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Induced changes in structural and thermal properties of polyethylene, polyamide-6 and their conjoint at high environmental temperature

M. Mekawy and A.A. Abd El-Megeed

National Institute for Standards
Tersa St. P. O. Box: 136 Giza,
Code. No. 12211, El-Haram, Egypt

Abstract

The effect of temperature on the stability of polyethylene and polyamide-6 and conjoint in films form was investigated by using differential scanning calorimetry (DSC) thermal analyses and X-ray diffraction technique. Differential scanning calorimetry (DSC) gives accurate values of glass transition temperature, melting temperature and changes in heat of fusion. X-ray diffraction technique was used to determine the crystallinity changes and crystallite size variation at different temperatures of setting. The smaller structural entities which result in are not perfect enough to be picked up in X-ray diffraction. Thus, differential scanning calorimetry technique, which is more sensitive than X-ray analysis, was used to confirm results. It was found that the conjoint polymer bears setting at high temperature rather than its two components (low density polyethylene and polyamide-6). Also, the conjoint suffers little changes in structure and its physical and mechanical properties are improved. So, its application in industrial and commercial uses is preferable.

The aim of the present work is to investigate the changes of some structural properties of low density polyethylene and polyamide-6 before and after conjoining them in one polymeric film. Heat setting for 150 hours in the range from 20ºC to 50ºC was applied to all of the samples to show the effect of environmental temperature on their structures.

Introduction

Polymers are conjointed to achieve two important purposes: firstly, low cost/price ratio and the allowance of recycling of degraded polymeric materials [1, 2], and secondly, for the production of materials with new improved mechanical properties. It was revealed that the modulus and tenacity of the polymeric conjoint are related to its composition ratio [3]. The morphology and compatibility of the conjoint of polyethylene and polyamide-6 at a dispersion phase of 50/50 composition has been studied before [4].

By studying the crystal behavior of the conjoint of polyesters and other thermoplastic polymers [5], it was found that the mechanical properties of the polymer conjoint have been improved. This depends strongly on the miscibility, size and form of dispersed phases, the character and size of interface domains and the distribution of residual stresses.

The degree of incompatibility has actually a tremendous effect on the mechanical properties of the conjoint. The resulting properties of the conjoint may be worse than the original polymers because of the strong difference between their chemical structures In blended polymers however, incompatibility arises from the very small entropy gained by mixing different species of macromolecules.

Compatibility of conjoins of polyolefins, and polyamides depends on functionalizing polyolefin which can react with the amino groups of polyamides giving rise to stabilized copolymers. This is performed by long and expensive chemical modification [6, 7, and 8] A recent method [9] was proposed to functionalize polyethylene by photo-oxidizing it first and then conjoining it with nylon-6. Structural, rheological and mechanical studies indicate that carbonyl and amino groups react producing stabilized conjoint polymer

Weathering may also bring about changes in the nature of the crystalline state, which in turn is governed by the nature of the crystal structure, degree of crystallinity, size and number of spherulites and orientation [10,11]. The crystallinity and the size of crystallites were found to be enhanced by thermal treatment. This treatment is supposed to remove crystal imperfection and to improve chain packing at the amorphous-crystalline inter phase [12]. However, few studies are available relating the effects of specimen crystallinity to polymer degradation and embrittlment.

La Mantia [1] used analyses of density, viscosity, tensile and dynamic mechanical results to investigate the effect of natural weathering on low density polyethylene (LDPE) and provided some structure and property correlations.

In the present study, X-ray diffraction was used to determine the crystallinity changes and crystallite size variation at different temperature settings. The smaller structural entities which resulted were not perfect enough to be picked up in X-ray diffraction. For, this case, differential scanning calorimetry, which is more sensitive than X-ray analysis, was used to confirm results.

Mechanical and Physicochemical properties of the studied materials

The polymers used in the present work are low density polyethylene, LDPE (E 340, SODP, FRANCE), Polyamide, PA-6 Type (Filmon CS, CAFFRO, ITALY); in the form of transparent film, without stabilizers. Both of these two polymers are conjointed at Arab Medical Packing Co. Egypt by pressing two sheets of both of them at certain temperature and pressure.

The conjointed films are used in the local markets in Egypt for commercial packing and textile uses. The thicknesses of these sheets as measured at different points with accuracy of ± 1µm are

LDPE = 67 ± 1µm
PA-6 = 86 ± 1µm
PE/PA-6 Conjoint = 87 ± 1µm

Polyethylene has a high degree of branching, with both long and short side chains, which sets a limit on its crystallinity. A small amount of oxygen is combined in its molecules. Low density Polyethylene LDPE is one of the polyolefin that undergo changes in carbonyl concentration, percent elongation and oxygen uptake in relationship to various kinds of weathering [13, 14, 15]. Winslow [16, 17, 18] described radical and non radical mechanisms proposed as routes of polyolefin degradation. It was found that vinyl and carbonyl index increased with exposure time. This increase could not be easily correlated to mechanical property reduction [19]. The crystallinity and the size of crystallites were found to be enhanced by thermal treatment [20]. This treatment is supposed to remove crystal imperfection and to improve chain packing at the amorphous-crystalline inter phase. Few studies, however, are available relating the effects of specimen crystallinity to polymer degradation and embrittlment.

Polyamide-6 is highly crystalline, and very well aligned or oriented polymer system with inter-polymer distances about 0.3nm [21]. Polyamide-6 is a polymer of poor heat conductivity and low heat resistance. Heat causes the polyamide polymers to become excited and this results in a break-down of inter-polymer bonding. Polyamides limps when warmed, its handle is restored as it is cooled because most of the broken bonds are reformed. The application of excessive heat to polyamide excites the polymers and the most of their textile material melts. Further heating will result in burning. Amide group works as an important constraint that limits the mobility of crystalline molecules, so crystalline regions seem to be quite rigid. Only train isomers conformations can be involved in the crystalline phase. Most of conformational changes (Trans and gauche-conformations) occur in the amorphous (disordered) phase, where hydrogen bonds are less organized, and, therefore the mobility is higher [20]. In an ordered phase, crystallinity i.e. crystalline Trans content, increases slightly by increasing temperature above 150ºC. This increase can be related to crystalline perfection and fold surface smoothing of crystalline layer. The hydrogen bonding in both crystalline and amorphous phases works as a pin prevent conformational mobility up to the point where sufficient energy is supplied to the molecules. As with the weathering of most polymeric materials, photo degradation is limited to the surface of polyamides. It is the polymer chains in the surface layer which undergo scission. The structure of the crystalline portions of polyamides has been determined from X-ray diffraction studies [13, 14, 15].

Experimental

Heat setting

Heat setting of all films was carried out in slake in the temperature range 20 - 50 ^{o}C for 150 hours. The treatment was done by putting films in an incubator model LT601

(U.K) with high capacity, heavy duty chamber and microprocessor controls. High efficiency polyurethane insulation helps to ensure stable temperature control over a wide operation range 0 ^{o}C - 50 ^{o}C (±0.1 ^{o}C) Cable access port is provided so that shakers or monitoring probes can be used. The microprocessor controls both heating and cooling junctions of the incubator. The resulting balanced airflow gives excellent temperature stability throughout the chamber. All measurements were performed 24 hours after incubation at 25 ^{o}C and 65.1 % relative humidity.

Thermal Analysis

A Shimadzu differential scanning calorimeter DSC-50 analyzer was used. The experimental work was carried out for all samples with heating rate of 10 ^{o}C/min using dry nitrogen as carrier gas at a flow rate of 50 ml/min. Samples run were repeated three times to ensure repeatability. The spectrum was recorded between room temperature and 400 ^{o}C.

X-ray Diffraction Analysis

The X-ray diffraction technique was used to quantify the crystallinity of the conjoint polymer. Scintag Irac diffractometer (USA) of $\mathrm{CuK}_{\text{á}}$ radiation was used operating at 45kv and 40mA, and wavelength ë=1.54 µm. The diffractograms were recorded continuously in the range of 2è = 5° – 60° at scan rate of 2°/minute.

