ABSTRACT

Title of Thesis : A Study on the Poly(ethylene terephthalate) / Fluoropolymer Blends

Chyan-nin Chiu, Master of Chemical Engineering, 1988

Thesis directed by : Dr. Wing T. Wong.
Assistant Professor.
Chemical Engineering Department

The rate of crystallization of Poly(ethylene terephthalate) (PET) can be improved by blending it with poly(ethylene co chlorotrifluoroethylene) (ECTFE; tradename Halar) so that it can be suitable for injection molding. The special advantage of this method is that molecular weight of the blend will not decrease so much as by adding nucleating agents. That is to say, the mechanical strength of the blend will not decrease very much compared with that of virgin PET.

A STUDY ON THE POLY(ETHYLENE TEREPHTHALATE) / FLUOROPOLYMER BLENDS

by
Chyan-nin Chiu

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Name of Candidate : Chyan-nin Chiu
Master of Chemical Engineering, 1988

Thesis and Abstract Approved : Aug. 4, 1988
Dr. Wing T. Wong
Assistant Professor
Chemical Engineering
Department
Date

Signature of other member
of the thesis committee.
Aug 8, 1988
Date

Signature of other member
of the thesis committee.
8/8/88
Date

VITA

Name : Chyan-nin Chiu

Permanent address :

Degree and date to be conferred : M.S.Ch.E., 1988

Date of birth :

Place of birth :

Secondary education :

New Jersey Institute of Tech.	2/87-10/88	M.S.Ch.E.	10/88
Private Tunghai University	9/80-6/84	B.S.Ch.E.	6/84

Major : Chemical Engineering

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I also want to thank my parents for their support and love, and wish that this thesis will be the most valuable Chinese Father's Day gift.

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CHAPTER ONE INTRODUCTION

Poly(ethylene terephthalate) (PET) is the reaction product of terephthalic acid and ethylene glycol. This reaction is a condensation reaction, so that the by-product of this reaction is water. Typical applications for PET include fibers (Dacron), films (Mylar) and soft drink bottles. The usage of Dacron is not limited to clothes only. Dacron can also be used as artificial tendons because of their biocompatibility.

PET is one of the few polymers that have been permitted to be used for containers of food. But post-consumer scrapes of PET containers can not be reused because they may be contaminated by dirt. If PET waste is treated by incineration, then there is a wastage in the limited petroleum resources on earth. Incineration may also cause air pollution. PET can not be just throw away, since it is not so easily weathered. It is reported that scientists have developed some weather-degradable plastics. However, they can not totally control the time of breakdown up to now. So the best way is to recycle it.

If the problem of reusing it cannot be solved, then the usage of PET will be limited. Some countries has banned the utilization of PET for food application. The reusage of PET has become a pressing topic now.

Some companies use recycled PET as fillers of dolls, but only limited quantities are used. Other companies has set up systems for recycling PET soft drink bottles. The bottles are cut by machine into pieces and then the PET is separated from HDPE, aluminum and paper by floatation process. These clean PET scrapes are commercially available and much cheaper than virgin PET. However, the problem of how to effectively use these PET scrapes has not been satisfactorily solved yet.

PET is characterized by their excellent physical and mechanical properties. However, PET is not suited for applications in injection molding, because of its slow crystallization rate. The goal of this thesis is to improve the rate of crystallization of PET so that it can be extensively used in injection molding.

Crystallinity is defined as the extent of crystalline order. When a polymer is orderly arranged, the space between molecular chains can be decreased. Hence the density is increased. Its mechanical strength is also increased because of the increase in friction between the polymer chains. Thus a polymer of higher crystallinity is stiffer than the same polymer of lower crystallinity. However it may become brittle. Its transparency usually decrease with increasing crystallinity because of scattering. Crystallinity can be measured in several ways :

1. by Densimeter :

When a body is immersed in water, it becomes lighter than in air because of the bouyance force of water. There is a relationship between this force and its density. High precision densimeter is now available commercially. Only about 20 seconds is required for measurement of each sample. The results are digitally displayed. By weighing a small amount of the sample in air and in a suitable liquid, the density of the sample is given by

$D=W/[W-(w\pm dw)]*(k-low)+low$

where W = weight in air;

w = weight in liquid;

dw = clamp's correction in liquid;

low = 0.0012 at 20°C, 50 % RH;

k = the density of liquid in which the sample is immersed.

By using this machine, crystallinity of a polymer can be calculated by the following equation :

Percentage of crystallinity = (density of sample - density of amorphous sample)/(density of crystalline sample - density of amorphous sample)

2. by Density gradient apparatus :

Two beakers of the same diameter are mounted on a platform which is higher than the top of a column. One beaker (beaker A) contains more dense liquid, the other (beaker B) contains less dense liquid whose quantity is more. These two beakers are connected with a siphon tube. Beaker B and the column are connected with another siphon tube. Since the liquid in beaker A is higher than that in beaker B, the liquid in beaker A will flow into beaker B automatically and the density of liquid in beaker A will decrease gradually. Thus the liquid in beaker B will flow into the column slowly with decreasing density. Thus the density of liquid in the column decrease with height. It will remain in this state unless it was disturbed.

A single column apparatus or three column apparatus is usually used. There are calibrated marker floats available. Since the density of liquid in these column varies with the height, the sample measured will stay at the height where its density is the same as that of liquid. The density of the sample can then be read directly. The sample must be polished, since even a small bubble will cause a big error in the result.

3. by X-Ray Diffraction.

The x-ray diffraction curves can be resolved into several single peaks. The area under a peak represents the relative amount of that contribution. Since a semicrystalline polymer consists of amorphous part and crystalline part, the relative amount of crystalline part in a polymer can be calculated. Thus the percentage of crystallinity can be known.

4. by Differential scanning calorimetry :

This will be discussed in the section under thermal analysis.

Any of the following methods may be used to improve the crystallinity of PET :

1. by adding nucleating agents :

Researchers have tried a number of inorganic and organic salts as nucleating agents. It has been proved that sodium benzoate and basic aluminum dibenzoate are excellent nucleating agents for PET (1). Although these kinds of nucleating agents are effective, they can cause decrease in molecular weight and hence lessen the mechanical strength of PET.

2. by blending it with another polymer :

Blending is often used in laboratory to produce a new material for specific purposes. These blends usually combine some of the merits of both components. Some blends of PET and other polymers have been widely applied. For examples :PET + nylon ; PET + PBT ; PET + PMMA ; linear PET + branched PET etc. Among these blends, some blends crystallize much faster than PET.

Linear low-density polyethylene (LLDPE), conventional polypropylene or low-molecular-weight polypropylene (LMWPP) have been shown to be powerful nucleating agents for PET (2). LMWPP has low molecular weight and narrow molecular weight distribution, so that it has low and stable melt viscosity. Since LMWPP has very low melting viscosity, it can be easily dispersed in another polymer. LMWPP also has high melting point, so that it can solidify first and nucleat the polymer which it blends with. Therefore, LMWPP works better than the other two.

Some low molecular weight ionomers have been used as efficient nucleating agents for PET, eg. ACLYN (a trademark of Allied-Signal INC.) and Surlyn (a trademark of Du Pont).

These ionomers work even better than Polypropylene. Each kind of ionomer contains a certain type of cation, eg. Ca, Mg, Na, Zn, etc..

It has been proved that the ionomers containing Na^+ are the best one. The reason has not been explained fully.

The crystallization of PET has also been shown to be accelerated significantly by alloying with PMMA (3). The reason is that the long PMMA chains cause decrease in the mobility of PET, so that the chance of the formaton of PET nucleation is increased. Another explanation is that it may results from the trans-esterification between these two polymers. This hypothesis needs further experiment to prove it.

There are several types of blending (4):

(1) By mechanochemical reaction
(2) With high shear equipment
(3) Melt blending
(4) Cryogenic or impact grinder

and there are also several kinds of mixers available for blending (4) :

(1) Banbury mixer
(2) Farrel continuous mixer (FCM)
(3) Corotating twin screw extruder
(4) Specific equipped, single-screw mixer
(5) Motionless mixer

(6) Gelimat (or continuous gelmet)

(7) Short, multi-flight screw extruder (L/D = 5)

The methods of blending may also be divided into the following catagories (5):

(1) Physical blending which includes :

a. Mechanical blends
b. Dissolve the polymer components in a mutual solvent

(2) Chemical blending which includes :

a. Interpenetrating network (IPN)
b. Lattices of uncrosslinked polymers
c. Inverse of IPN formation (or solution grafting technique)

The properties of polyblends (4) :

(1) For miscible polyblends :

A miscible polyblend can be regarded as a homogeneous system. It behaves like a pure substance. Its properties can be predicted from the properties of its components by the following simple equation :

$P = P_1*F_1+P_2*F_2+I*F_1*F_2$

where P = property

F1,F2 = composition

I = interaction terms

(2) For immiscible polyblends :

An immiscible polyblend is a nonhomogeneous system which contains dispersed phase and continuous phase. The interaction between dispersed phase and continuous phase is complex. The morphology also affects the properties of the whole system. The properties of this system is difficult to predict. we usually use a semiempirical equation as follows :

P/P1 = (1+A*B*F2)/(1-B*F2*U) (semiempirical)

where A > 0 and depend on :

- a. Shape and orientation of the dispersed phase
- b. Nature of the interface :

F_1,F_2 = composition

P = properties

B is a function of A, P_1 and P_2

U is a function of F_m

F_m = maximun packing volume fraction

Since different species have different thermal properties, eg. heat capacity, heat of melting, heat of vaporization, glass transition temperature, melting point etc. The details in a sample can be known simply by measuring its thermal properties. There are several methods available for thermal analysis (6):

1. Differential Scanning Calorimetry (DSC) :

The operating principles of DSC is that it maintains the sample and a reference at the same temperature and measures heat capacity versus temperature. DSC was chosen as a primary analytical method in this thesis for the determination of crystallization kinetics.

2. Differential thermal analysis (DTA) :

The principle of DTA is that it supplies the same amount of energy to both sample and reference holder and measures temperature difference between sample and reference. DTA curves are quite similar to DSC curves since temperature difference is proportional to heat capacity.

3. Thermogravimetric Analysis (TGA) :

TGA uses high sensitive balance to measures the percent of weight remaining of a sample versus temperature. Since when a polymer decomposes, its weight changes. By monitoring the weight of a sample, the decomposition temperature and stability of this sample can be determined.

4. Thermomechanical Analysis (TMA) :

It measures the mechanical response of a polymer versus temperature. Since some polymer must serve under abnormal temperature, especially those polymers used as engineering plastics, TMA must be used instead of ordinary mechanical test to gain data for design.

Fluoropolymers are famous for their thermal stabilities at high temperature, so that they are suited for blending with PET. Furthermore, most of them are excellent lubricants. They may decrease the friction between polymer chains and promote crystallization process. On comparing the nonisothermal DSC curves of Foraflon(tradename of PVDF), Aclon(tradename of CTFE), Voltalef(tradename of CTFE) and Halar(tradename of ECTFE), it was observed that Halar was the best one for blending with PET since its Tcc and Tm are the highest one among them. It was thus decided to blend PET with Halar, since blending would not cause the decrease in molecular weight of the polymer. Halar indeed has the effect of initiating the crystallization of PET.

CHAPTER TWO PHYSICAL PROPERTIES

PET has a melting point of 265°C. Its specific gravity is between 1.34 and 1.39. PET has very good mechanical properties. Its tensile strength is 8500-10500 psi., tensile modulus is $4x10^5$-$6x10^5$ psi. Ultimate elongation is 50-300 %. However, PET crystallizes slowly and this limits its utilization.

Fluoropolymers are characterized by their thermal stabilities, toughnesses and chemical resistances. The rationale for choosing fluoropolymers to blend with PET is because of their thermal stabilities and high melting points.

Foraflon (PVDF) has amelting point of about 170°C. They decompose at 350°C and liberate hydrofluoric acid.

The main component of Voltalef and Aclon is polychlorofluoroethylene (PCTFE). The crystalline melting point of PCTFE is 218°C. The melting points of Voltalef and Aclon are slightly different from this value because they contain certain additives.

Halar (ECTFE) has a melting point of 240°C. It decomposes rapidly at 350°C and give out HCl and HF gases.

On comparing Foraflon, Voltalef, Aclon and Halar, it was found that Halar has the highest melting points among them and is quite stable at high temperature. Halar was thus chosen to blend with PET.

CHAPTER THREE EXPERIMENT

3.1 Preparation of Samples

The components for blending were dried in vacuum overnight in order to avoid degradation of PET induced by moisture. The temperature needed is usually about 100 to 116°C. However, Kraton and J-von are not stable at high temperature. They had to be dried at low temperature for only a few hours.

A C.W. Brabender Plasti-Corder was used to blend our polymers. It is a recording torque rheometer and processes polymers in batch style. It heats polymer by electric power and the temperature is not the same at every place. The temperature of polymers was measured by a thermocouple so that an average temperature of the blend would be obtained. The blending speed was 24 rpm (the lowest speed) such that the breakage of polymer chain by shear force could be largely avoided. The setting of blender was 295°C. since the processing temperature of blending must be (4) :

1. much higher than the glass transition temperature of each component (for amorphous polymer) or

2. much higher than the melting temperature of each component (for semicrystalline polymer)

The temperature of mixing was chosen such that the viscosities of components were about the same. This insured optimal mixing (7). Since the viscosity of Halar was much higher than the viscosity of PET, polymer will degrade before it can reach this temperature. The temperature of blender was set at 295°C which is the maximun possible temperature.

