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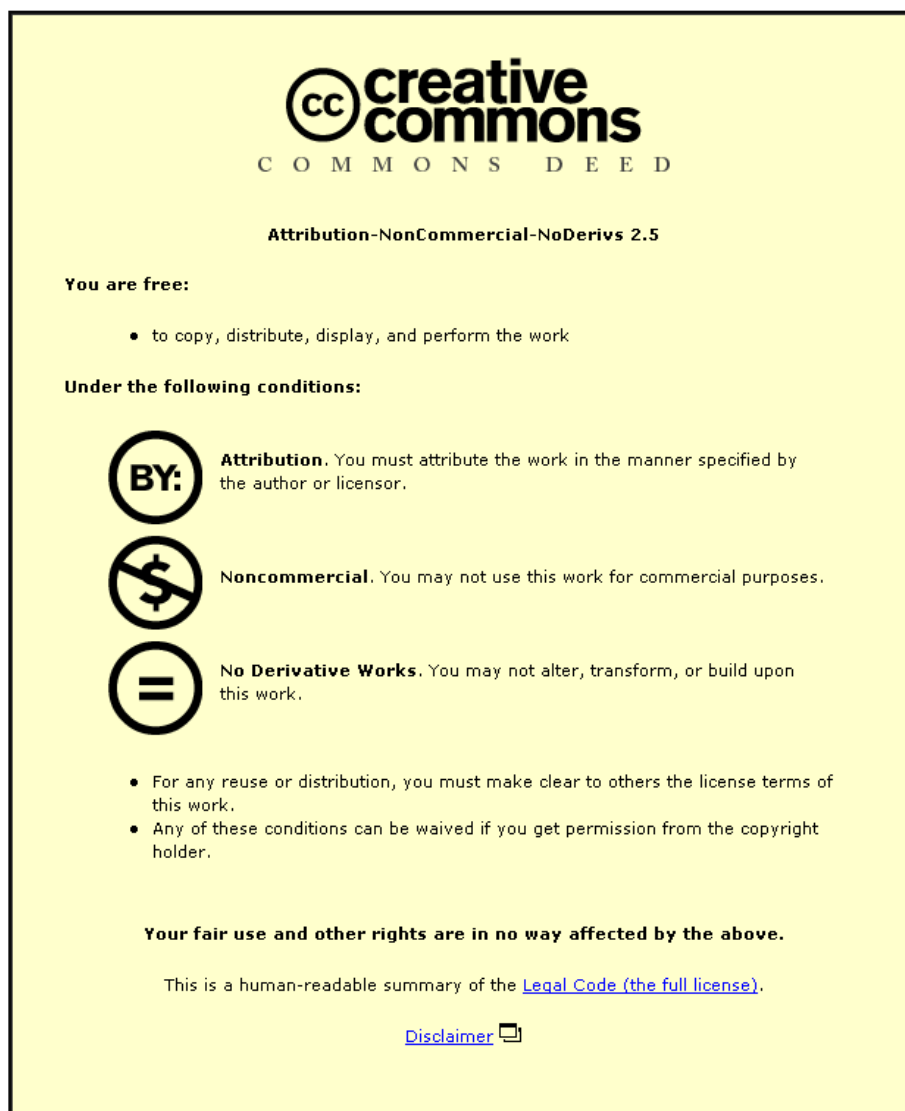
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PLASTICIZATION OF POLY(VINYL CHLORIDE):
PVC/PLASTICIZER COMPATIBILITY AND ITS RELATIONSHIP
WITH PROCESSING AND PROPERTIES OF PLASTICIZED PVC

by

Luis Francisco Ramos-deValle

A Doctoral Thesis

Submitted in partial fulfilment of the
requirements for the award of the degree of

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of the

Loughborough University of Technology

1988

Supervisor: Dr Marianne Gilbert

Inst. of Polymer Technol. and Materials Eng.
Loughborough University of Technology
Loughborough, Leics. LE11 3TU, Great Britain

Certificate of Originality

This is to certify that I am responsible for the work submitted in this thesis, and that neither this thesis nor the work contained herein have been submitted to this or any other institution for a degree.

L.F.Ramos-deValle

to the memory of my dearest father

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SYNOPSIS

The compatibility of suspension PVC with a series of twelve different plasticizers was determined using the estimated values of compatibility predictors, such as the Hildebrand solubility parameter, as well as actual measurements of compatibility, such as the solid-gel transition temperature and the Flory-Huggins interaction parameter. Different relative orders of compatibility were obtained between the plasticizers studied using the two different approaches.

Then, using the twelve different plasticized PVC compounds, the ease of fusion during processing (Brabender mixing and compression moulding) was evaluated and found to be closely related to the PVC/plasticizer compatibility. It was found that the more compatible the plasticizer, the more rapid the fusion during processing, but the higher the torque peak during Brabender mixing. It was also found that the temperature at the fusion peak in a Brabender torque rheometer is closely related to the various parameters used to measure the compatibility, (e.g. the solid-gel transition temperature, the interaction parameter, and the activity parameter). Finally, the rheological and tensile properties of plasticized PVC were determined and it was found that both the rheological and tensile behaviour are highly dependent on the level of fusion of the PVC compound, which in turn depends on the plasticizer type. However, once a high level of fusion is attained, these properties depend more on the viscosity of the plasticizer and the glass transition temperature of the compound.

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Chapter 1

INTRODUCTION

1.1 General

Poly(vinyl chloride) "PVC" was first recognised and characterized more than 100 years ago¹, but due to its poor thermal stability it was not until about 1930, with the development of suitable stabilizer systems, that it started to gain commercial importance. It is now one of the world's leading synthetic polymers, with a total production of about 15 million tonnes in 1980.

Commercial manufacture is mainly by suspension, mass, emulsion, and microsuspension polymerization. The suspension and mass processes both produce a free flowing powder having the same general appearance and a mean particle size around 100 μm . The microsuspension and emulsion processes produce a powder, which while still in latex form has a mean particle size ca 1 μm , but when spray dried, agglomeration occurs and the mean particle size goes up to 50 μm . All PVCs however have particulate substructures.

Suspension and mass PVCs are usually porous and their grains of around 100 μm are made up of much smaller primary particles of around 1 μm .

In the case of microsuspension and emulsion PVCs, the particles still in latex may be considered as primary particles, whereas the agglomerates produced after spray drying may be considered as grains.

The primary particles are in turn made up of even smaller particles. Fibrillar structures have been observed²⁻⁴ at the 0.01 μm size level, and these are referred to as microdomains.

1.2 Suspension Polymerization

By far the majority of PVC is produced by the suspension process. The vinyl chloride monomer (VC) is suspended, as droplets, in a water phase, with vigorous agitation and in presence of a dispersant. A free radical initiator soluble in monomer is used and polymerization occurs within the suspended droplets via a free radical mechanism⁵. The polymerization of VC is very exothermic and thus the ability to remove heat is the limiting factor in attempting to reduce the reaction time.

A simple formulation for suspension polymerization may consist of:

water	150-200	parts by weight
VC monomer	100	
pH regulator	0.05	
dispersant	0.1	
initiator	0.06	

Water is first charged to the reactor. The pH regulator is then added followed by the dispersant. The initiator is then sprinkled onto the aqueous phase immediately before sealing the reactor which is then evacuated to remove O_2 . VC is finally charged and heating up commences. Reaction temperature, which is the main molecular weight control, is commonly between 50-70 C.

When the desired conversion has been reached, usually 75-95% after ca 6 hours of reaction, the reaction is stopped and the remaining VC recovered. The product slurry is treated at elevated temperatures to minimize the residual VC, then dewatered, and finally dried.

Initiation is by means of azo- or peroxy-compounds that decompose to form free radicals at the desired temperature. PVC is insoluble in the VC, therefore it precipitates once a critical size is attained.

It has been reported^{6,7} that the PVC chains that precipitate regroup in numbers of 5-10 macromolecules, forming the microdomains of 0.01 μm . These have a very short half life⁶ after which they reagglomerate to form the primary particles. These primary particles are already formed at conversions of 0.5%.

It has also been reported^{8,9} that at low polymerization rates, a definite substructure is observed within the primary particles, but at high polymerization rates, the primary particles appear smaller and with no obvious substructure. These high polymerization rates correspond to those used commercially and account for the fact that the primary particles appear as solid spheres with no visible substructure.

1.2.1 Effect of Temperature

In absence of other reactive agents, the molecular weight (MW) of PVC is controlled by the polymerization temperature⁸.

As temperature increases molecular weight decreases. In practice, the MW of PVC is expressed as ISO viscosity numbers or as K values, both of which are obtained from simple solution viscosity measurements. Commercially, the K values range between 50 and 75, for which the polymerization temperatures range between 75 and 45 C, the higher temperatures producing the lower K values.

The polymerization temperature also has a profound effect on the porosity of the PVC grains. As temperature increases porosity decreases⁸.

1.2.2 Effect of Conversion

Commercially, conversion varies from 75 to 95%. The upper limit is simply defined by the very low reaction rate beyond this point.

Experiments have shown^{10,11} that the PVC K value changes by no more than 3 units over the range from 10 to 90% conversion. This implies that the K value is determined during the first 10% conversion.

Conversion also has a very large effect on product porosity. Porosity decreases with increasing conversion^{12,13}.

1.2.3 Effect of Dispersant

The dispersant contributes to control of the particle size distribution and also has a major effect on the particle substructure, e.g. porosity¹⁴⁻¹⁶. The primary dispersant usually consist of a water soluble polymer, such as, poly(vinyl alcohol), substituted celluloses, or a mixture. It has been found¹⁷ that the

PVC capacity for plasticizer absorption is related to the surface activity of the dispersant. A dispersant having high surface activity (low surface tension) would produce a PVC of low apparent density but high porosity, and viceversa.

However, the surface activity of these materials is limited and additional secondary dispersants are sometimes used to further increase porosity^{18,19}. Examples are sodium lauryl sulphate and sodium dioctyl sulphosuccinate.

1.2.4 Effect of Agitation

Together with the dispersant, agitation controls the stability of the suspension during polymerization and the particle size of the product. It has been found²⁰ that particle size reaches a minimum with increasing agitator speed. Agitation also affects porosity, i.e. porosity increases with agitation.