The crystallinity index (Cr.I) which is a time-save empirical measuring of relative crystillinity for LDPE, PA-6, and their conjoint was computed using the relation of Segal et al [21]:

$$Cr.I = (I_f - I_s \; / I_f \; \times 100 \qquad (1)$$

Where, I_f is the peak intensity of the fundamental band, I_s is the peak intensity of the secondary band at 2è = 6^{o} - $8^{o.}$

Table 1: The DSC thermograms of the LDPE

Materials	Peak ^{o}C	Heat of fusion j/g	Onset ^{o}C	Endnset ^{o}C
a PE-20	108.0	135.00	85.87	127.62
b PE-30	107.66	181.13	80.26	127.45
c PE-40	107.89	109.72	82.77	128.07
d PE-50	108.02	123.41	88.40	128.90

Table 2: The DSC thermograms of the PA-6

Materials	Peak ^{o}C	Heat of fusion j/g	Onset ^{o}C	Endnset ^{o}C
a PA-20	218.99	68.18	201.03	230.44
b PA-30	220.38	71.91	204.56	229.31
c PA-40	219.56	71.39	201.54	232.79
d PA-50	220.12	66.71	202.88	231.49

Results and Discussion

Thermal analyses

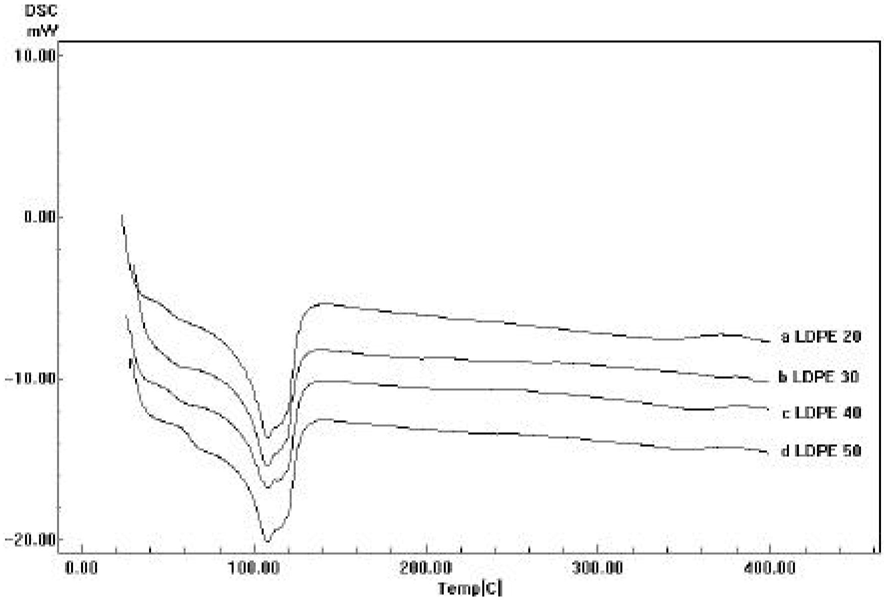

Figure 1. The DSC thermograms for LDPE at temperatures 20, 30, 40 and 50 °C.

For LDPE the endothermic peaks are broadened by increasing heat setting temperature up to 50 °C (which are indicated as a PE-20, b PE-30, c PE-40 and d PE-50 respectively). Also, changes in heat of fusion and melting temperature are shown in figure (1) and table (1).

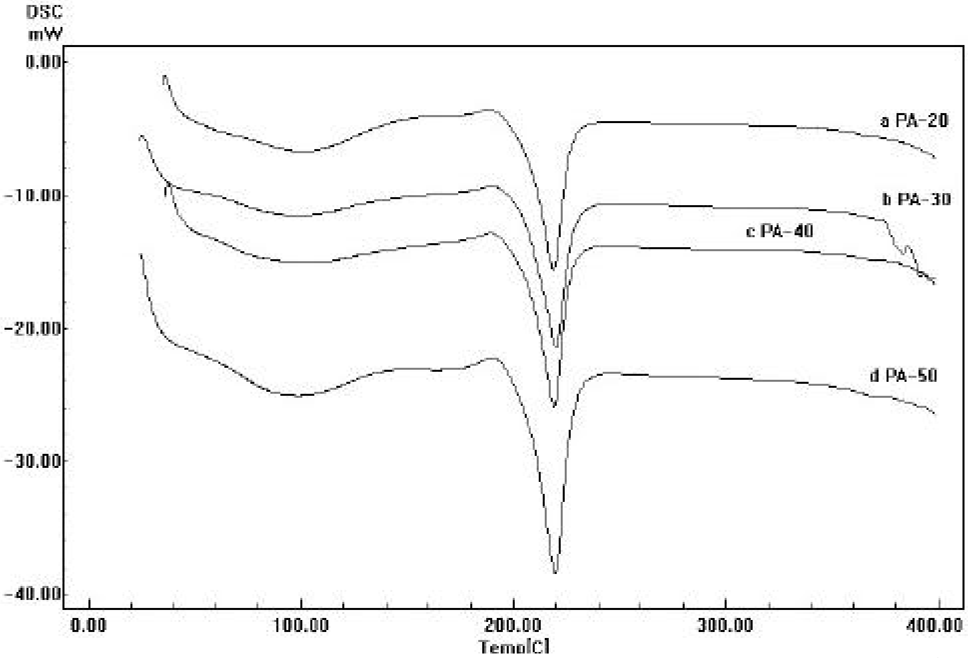

Figure 2: The DSC thermograms for PA-6 at temperatures 20, 30, 40 and 50 °C.

Figures (1-3) show the differential scanning calorimetry (DSC) curves for LDPE, PA-6 and their conjoint at different temperatures. Differences in the shape and area of the melting endotherms are clear.

The PA-6 samples at heat setting of 20, 30, 40 and 50 °C (which are indicated as a PA-20, b PA-30, c PA-40 and d PA-50 respectively) show one endothermic peak in the DSC curves.

Small changes in temperature and heat of fusion are observed as shown in figure (2) and table (2). Change in endothermic peak area is also noticed.

For the conjoint polymer two peaks are clearly observed at all temperatures of heat setting (which are indicated as a Blend-20, b Blend -30, c Blend -40 and d Blend-50 respectively). The first peak indicates the presence of LDPE, while the second indicates the presence of PA-6. It is clear from figure (3) and table (3) that the heat of fusion at both peaks is much lower than in case of the parent polymers especially for the peak corresponding to PA-6.

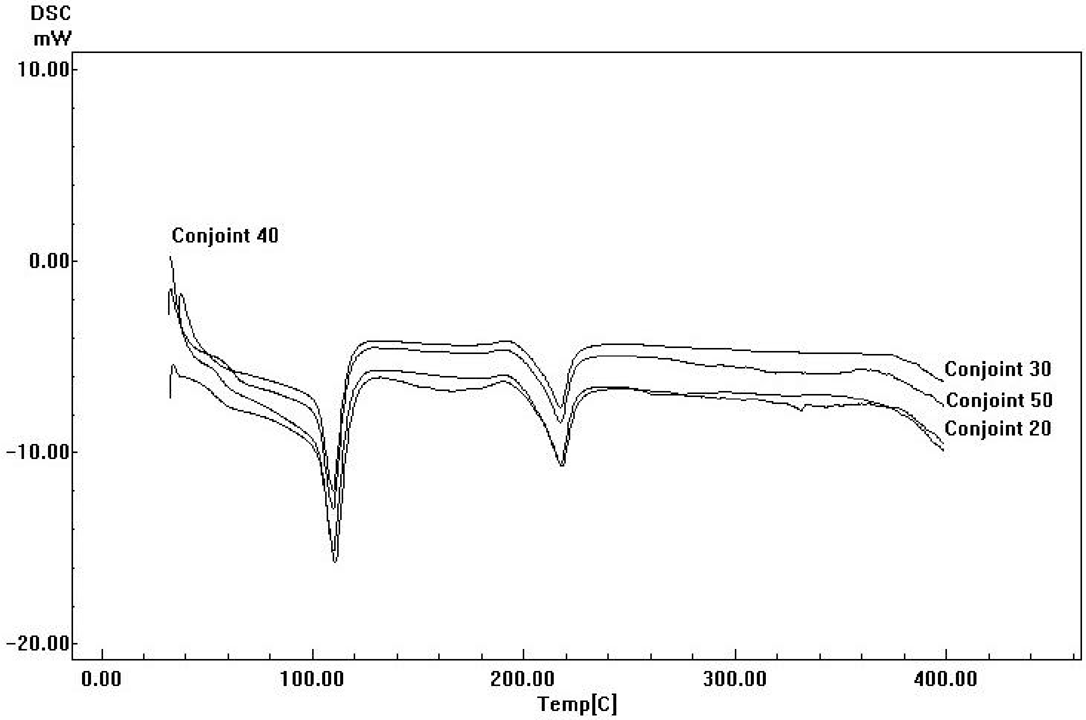

Figure 3: The DSC thermograms for the Conjugate of LDPE and PA-6 at temperatures 20, 30, 40 and 50 °C.