Nitrogen gas can be used to prevent the possible degration of polymers during blending. While taking samples, it was necessary to press them into thin films so that they would be suitable for DSC. Either liquid nitrogen or ice was used to quench samples and get amorphous products.

Before each batch of blending, polyethylene was used to clean the blender. The blender has to be carefully cleaned since any little bit of contamination could change the properties of this blend. Before blending, at least half an hour was required to let system reach thermal stability. A stop watch was started and at the same time polymer was fed into the blender. Samples were taken at 5 and 10 minutes respectively. When taking samples, they were pressed on a cool steel plate to quench them. Films prepared in this manner could be used for DSC analysis.

3.2. Measurement and Discussion

3.2.1 Differential Scanning Calorimetry (DSC) :

A Perkin Elmer DSC 2-B was used for thermal analysis. The DSC was connected to an AT&T personal computer for data aquisition. These samples were cut small enough such that they could be able to be sealed in small aluminum pans. These samples were then dried in oven overnight. After weighing, the samples were sealed in aluminum pans and kept in a dessicator.

The machine was warmed up and allowed to reach stable state. Calibration was performed using standard indium and zinc samples. A computer was connected to this machine for data aquisition. Data was stored in 4.5 in. floppy discs. Simpson rule for integration was used to compute areas under isothermal crystallization curves.

When a polymer melts or crystallizes, there will be a peak on the graph because it absorbs or gives out the latent heat. Before scanning, the sample was heated up to 280^{o}C and held there 10 to 15 minutes to eliminate previous thermal history of the polymer.

1. Nonisothermal Scanning :

The DSC and chart recorder were set at 1 mca/s, 50 mv, 1 cm/min. The polymer was quenched at a rate of 320^{o}C/min. from

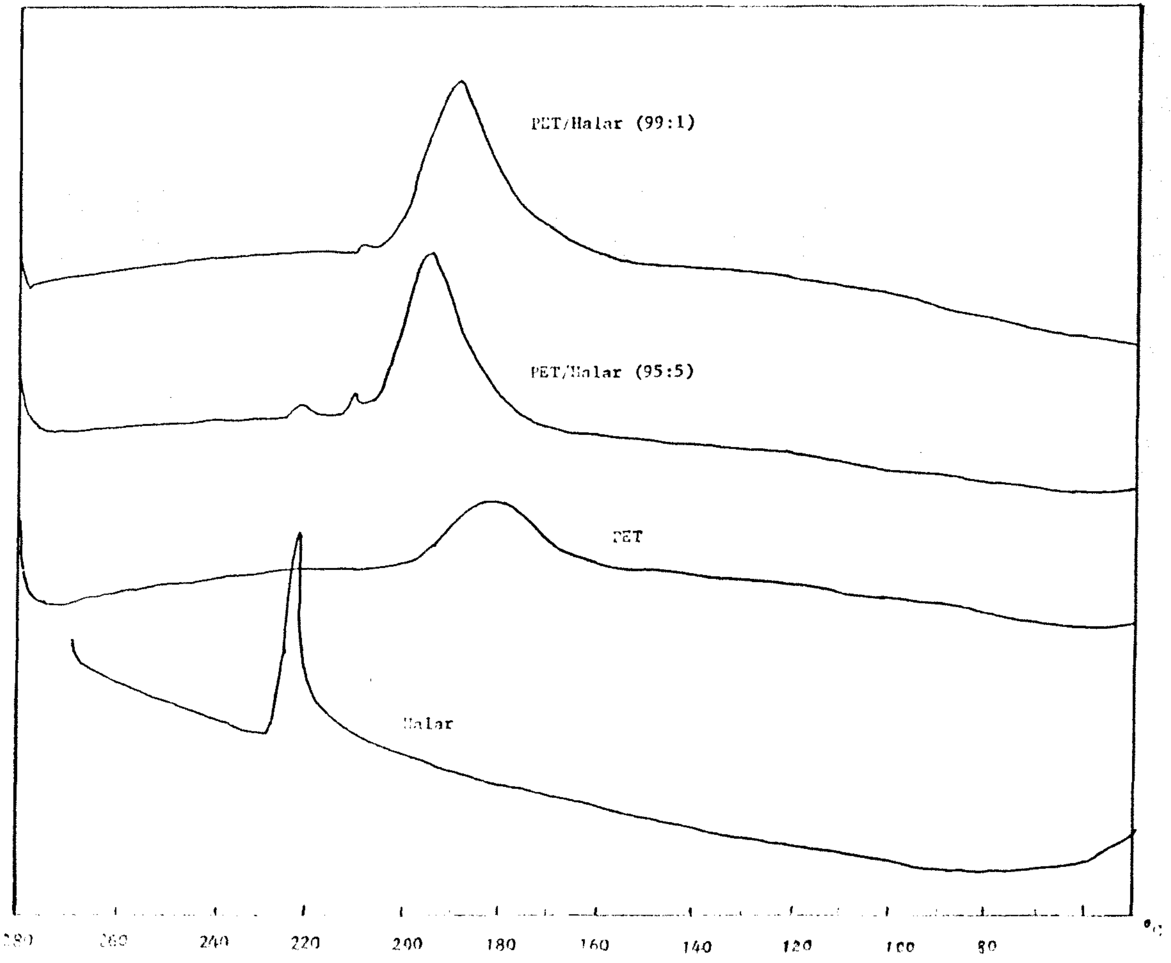

Figure 1 : Nonisothermal DSC curves of PET, Halar and PET/Halar (99:1) in cooling process.

280°C . This causes the polymer to exist in an amorphous state (i.e. almost no crystal forms). The polymer is then scanned at a rate of 10°C/min. from 50 to 280°C, and then cooled down to 50°C at the same rate.

Table 1 : The peaks in DSC curves for fluoropolymers without processing in blender :

Polymer	Tg	Tch	Tm	Tcc
Foraflon (PVDF)	-	-	163,169[a]	134
Aclon (CTFE)	-	-	205.5	171
Voltalef (CTFE)	-	-	209	154
Halar (ECTFE)	-	-	237.5	221.5
Halar (ECTFE) (amorphous)	-	-	238.5	221.5

Unit : °C.

Tch : the crystallization peak on heating curve.

Tm : the melting peak on heating curve.

Tcc : the crystallization peak on cooling curve.

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[a] Foraflon contains some additives.

As shown in table 1, Foraflon contains some additives because it has two peaks for Tm. Thus it was not suitable for this work. Since Tcc and Tm of Halar is the highest one among the fluoropolymer studied, Halar was chosen to blend with PET in an attempt to improve the crystallization of PET. The criteria for this selection is as follows :

A good nucleating agent must solidify as soon as possible during the process of cooling, so that this nucleating agent can have the effect of promoting crystallization.

Table 2 : The peaks in DSC curves for PET processed in blender (as a refernce to the blend of PET)

Blending time (min.)	Tg	Tch	Tm	Tcc
5(without holding)	81.5	136	247,251	-
5	81	139	249	182.5
20	81	136	251	188
25	80	133	252	193.5
35	79.5	133.5	251	193

Table 3 : The peaks in DSC curves for blend of PET and Halar (99:1)

Blending time (min.)	Tg	Tch	Tm	Tcc
5(without holding)	81.5	131	250	-

5	81	128	249	209,189.5
20	83	125	249.5,251.5	209.5,189
25	-	-	249,250	210.5,191.5
35	-	-	251	210,193

By comparing table 2 and table 3, it was observed that PET gained an extra peak for Tcc after adding Halar into it. This peak indicates that PET/Halar crystallizes earlier than PET during the cooling process.

Before holding at 280°C for 10 min, Tch peak of PET/Halar blend is much bigger than that of after holding as shown in fig.1. This proves that the crystallization of PET/Halar system is substantial. During its quenching step, it has finished most of its crystallization.

Table 4 : The peaks in DSC curves for blend of PET and Halar (95:5)

Blending time (min.)	Tg	Tch	Tm	Tcc
20	-	-	249.5	222,211,192
25	-	-	251	221,210,192
35	-	-	251	221,211,195

Table 5 : The peaks in DSC curves for blend of PET and Halar (other mixing ratio; 15 min.) :

Mixing ratio	Tg	Tch	Tm	Tcc
99.5 :1	-	125	249	209.5,182
9:1(without holding)	80	127.5	250	221.5,210.5,185
9:1	80	125	249.5	221,210,184
1:1(without holding)	-	123	238.5,250.5	221.5,211,187
1:1	-	125	239.5,250	221.5,210.5,188

From the data above, it was found that Halar can initialize the crystallization of PET. However, there are more than one peak for Tcc, so it is obvious that PET and Halar are immiscible. By comparing Tcc of PET, Halar and PET/Halar in fig.2 and table 4 &5, it was found that one of those Tcc peaks belonged to PET, another belonged to Halar, the middle one might belong to the interface of PET and Halar. For lower percentage of Halar (< 1 % ; see table 3), the DSC of PET/Halar blend only has two peaks; one belongs to PET and another must be for the interface of PET and Halar. The peak for Halar is too weak to be identified.

When the percentage of Halar is 50 %, the PET/Halar blend has two peaks for Tm, this can also be regarded as an evidence of immiscibility. A homogeneous material only has

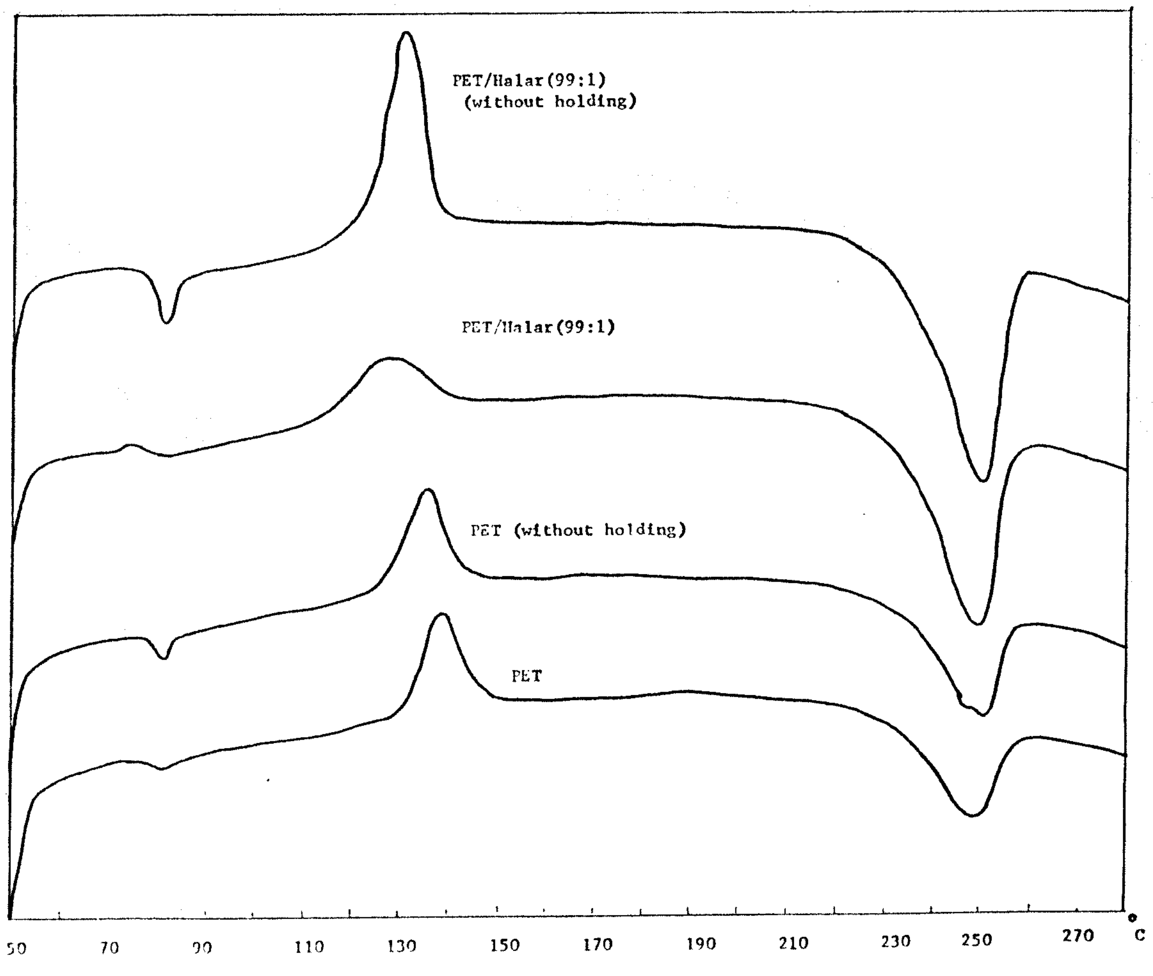

Figure 2 : Nonisothermal Curves of PET and PET/Halar(99:1) in Heating Process.

one peak for Tcc and Tm respectively.

Usually, the immiscibility of polymers may cause the decrease in mechanical strength. It was felt that a compatibilizer (eg. J-von 3000-33A, J-von 3000-60A, Kraton 1657 etc.) could be used to improve the miscibility of PET and Halar.

