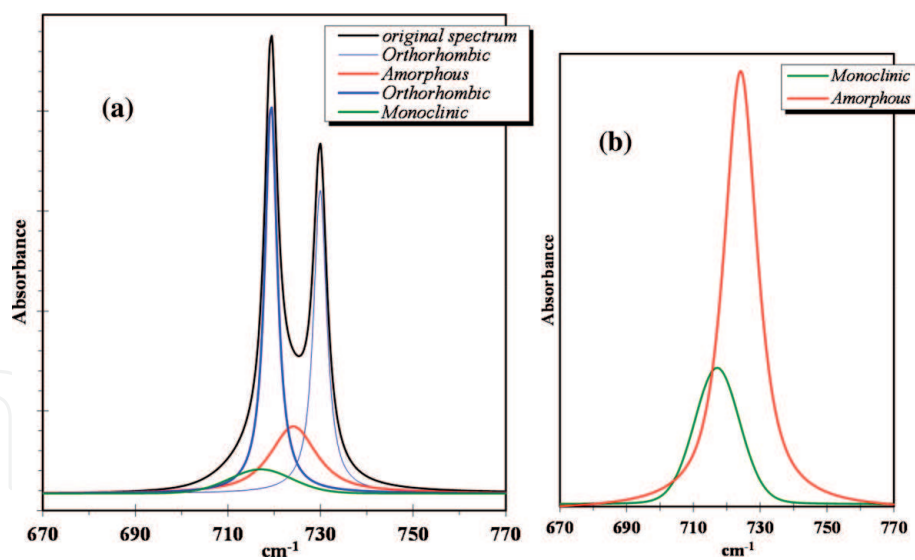


Figure 13.
FTIR spectrum in the rocking region showing three phases (orthorhombic, monoclinic, amorphous) of LDPE/16%Cu composite (a). Monoclinic and amorphous band evolution (b).

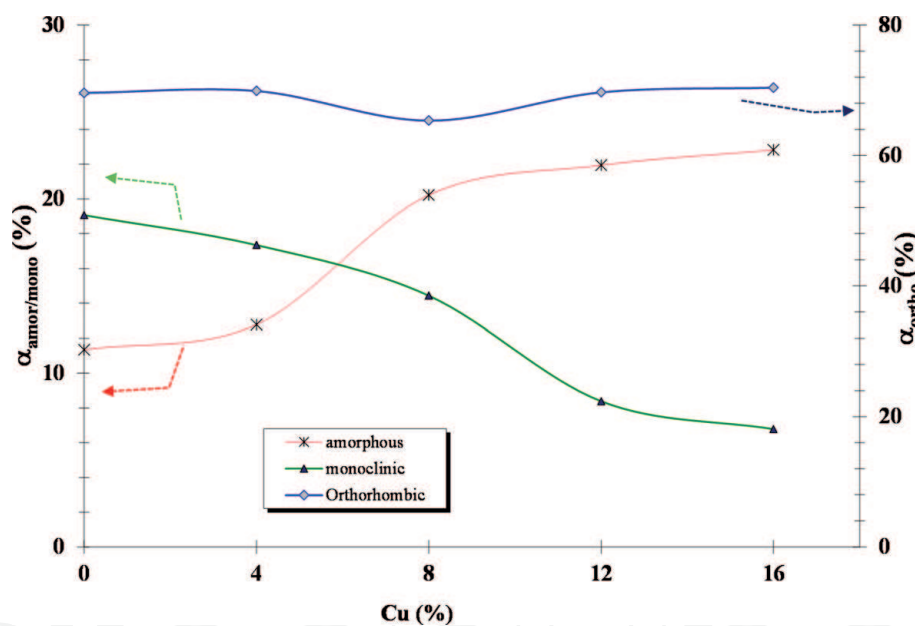


Figure 14.
Fractions of crystalline and amorphous phases of LDPE as functions of copper particle content in LDPE determined by FTIR using three-phase model simulation.

above and supporting the fact that the changes in the polymer phase composition due to the presence of the copper micro-particle is better seen when considering the existence of the network phase. The copper micro-particles lower probably the total crystallinity of the polymer matrix considering a three phase model, and do not show any effect when considering a two phase model [25].

The physical reason probably due to the fact that the copper particles may oppose to the formation of physical entanglements in their close environment. In consequence, the entanglements concentration as well as of the network phase content decrease with the increase of fraction copper and so does the network phase content. Other than the effect of copper micro-particles the polymer matrix seems to adopt the relaxed conformation of the amorphous phase due to the decrease of the entanglements concentration. The orthorhombic phase was not affected by the presence of copper micro-particles. However, with copper nanoparticles seen to

have a clear effect on the long-range order of LDPE matrices in LDPE/Cu nanocomposites [38]. The difference might be due to the influence of the size effect of the copper nanoparticles.

4. Conclusion

LDPE/Cu composites prepared in solution was characterized by optic, spectroscopic and thermal analysis. The optical observation suggested that the copper powder particle distributions were found to be relatively uniform at both low and high copper contents. The presence of copper particles can improve the thermal stability of the composite since a maximum increment of 14°C is obtained comparing with the pure LDPE as shown on the TGA thermogram results. The results of DSC in standard conditions show that Cu content has little influence on the crystallinity X_c of LDPE. However, the trace of DSC at non-standard conditions suggested that the presence of copper microparticles has more effect on the network phase than that can be observed on the crystalline long range order phase. FTIR spectroscopy was used to study the phase content of LDPE in LDPE/Cu non-oriented composite films by investigate the CH_2 rocking vibrations. Spectral simulation of the transmission spectra performed using a tow phase model show that the copper contents does not any effect in the phase composition of the LDPE matrix. According of three phases model the amount of the orthorhombic phase was found to be constant. However, the amorphous and the network phase fraction were found to respectively increase and decrease with the increase of copper particles load in the film. The presence of an inorganic filler (Cu) in an organic polymer matrix (LDPE) forms a hybrid material that merges the properties of the two families of materials that compose it. This type of LDPE/Cu composite material which exhibited good structural and thermal stability as a function of the Cu fraction can be used as a phase change material (PCM) by the addition of a suitable oil phase.

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