Table 3: The DSC thermograms of the Conjugate.

Materials	Peak °C		Heat of fusion j/g		Onset °C		Endnset °C	
a conjoint -20	110.84	218.37	105.34	22.75	95.34	203.48	121.72	226.98
b conjoint -30	109.95	217.65	153.66	21.45	95.42	203.59	119.03	225.08
c conjoint -40	110.0	217.66	114.97	22.02	101.00	203.28	118.07	225.36
d conjoint -50	109.97	217.73	156.86	22.84	94.24	203.55	119.65	224.54

The variation in the endothermic peak shape is attributed to the different degrees of crystillinity at different temperatures of heat setting [22]. In case of LDPE the increase in crystillinity with oxidation seams to be due to the replacement of C-H bonds by C=O bonds in the amorphous region [23], i.e. changes in the chemical bonds and hence changes in the molecular configuration of the polymer. LDPE consists of skeletal structure of crystalline lamellae interlaced with tie chain in a disordered arrangement. The broken chains in amorphous regions allow the free fragments to relax in a more compact arrangement. The probable point of attack in LDPE is the tertiary hydrogen on the chain at branch points. This polymer also undergoes some cross-linking when heated or worked at high temperatures. LDPE undergoes serious modification during photo oxidation due to the increase in carbonyl groups, change in molecular weight and formation of cross-linking [1]. The rate of photo oxidation of LDPE is temperature dependent and approximately is doubled for each 10^oC increase. It is well known that photo oxidation proceeds by the same free radicals chain mechanism operating in the thermal oxidation of hydrocarbons. So oxidative breakdown should be facilitated by the presence of hydrogen attached to tertiary carbon atoms.

In case of LDPE, the inter-phase (the transition from well ordered crystals to random amorphous chain) is expected to be more prominent feature of the morphogical structure due to the disturbance of the branch points in the crystal. The increase in the molecular weight has been shown to increase the fraction of this inter-phase.

The chang in endothermic peak and heat of fusion in case PA-6 can be explained as follows: There are two important groups in PA-6, the polar amide groups- CO-NH- which link together separate parts of chains consisting of methylene groups and, the amino group - NH_2, found at the ends of polyamide polymers. At higher temperatures the amide group works as an important constraint that limits the mobility of the crystalline molecules and most of the conformational changes occur in the amorphous phase. The hydrogen bonds in polyamide polymer systems are formed from these two chemical groups (radicals). The inter-polymer distance of polyamide is on average about 0.3 nm, which enables polyamide to form an optimum number of strong uniform hydrogen bonds. This makes polyamides very crystalline polymer systems. There are also carboxyl groups -COOH, at the ends of the chain in a small number due to the high molecular weight of polyamides and these groups may be blocked. Extended macromolecules are interconnected in crystalline regions by intermolecular Van der Waal's forces and hydrogen bonds. Hydrogen bonds are formed between the >NH and >C-O groups of adjacent chains and play a particularly important role in the stabilization of super molecular structure of polyamide. Since polyamides are strongly self-associated polymer, the development of order is reflected as distribution of conformation along the chains and strong molecular interaction due to the hydrogen bonds with respect to the conjoint [24]. Correlating between X-ray diffraction and thermal analysis results, no remarkable change is observed in crystallite size or in crystillinity index, which means that there is no change in its structure during heat process. It is also clear from figure (4) that by conjointing of LDPE and PA-6 in one film, it bears high temperature than each of the parent polymers (LDPE and PA-6).

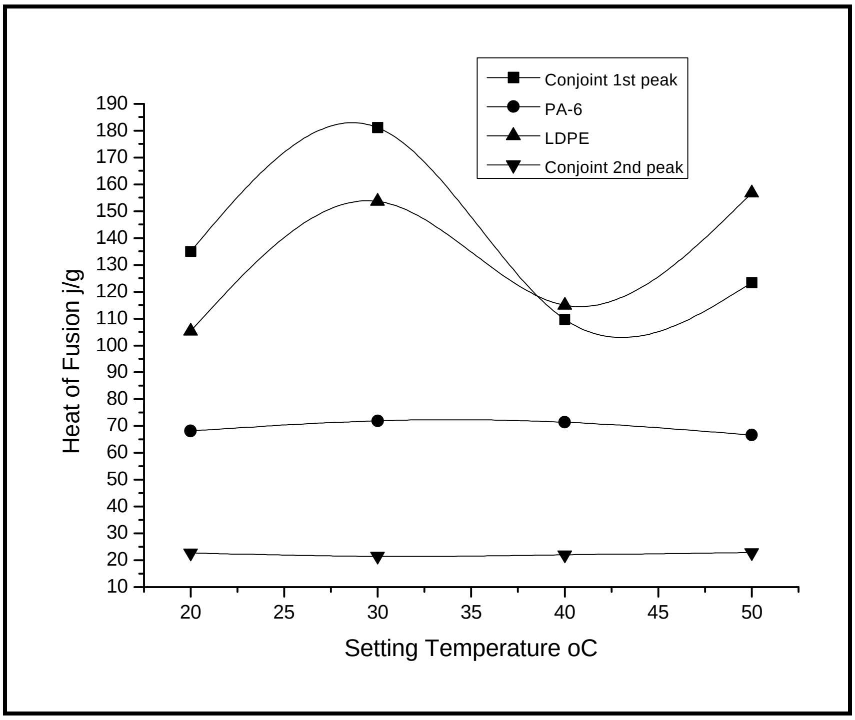

Figure 4: The variation of the heat of fusion with the setting temperature.

Figure (4) also shows the variation of the heat of fusion for the polymers used in the present work at the setting temperatures 20, 30, 40, and 50°C. From the figure it is clear that the conjoint second peak has the minimum value of heat of fusion. It varies from 21.45 j/g to 22.84 j/g. For PA-6 the heat of fusion varies from 66.71 j/g to 71.91 j/g. However for LDPE it has a maximum heat of fusion value of 181.13 j/g which drops to 109.72 j/g at 40°C. For the conjoint, the first peak has a maximum heat of fusion 156.86 j/g at the heat setting of 30 °C and drops to 105.34 j/g at 40 °C.

X-ray diffraction

X-ray diffraction technique was used by many authors to characterize the change in the crystal structure parameters of polymers the apparent crystal size, the degree of crystal orientation and the lattice strain along the axis of the crystal unit cell. Analysis yields a great deal of valuable information on the configuration of the polymers including their macromolecules and the size of thier ordered regions. X-ray studies are also very helpful in predicting relative amount of amorphous and crystalline phases, rather than their identification, from the heights of the characteristic peaks. The main physical properties of polymers, including their mechanical properties, are strongly dependent upon the amount and the nature of crystalline and amorphous regions, i.e. on super-molecular organization, and not only on the chemical structure.

This amount is also responsible for chemical reactions absorbitivity in case of polymeric fabrics. Reactivity increases by increasing the amorphous part of the polymer. The degree of crystallinity can be determined by measuring peak heights with proper attention to experimental details. X-ray diffraction (XRD) analysis was used to check the crystalline formation of PE,PA-6 and their conjoint at different temperatures of heat setting [25].

Figure 5(a-l) represents the typical X-Ray Diffraction (XRD) for the (LDPE), (PA-6), and their conjoint. A noticeable change was found in the intensity of XRD peaks. The band intensity for peaks are drawn in figure 6(a, b and c).