The compatibility of a polymer pair depends on both temperature and composition. It can be predicted by X_{AB}, polymer-polymer interation parameter (5).

Under metastable compositions, the polymer mixtures are homogeneous because separation is difficult under high viscosity . The binodal curve is the boundary between stable and metastable compositions. On the other hand, the spinodal curve is the boundary between metastable and unstable compositions. The phase diagram can be derived from Flory-Huggins theory (5).

"A good compatibilizer must adhere well to the primary blend components rather than just a rubber (8)". Block and graft copolymer has a compatibilizing effect if it correspond to the polymers used in the blend (5). Compatibilizer may be formed adventitiously during the mixing operation (9).

Kraton is a thermoplastic rubber. Its structure is plastic-rubber-plastic. The structure of Kraton D is styrene-butadiene-styrene or styrene-isoprene-styrene. The structure of Kraton G is styrene-ethylene/butadiene-styrene. Kraton G has better oxidation and weather resistance, higher service temperature range and better processing stability than Kraton D (10).

Kraton G1652 has been used as a compatibilizer for some system, e.g. PS + HDPE ; PS + PP ; PET +HDPE .Since the structure of both HDPE and Halar (ECTFE) are linear, it can be expectd that the Kraton G1652 would be an effective compatibilizer for PET + Halar system. Kraton G1657 was used because it was more stable under high temperature. After several experiments had been conducted, it was found that Kraton G1657 was not effective for this system.

J-von is another kind of compatibilizer, whose chemical structure and most of its properties are similar to Kraton. J-von 3000-60A is more stable at high temperature and harder than J-von 3000-30A. Experiments proved that both of them failed to compatibilize PET/Halar system.

Although PET and Halar are immiscible, it can not be assumed that the mechanical strengh of this system is weak. In reality, its mechnical strength may be only a little bit weaker. It is thus necessary to check its mechanical properties.

Table 6 : The peaks in DSC curves for blend of PET, Halar and J-von 3000-33A (8:1:1)

Blending time(min)	Tg	Tch	Tm	Tcc
15	-	125	252	216,194.5

J-von 3000-33A is not effective for PET/Halar system, because there are two peaks for Tcc as shown in table 6. Since J-von 3000-60A was more stable than J-von 3000-33A at high temperature, J-von 3000-60A was tried.

Table 7 : The peaks in DSC curves for blend of PET, Halar and J-von 3000-60A (8:1:1) (mix Halar and J-von first)

Blending time (min)	Tg	Tch	Tm	Tcc
15	-	-	250.5	219,196

Table 8 : The peaks in DSC curves for blend of PET, Halar and J-von 3000-60A (92.5:5:2.5)

Blending time (min)	Tg	Tch	Tm	Tcc

20	80	125	250	220.5,208,191.5
25	80	125	241,250	220,208,192
35	-	123	249.5	220,208,194.5

From table 7 & 8, J-von 3000-60A is shown to be ineffective as a compatibilizer for PET/Halar system. Another compatibilizer - Kraton 1657 was tried.

Table 9 : The peaks in DSC curves for blend of PET, Halar and Kraton 1657 (8:1:1)

Blending time(min)	Tg	Tch	Tm	Tcc
15	81	127	249.5	210,185

Table 10 : The peaks in DSC curves for blend of PET, Halar and Kraton 1657 (92.5:5:2.5)

Blending time (min)	Tg	Tch	Tm	Tcc
20	80	126	250	221.5,210.5,191
25	81	127	252	222,211,190.5
35	79	126.5	251	221,210,193

From table 9 & 10, Kraton 1657 is also not an effective compatibilizer for PET/Halar system.

Table 11 : The peaks in DSC curves for blend of PET and J-von 3000-60A (95:5)

Blending time(min.)	Tg	Tch	Tm	Tcc
20	79	135	251	194
25	79	135	244.5,250	198
30	79	137	249.5	194.5

Table 12 : The peaks in DSC curves for blend of PET and Kraton 1657 (95:5)

Blending time(min.)	Tg	Tch	Tm	Tcc
20	80.5	135	249.5	189,186
25	81	137	252,254	186
35	79	133.5	250.5	192

Table 13 : The peaks in DSC curves for blend of Halar and J-von (1:1)

Blending time(min.)	Tg	Tch	Tm	Tcc
15	-	148	234	217,93

From table 11 to 13, it is obvious that PET/J-von blend, PET/Kraton blend and Halar/J-von blend are all nonhomogeneous.

2. Isothermal Scanning :

The polymer was cooled down at rate of 320 deg.C/min. from 280 deg.C to the desired temperature. When the temperature reached eqilibrium, data aquisition and chart recorder was started.

The data for tmax is the follows :

Table 14 : tmax of PET and PET/Halar (99:1) for blending 5 min.; blender was set at 295^{o}C

TEMP.	V-PET	PET/HALAR(99:1)
160	.9	.35
170	.867	.40
180	.85	1.45
190	1.2	2.225
200	2.15	3.15
210	4.85	5.425

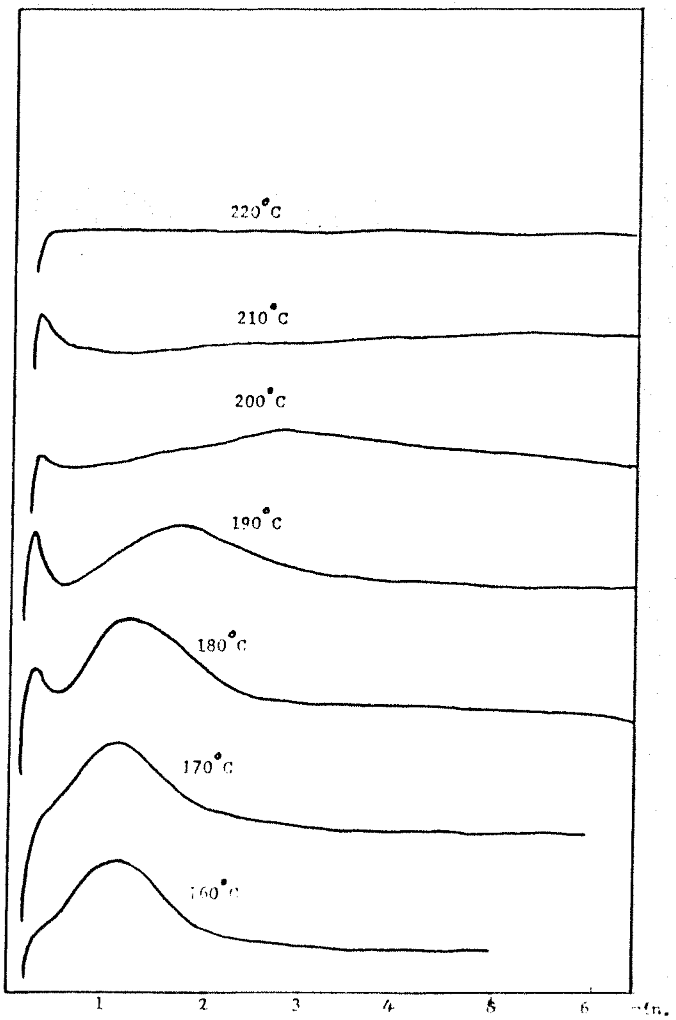

Figure 3 : Isothermal DSC Curves for PET (Processed in Brabender Blender for 5 min.)

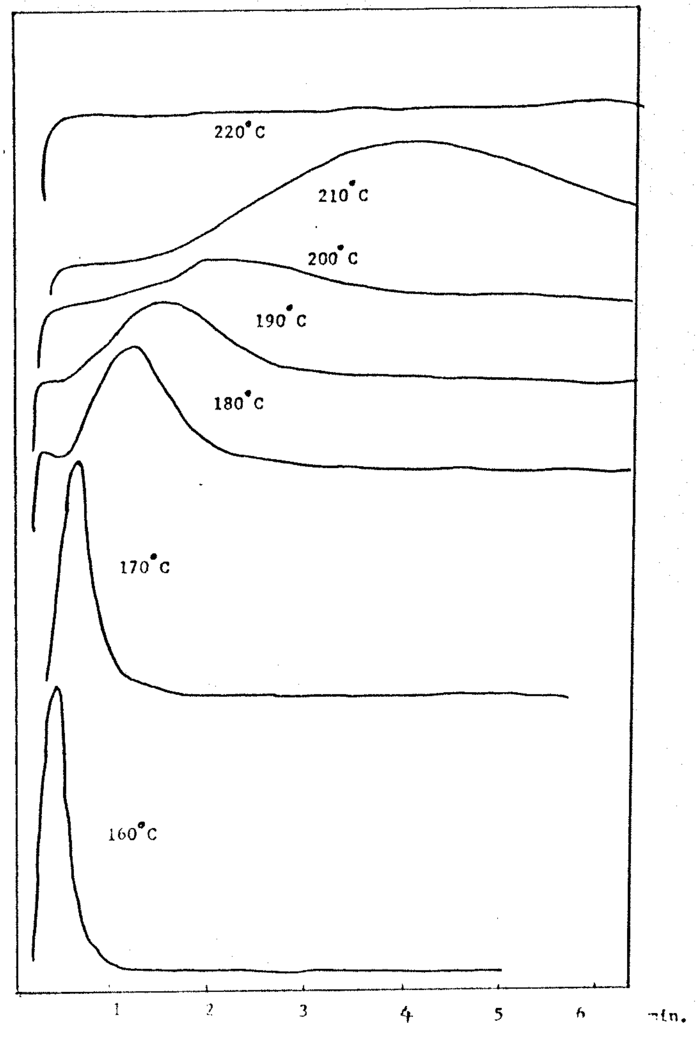

Figure 4 : Isothermal DSC Curves of PET/Halar (99:1) (Processed in Brabender Blender for 5 min.)

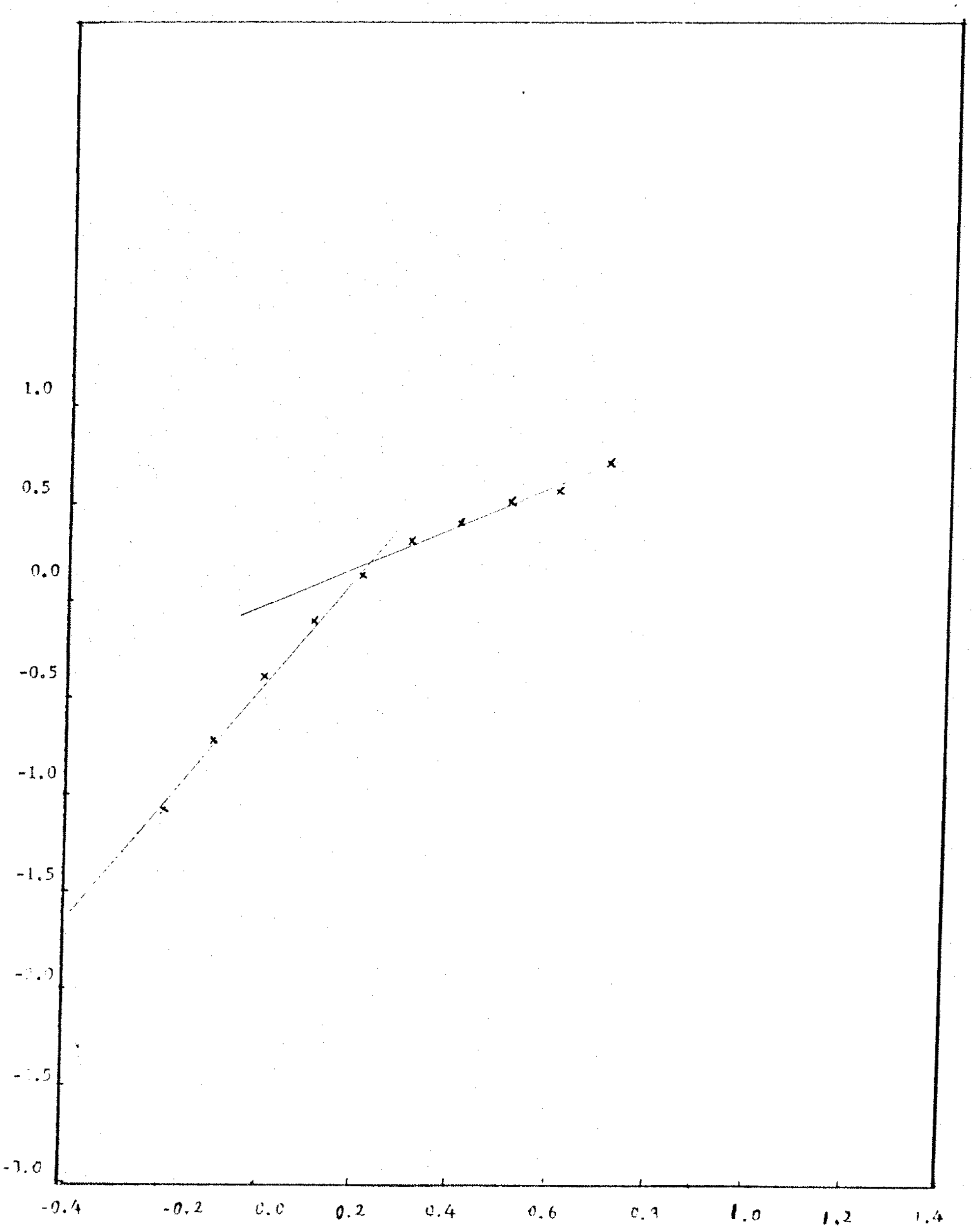

Figure 5 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET at 160°C.