1.2.5 Initiator

Most initiators used for VC polymerization decompose by first order kinetics ($d[I]/dt = k_1[I]$). The rate of initiation is proportional to initiator concentration $[I]$, which decreases with time t . The rate constant k_1 is characteristic of each particular initiator and depends on temperature, i.e. as temperature increases k_1 increases. Typical initiators with their corresponding half life times are listed in Table 1.1. [The half life is the time required for a given reactant to decrease its initial concentration to one half]. Initiators with half life times of about 2 hours are commonly used in the polymerization of VC.

Table 1.1 Half-lives of Initiators used in VCM Suspension Polymerisation (48)

Initiator	Half-life (min)		
	50°C	60°C	70°C
Azodi-isobutyronitrile	4200	1080	300
Azobis(2,4-dimethylvaleronitrile)	420	120	35
<i>t</i> -Butyl perpivalate	1300	360	100
Dibutyl peroxydicarbonate	300	70	18
Di(2-ethylhexyl) peroxydicarbonate	250	60	15
Di(<i>t</i> -butylcyclohexyl) peroxydicarbonate	250	60	15
Lauroyl peroxide	3000	800	200
Benzoyl peroxide	—	3000	800
Acetyl cyclohexylsulphonyl peroxide	80	18	4

The most popular initiators are the peroxy dicarbonates.

It has been found^{10,11} that the PVC K value changes by no more than 5 units over the range of initiator concentration of 0.01-1.0%. Initiator concentration in commercial polymerization varies from 0.01 to 0.1%. This means that the K value (i.e. the MW) is apparently not affected by initiator concentration.

1.2.6 Oxygen

Oxygen has to be removed from the reactor since it is a very powerful inhibitor of the VC homopolymerization. In its presence, VC copolymerizes with O₂ to give poly(vinyl chloride peroxide) (-CH₂-CHCl-O-O-), which decomposes to give HCl, and unsaturated and carbonyl containing PVC molecules.

1.3 Morphology of PVC

The terminology used to describe the PVC morphology is summarized by Geil²¹ and by Allsopp²². Figure 1.1 gives a simplified representation of a PVC grain.

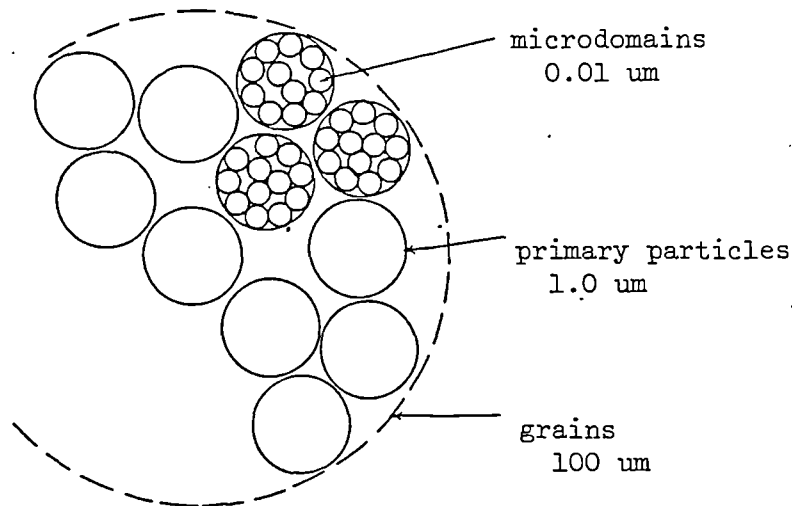


Fig.1.1. Schematic representation of a PVC particle. (21/22)

In suspension polymerization, many combinations of agitation regimes and dispersant systems are possible, but in essence 3 main routes occur²²;

- route 1: Monomer droplets are extremely well dispersed and are completely stable against coalescence, and remain as individual droplets to give a spherical fine sub-grain of low porosity.
- route 2: An intermediate level of dispersion is applied so that the droplets undergo controlled coalescence to produce a grain of irregular shape, intermediate size, and higher porosity. A wide variety of products can be prepared by minor variations in the agitation regime/dispersant system combination.

--route 3: Inadequate dispersion is applied and the droplets coalesce freely at low conversion to give eventually one large grain the size of the reactor.

On a macro scale, Tregan and Bonnemayne²³ have presented a useful classification of the possible structures of PVC. This classification is reproduced in Figure 1.2.



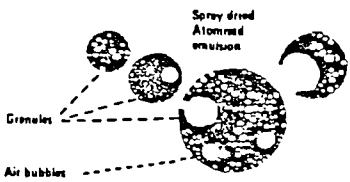
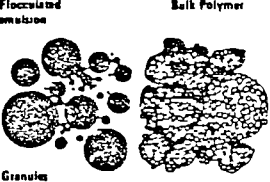
CELLULAR GRAINS (SUSPENSION)			
Microstructure & transparency of particles immersed to equilibrium in DOP	UNICELLULAR	MULTICELLULAR	PARACELLULAR
	Closed pore opaque grain - "Black". Two media with very different refractive indices air □ solid ■ Pronounced light dispersion		
	Open pore semi-opaque grain - "Translucent". Two media with similar refractive indices liquid □ solid ■ Slight light dispersion	Inter A	2 A
	Non-porous transparent grain - "Clear". Spherical droplet with homogeneous refractive index solid ■ No light dispersion	Inter B	2 B
	1B		
	1T		
	1C		
NON-CELLULAR GRAINS (EMULSION-BULK)			
Spherical			
Undefined			

Fig.1.2. Classification of PVC grains, (23)

A sample of PVC is immersed in DOP, and after equilibrium swelling it is viewed at low magnification (x100) by transmitted light. This permits classification of PVC grains into 3 basic structures:

blacks.- Grains containing closed pores which are not wetted by DOP, leaving entrapped air within the grains. This gives two regions of marked refractive index difference. Pronounced diffraction occurs at the PVC-air interface, giving rise to black zones.

translucent.- Grains containing a great amount of open pores, giving two regions of very similar refractive index. Slight diffraction occurs at the PVC-DOP interface, giving rise to a translucent appearance.

clears.- Solid grains containing little or no porosity. The refractive index of the grain interior is constant (that of PVC). Diffraction occurs only at the surface, giving a clear appearance.

As polymerization conditions tend to route 2 the translucent type is more typical, whereas for route 1 the clear type tends to be typical.

1.3.1 Suspension Polymerization: Macro Scale

The combination of agitation regime and dispersant system will determine the mean size of the VC droplets in suspension, which usually ranges from 5 to 150 μm , and will in turn determine the extent to which the reaction follows route 1 or 2. In any case, experiments have shown that a membrane forms around the droplets, which becomes more coherent with conversion. At ca 30% conversion the membrane is strong and stable. During this time, density changes within the droplets, as VC (850 kg/m^3) converts to PVC (1400 kg/m^3). This 40% contraction can be absorbed in two ways²². A uniform contraction of the droplet can occur progressively throughout the reaction, but this would produce a solid grain with almost no porosity.

Alternatively, this contraction can be arrested by forming an open structure at the time the primary particles coagulate. As this structure becomes stronger with conversion, it reaches a point where it is sufficiently coherent to resist the forces of contraction and the volume of the grain is fixed. All other changes in density, otherwise leading to uniform contraction, will create porosity. At ca 65% conversion the remaining VC is dissolved in the PVC grains, and as polymerization proceeds (i.e. VC converts to PVC) the pressure within the grains decreases and the grains collapse with folding and rupturing of the surface.

Changes in the macro scale level of structure have a marked influence on the bulk properties of the polymer, such as: particle size, particle size distribution, apparent density, and powder flow.

1.3.2 Suspension Polymerization: Micro Scale

Within the VC droplets, the first PVC that forms coagulates to form 0.1 μm particles at conversions below 2%. These particles remain discrete and stable, but as conversion reaches 5-10% they become unstable and flocculate to form agglomerates of ca 1 μm . Depending on the polymerization conditions, different arrangements of these agglomerates are possible. Loose packing will produce highly porous grains while close packing will produce grains of low porosity.

Both temperature and agitation have a marked influence on the grain structure²². Although temperature is mainly used to control the molecular weight, it also has an effect on porosity, i.e. as

temperature increases porosity decreases. Besides, as the level of agitation increases, the grain structure changes from dense and spherical to porous and irregular.

Changes in the micro scale level of structure have a marked influence on many polymer properties, such as; porosity, surface area, plasticizer absorption capacity, and ease of fusion.

1.3.3 Suspension Polymerization: Sub Micro Scale

The main features of interest at this scale are the microdomains, ca 0.01 μm in size, and the domains, ca 0.1 μm . The existence of the microdomains has been reported by various authors^{3,24-26}. Examination of suspension and mass PVC, obtained at very low conversions, has shown clear evidence of the existence of the 0.1 μm domains²⁷, which have also been reported on commercial PVC²⁸⁻³⁰.

Evidence for the existence of domains in plasticized PVC has been provided by Geil and coworkers^{31,32}. This confirms that the 0.1 domains are real entities.

It has been suggested that there is a crystalline nucleus associated with the basic microdomain structure. Using laser Raman spectroscopy on material isolated at ca 2% conversion, (as mentioned above, at ca 2% conversion the sample consists largely of 0.1 μm particles, i.e. domains), it was shown that this material is indeed more crystalline²⁷. X ray measurements on PVC showed a two phase structure consisting of crystallites in an amorphous matrix³³.

The arrangements of crystallites can exhibit various degrees of order which depend on the thermal history. Annealing enhances crystallinity and produces a certain degree of order. Without annealing, the crystalline arrangement remains disordered.

In commercial PVC powder, the 1 μm primary particles are easily identified but not the other smaller species. After processing however, in addition to the primary particles, the 0.1 μm domains are also observed. This in turn suggests that the 0.1 μm domains retain their original identity even after processing.

Changes in the sub-micro scale level of structure have a marked influence on some polymer properties, such as: hot plasticizer absorption, solvent dissolution, and flow and viscoelastic properties of the melt.

1.3.4 Summary

The size and shape of the final grain depend largely on the macro scale morphology produced in the droplet coalescence step. This depends on the extent to which the reaction follows route 1 or 2. Depending on the macro scale morphology a variety of structures can be obtained. a).- Following route 1, various degrees of flocculation can occur within the VC droplets to give 1C, 1B, or 1T grains, according to Figure 1.2. The final type of grain will depend on polymerization conditions. b).- Following a route intermediate between 1 and 2, coalescence starts to occur amongst VC droplets, and depending on polymerization conditions, inter A or inter B grains are obtained. c).- Following route 2, 2A grains will be produced.