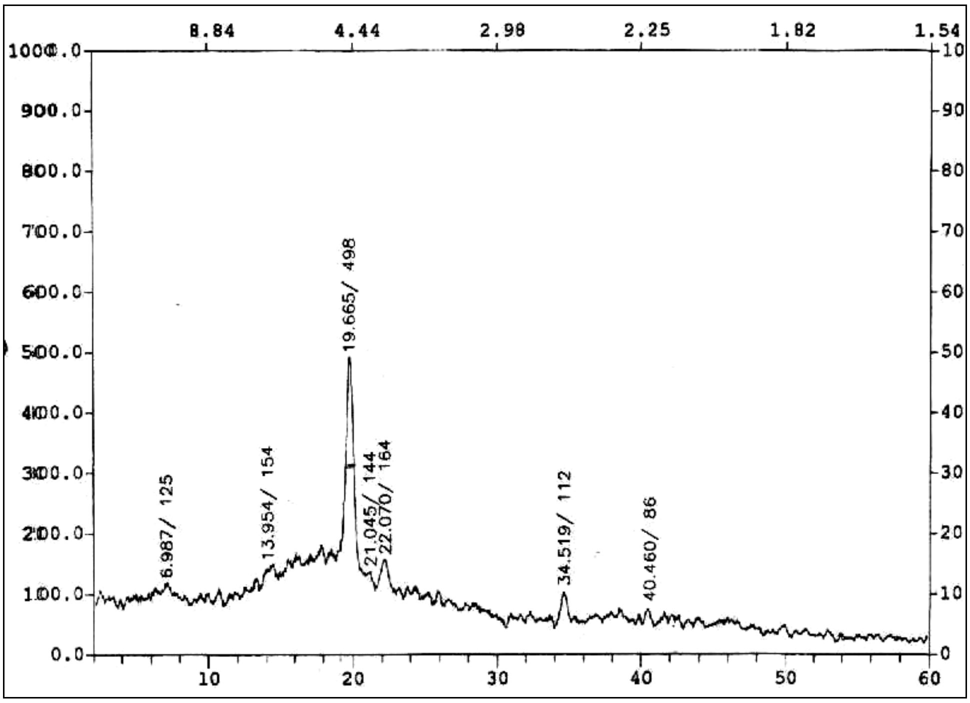

Figure 5(a). XRD for Polyethelene at 20°C.

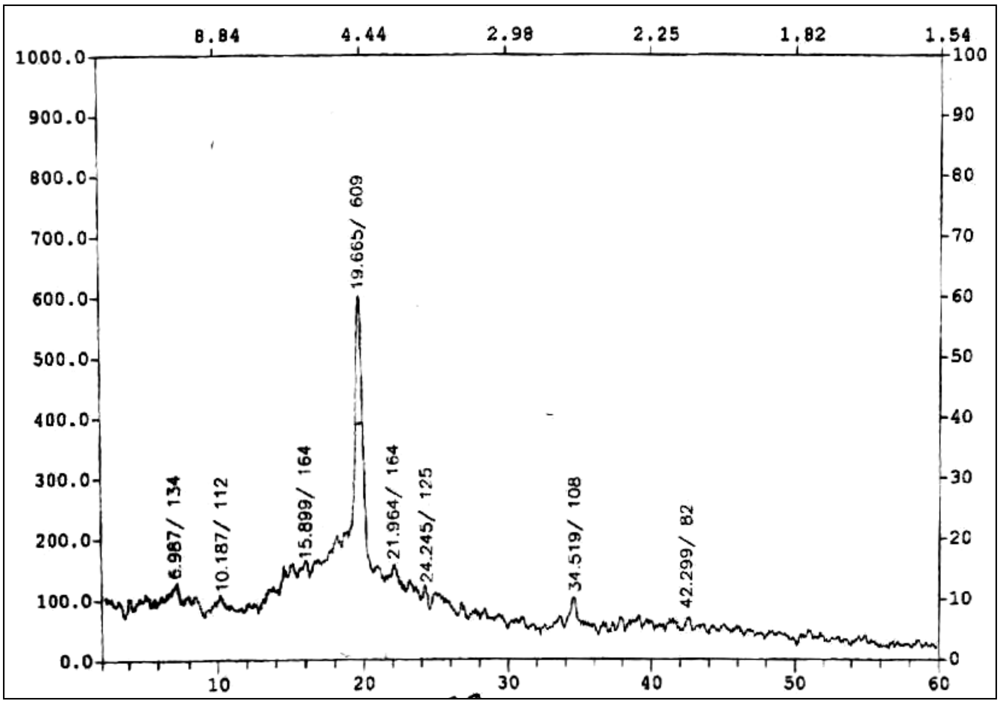

Figure 5(b). XRD for Polyethelene at 30^{o}C.