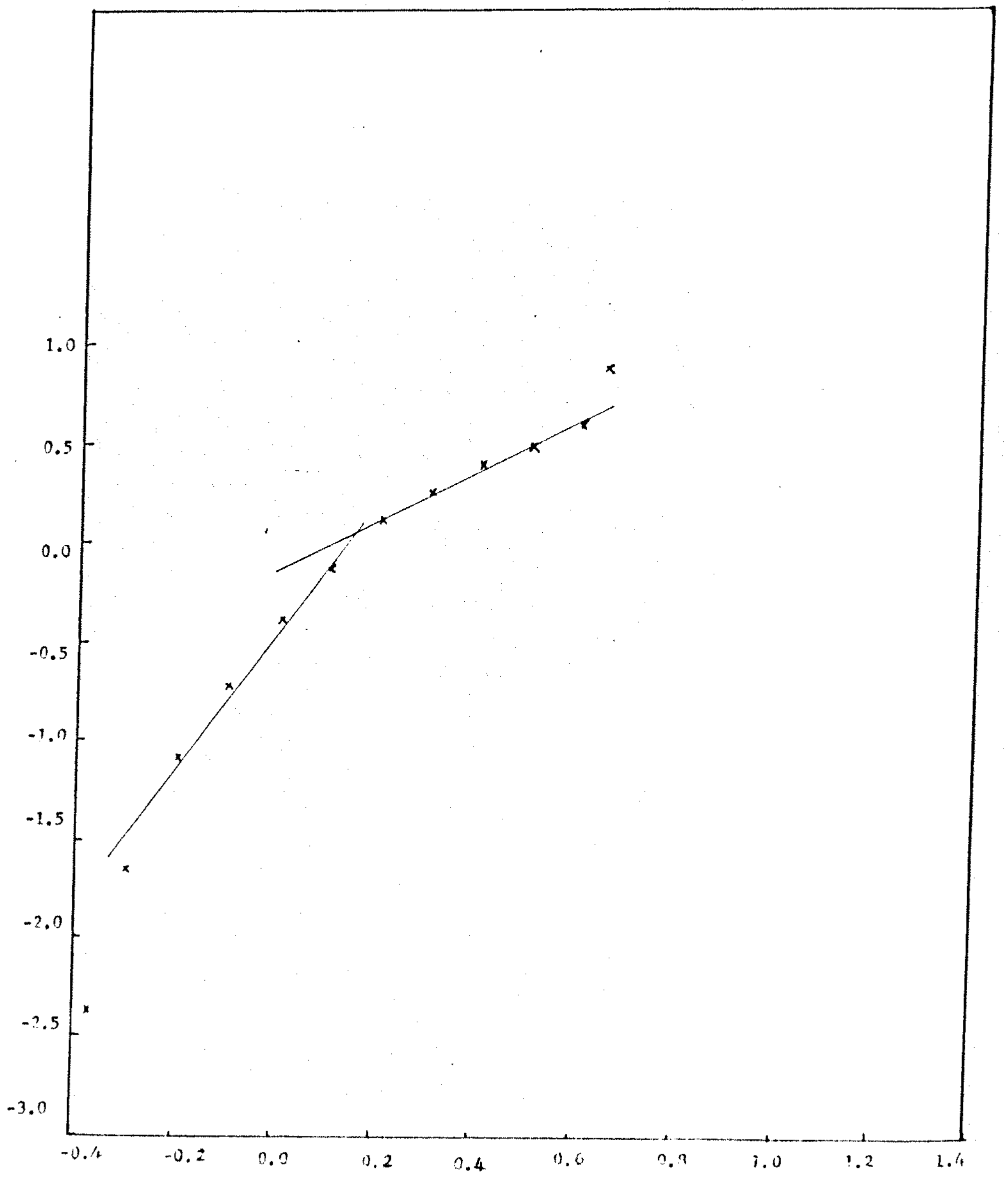

Figure 6 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET at 170°C.

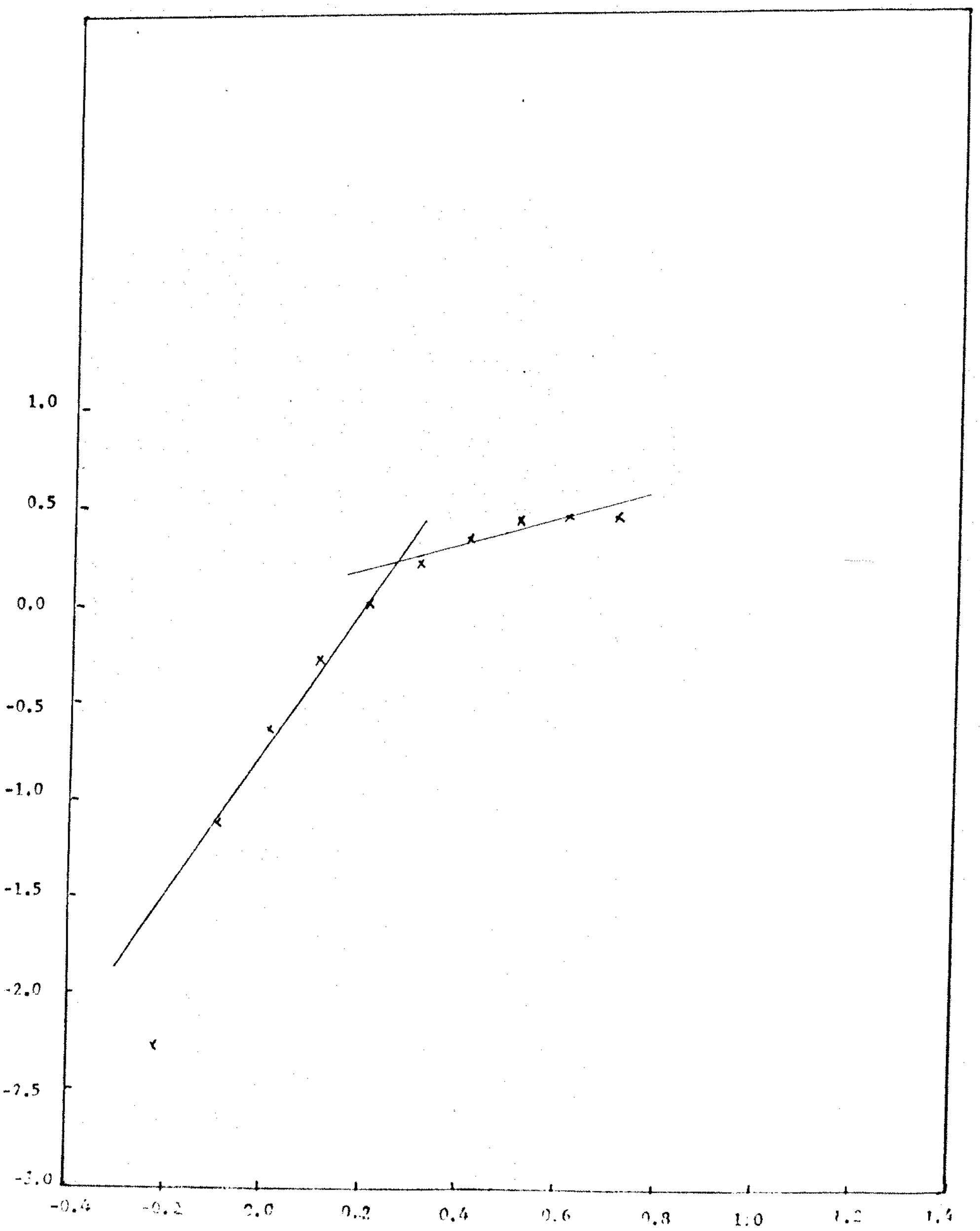

Figure 7 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET at 180^{o}C.

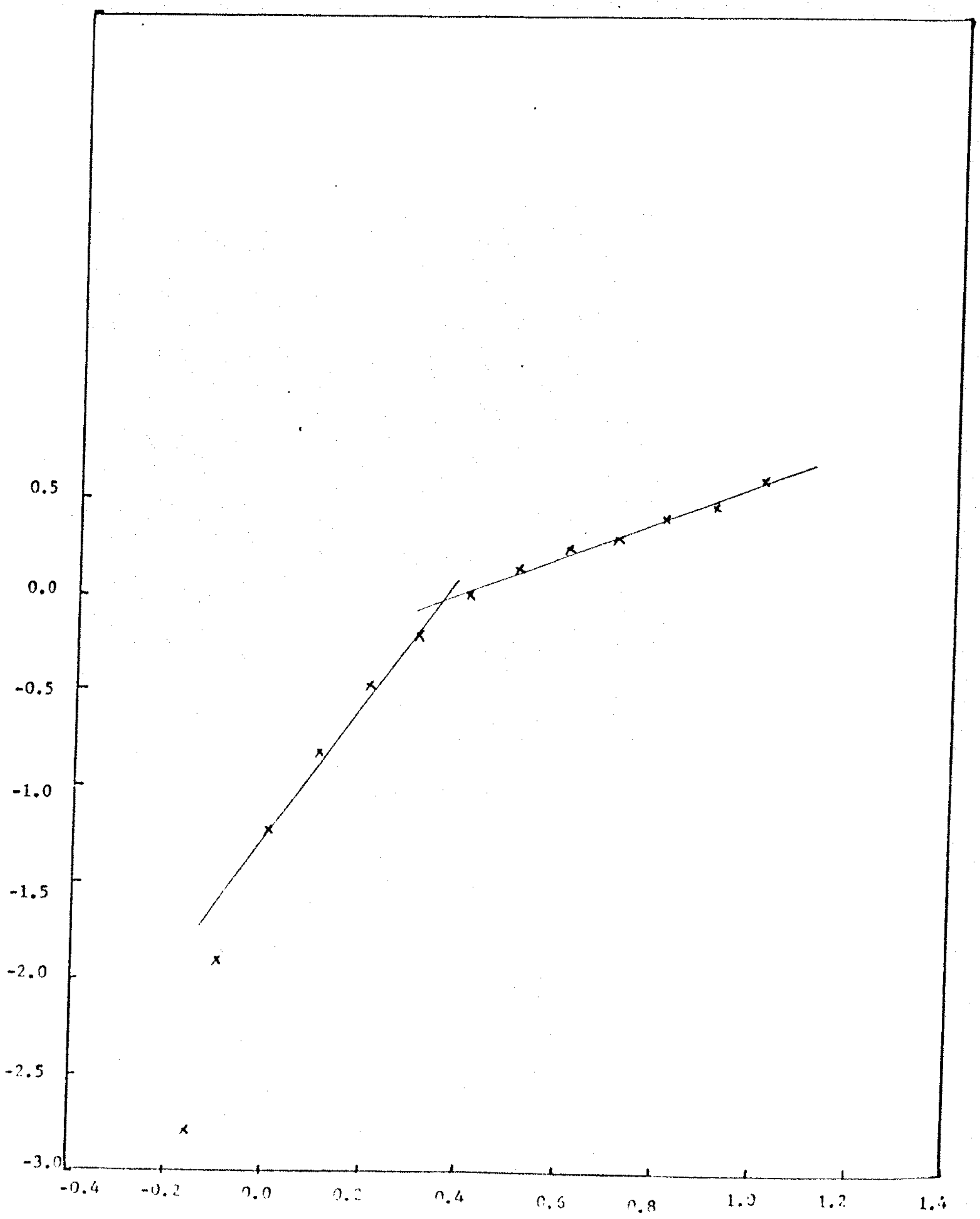

Figure 8 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET at 190°C.