Most commercial PVCs for flexible applications tend to consist of inter A and 2A type grains, having high porosity and surface area. For rigid applications on the other hand, they tend to consist of inter B or 1T type grains, which have lower porosity and higher apparent density.

Control of morphology on the micro and sub-micro scale is not as well established as in the macro scale; nevertheless, temperature, agitation, and the presence of dispersants do have a considerable effect. In suspension polymerization the change in morphology in one scale is often reflected by changes in morphology on the other scales. This interrelationship must always be considered in total, no one parameter can be changed independently from others.

1.4 Crystallinity

The first proof of crystallinity in commercial PVC was shown by Natta and Corradini³⁴. In addition, they noted a strong tendency for the C-Cl groups of PVC to arrange themselves in a syndiotactic configuration. Later it has been reported that syndiotacticity may reach ca 50% in commercial PVC³⁵.

There are differences of opinion concerning the amount of crystallinity in commercial PVC, however most workers consider it to be around 10%.

Juijn et al^{36,37} and Keller et al^{38,39} have proposed that crystallinity of PVC consist of relatively well developed crystals and less well developed crystals. These were designated by Keller

et al as A and B crystals respectively, and by Juijn et al as primary and secondary crystallinity respectively. Juijn et al also suggested that primary crystallinity is converted to secondary crystallinity during processing.

The existence of a para crystalline structure has also been reported⁴⁰. This is considered as nematic or smectic liquid crystals. The extent of this para crystalline structure will depend on the thermal history of the material³⁶.

Crystalline melting points, obtained by various extrapolation techniques^{41,42}, are between 205-235 C.

Nardi⁴³ determined the crystallinity of an unplasticized PVC sample to be 10%, but on stretching this to 500% to form a fibre, he found that crystallinity had increased to 40%. On further treatment with ultrasonic irradiation (for 6 min) the crystallinity increased to 70%. Apparently, the structural ability for greater crystallinity was always present, but mobility of the polymer chains was inhibited by the rigidity of the structure.

Plasticization aids mobility and facilitates chain reaccommodation into ordered segments and thus will tend to increase crystallinity⁴⁴.

In 1949, Alfrey et al⁴⁵ reported that PVC plasticized with trioctyl phosphate showed definite crystallinity, and orientation increased this crystallinity. They concluded that plasticized PVC exhibits a 3-dimensional gel structure where crystallites act as physical crosslink points, and that

the mechanical properties of a given formulation can therefore be considerably altered by suitable recrystallization procedures.

Processing can also affect crystallization. As processing (milling, mixing, or extrusion for example) tends to decrease the entanglements, the PVC macromolecules tend to orient in the direction of flow, and this in turn will favour the development of molecular order. This order may be crystalline or para crystalline.

Hosada⁴⁶ demonstrated the effect of milling on the crystallinity of a PVC compound with 20 phr DOP (dioctyl phthalate). [In order to measure the crystallinity, he first assumed that this will act as physical crosslink points, and then measured the crosslinking level by swelling the PVC samples in DOP at 85 C]. He found that while milling at 160C, the crystallinity increased with milling time. That is, milling time increased orientation, which in turn increased the molecular order. Milling above 160C decreased the amount of crystallinity due to melting.

This ability to crystallize tends to decrease with higher plasticizer concentrations³⁶.

It appears therefore that the ability to crystallize tends initially to increase with the addition of plasticizer⁴⁴, but after a certain point this ability tends to decrease with further addition of plasticizer³⁶. This crystallinity produces a network structure which imparts the toughness and strength characteristic to plasticized PVC⁴⁷.

1.5 Fusion: Effect of Temperature, Pressure, and Shear

PVC must undergo fusion in every fabrication process in order to achieve its best mechanical properties. During this process of fusion the PVC polymer passes from a grain structure with very poor mechanical strength, to a fused mass with a high degree of molecular entanglement possessing very good mechanical strength.

This process of fusion is affected by a combination of such external parameters as temperature, pressure, and shear.

Starting with a dry blend, if heat is applied alone, little change occurs until a temperature of ca 150 C is exceeded. Then loss of porosity and increase in density are observed⁴⁸.

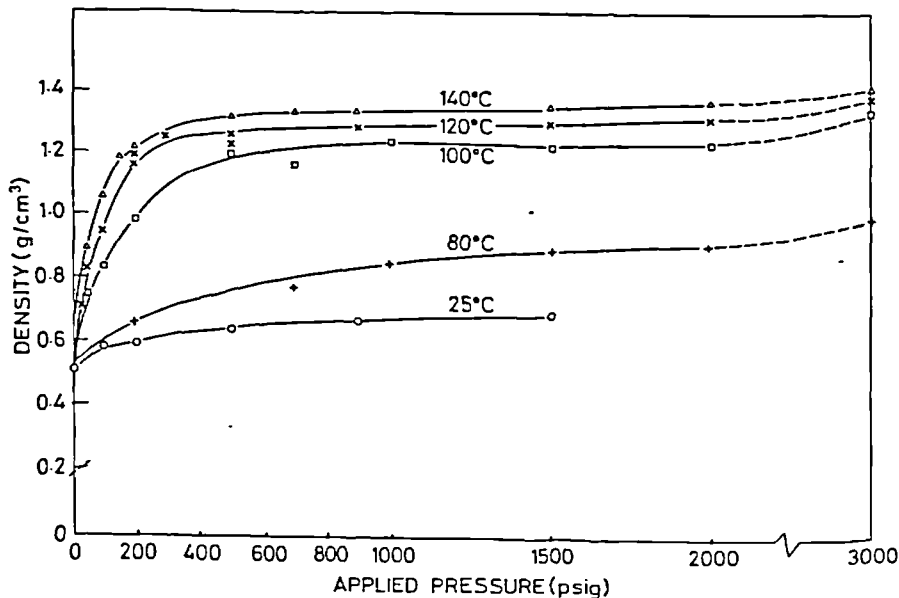


Fig.1.3. Densities of 'Corvic' S67/111 mouldings produced at different temperatures and pressures. (48).

When heat and pressure are applied together, for example, increase in density occurs at temperatures as low as 100 C, at pressures ca 3.5 MPa (35 Kg/cm²). This is shown in Figure 1.3⁴⁸.

Apparently, the lowest temperature for an appreciable increase in density to occur, as the applied pressure increases, is limited by the T_g (glass transition temperature). But the more the temperature exceeds T_g, the lower the applied pressure needed to produce an appreciable increase in density.

If shear is applied, significant changes occur⁴⁸. At low pressures, there is low compaction and shear is not transmitted through the powder material. At higher pressures, more compaction results and shear can now be transmitted more effectively through the material, resulting in higher temperatures and more fusion.

Higher temperatures will tend to shift the whole process to lower pressures, due to the onset of fusion making transmission of shear more effective, even at low pressures.

In extrusion for example, the more rapidly the dry blend reaches a temperature in excess of ca 120 C, the lower the pressure required to compact the powder and make the transmission of shear effective. Once the shear component is added the rate of fusion increases rapidly.

Under conditions of transmission of shear, the higher the applied shear, the more rapidly a given level of fusion is achieved. Besides, the shear exerted on a material depends on its melt viscosity, i.e. at

given operating conditions, the shear increases with the melt viscosity of the material.

The effect of different combinations of temperature, pressure, and shear on the fusion characteristics of PVC are described below using a single screw extruder and a Banbury internal mixer.

1.5.1 Fusion in a Single Screw Extruder

A given PVC formulation was processed in a single screw extruder. After a given processing time, the extruder was stopped and cooled down. Then it was stripped and the state of the sample was examined along the screw and die⁴⁸.

It was found that in the first part of the screw the powder is simply compacted. Further along the screw the PVC grains start to show a high level of densification, with the additives distributed at the grain surface. Mid way along the screw, grain densification is complete, with almost complete fusion of the grains, but the additives still remain concentrated at the grain surface. Between the end of the screw and the forward side of the breaker plate the grains become highly elongated and homogenization of PVC and additives becomes very good. The material that leaves the die is thus a well fused and homogeneous material.

1.5.2 Fusion in a Banbury Internal Mixer

A given PVC formulation was processed in a Banbury and discharged at different temperatures between 110 and 200 C for examination⁴⁸.

It was found that between 110 and 140C, Comminution of the grains is dominant and this leads to the formation of agglomerates, which consist of bound fragments of comminuted grains. At 140 C, the agglomerates accounted for the majority of the mass and the remainder consisted of fragments of grains. The primary particle structure was maintained and there were signs of densification. Between 140 and 170C densification of primary particles took place, but the primary particle structure was still evident. The additives were well dispersed throughout the matrix. At 180C, the sample was highly densified but the primary particle structure may still be observed. Finally at 200 C, the sample consisted of an apparently homogeneous fused matrix. No memory of primary particle structure was found and the additives were uniformly distributed.

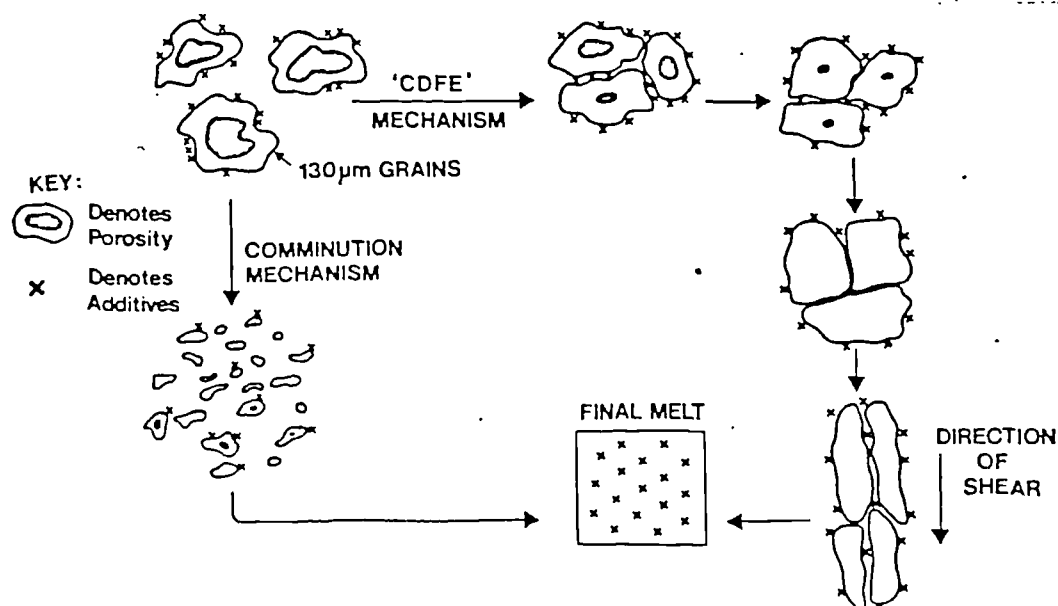


Fig.1.4. Mechanism of gelation during processing. (48),

The mechanism of fusion proposed by Allsopp is summarized in Figure 1.4. If conditions are such that shear is applied before densification is complete, e.g. Banbury and Brabender mixing, grain comminution results, but if grain densification is complete before shear is applied, e.g. extrusion, two roll milling, and compression moulding, then compaction-densification-fusion-elongation (CDFE) results⁴⁸.