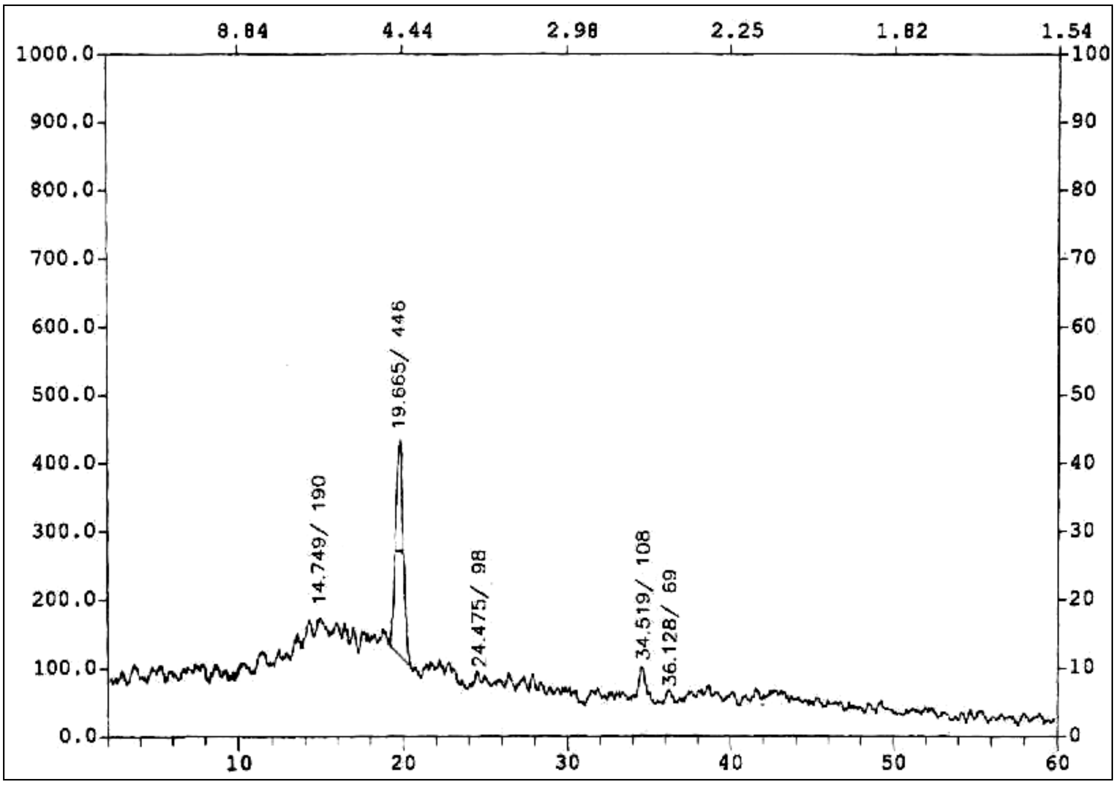

Figure 5(c). XRD for Polyethelene at 40^{o}C

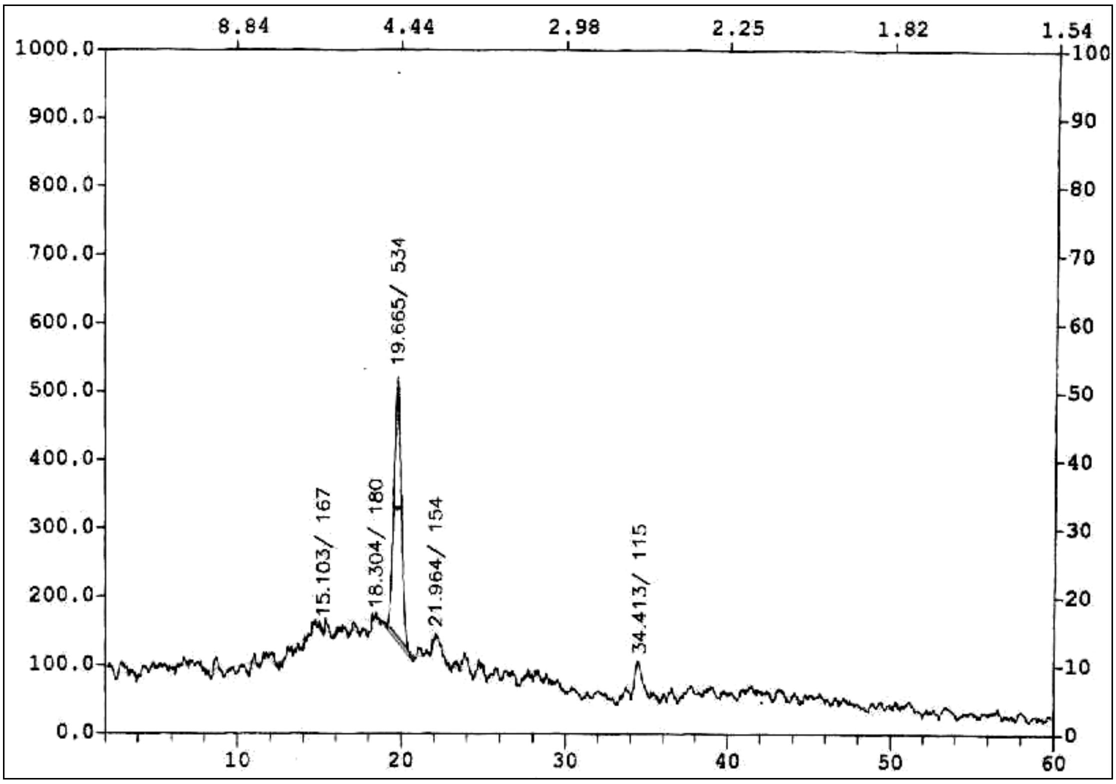

Figure 5(d). XRD for Polyethelene at 50°C

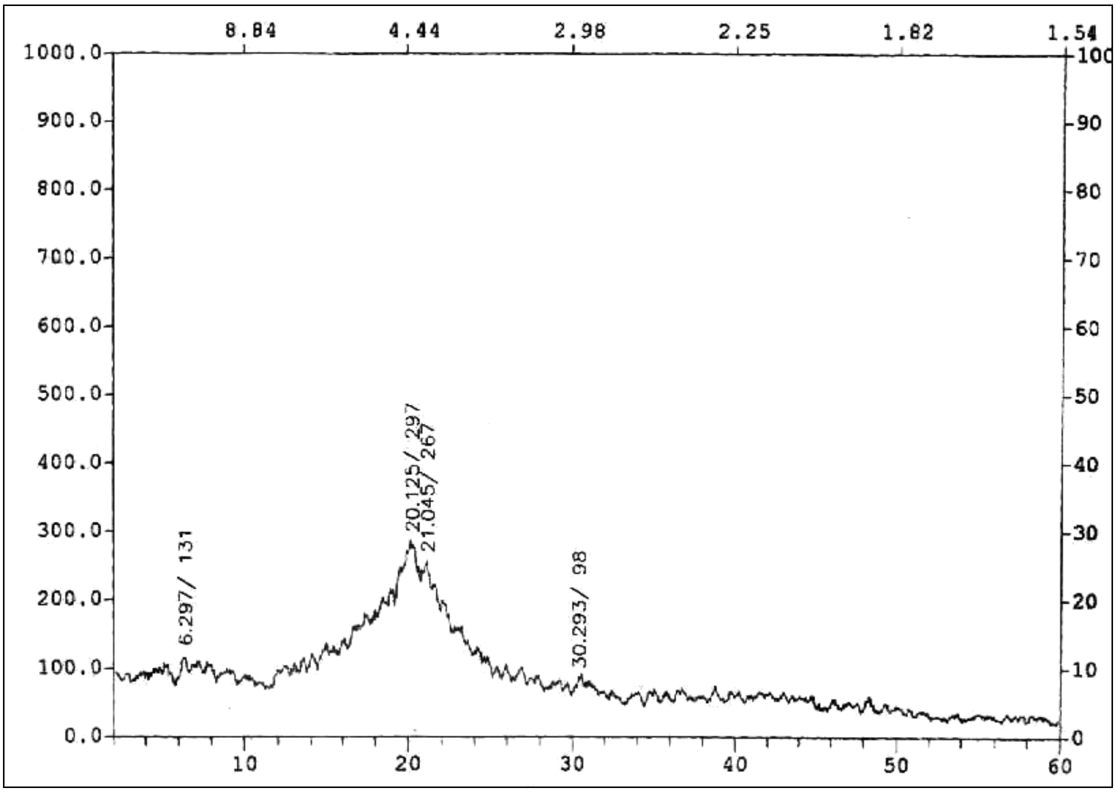

Figure 5(e). XRD for Polyamide-6 at 20°C

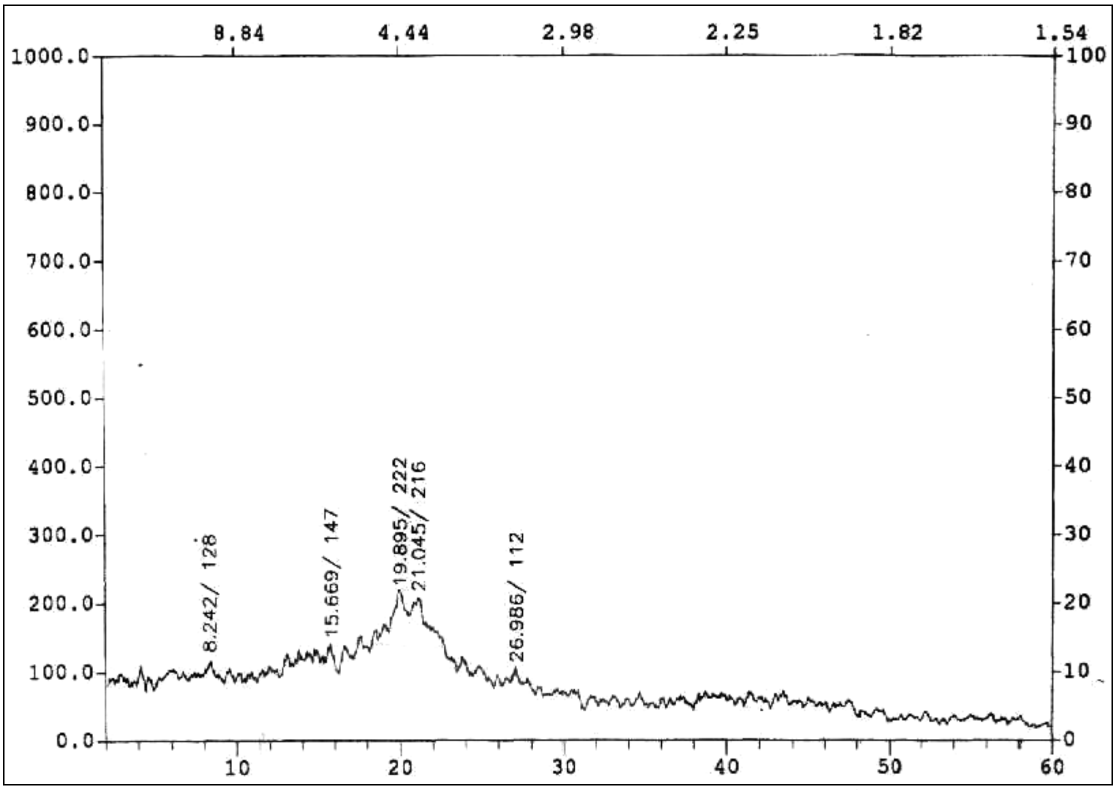