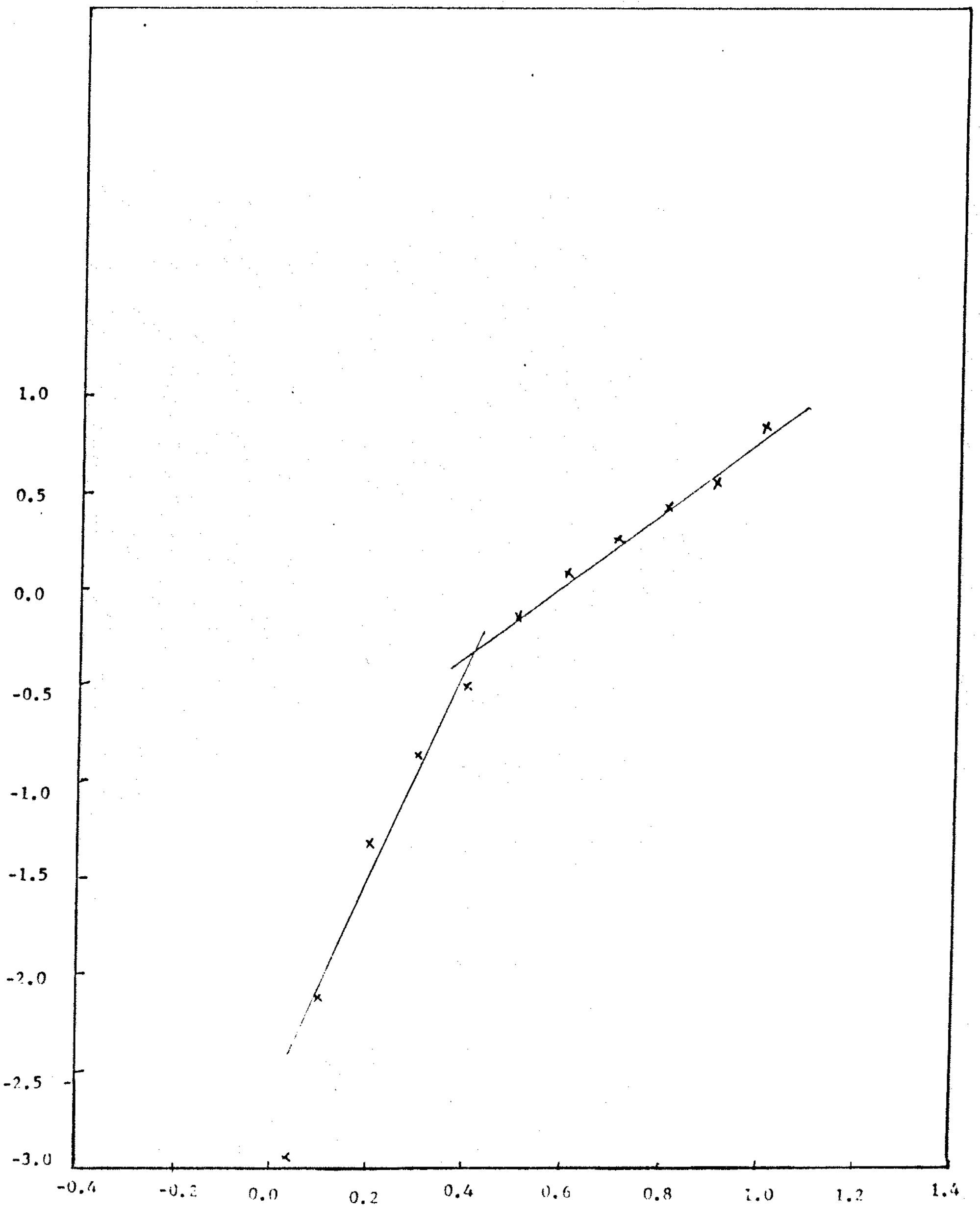

Figure 9 : log(-ln[1-x(t)/x(infinite)]) versus log(t) for PET at 200^{o}C.

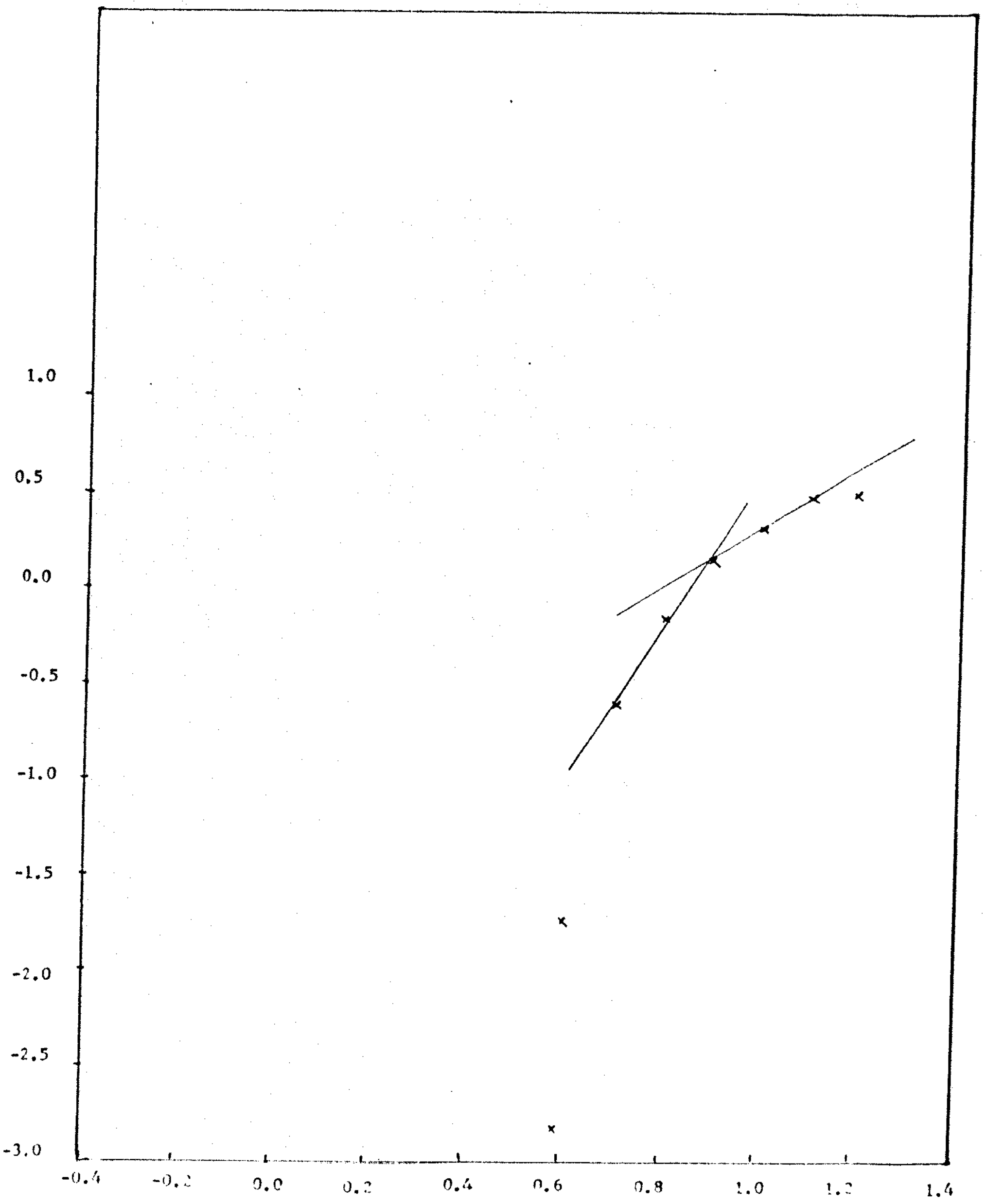

Figure 10 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET at 210°C.

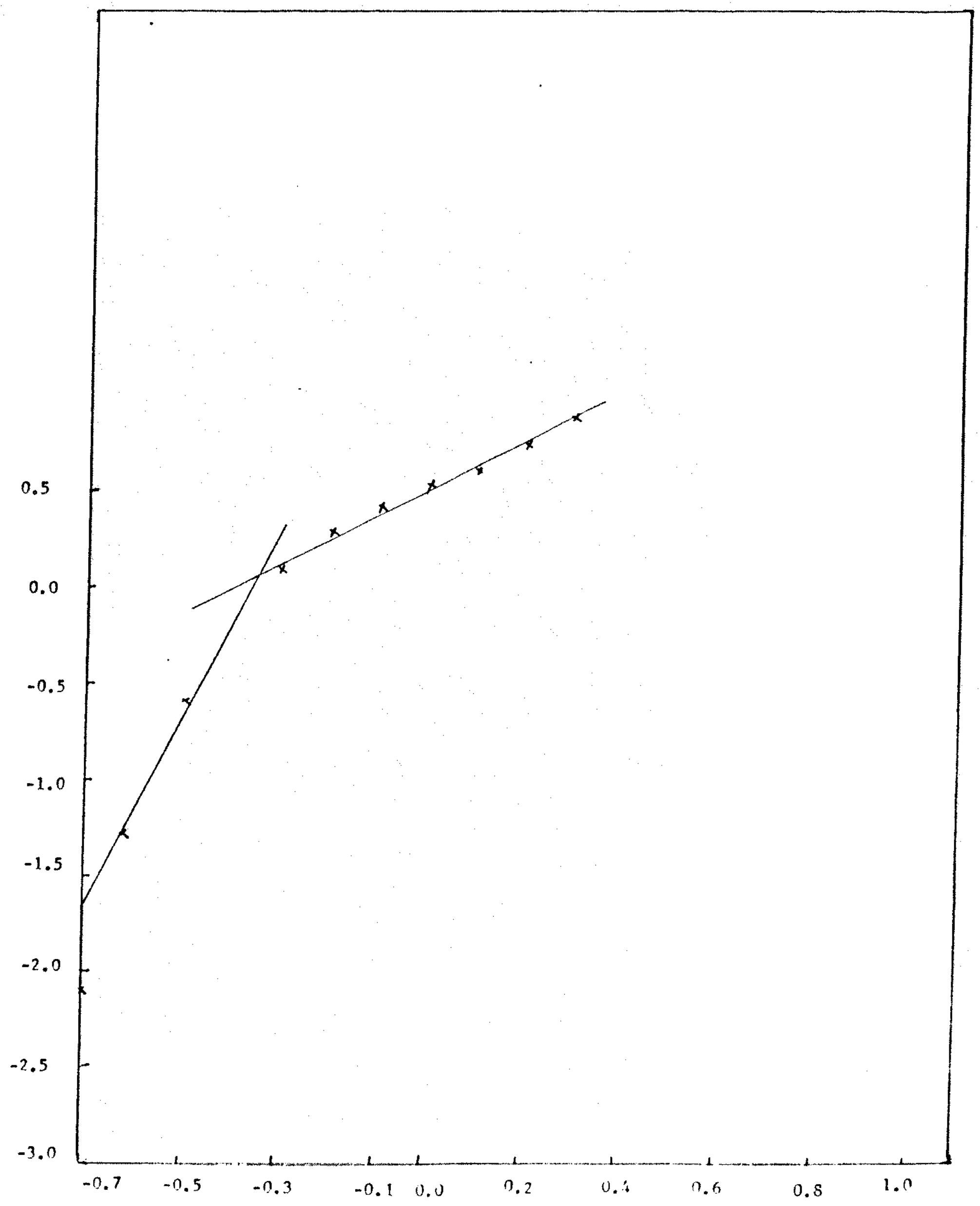

Figure 11 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET / Halar (99:1) at 160°C.

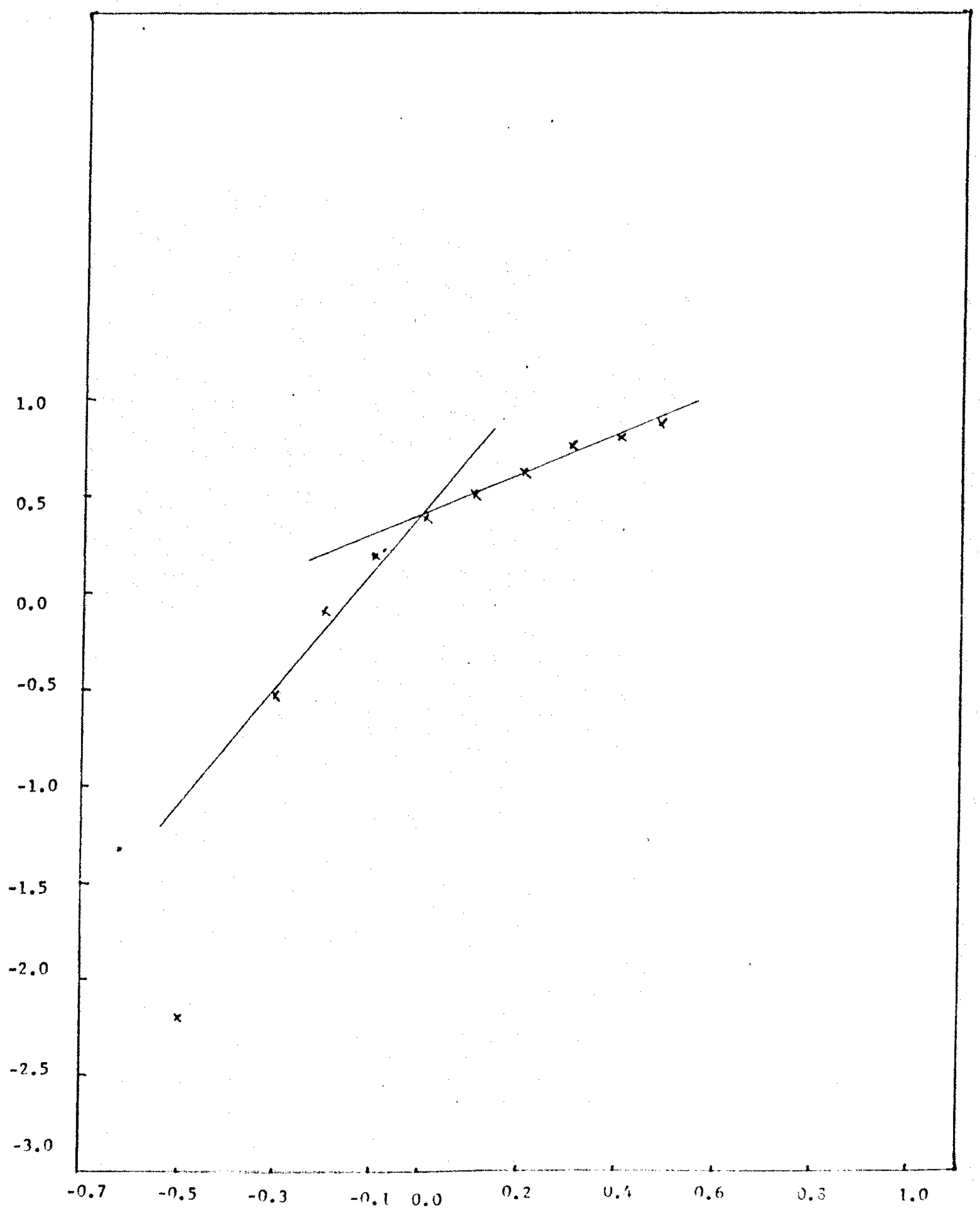

Figure 12 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET / Halar (99:1) at 170°C.