1.5.3 Breakdown of the Particulate Structure and Development of the Molecular Network

During mixing in a Brabender torque rheometer, a PVC compound is subjected to temperature and shear and it passes through all the stages of fusion. According to Faulkner², these may be studied by examining the torque changes as a function of temperature.

The rate at which temperature and shear affect the grains depends on; powder to powder and powder to metal friction, cohesion of the primary particles within the grains, and size and distribution of the grains. At any rate however, the grains will be broken down.

As the process of mixing commences, breakdown of grains proceeds and a point is reached at which the ratio of the remaining grains to the newly released primary particles passes through a value which results in a maximum of the packed density of the mix. At this point the torque - temperature trace shows a relatively small torque peak.

The further influence of temperature and shear will start to break down the primary particles. At this

point Faulkner observed the development of a mixture of primary particles in a matrix of what appear to be the microdomains. A point is now reached at which the ratio of the primary particles to the microdomains passes through a value which results in a maximum of the packed density of the mix. A relatively large torque peak appears at this point which is usually referred to as the "fusion peak" (Figure 2.3).

Beyond the second peak breakdown continues, the primary particles largely disappear, and a third relatively small torque peak appears, at which point Faulkner identified a mixture of microdomains in a matrix of true melt. He showed that the temperature at which this peak occurs is related to the PVC molecular weight and to the applied shear. In addition, he demonstrated a similar relationship between the point at which the activation energy for flow changes (from low to high), and the PVC MW and the applied shear. He inferred from this, a relationship between the third peak and the change from particulate flow (with low activation energy) to molecular deformational flow, i.e. melt flow, (with high activation energy).

True melt flow behaviour should be found at this peak and beyond. At this stage however, thermal degradation of PVC tends to obscure the details.

The microdomains initially contain the molecular chains localised by the crystallites. But as temperature increases, the crystallites start to melt and the molecular chain mobility increases. Shear also begins to destroy the particle boundaries, which permits diffusion of chains across the fading boundaries and promotes entanglements with chains from

other domains. The greater the heating and shearing, the more the diffusion and entanglement of chains between different domains.

The molecular manifestation of increasing fusion during processing is therefore, increasing molecular mobility and hence increasing entanglement. On cooling, the crystallites are reformed from chain segments, and the newly formed network is fixed in place. The degree of fusion thus can be measured by the degree to which this network is formed.

1.5.4 Fusion and Melt Rheology

The melt rheology of a PVC compound is highly dependent on the state of fusion of the PVC. Berens and Folt⁴⁹⁻⁵¹ studied the flow of PVC in a capillary rheometer and identified the particulate flow. They found that some particles survived even after extrusion at temperatures around 180 C. When testing emulsion PVC for example, the surviving particles were similar in size to the original particles, i.e. ca 1 μm . With suspension PVC however, the original grains (ca 100 μm) had disappeared and the surviving particles were similar in size to the primary particles, i.e. ca 1 μm . They noted that the die swell increased monotonically with the extrusion temperature. Berens and Folt explained this assuming decreasing dependency on particulate flow and increasing dependency on molecular deformational flow.

The work of Berens and Folt explained the flow "anomalies" previously reported⁵²⁻⁵⁵ by many investigators and remains the basis of present understanding in relation to the flow of PVC⁵⁶⁻⁶⁰.

The change from particulate flow to molecular deformational flow is accompanied by a change in the activation energy for flow, from relatively low to relatively high respectively.

Using EM and X ray analysis, Singleton et al^{31,61} identified the 0.01 μm microdomains in plasticized PVC. They found that compression moulding seemed to increase the microdomain size, whereas injection moulding destroys them. Extrusion above a certain temperature " T_f " resulted in the destruction of the microdomains, whereas below T_f the microdomains persisted. Then they plotted the apparent melt viscosity versus the inverse of the extrusion temperature and observed a noticeable change in slope, i.e. in the activation energy, at T_f .

Soni⁶² found that in samples processed below T_f , the plasticizer concentrates in the areas between the 0.01 μm microdomains. He suggested that the microdomains contained a crystalline core which constrained the molecular structure and prevented the absorption of plasticizer. He demonstrated that when processed above T_f , the microdomains are destroyed and the plasticizer homogeneously distributed in the PVC.

The melt viscosity of a fully fused PVC compound increases with the PVC MW and decreases with the plasticizer content^{56,63}. As with many other thermoplastics, the melt viscosity decreases with increasing temperature and shear rate^{56-60,63}.

As mentioned above, the melt viscosity is affected by the state of fusion. Incomplete fusion will result in particulate flow, whereas complete fusion will result in molecular deformational flow. At a given

test temperature, the viscosity of a completely fused compound will be greater than when fusion is not complete^{64,65}.

1.6 Assessment of Fusion

Fusion of PVC is the progressive breakdown of particulate structure, with the parallel development of a molecular network. The state of fusion achieved can therefore be assessed either by noting the state of particulate breakdown or by noting the state of molecular network formation⁶⁶.

1.6.1 Electron Microscopy (EM)

The most obvious way to study the breakdown of particles in PVC, is simply to observe this with a microscope. One instrument is the Scanning Electron Microscope (SEM), but it is essential that the specimen preparation is carried out in the right manner. For example, it is recommended to examine the metal coated surface of a sample previously fractured at ca 100 C below its Tg. The main limitation though, is that only a very small area of the sample is examined. EM has been widely used to study the morphology of PVC^{2,31,32,61,67}.

1.6.2 Brabender Mixing

Another device to assess the progress of fusion is the Brabender mixing chamber⁶⁸. The mode of operation can be either temperature programmed Brabender mixing² or the modified Brabender mixing described below⁶⁹.

The reference dry blend is placed in the Brabender mixing chamber, which is at a predetermined high temperature, e.g. 180 C. Mixing commences and the temperature of the PVC sample will rise from room temperature to the mixing chamber temperature and will slightly exceed it until a heat balance is reached between the sample and its surroundings. The resultant plot of torque versus temperature will show the essential fusion peak, and will be the reference fusion curve.

Any other sample to be assessed for fusion is first reground and then processed in the Brabender mixing chamber, as described above, to obtain its torque-temperature trace. The basis of the test is to compare the two curves. It is found that after differences at the lower temperatures, the sample curve joins the reference curve, and the point at which they rejoin indicates the state of fusion of the sample. The higher the temperature at which they rejoin, the higher the state of fusion of the sample. Comparisons however are subjective and interpretation is not always easy. Furthermore, the formulation of the reference dry blend has to be the same as that of the sample.

1.6.3 Optical Microscopy

Summers et al^{70,71} developed a technique for the identification of primary particles and the assessment of the state of fusion of a PVC sample, by first swelling the processed samples in acetone, then shearing the swollen samples between glass slides, and finally examining them through an optical microscope.

An effective discrimination can be carried out between unagglomerated primary particles, agglomerated primary particles, and an apparent continuous mass, in samples processed respectively at lower, intermediate, and higher temperatures.

1.6.4 Capillary Rheometry

This is intended to examine the elastic effects of the PVC compound, which in turn are due to the formation of a molecular network⁷²⁻⁷⁵. The equation that applies is:

$$P = 2 \sigma (L/R) + 2 \sigma (n + S_r/2) \quad (1.1)$$

where P is the pressure needed to extrude a sample through a die of length L and radius R, σ is the shear stress at the die wall, and n is the Couette viscosity and S_r the recoverable shear strain⁷⁶. It can be said that the first term represents the viscous effects, whereas the second term represents the elastic effects. If a die with a very short L/R is used, the elastic term predominates. Besides, the testing conditions can be such that the elastic effects of the PVC sample are enhanced over the viscous effects. Elastic effects are enhanced by lower temperatures and higher shear rates. [Apart from the fact that the test temperature has to be above the T_g of the sample, the combination of temperature and shear rate is determined by equipment limitations].

Samples of varying levels of fusion are first prepared by processing a PVC dry blend at different temperatures, e.g. from 130 to 200 C. The processed samples are then tested in the capillary rheometer, and

the pressure "P" needed to extrude each sample is recorded. A plot is finally prepared of the extrusion pressure versus the processing temperature, to give a reference fusion curve similar to the one shown in Figure 1.5. This reference curve can now be used to evaluate the degree of fusion of other samples of exactly the same formulation and processed in the same equipment as the reference.

A sample of unknown fusion will give a pressure "P_{sample}", and its degree of fusion is determined as:

$$\% \text{fusion} = (P_{\text{sample}} - P_{\text{min}}) / (P_{\text{max}} - P_{\text{min}}) \times 100 \quad (1.2)$$

where P_{max} and P_{min} refer to the maximum and minimum pressures in the reference curve.