Figure 5(f). XRD for Polyamide-6 at 30°C

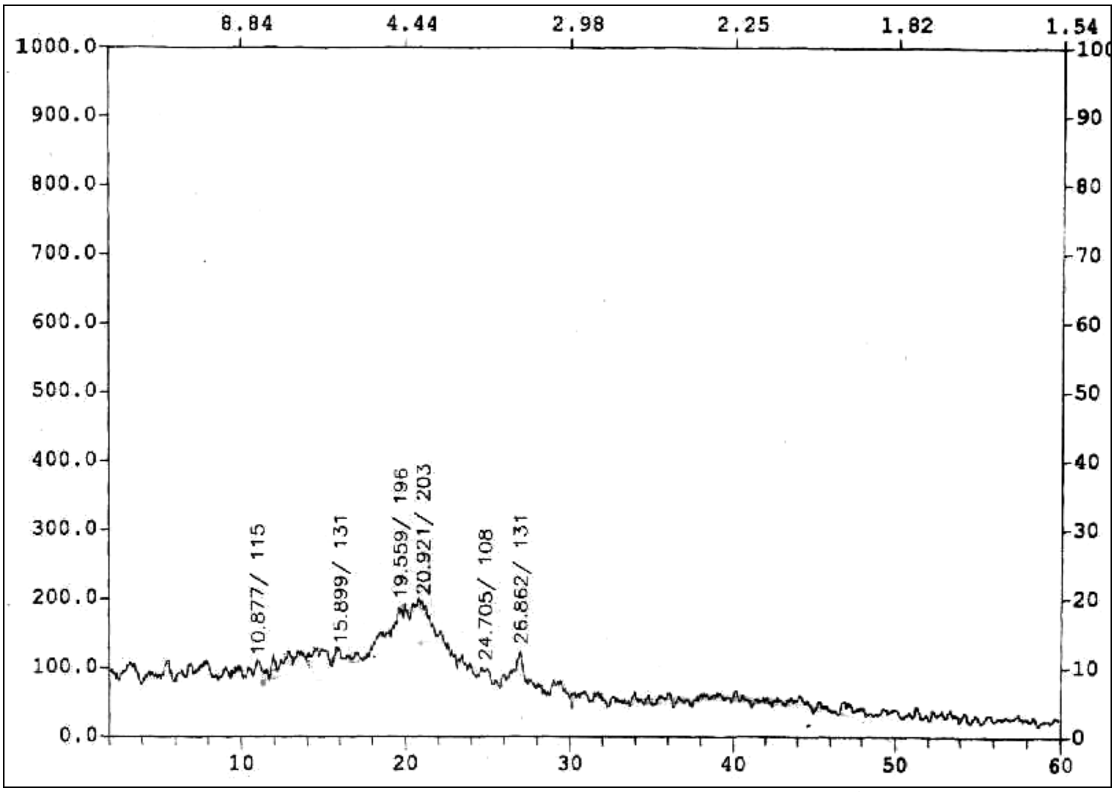

Figure 5(g). XRD for Polyamide-6 at 40°C

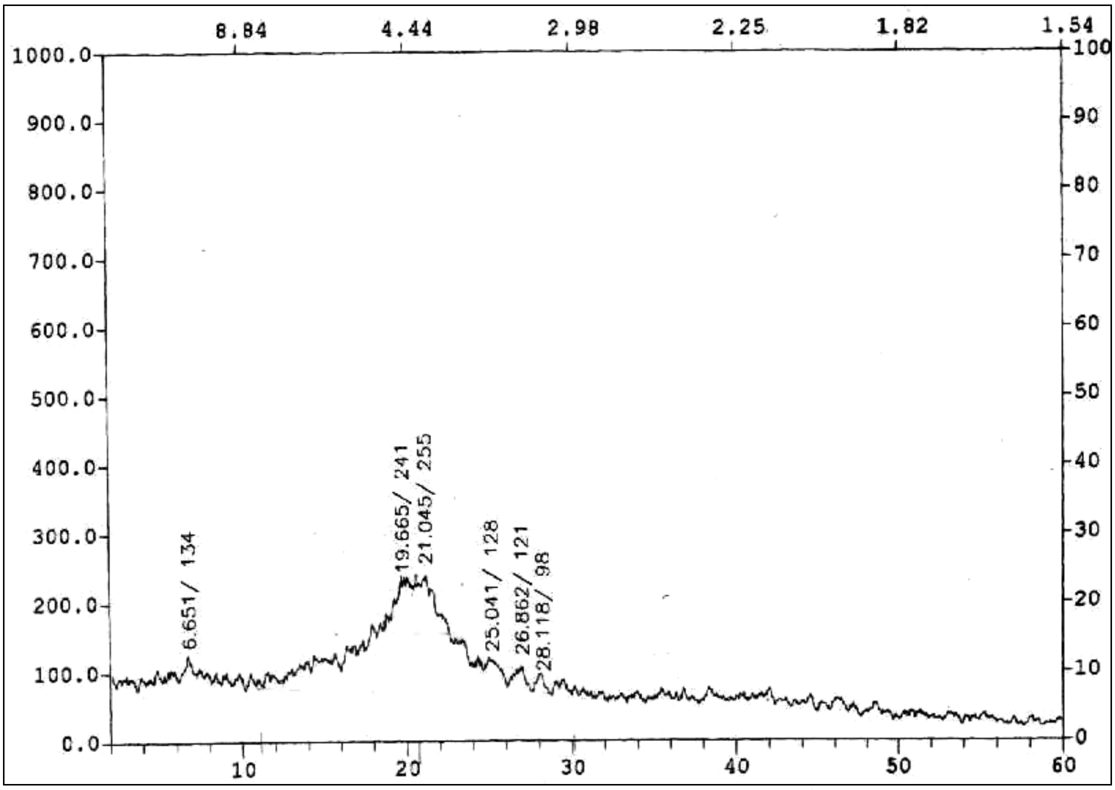

Figure 5(h). XRD for Polyamide-6 at 50°C

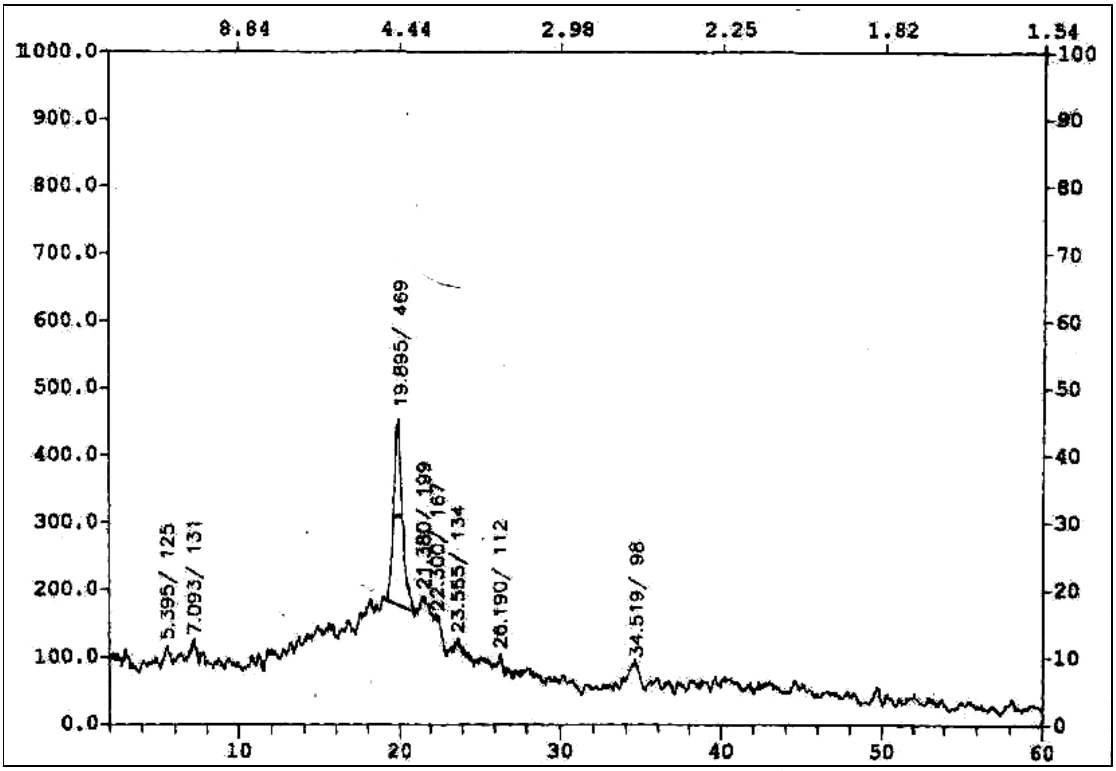

Figure 5(i). XRD for Conjoint at 20°C