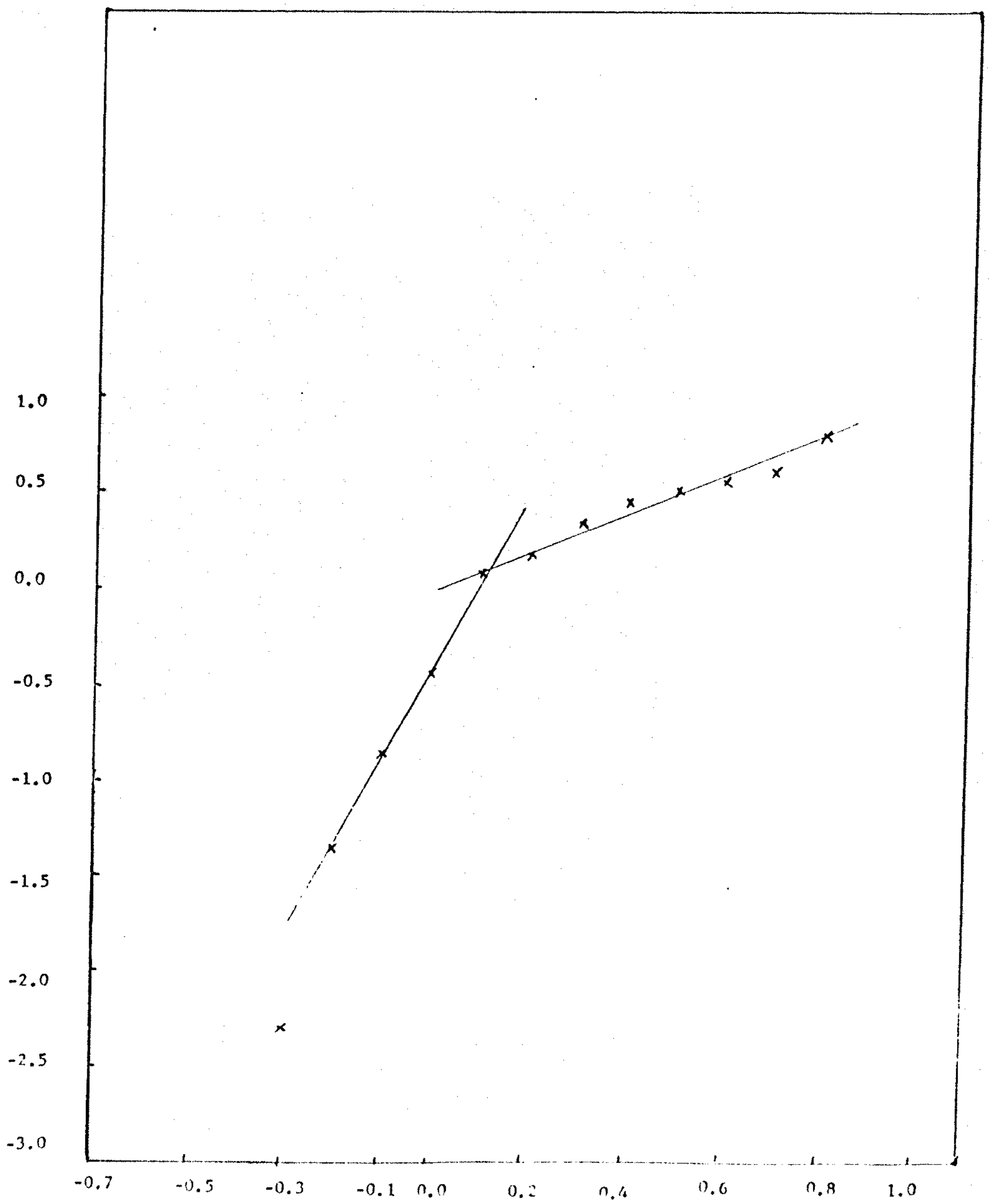

Figure 13 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET / Halar (99:1) at 180°C.

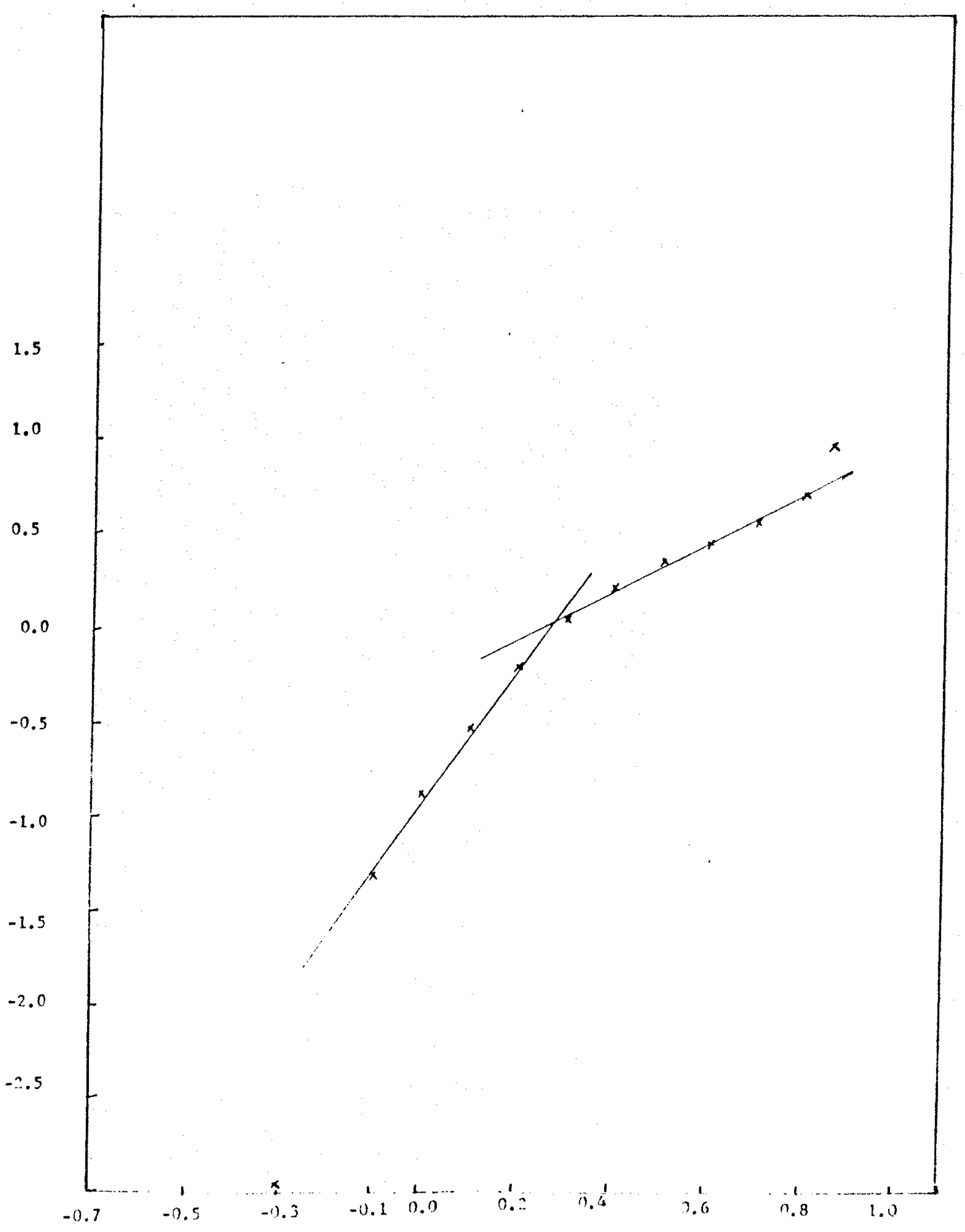

Figure 14 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET / Halar (99:1) at 190°C.

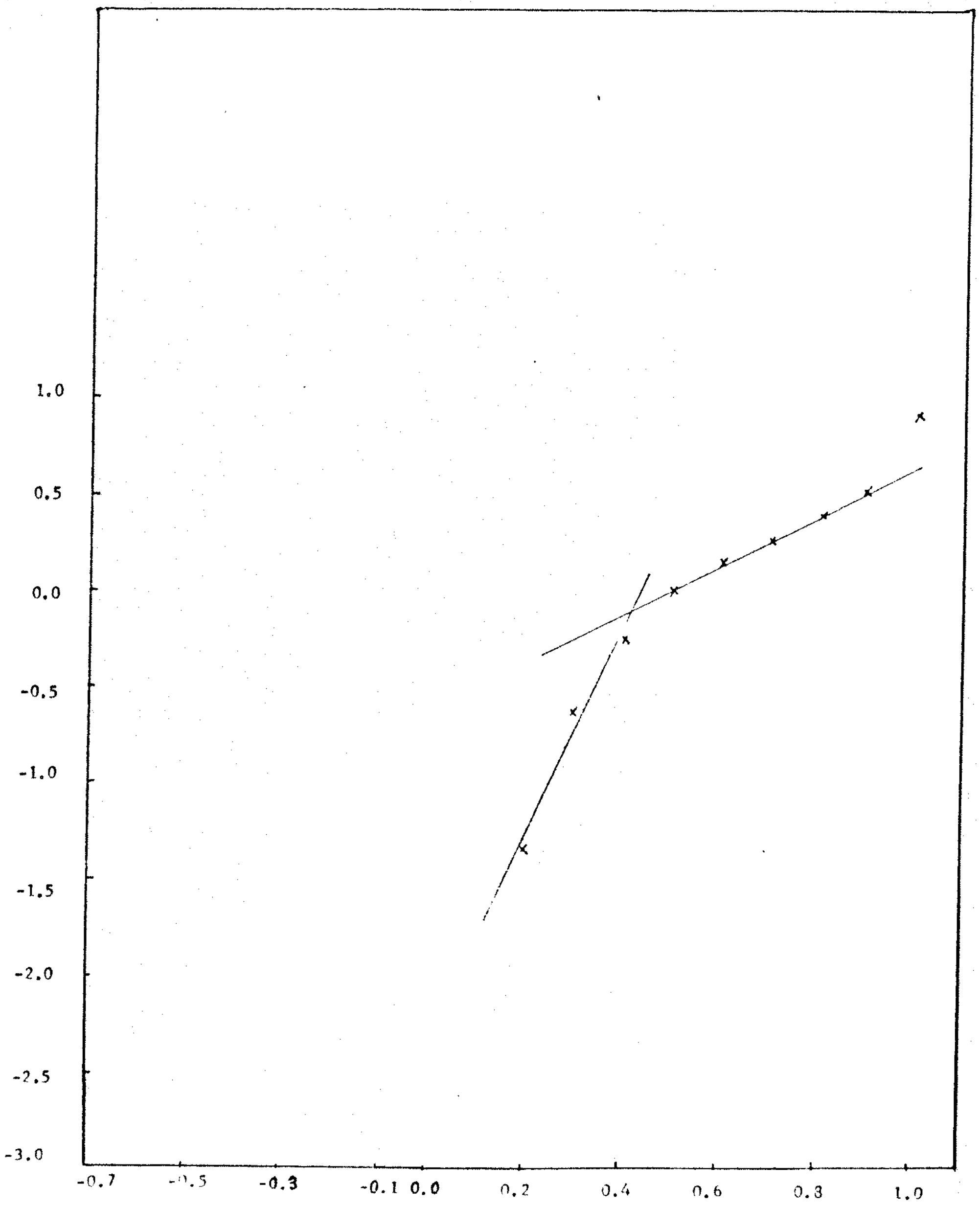

Figure 15 : log{-ln[1-x(t)/x(infinite)]} versus log(t) for PET / Halar (99:1) at 200°C.

From fig.3, fig.4 and table 14, it is obvious that Halar increase the crystallization rate of PET at 160 and 170°C. However, Halar decrease the crystllization rate of PET at higher temperature.

Table 15 : tmax of PET and PET/Halar (99:1) for blending 25 min.; blender was set at 295°C

TEMP.	V-PET	PET/HALAR(99:1)
160	.51	.15
170	.45	.30
180	.75	.70
190	.80	1.0
200	1.4	1.6
210	2.8	3.1

Table 16 : tmax of PET and PET/Halar (99:1) for blending 5 min.; blender was set at 285°C

TEMP.	V-PET	PET/HALAR(99:1)
160	.4	.2
170	.325	.4
180	.475	.55
190	.575	.8

200	.875	1.0
210	1.55	1.9
220	3.05	4.3

Five minutes is a better blending time at 295°C setting becuase most of the polymer in the blender is already molten. At that time only a little polymer clinging to blades does not melt which is unavoidable. Twenty-five minutes is surely too long and can cause the breakdown of polymer chain resulting in high crystallization rate as shown in table 15.