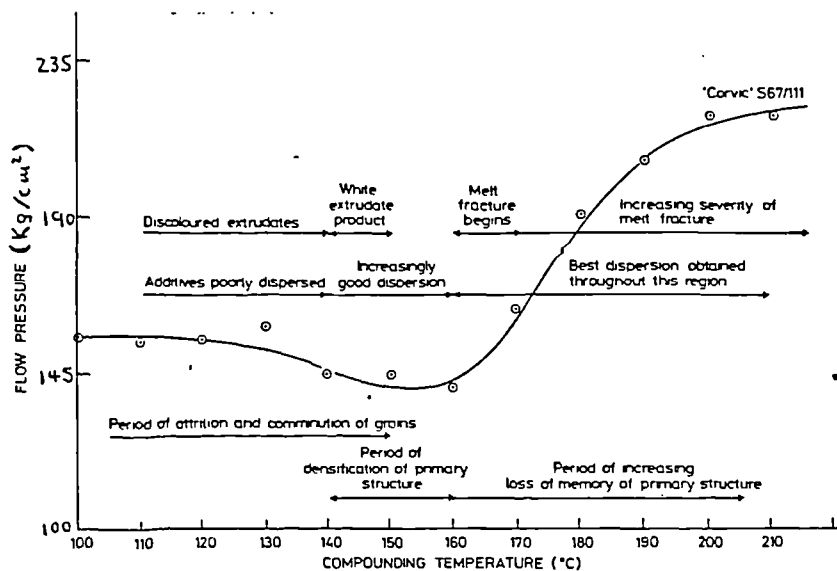


Fig.1.5. The zero length die flow curve of 'Corvic' S67/111 (subdivided into regions on phenomenological and morphological features). (48)

Application of the CR (capillary rheometry) experiment to plasticized PVC produces the same type of S shaped curve as with unplasticized PVC, but with a considerable shift to lower temperatures^{75,77,78}. At the same time, the maximum pressures decrease with plasticizer concentration.

SEM examination⁷⁵ of samples processed at different temperatures shows that at 90 C the grains are still intact (at the minimum in the CR curve). At 115C the primary particles are clearly visible and some have been drawn to form fibrils (going up in the CR curve). At 160 C melting of the primary particles is widespread, but their structure is still visible (near the maximum in the CR curve). At 190C a formless matrix is observed and fusion appears complete, at least at the scale of the primary particles (coming down in the CR curve, after the maximum).

1.6.5 Extrudate Distortion or Melt Fracture

In this respect, Rudin^{64,79} derived the equation:

$$D/D_o = \exp[-4L / (R\dot{\gamma} \tau)] \quad (1.3)$$

where D is the observed severity of extrudate distortion of a material extruded through a die of length L and radius R at a shear rate $\dot{\gamma}$, and D_o is the corresponding severity of extrudate distortion with a die of zero length and same radius. τ is the relaxation time characteristic of the material. This equation predicts, that the extrudate distortion will increase with the relaxation time.

The relaxation time is affected by the process of entanglement/disentanglement. That is, entangled molecules will increase the relaxation time, since a disentangled molecule can adjust to a relaxed position faster than an entangled molecule.

Since fusion of PVC is accompanied by the development of entanglements between PVC molecules, the process of fusion can be followed by measuring the extrudate distortion of PVC samples processed at different temperatures.

However, shearing during processing tends to reduce the entanglement (combing out effect)^{46,79,80}, so that during processing at a given temperature, the extrudate distortion will tend to be more severe in samples processed at low shear than in samples processed at high shear.

1.6.6 Solvent Testing

If either an unfused or a fully fused PVC sample is put in a suitable solvent, it will swell,

but the mechanical effect of such swelling will depend on the extent of fusion of the PVC sample. In a well fused sample, the swelling will have little effect on the cohesion of the sample due to the restraining effect of the molecular network. In a poorly fused sample, this swelling will now cause some disintegration of the sample due to the lack of a molecular network that holds the particles together. This is therefore very well suited to distinguish between a poorly fused and a well fused sample. Nevertheless, it is difficult to try to distinguish between different well fused samples⁸¹.

Acetone is the most widely used solvent for swelling of PVC samples, though methylene chloride and methyl ethyl ketone have been suggested as alternatives.

The test specimens should be "well cut" pieces of the final product. For example, any heterogeneity of the degree of fusion in a pipe may be missed if a whole piece of pipe is used, since the outside surfaces are almost always fully fused and will contain the disintegration of the possibly less well fused inner particles.

1.6.7 Dynamic Mechanical Analysis

This is a well known method for studying the viscoelasticity of the materials. The dynamic shear modulus G , and its elastic G' and viscous G'' components can be measured. G' is related to the elastic recoverable deformation of the material, whereas G'' is related to the viscous non-recoverable deformation.

If a PVC sample were tested, a relationship between G' and the degree of fusion would be expected. Den Otter⁸² found that G' changed with fusion level. First, a rigid PVC formulation was extruded at different screw speeds. Then he found that the G' of the extruded samples increased with the screw speed, i.e. with the state of the fusion of the sample. [He assumed that the higher the screw speed, the higher the state of fusion of the extrudate].

At the same time, lower test temperatures were more discriminating in showing up the differences in the state of fusion (around 140 C in his case).

1.6.8 Thermal Analysis

The most recent method for measuring the state of fusion of a PVC sample was reported in 1981 by Gilbert and Vyvoda⁸³.

In this test, PVC samples processed at different temperatures, are examined in a Differential Scanning Calorimeter from ca 20 C to ca 240 C, at 20C/min. Two endothermic peaks are observed, which correspond to peaks A and B in Figure 1.6. Endotherm B represents the melting of the relatively well developed crystals, or primary crystallinity according to Juijn et al^{36,37}. The nature of endotherm A is not yet fully understood but it is suggested⁸³ that it is due to the formation of imperfect ordered regions, which are produced as a PVC network develops, and which melt on reheating.

As the processing temperature is increased, i.e. as the level of fusion in the sample is increased, endotherm B decreases in size and moves to higher temperatures, and this is accompanied by an increase in size of endotherm A. Therefore, as suggested by Gilbert and Vyvoda, the increase in size of endotherm A should be related to the degree of fusion of the sample. They also noted that the onset of endotherm B corresponded to the actual processing temperature. Similar observations were made by Illers⁸⁴, who found that the onset of endotherm B corresponded to the previous annealing temperature, as observed in Figure 1.7.

Processing of PVC therefore, either at high shear or at low shear, or even simple annealing, will produce approximately the same thermal effect on the PVC ordered structures.

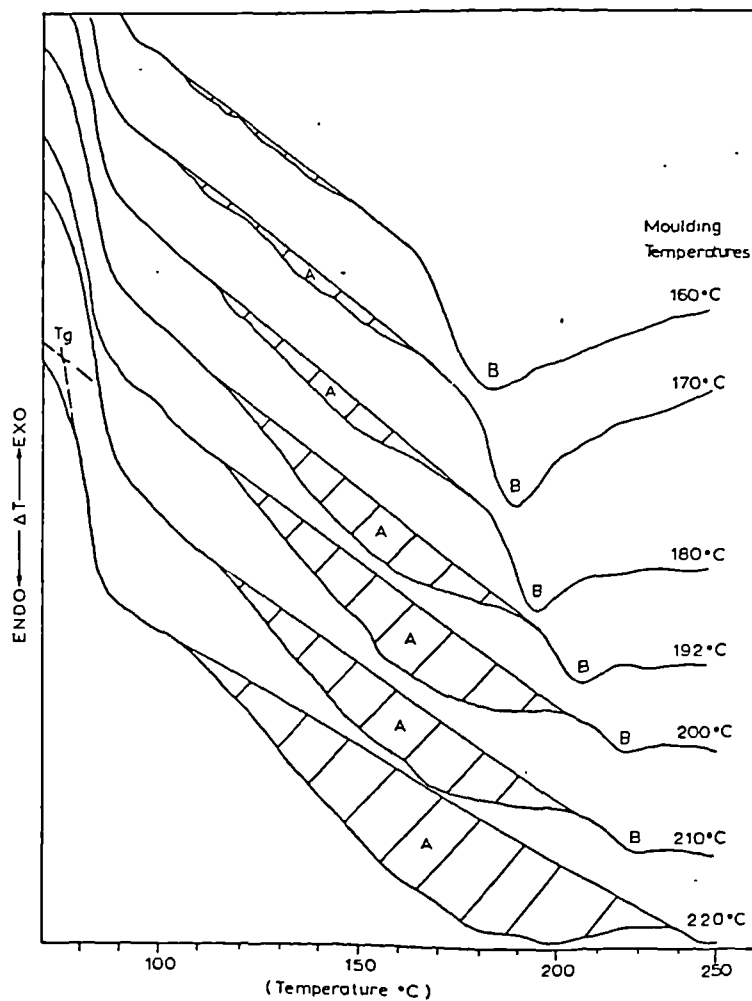


Fig.1.6. DuPont thermal analysis of an unplasticised PVC compound compression moulded at different temperatures. (83)

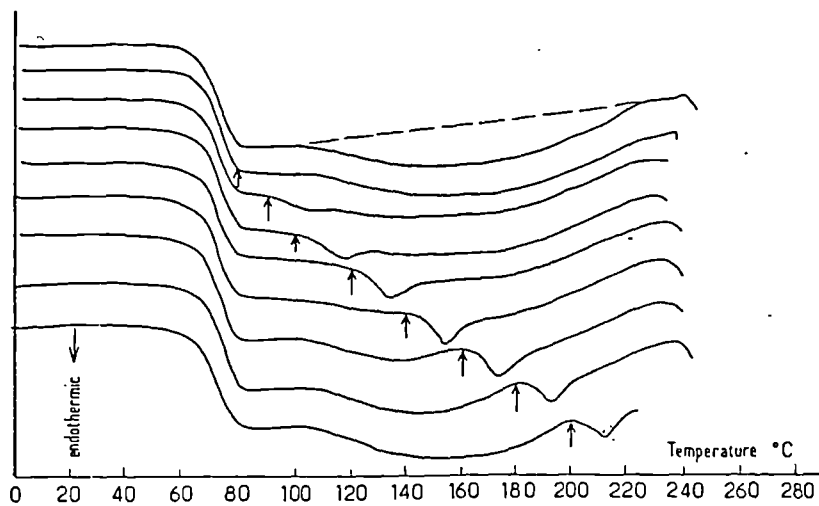


Fig.1.7. Differential scanning calorimetry of a suspension PVC sample cooled at 20°C/min from 240°C and annealed 5 min at the indicated temperature (1). (84)

1.7 Principles of Formulation

The basic ingredients of a flexible PVC composition are PVC, plasticizer, and stabilizer. In practical cases however, other ingredients such as, lubricants, processing aids, and fillers are also included.

1.7.1 The PVC

The most important characteristic of any polymer is its molecular weight. In PVC this is usually specified as the ISO viscosity number or as the K value. Both are based on solution viscosity measurements.

For flexible compositions, the K values are typically between 65 and 72, with the higher values used where the mechanical properties are very important and the lower values where the emphasis is on easy processing.