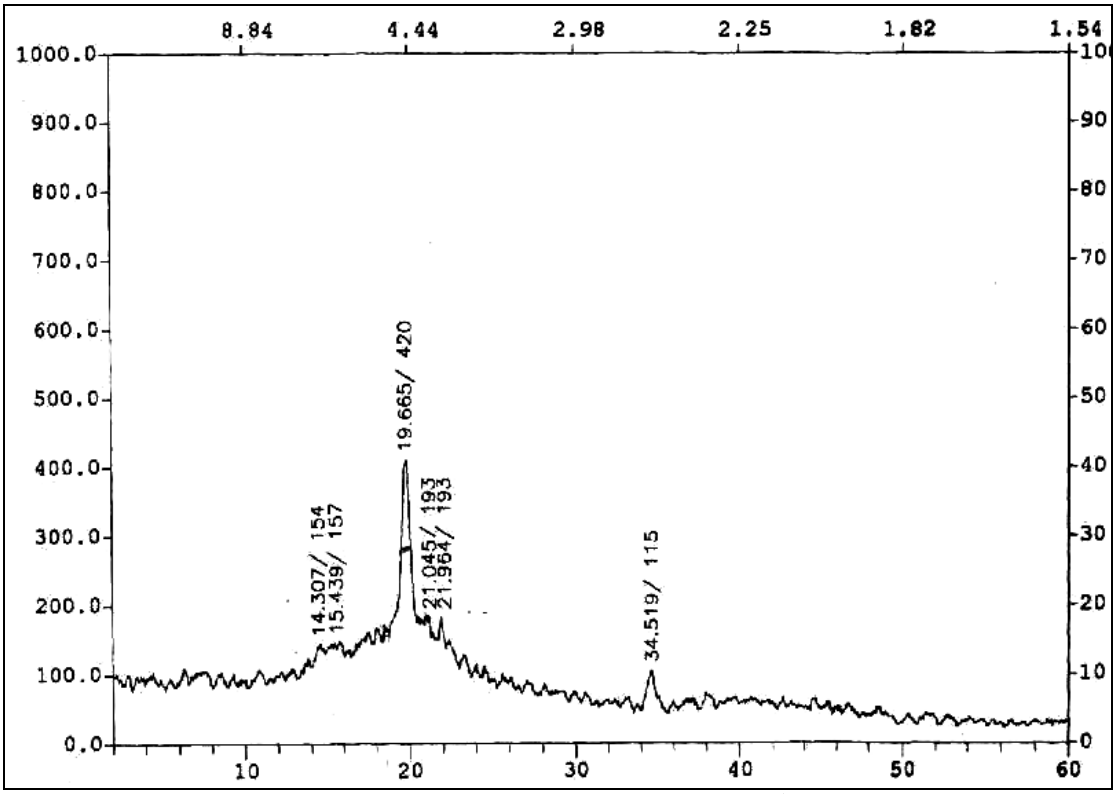

Figure 5(j). XRD for Conjoint at 30^{o}C

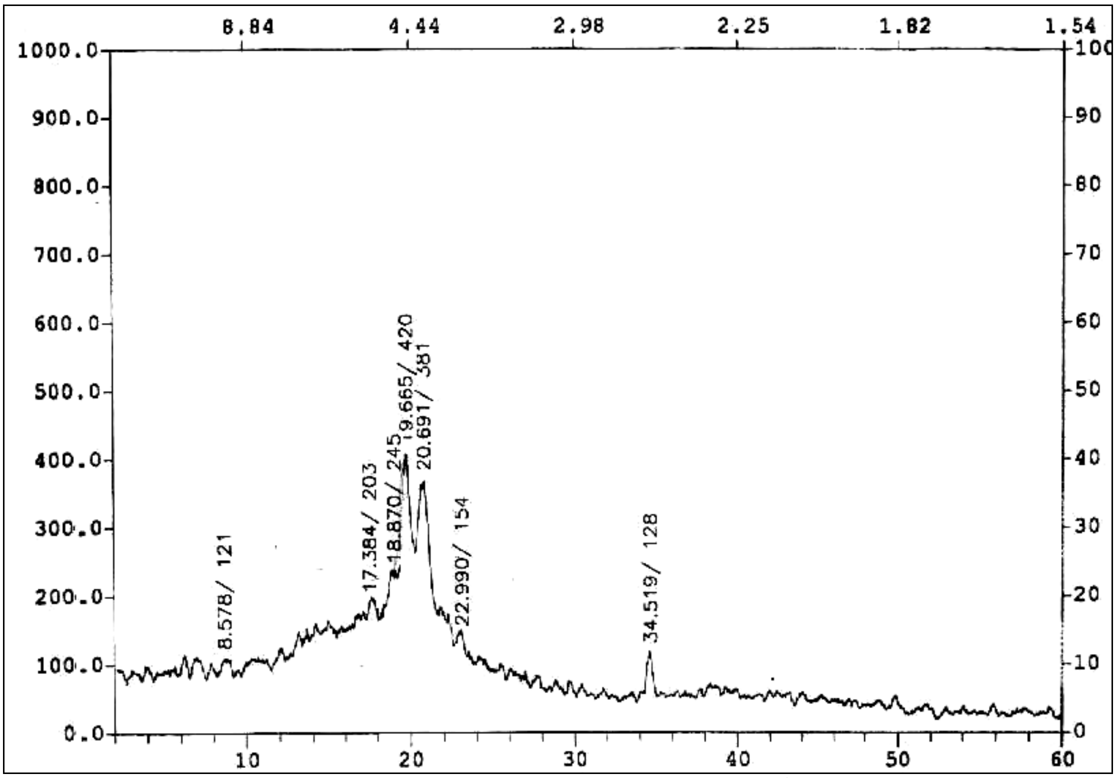

Figure 5(k). XRD for Conjoint at 40^{o}C

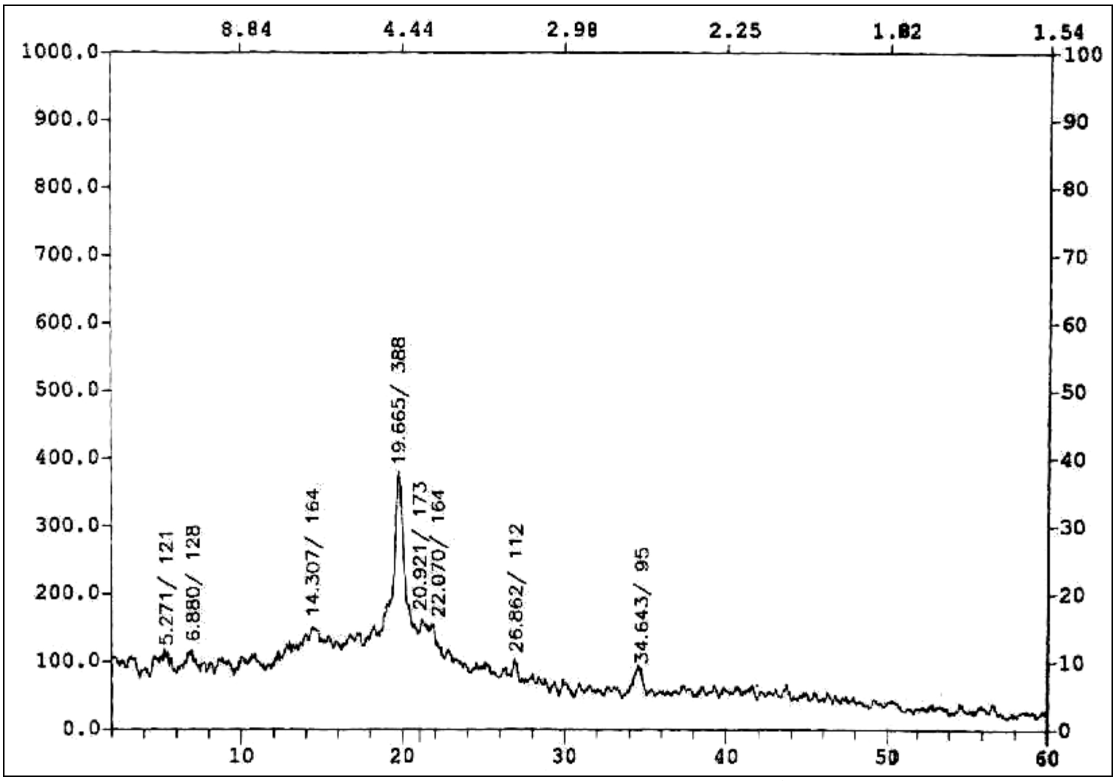

Figure 5(l). XRD for Conjoint at 50°C

The band intensities for peaks are drawn in figure 6(a, b, and c)