Setting at 285°C is too low and also cause breakage of polymer chain due to excessive shear caused by the high viscosity as shown in table 16. Actually, for the process of industry (eg. injection molding), five minutes is long enough.

Using a computer program, log{-ln[1-x(t) / x(infinite)]} and log(t) are calculated, as shown in table 17 to 27. These curves can be fit by two straight lines, as shown in fig 5 to 15. The slope of each line is the n in Avrami equation and its intercept is the k in Avrami equation, as shown in table 28.

Table 17 : data obtained from isothermal crystallization at 160°C for PET processed by Brabender blender

log(t)	log{-ln[1-x(t)/x(∞)]}
-0.367	-2.28
-0.201	-1.074
-0.102	-0.719
0.00432	-0.380
0.1038	-0.0956
0.201	0.143
0.3032	0.3186
0.4031	0.4347
0.501	0.5150
0.6010	0.5858
0.698	0.7323

Table 18 : data obtained from isothermal crystallization at 170°C for PET processed by Brabender blender

log(t)	log{-ln[1-x(t)/x(∞)]}
-0.3665	-2.378
-0.3018	-1.647
-0.20066	-1.0778
-0.1024	-0.7231
0.00432	-0.3868
0.1038	-0.1045

0.2014	0.1213
0.3032	0.2867
0.4031	0.4103
0.5011	0.5173
0.6010	0.6295
0.6503	0.9197

Table 19 : data obtained from isothermal crystallization at 180°C for PET processed by Brabender blender

log(t)	$\log\{-\ln[1-x(t)/x(\infty)]\}$
-0.2218	-2.269
-0.1079	-1.113
0.00	-0.6304
0.1004	-0.2688
0.2041	0.0344
0.3010	0.233
0.4014	0.3644
0.5024	0.4520
0.602	0.4784
0.6990	0.4579

Table 20 : data obtained from isothermal crystallization at 190°C for PET processed by Brabender blender

log(t)	log{-ln[1-x(t)/x(∞)]}
-0.155	-2.777
-0.1079	-1.920
0.00	-1.237
0.1004	-0.8255
0.2041	-0.472
0.301	-0.203
0.4014	-0.00046
0.5024	0.1405
0.602	0.2446
0.701	0.3144
0.801	0.4003
0.901	0.4777
1.00	0.5962

Table 21 : data obtained from isothermal crystallization at 200°C for PET processed by Brabender blender

log(t)	log{-ln[1-x(t)/x(∞)]}
0.04139	-2.9362
0.1004	-2.108
0.204	-1.323
0.301	-0.8787
0.4014	-0.501

0.502	-0.1568
0.6021	0.0796
0.701	0.259
0.801	0.4186
0.901	0.547
0.9965	0.8292

Table 22 : data obtained from isothermal crystallization at 210°C for PET processed by Brabender blender

log(t)	log{-ln[1-x(t)/x(∞)]}
0.5888	-2.8268
0.602	-1.742
0.7007	-0.6260
0.8007	-0.185
0.9009	0.1195
1.000	0.2955
1.100	0.461
1.200	0.4654
1.301	0.4476

Table 23 : data obtained from isothermal crystallization at 160°C for PET/Halar (99:1) processed by Brabender blender

log(t)	$\log\{-\ln[1-x(t)/x(\infty)]\}$
-0.699	-2.106
-0.62	-1.28
-0.495	-0.575
-0.301	0.099
-0.208	0.295
-0.108	0.431
0.00	0.532
0.100	0.614
0.204	0.745
0.301	0.883

Table 24 : data obtained from isothermal crystallization at 170°C for PET/Halar (99:1) processed by Brabender blender

log(t)	$\log\{-\ln[1-x(t)/x(\infty)]\}$
-0.495	-2.195
-0.301	-0.525
-0.208	-0.105
-0.108	0.191
0.00	0.384
0.1044	0.517
0.204	0.625
0.301	0.762

0.401	0.797
0.480	0.874

Table 25 : data obtained from isothermal crystallization at 180°C for PET/Halar (99:1) processed by Brabender blender

log(t)	log{-ln[1-x(t)/x(∞)]}
-0.301	-2.295
-0.208	-1.356
-0.108	-0.865
0.00	-0.431
0.1004	0.0858
0.204	0.176
0.301	0.329
0.401	0.4380
0.5024	0.513
0.602	0.563
0.701	0.614
0.795	0.779

Table 26 : data obtained from isothermal crystallization at 190°C for PET/Halar (99:1) processed by Brabender blender

log(t)	log{-ln[1-x(t)/x(∞)]}

-0.301	-2.94
-0.108	-1.328
0.00	-0.883
0.1004	-0.522
0.2041	-0.198
0.301	0.0443
0.401	0.221
0.502	0.3485
0.602	0.442
0.701	0.552
0.801	0.709
0.857	0.957

Table 27 : data obtained from isothermal crystallization at 200°C for PET/Halar (99:1) processed by Brabender blender

log(t)	$\log\{-\ln[1-x(t)/x(\infty)]\}$
0.201	-1.346
0.303	-0.638
0.403	-0.260
0.501	-0.00735
0.601	0.152
0.702	0.277
0.800	0.401

0.900	0.531
1.01	0.925

Table 28 : the values of n's and k's in Arami equation for PET and PET/Halar(99:1) system

Temp.	PET				PET/Halar(99:1)			
	stage 1		stage 2		stage 1		stage 2	
	n	k	n	k	n	k	n	k
160	2.75	-1.6	0.93	-0.3	4.2	-2.1	1.31	-0.43
170	3.38	-1.8	1.14	-0.55	2.98	-1.68	1.29	-0.3
180	3.93	-2.3	0.64	-0.18	4.44	-1.55	0.98	-0.7
190	3.22	-2.5	0.91	-0.68	3.52	-0.94	1.5	-1.23
200	4.00	-2.6	1.92	-1.8	5.5	-2.67	1.38	-1.58

3.2.2 Viscosity

A Kayeness capillary rheometer 2052 (manufactured by Kayeness, Inc. Honey Brook, P.A.) was used to measure the melt viscosity of polymers. This rheometer is computer controlled. The samples were dried in oven at 110^{o}C over night. About eight grams of polymer was filled in the heat chamber of the viscosimeter and a packing rod was pushed down the fill tube to push and squeez out as much air as possible.

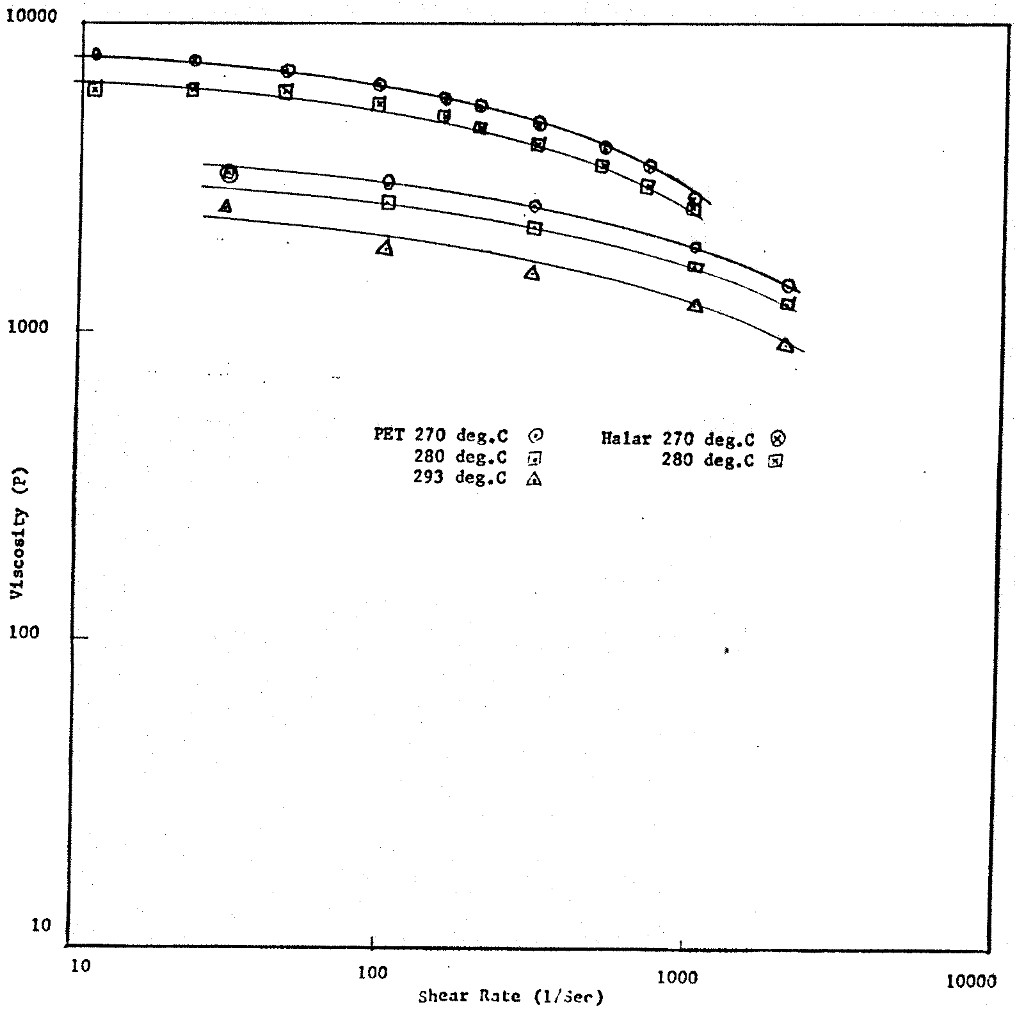

Figure 16 : Melt Viscosity of PET and Halar (without Processed by Injection Molding)

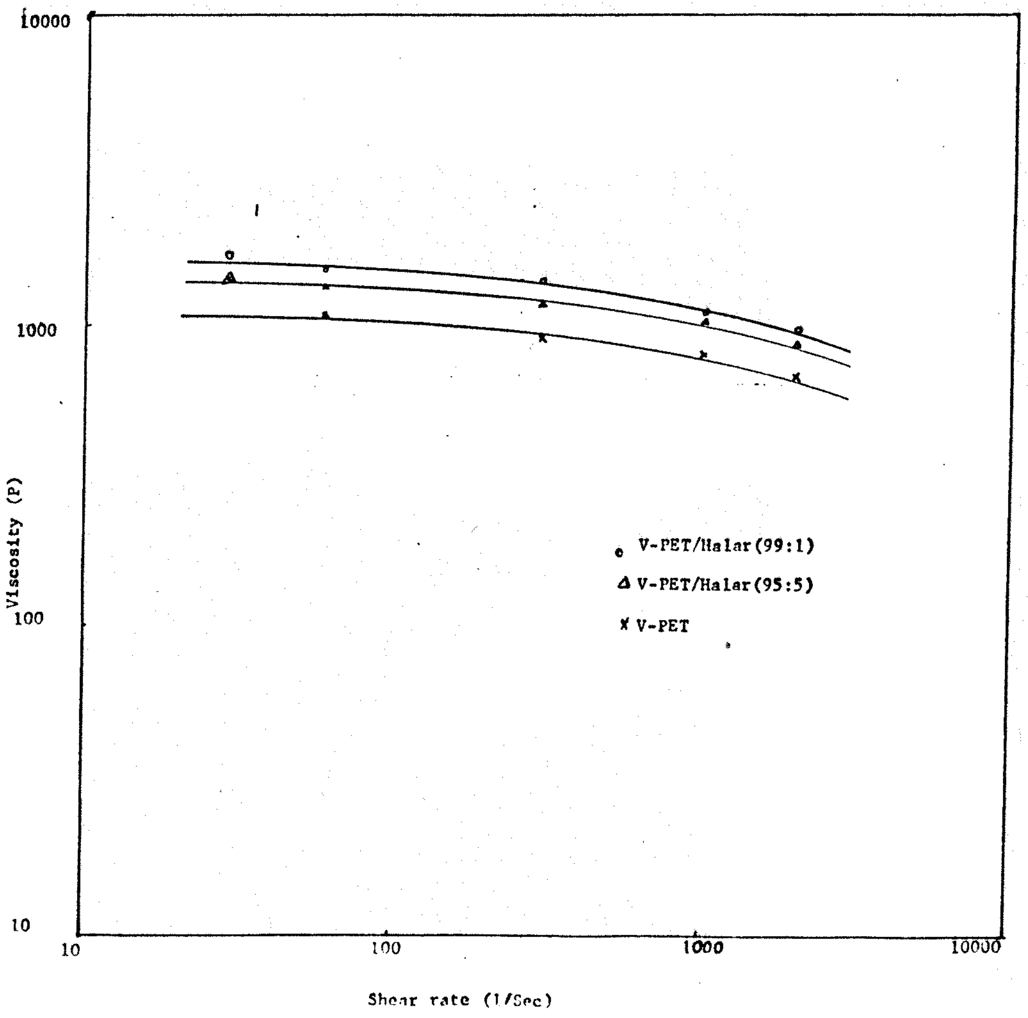

Figure 17 : Melt Viscosity of PET and PET/Halar Blend (99:1 and 95:5) (Processed by Injection Molding)

Melt time of 8 minutes was used (but only 2 minutes for Halar) to insure that the polymer was completely melted. Five shear rates were entered into the computer and the test was started. At the end of test run, viscosity, forces, shear rates were obtained from the computer printout.