The PVC intended for flexible applications should also possess a high level of porosity. In practice, the absorption of plasticizer at ambient temperatures (cold plasticizer absorption) is taken as a measure of grain porosity. CPA levels between 30 to 35% are typical of PVCs designated for flexible applications, whereas levels between 15 to 20% are typical for rigid applications. Increasing grain porosity results in lower apparent densities, and densities of 450-500 kg/m³ are typical of flexible grades, whereas densities of 550-600 kg/m³ are typical of rigid grades.

1.7.2 The Plasticizer

The main objective of plasticizers in PVC is to obtain a flexible and soft product, simply referred to as plasticized or flexible PVC.

The most widely used plasticizers for PVC are esters of phthalic acid, esters of adipic acid, and organic phosphates. The choice of plasticizer is generally dictated by the end product requirements, such as; mechanical properties, high or low temperature performance, permanence, electrical properties, weathering, flammability, toxicity, and always cost.

The choice of plasticizer will also have a pronounced effect on the flow properties of the melt. The more active plasticizers will show higher absorption by PVC and more ease of fusion, but at the same time they will more readily facilitate the formation of a melt structure which will increase the melt viscosity and the elasticity of the compound.

1.7.3 The Stabilizer

Heat stabilizers are essential to protect the PVC from degradation at the temperatures encountered during processing. Stabilizers may include inorganic metal salts, metal soaps and complexes, organo tin compounds, epoxy compounds, and organic phosphites. However, some of these have a direct effect on the process of fusion and on the flow properties of the melt. Metal soaps of limited compatibility with PVC may act as external lubricants and organo tin compounds, generally more compatible, may act as internal lubricants.

1.8 Definition of a Plasticizer

The use of plasticizers in PVC may have two completely different purposes; to modify the properties of the material during processing, or to modify the properties in the final product. Table 1.2 presents the major effects of plasticizers in each of these two categories. Plasticizers used for the purpose of making the final product flexible and soft may have ancillary effects during processing, and vice versa. In order to make a flexible product, the amount of plasticizer incorporated into PVC normally varies between 30 and 100 phr.

Table 1.2 Some Physical Functions of Plasticizers (109)

<i>As processing aids</i>	
Lower the processing temperature	Increase tackiness
Lower the hot melt viscosity	Decrease blocking action
Reduce nerve	Improve flow-out (paint)
Increase lubricity	Improve wetting
Reduce sticking during milling	Lower the film-forming temperature (of latexes)
Reduce sticking in mold	
<i>As end-use plasticizers in the plasticization concentration range</i>	
Soften the resin	Increase the temperature range of usefulness
Lower the modulus	Increase adhesion
Lower the tensile strength	Increase blocking action
Increase elongation or distensibility	Decrease blocking action
Increase flexibility	Improve slip or reduce friction
Increase tear strength	Improve surface appearance, gloss, etc.
Increase toughness	Decrease static charge
Increase impact resistance	
Lower the glass transition temperature	
<i>In the antiplasticization concentration range^a</i>	
Increase modulus	Increase hardness
Increase tensile strength	Increase brittleness

^a Only in some resins such as PVC and polycarbonate, and at low plasticizer concentration. Some other resins may show little or no antiplasticization effects.

Plasticizers decrease the T_g of the compound and broaden the elastomeric range of the final product, i.e. the temperature difference between T_g and T_m (melting temperature) is increased⁸⁵. These two effects increase with plasticizer concentration.

1.8.1 Plasticization

Plasticization occurs as plasticizer molecules become homogeneously distributed between polymer molecules. This weakens (or dilutes) the intermolecular forces of attraction between polymer chains and increases their flexibility.

Three major theories have been proposed to explain plasticization. The lubricity theory, the gel theory, and the free volume theory. The first two were developed concurrently by many workers⁸⁶ during the first half of this century. They are two separate theories, but are so intermingled that are commonly used together to explain different parts of the plasticization phenomenon. The free volume theory is based on the free volume between atoms and molecules, which has now been measured and used in the mathematical explanation of flow phenomena.

1.8.1.1 The Lubricity Theory

This considers the resistance of a polymer to deformation, i.e. its rigidity, to result from intermolecular friction. Like oil between two moving parts acts as a lubricant, the plasticizer acts as a lubricant to facilitate the movement of the macromolecules over each other. Little effort is made to explain how this happens, and the only explanation

is to say that as the polymer is flexed, the macromolecules must slide over each other, and that the plasticizer lubricates these moving parts^{87,88}.

1.8.1.2 The Gel Theory

This considers the rigidity of a polymer to result from an internal three dimensional structure. This gel is formed by loose attachments along the polymer chains. Originally, many points of attachment are present and the material is very rigid. The plasticizer breaks many of these attachments, which could be due to van der Waals forces, hydrogen bonding, or crystalline crosslinking. This produces the same result as if far less points of attachment had been present at the beginning. The rigidity is reduced and according to the theory this is enough to cause flexibility^{89,90}.

1.8.1.3 The Free Volume Theory

According to this theory, the progressive transition from rigid to flexible is due to an increased mobility of the polymer molecules. This mobility is in turn facilitated by an increase in the free volume, brought about by the plasticizer.

The concept of free volume may be expressed as^{91,92}:

$$V_f = V_T - V_o \quad (1.4)$$

where V_f is the free volume, V_T is the volume at temperature T , and V_o is the volume at absolute zero.

Figure 1.8 presents some basic concepts of free volume. In a dilatometric experiment, when an amorphous polymer is cooled, its volume decreases with decreasing temperature until a temperature " T_g " is reached at which the material passes from elastomeric to glassy. As temperature is further decreased, the decrease in volume continues but at a slower rate, Fig. 1.8 A. If the first part of this curve a (elastomeric portion) is extrapolated to absolute zero, a specific volume V_l^0 is obtained which is too small to represent the hypothetical volume of the material. But if the second part of this curve a (glassy portion) is extrapolated to absolute zero, a specific volume V_g^0 is obtained which is too large to represent the hypothetical volume of the material. The hypothetical volume V_0 , which lies between V_l^0 and V_g^0 , represents the true occupied volume, and it may be assumed that V_0 remains constant with temperature, curve b. The area between curves a and b represents the free volume, Fig. 1.8 B.

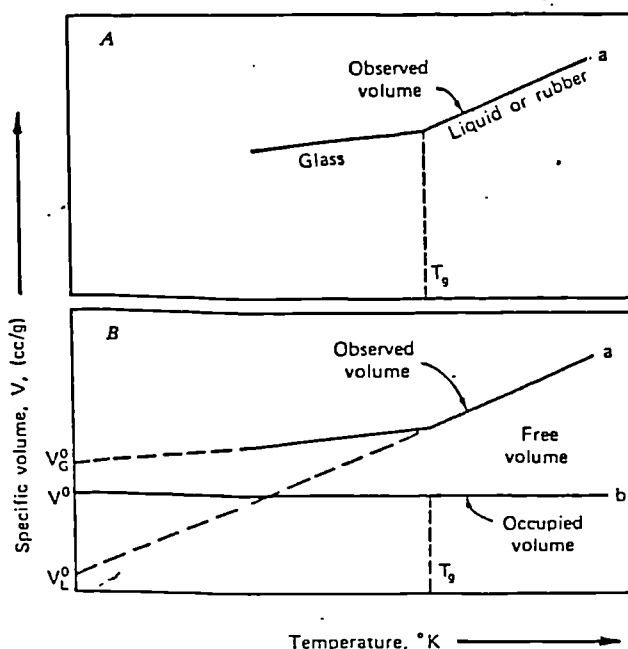


Fig.1.8. Thermal expansion and free volume of a polymer or a noncrystallizing plasticizer. V = specific volume: V_g^0 = specific volume at absolute zero for hypothetically pure and perfectly ordered material: V_g^0 and V_l^0 = specific volumes of the glass and liquid extrapolated to 0° K: T_g = the observed glass transition temperature. (109)

Essentially, the free volume remains constant at all temperatures below T_g ⁹³. Furthermore, the amount of free volume at T_g is approximately the same for polymers of all kinds, such as; silicones, PTFE, NR, PAN, PC, etc.⁹⁴. At T_g , the free volume has been calculated to constitute from 12 to 17% of the total volume⁹⁵.

Because an increase in the free volume permits an increase in the motion of the polymer molecules, the study of plasticization is therefore the study of ways to increase the free volume.

Free volume comes from three different sources; 1) motion of chain ends, 2) motion of side chains, and 3) motion of the main chain. These motions and therefore the free volume may be increased by:

- 1).- increasing the number of chain ends, i.e. decreasing molecular weight.
- 2).- increasing the number of side chains, i.e. increasing branching.
- 3).- increasing the chance for main chain movement by decreasing the steric hindrance and the intermolecular attraction, i.e. internal plasticization (or copolymerization).
- 4).- inclusion of compatible compounds of lower molecular weight that act as if they do all the three points above, i.e. external plasticization.
- 5).- increasing the temperature.

Kanig⁹¹ derived a relationship to predict the lowering of T_g of pure polymers by the addition of plasticizers. From this he predicted that:

- 1).- The smaller the plasticizer molecule, the more efficient it is in lowering T_g .
- 2).- The efficiency of plasticizers in lowering T_g decreases with increasing concentration, i.e. the first amounts of plasticizer are more effective, and increasing amounts are progressively less effective.
- 3).- Within limits, the smaller the affinity between polymer/plasticizer, as compared to polymer/polymer, the more efficient is the plasticizer, i.e. a good plasticizer is a poor solvent.
- 4).- Within limits, the smaller the affinity between plasticizer/plasticizer, as compared to polymer/polymer, the more efficient is the plasticizer, i.e. the viscosity of the plasticizer should be low.

Regardless of which theory seems most appropriate, it appears that solvents or plasticizers are attracted to the macromolecules, but not to be bound permanently. Instead, there is a dynamic equilibrium between solvation and desolvation, in which a certain fraction of the points of attachment between polymer chains is masked by the solvent or plasticizer under a given set of conditions such as, concentration, temperature, and pressure. This is the basic concept of Doolittle's "mechanistic theory of plasticization"⁹⁶. This theory supplements the lubricity, gel, and free volume theories.

Figure 1.9 presents a visual concept of plasticization, where the polymer is represented according to the fringed micelle theory with small areas of order among large areas of disorder. The areas of order may be ordered enough to be crystalline regions. The plasticizer molecules are represented by "dots with branches".