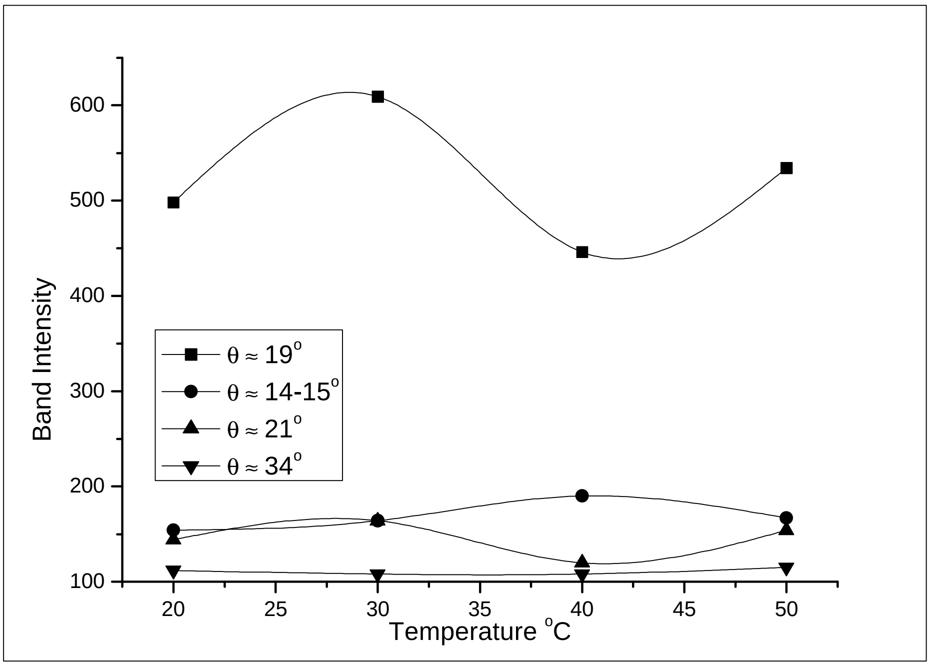

Figure 6(a). Band Intensity for Polyethelene

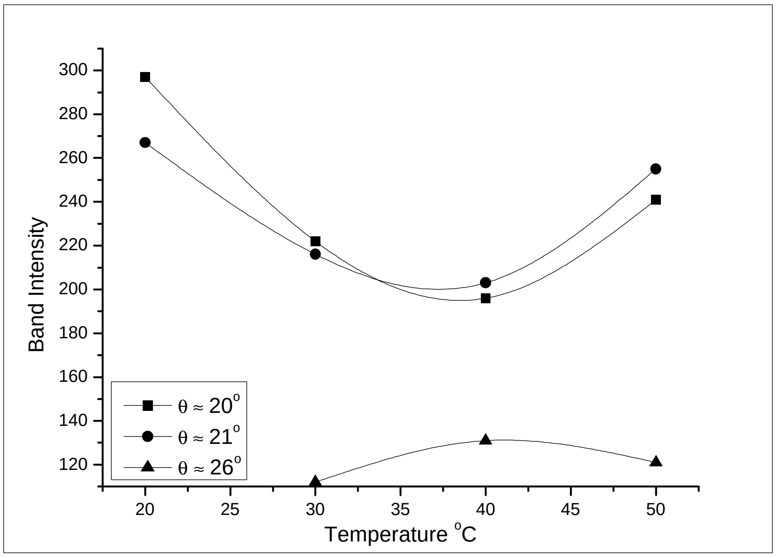

Figure 6(b). Band Intensity for Polyamide-6

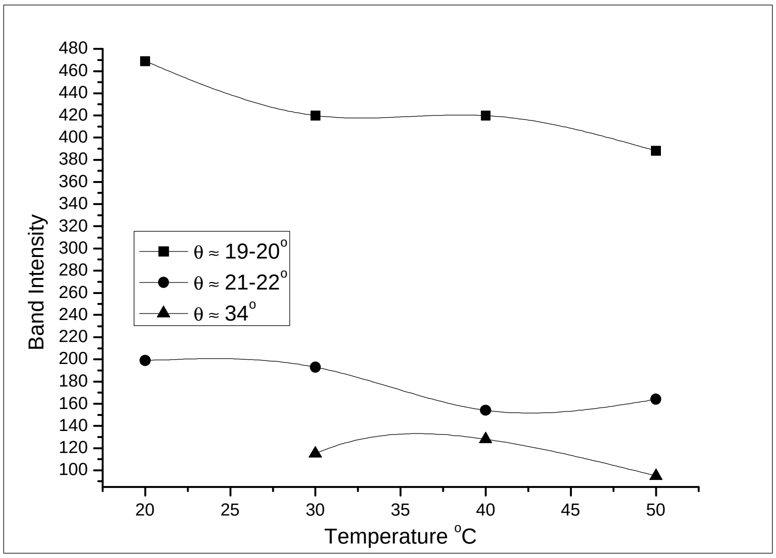

Figure 6(c). Band Intensity for Conjoint

Crystallite size was determined by measuring the peak width in X-ray diffraction patterns for each polymer at different heat setting temperature. It can be concluded by using the formula:

$$t = \frac{0.89\, l}{b \cos q_{hkl}} \qquad (2)$$

Where ë is the wavelength of X-ray, *t* is the crystal dimension perpendicular to the hkl plane, $è_{hkl}$ is the Bragg’s angle for this plane and *â* is the width of the half maximum intensity in radians. The crystal dimension *t* is then inversely proportional to *â*.

Figure (7) and table (4) represent a relation between half-band-width (h.b.w) versus different temperatures of heat setting for the three polymers under investigation. For LDPE, no remarkable change in h.b.w of the fundamental band is observed up to 50°C setting. On the other hand the h.b.w for polyamide-6, drop drastically at 30°C followed by slight drop at 40°C, and increase again at 50°C. With respect to the conjugate polymer of PE and PA-6, no change is observed at all setting temperatures indicating stability of crystallite size.

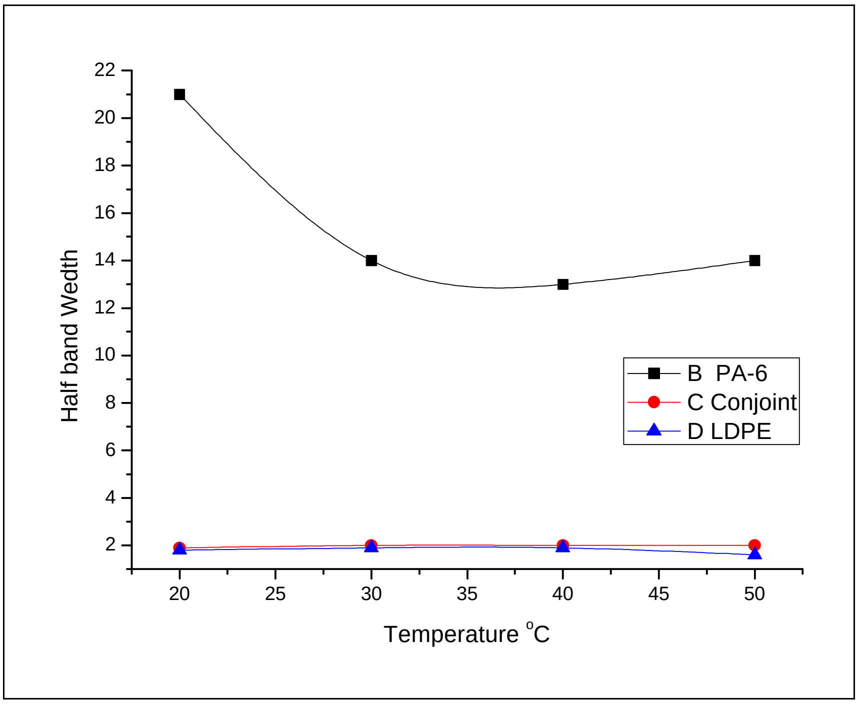

Figure 7: Relation between half-band-width (h.b.w) and temperatures of heat setting for the three polymers under investigation

Table 4: Percentage change in band intensity (ÄI%) versus temperature of heat setting for LDPE, PA-6, and their conjoint:-

Sample	Temperature °C	ÄI%
LDPE	20	0
	30	- 25.253
	40	- 37.374
	50	- 18.855
PA-6	20	0
	30	+ 22.289
	40	- 10.442
	50	+ 7.229
Conjoint	20	0
	30	- 10.448
	40	- 10.448
	50	- 17.271

Conclusion

We have studied the mechanical and thermal properties of three polymeric materials; LDPE, PA-6 and their conjoint. The stability of heat setting polymers for certain time can be determined by using two useful and accurate techniques, X-ray diffraction analysis and differential scanning calorimetry. The changes in structural and thermal properties of the studied polymers are probably due to the change in the molecular configuration as a result of the change in temperature of heat setting. It was found that conjoint of LDPE and PA-6 bears high temperature than each of the parent polymers (LDPE and PA-6). Also, the conjoint has little changes in structure and its physical and mechanical properties have been improved. So, its application in industrial and commercial uses is preferable.

Acknowledgements

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