Three experiments were run for each temperature and the average value of them is shown in table 29 to 31. A plot of viscosity versus shear rate was made on log-log paper. As shown in fig.16, the viscosity of Halar is much higher than that of virgin PET. The viscosities of PET/Halar blend (99:1 and 95:5) is higher than that of PET and Halar, as shown in fig.17.

Table 29 : viscosity of virgin PET (without processed by injection molding)

Shear rate (1/sec)	270°C	280°C	293°C
30	3326	3302	2533
100	3025	2659	1845
300	2597	2206	1562
1000	1904	1658	1231
2000	1423	1259	922

unit : poise (P).

Table 30 : viscosity of Halar (without processed by injection molding) :

Shear rate (1/sec)	270°C	280°C
11	7931	6066
23	7635	6184
46	7043	6096
93	6355	5511
152	5738	5026
199	5394	4590
304	4741	4084
503	3967	3469
709	3426	3034
996	2719	2606

Table 31 : viscosity of V-PET and V-PET/Halar (99:1 & 95:1) (after processed by injection molding) at 280°C :

Shear rate (1/sec)	PET	PET/Halar (99:1)	PET/Halar (95:5)
29	1372	1657	1349
99	1051	1448	1246
298	883	1309	1107
996	756	1047	975

1992	649	910	828

3.2.3 Microscope

The sample of PET/Halar blend was heated slowly until it melt completely. Under microscope, several small bubbles were observed as shown in fig.18, which should be Halar surrounded by PET because the viscosity of Halar is much higher than PET.

The sample was cooled down and observed under polarized light. Since the amorphous region would be dark and the crystallized region would be bright, the temperature range under which it crystallize can be estimated and compared with the result obtained from DSC. Under cross polarized light, it was found that the crystal of PET/Halar blend was small and its density was very high, as shown in fig.19. Figure 20 and 21 show the crystal of PET and Halar formed from melt.

3.2.4 Injection Molding

Although the immisciblity of PET and Halar may cause the decrease of mechanical properties, it can be a good product if the decrease is not serious. This only can be done after testing the properties of bone-like samples made by injection molding.

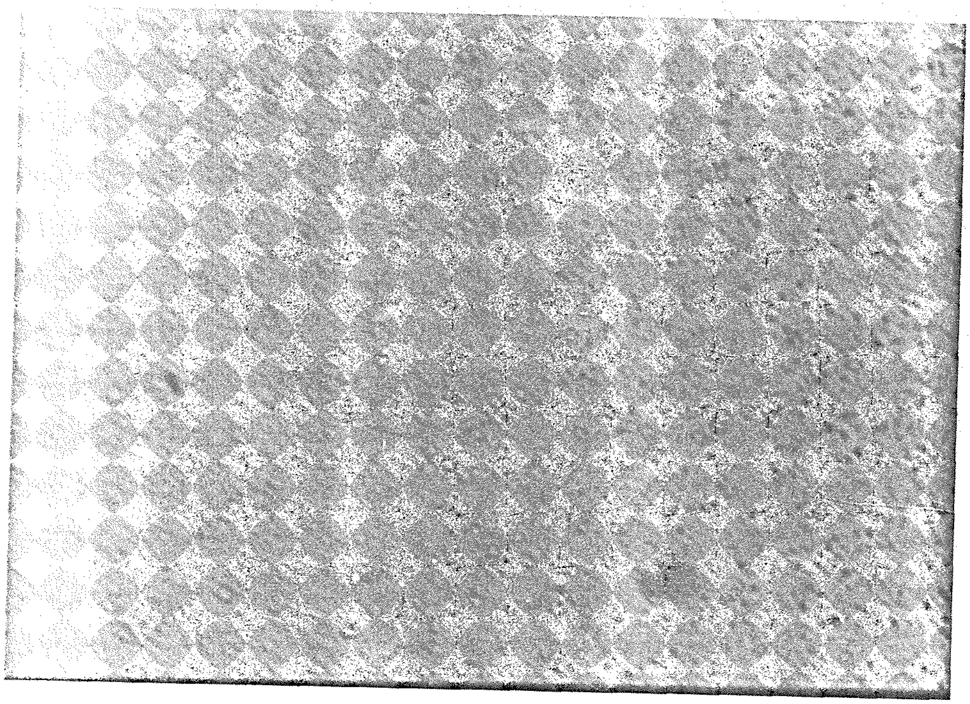

Figure 18 : Photomicrograph Taken at 280°C Showing Phase Separation of Halar Dispersed in a Continuous PET Phase. (x 200)

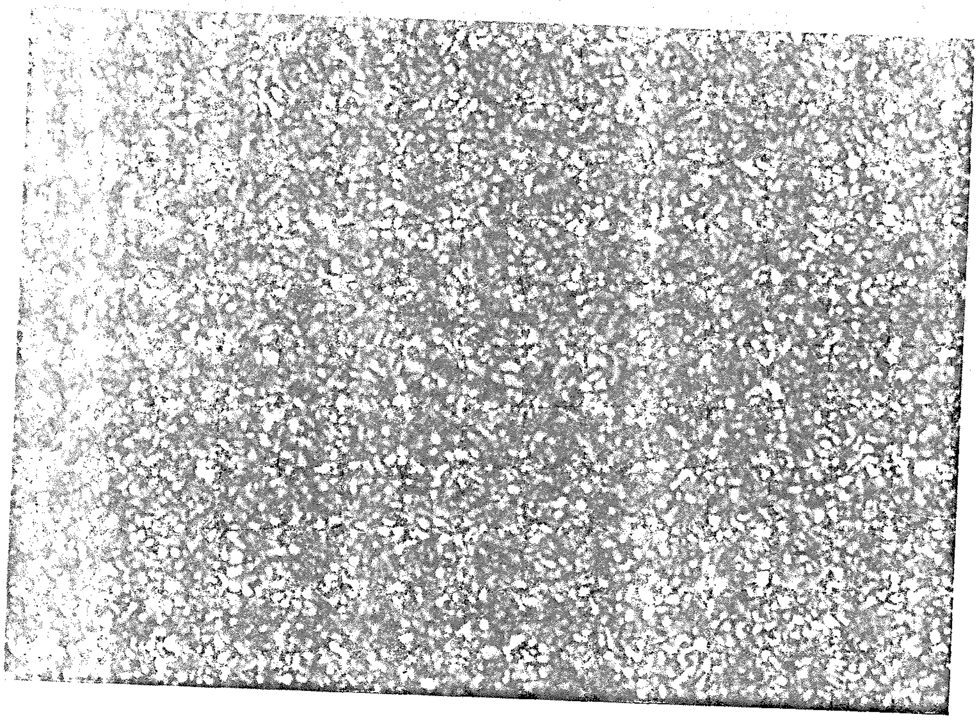

Figure 19 : Crystal Formed from Melt of PET/Halar (99:1) Blend while Cooling from 280°C to Room Temperature Observed in the Optical microscope between crossed polarizers.(x 200)

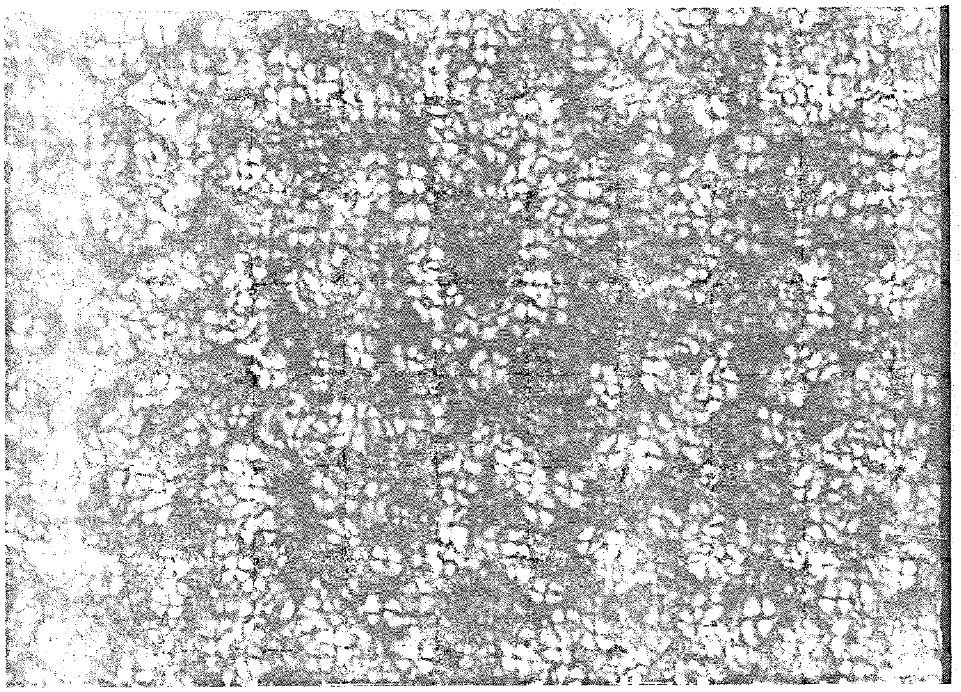

Figure 20 : Crystal of PET Formed from Melt while Cooling from 280°C to Room Temperature Observed in the Optical microscope between crossed polarizers. (x 200)

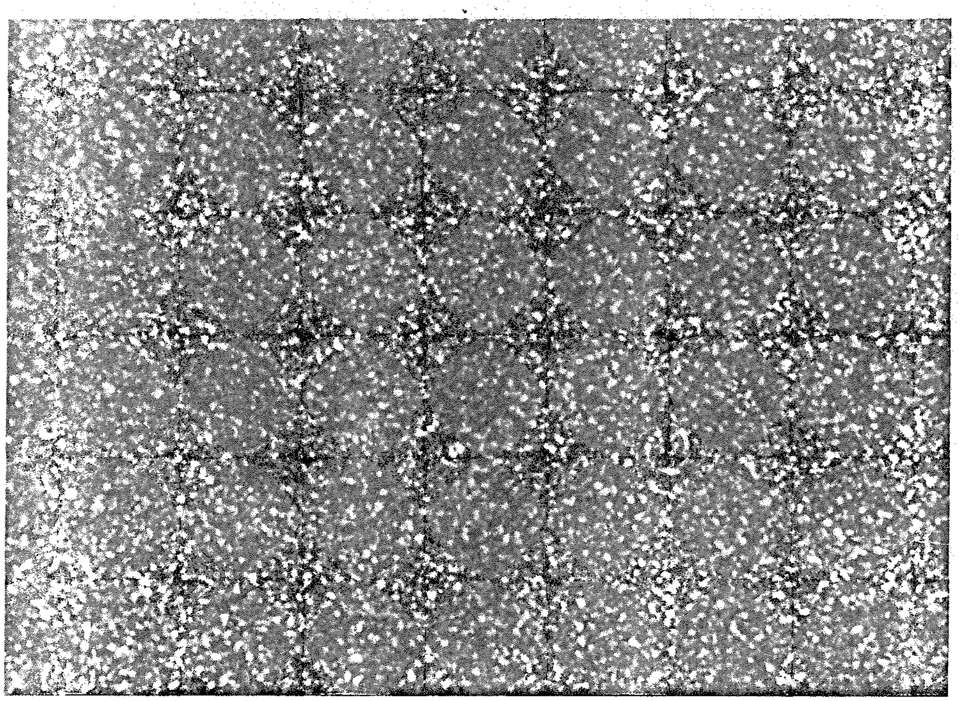

Figure 21 : Crystal of Halar Formed from Melt while Cooling from 280°C to Room Temperature Observed in the Optical microscope between crossed polarizers. (x 200)

After testing mechanical properties, tensile strength, tensile modulus, flexural strength and flexural modulus of polymers can be calculated.

Table 32 : Tensile strength and tensile modulus of PET/Halar (99:1)

Run	Tensile strength (psi)	Tensile modulus (psi)
1	7741	134939.2
2	7520	126017.6
3	7648	125654.4
Ave.	7636.33	128870.4

Table 33 : Tensile strength and tensile modulus of PET/Halar (95:5)

Run	Tensile strength (psi)	Tensile modulus (psi)
1	7392	120718.4
2	7472	123076.8
3	7728	122947.2
Ave.	7530.67	122247.467

Table 34 : Flexural strength and flexural modulus of

PET/Halar(99:1)

Run	Flexural strength (psi)	Flexuarl modulus (psi)
1	11788.8	327680.2
2	11904	329031.68
3	12019.2	349941.76
Ave.	11904	335551.15

Table 35 : Flexural strength and flexural modulus of PET/Halar(95:5)

Run	Flexural strength (psi)	Flexural modulus (psi)
1	11404.8	316416
2	11520	314695.68
3	12096	351682.56
4	11865.6	328642.56
Ave.	7530.67	327859.2

From table 32 to 35, we found that the mechanical strength of PET decrease a little after blending with Halar.

CHAPTER FOUR CONCLUSION

Since the blend of PET/Halar has three peaks for Tcc in nonisothermal DSC curve, it was deduced that PET and Halar are immiscible. From microscopic examination, this deduction was confirmed. From the viscosity tests, it was further confirmed that the small bubbles was Halar because viscosity of Halar is much higher than that of PET. The great difference in viscosity is an important factor that results in the immiscibility of PET and Halar.

Under polarized light, small dots of crystals of high density was observed. This proved that the crystallization was initiated by Halar as suggested before.

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