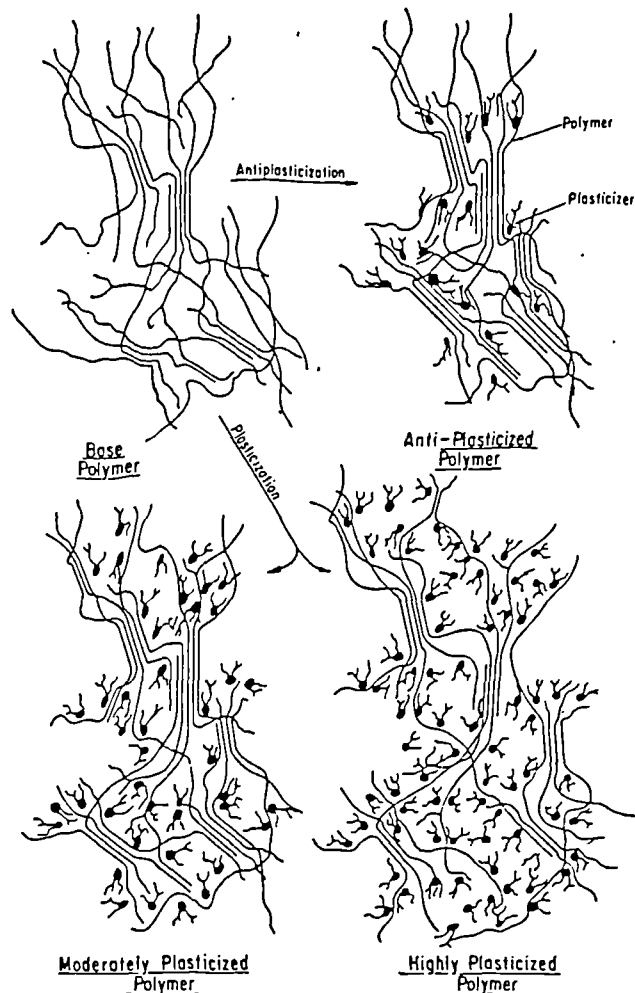


Fig.1.9. Stylized concept of plasticization of a resin, explaining antiplasticization and plasticization. (109)

1.8.2 Stages in Plasticization

Many workers⁹⁷⁻¹⁰² have described the process of PVC plasticization.

- 1).- the plasticizer wets the resin and fills the available pores of the grains.
- 2).- the plasticizer solvates the surface of the PVC grains.
- 3).- the plasticizer is absorbed into the PVC grains with swelling of the amorphous regions.
- 4).- the plasticizer dissociates the polar and hydrogen bondings and dissolves the amorphous regions.
- 5).- the plasticizer aids in the breakdown of the molecular structure and in the dissolution of the crystalline regions.

In the first step there is a rapid and irreversible plasticizer uptake as the plasticizer molecules penetrate the pores of the PVC grains. This is a capillary action and hence depends on the grain morphology.

The second step can be considered as an induction period for the absorption that occurs in the third step. The presence of dispersants on the surface of suspension PVC grains for example, can prolong this induction period¹⁰⁰. This period decreases and eventually disappears with increasing temperature.

The third step involves the absorption of plasticizer, which is a simple diffusion process, during which the total volume of PVC/plasticizer decreases while the PVC particles swell. It has been observed¹⁰¹ that the PVC capacity for plasticizer absorption and the rate of plasticizer absorption vary with temperature and plasticizer type and also with the PVC grain structure.

The fourth step, which involves dissociation of the polar and hydrogen bonding, occurs probably in parallel with the third step but is much slower. Dannis¹⁰⁰ found that the dielectric constant increases during plasticization, due to dissociation of the resin polar groups, at a rate that increases with temperature and with plasticizer activity. In this step, disentanglement of polymer molecules may occur.

The fifth step involves the breakdown of the ordered structures. By the end of the fourth step, all plasticizer has been absorbed and dissociation of polar and hydrogen bonding has taken place. If the

polymer were totally amorphous and with no structural order, it should be completely plasticized. However, a semicrystalline polymer such as PVC has some structural order. This order must be broken down (dissolved in plasticizer) to obtain complete and intimate plasticization. This step is related to the polymer/plasticizer compatibility.

If a PVC/plasticizer dry blend is compression moulded at 130 C after the fourth step, the result is not a truly plasticized PVC product⁹⁹. However, when sufficient energy is put into the system by moulding at a higher temperature or by processing under high shear before moulding at 130 C, the ordered structures are broken down and plasticization is complete.

1.8.3 Antiplasticization

Many polymers tend to become more ordered when small amounts of plasticizer are added. This results in a more rigid polymer with higher modulus and lower elongation. This is antiplasticization. Antiplasticization effects have been observed in many polymers, for example, PMMA, PC, and PA66, which vary from completely amorphous to highly crystalline¹⁰³. Thus, antiplasticization, due to increases in molecular order, is not necessarily accompanied by crystallinity, but hydrogen bonding, van der Waals forces, and steric hindrance may also be involved.

Antiplasticization in PVC was first reported by Brous and Semon¹⁰⁴ in 1935. At that time nevertheless, they considered it an apparent discrepancy due to the difficulty of producing good test specimens with less than 15% plasticizer.

Antiplasticization produces a plasticization threshold which must be passed before the "normal" effects of plasticization are observed. The plasticizer concentration needed to pass this threshold depends on the plasticizer type. This concentration will be greater for more polar, more globular plasticizers, e.g. more aromatic plasticizers, than for less polar, more linear plasticizers, e.g. more aliphatic plasticizers¹⁰⁵. This plasticization threshold shifts to lower plasticizer concentrations as temperature is increased.

For PVC, Horsley¹⁰⁶ showed by X ray diffraction that small amounts of DOP (up to ca 15%) progressively increase the intensity and sharpness of the halo pattern, indicating that the increase in order may include crystallinity. Further amounts of DOP result in a decrease of the halo intensity. This apparent increase and decrease in crystallinity paralleled exactly the increase and decrease in modulus. Horsley also showed that quenching the PVC/DOP melt produced a plasticized compound with no antiplasticization effects, whereas annealing at 65 C converted it to a compound with antiplasticization effects.

Crystallinity may increase with larger amounts of plasticizer, but the amorphous regions become highly swollen until the whole mass becomes softer.

Elastomeric plasticizers, such as NBR, tend to show no antiplasticization effects.

1.8.4 Efficiency of a Plasticizer

The efficiency of a plasticizer refers to its ability to impart a desired property. The more the amount of plasticizer required to produce the desired effect, the less efficient it is. In this respect, many attempts have been made to compare the efficiency of plasticizers by one simple number called "the efficiency factor". But whereas some properties, such as the cold flex temperature and the T_g tend to vary linearly with plasticizer concentration, some other properties, such as the tensile properties do not¹⁰⁵. This is further complicated by the antiplasticization effect, which shows up in the tensile properties but not in the cold flex temperature or the T_g . Nevertheless, the efficiency factor is very useful for comparison of plasticizers for a specific end use. Usually the comparisons are based on the amount of plasticizer needed to produce a given modulus, softness, cold flex temperature, etc. But the relative efficiency would be different depending on the property taken to establish it.

1.8.5 Polymer/Plasticizer Compatibility

Compatibility means the ability of two or more substances to mix intimately and stay together to form a homogeneous composition of useful properties. In a narrow sense this would imply thermodynamic compatibility, however there are blends which are thermodynamically not compatible but have very useful properties. Most theoretical studies of compatibility have involved solvents and the results have been applied to plasticizers. But plasticizers are rarely good solvents for most plastics¹⁰⁷.

Very early efforts to explain compatibility were based on the idea of "like dissolves like", and one good study of structural similarities to explain the compatibility of plasticizers is due to Kirkpatrick¹⁰⁸.

According to thermodynamics two substances will be miscible when the Gibbs free energy of mixing " ΔG_m " is negative:

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (1.5)$$

where ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing, and T is the absolute temperature.

Application of the theory has led to the measurement of the internal pressure " P_i ", the Hildebrand solubility parameter " δ ", and the Flory Huggins interaction parameter " χ ", as indicators of compatibility.

A predictor of compatibility is different from an actual measure of compatibility. The use of two or more predictors together is common practice. As well as to predictors, actual measurements of compatibility at one or more concentrations may be used to fix the limits of compatibility.

1.8.5.1 Internal Pressure

This is one of the most basic concepts that have been applied to solubility or compatibility¹⁰⁹⁻¹¹¹. This is based on the fact that changes in the internal energy are directly related to the forces of attraction that hold the molecules together, and therefore related to the solvent power

According to thermodynamics:

$$(\delta E / \delta V)_T = T(\delta P / \delta T)_V - P = P_i \quad (1.6)$$

where E is the internal energy, V is the molar volume, $(\delta P / \delta T)_V$ represents the variation of pressure with temperature at constant volume, P is the external hydrostatic pressure, and P_i is the internal pressure.

The internal pressure P_i is zero for ideal gases, but due to the forces of attraction between molecules (van der Waals forces), it is different from zero for most real gases.

From thermodynamics, $[(\delta P / \delta T)_V = - (\delta V / \delta T)_P / (\delta V / \delta P)_T]$ therefore, P_i is commonly determined at a given temperature T, from the coefficient of thermal expansion " α " $(1/V (\delta V / \delta T)_P)$ and the coefficient of compressibility " β " $(- 1/V (\delta V / \delta P)_T)$.

$$P_i = T(\alpha / \beta) - P \quad (1.7)$$

On the other hand, vaporization may be visualized as the process of separating the molecules from their normal equilibrium distance at which they are held by their cohesive energy. The CED (cohesive energy density) can be calculated from the molar energy of vaporization " ΔE_v " and the molar volume "V" by:

$$CED = \Delta E_v / V \quad (1.8)$$

and if the vapour behaves as an ideal gas:

$$CED = (\Delta H_v - RT) / V \quad (1.9)$$

where ΔH_v is the molar heat of vaporization.

Both, the internal pressure and the cohesive energy density are measurements of energy and are related to the solvent ability in such a way that two substances with the same P_i or the same CED values should be miscible.

According to Hildebrand¹¹² P_i /CED is nearly unity for van der Waals substances, but this does not hold for materials with hydrogen bonding or polar groups. P_i /CED for example, becomes much less than one for substances with strong hydrogen bonding or polar groups, but is greater than one for substances with strong forces of repulsion and weak forces of attraction. P_i /CED is between 1.05 and 1.30 for the more common solvents and plasticizers.

P_i and CED are affected by temperature^{113,114} as shown in Figure 1.10. Since dP_i/dT or $dCED/dT$ differ for different materials, it is possible to have a polymer/plasticizer system that is compatible at one temperature but incompatible at some other temperature.

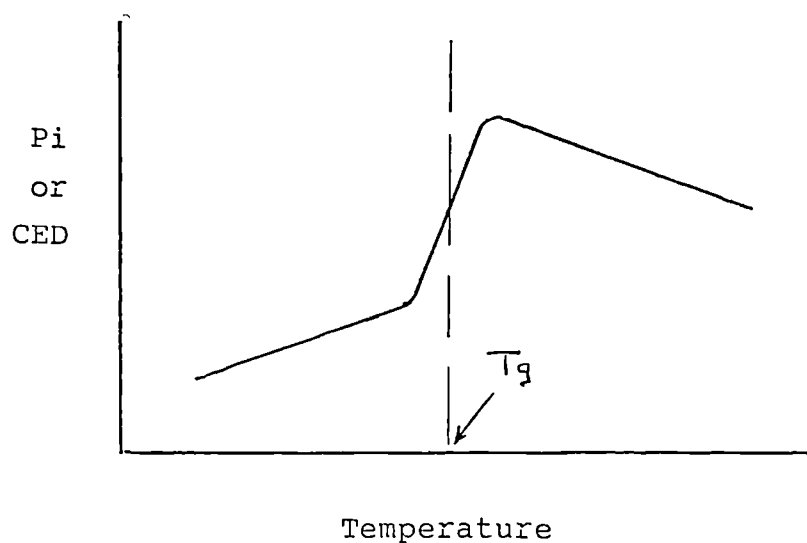


Fig.1.10: Typical variation of P_i or CED with temperature

1.8.5.2 Hildebrand Solubility Parameter

The Hildebrand solubility parameter " δ " is identical to the square root of the CED, i.e.

$$\delta = (\text{CED})^{1/2} \quad (1.10)$$

Let δ_1 and δ_2 represent the solubility parameters of the solvent (plasticizer) and solute (polymer). According to theory¹¹⁵, the enthalpy of mixing " ΔH_m " is proportional to $(\delta_1 - \delta_2)^2$. Thus, if δ_1 approaches δ_2 , then ΔH_m approaches zero, and the free energy of mixing " ΔG_m " becomes negative. Therefore, as δ_1 approaches δ_2 , the two substances tend to become miscible.

The most reliable method for the determination of solubility parameters of plasticizers would be to calculate these from the molar energy of vaporization and the molar volume. But energies of vaporization are rarely known for plasticizers and almost impossible for polymers.

The method devised by Small¹¹⁶ to estimate the values of δ has been very useful for many plasticizers and also for polymers. He found a set of additive constants for the more common groups in organic molecules to account for the observed magnitude of the solubility parameter. These constants (Small constants) are designated by F , so that:

$$\text{CED} = (\Sigma F/V)^2 ; \quad \delta = \Sigma F/V \quad (1.11)$$

where V represents the molar volume.


Table 1.3 presents a list of the F values of the more common groups and Figure 1.11 shows the estimation of solubility parameters for one common plasticizer (BBP or butyl benzyl phthalate) and PVC.

Hoy¹¹⁷ has published a revised set of Small constants based on vapour pressure measurements. Fedors¹¹⁸ reported a historical survey and extended this with his own method that predicts ΔE_v and V purely from the chemical structure. He also shows how to adjust δ with changes in temperature.

With respect to compatibility (as predicted by the solubility parameter) and its relation with the ease of fusion of PVC, it was first reported that there appeared to be no correlation between them¹¹⁹. After re-examination however, it was realized that the solubility parameter predicted compatibility at room temperature, whereas fusion occurred at elevated temperatures.

However, solubility parameters decrease with temperature. This decrease ($-d\delta/dT$) is roughly seven times greater in plasticizers than in PVC. Consequently, the solubility parameter of a plasticizer such as BBP (butyl benzyl phthalate) or TCP (tri crecyl phosphate) (9.88 and 9.86 respectively) will rapidly approach that of PVC (9.66) during processing at elevated temperatures, which results in increased compatibility and ease of fusion. On the other hand, plasticizers with solubility parameter lower than that of PVC will tend to be even less compatible at elevated temperatures.

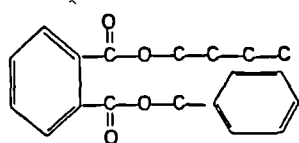
Table 1.3 Group Molar Attraction Constants for Determination of Solubility
Parameters (Small Constants) (116)

Group	$(\text{cal cm}^3)^{1/2}/\text{mol}$	Group	$(\text{cal cm}^3)^{1/2}/\text{mol}$
CH ₃ —	214	CN	410
—CH ₂ —	133	Cl single	270
	28	Cl twinned	260
—CH			
—C—	—93	Cl triple	250
CH ₂ =	190	Br single	340
—CH=	111	I single	425
>C=	19	CF ₂ <i>n</i> -fluorocarbons	150
CH≡C—	285	CF ₃ <i>n</i> -fluorocarbons	275
—C≡C—	222	—S—	225
Phenyl	735	SH thiols	315
Phenylene (<i>o</i> , <i>m</i> , <i>p</i>)	658	O—NO ₂ nitrates	~440
Naphthyl	1146	NO ₂ (aliphatic)	~440
Ring, 5	105–115	NO ₂ (aromatic ortho)	280
Ring, 6	95–105	PO ₃ (phosphite)	68
Conjugation	20–30	PO ₃ ⁺ (alkyl phosphonate)	233
H—	80–100	PO ₄ (organic)	~500
O Ethers	70	—N— (sulfonamide)	~600
 Epoxy oxygen	255	—SO ₂ — (sulfonamide)	~500
CO Ketones	275	O	
COO Esters	310		
O—CO ₂ Carbonate esters	325	—C—NH ₂	~740
		O	
		—C—N	~500
—O—O— Alkyl peroxide	158		

* Values given are from Small unless designated otherwise and are for 25°C.

Estimation of Solubility Parameters

For Plasticizers and Solvents



Butyl Benzyl Phthalate

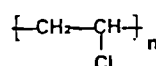
Mol Wt. 312.4
d 1.12

F
1 CH₃ 214
4 CH₂ 532
1 Phenyl 735
1 Phenylene 658
2 COO 620

ΣF = 2759

$$\delta = \frac{2759}{312.4/1.12} = 9.82$$

For Polymers



PVC Repeating Unit

Unit Wt. 62.5
Polymer d 1.4

F
1 CH₂ 133
1 CH 28
1 Cl 270
ΣF = 431

$$\delta = \frac{431}{62.5/1.4} = 9.66$$

Fig.1.11. Estimation of solubility parameters of plasticizers and resins by the method of P. A. Small and illustrated by BBP and PVC

1.8.5.3 Dielectric Constant

Apart from the solubility parameter Darby, Touchette, and Sears¹²⁰ used the dielectric constant as a second predictor of compatibility. This is easily obtained after measuring the capacitance of a cell containing the substance as the dielectric. The dielectric constant is a measure of the intermolecular forces and their effect on the ability of the molecule to adapt itself to the electric forces of the environment.

They recommended the use of both, the solubility parameter and the dielectric constant, to predict more accurately the compatibility of a plasticizer. They showed that for a plasticizer to be compatible with PVC (i.e. no exudation) its dielectric constant should be between 4 and 8, and the more compatible plasticizers between 5 and 6.

1.8.5.4 Polarity Parameter

This was devised as a very simple way of correlating the chemical structure of plasticizers with their performance in PVC¹²¹.

First, the ratio of non-polar/polar elements of the plasticizer molecule is determined as "Ap/Po"; where Ap represents the number of non-polar, aliphatic carbon atoms in the plasticizer molecule, excluding the aromatic and carboxylic C atoms, and Po represents the number of polar groups present, such as ester or ether groups for example. [The Ap/Po ratio increases as polarity decreases].

For example, DOA (dioctyl adipate) has two aliphatic alcohol chains containing 8 C atoms plus an aliphatic acid chain containing 4 C atoms (carboxylic C atoms are excluded), and has 2 ester groups. The Ap/Po ratio is therefore 20/2 i.e. 10. Similarly, DOP (dioctyl phthalate) has two aliphatic chains containing 8 C atoms (aromatic and carboxylic C atoms are excluded), and has 2 ester groups. The Ap/Po ratio is therefore 16/2 i.e. 8. Finally, TOP (trioctyl phosphate) has three aliphatic chains containing 8 C atoms and has 3 polar groups. The Ap/Po ratio is therefore 24/3 i.e. 8.

It has been shown that the Ap/Po ratio of many plasticizers correlates well with a number of properties, including density of plasticizer, solid-gel transition temperature of PVC in excess plasticizer, and modulus and efficiency of plasticized PVC compounds^{121,122}.

Since the activity of a plasticizer depends on its polarity, as well as on its molecular size, it has been mentioned later^{77,122} that the Ap/Po ratio multiplied by the plasticizer molecular weight gives a better correlation. This is the polarity parameter " ϕ " defined by:

$$\phi = (\text{Ap/Po}) \times \text{MW} / 1000 \quad (1.12)$$

where the factor "1000" is used only to produce numbers in a convenient scale.

1.8.5.5 Flory-Huggins Interaction Parameter

This is based on actual physical measurement on a polymer/solvent or polymer/plasticizer mixture. A number is calculated, called the interaction parameter, and this represents the compatibility of the system. Such an interaction parameter is therefore specific for that particular system. The most popular is the Flory-Huggins interaction parameter " χ "¹²³.

From thermodynamics and from their statistical mechanical approach, they obtained:

$$\Delta G_m = RT(n_1 \ln v_1 + n_2 \ln v_2 + \chi n_1 v_2) \quad (1.13)$$

where ΔG_m is the Gibbs free energy of mixing, R is the gas constant, T is the absolute temperature, n_1 and n_2 are the number of moles of solvent and solute respectively, v_1 and v_2 are the volume fractions of solvent and solute respectively, and χ is the Flory-Huggins interaction parameter. This interaction parameter is not truly a constant for it may vary with concentration, MW, and temperature¹²³⁻¹²⁵. Nevertheless, many equations that involve χ have been developed and various types of measurements can be correlated with the polymer/plasticizer compatibility¹²⁵.

According to theory, the dividing line between compatibility and incompatibility lies at $\chi = 0.55$. Plasticizers with χ less than 0.55 should be compatible and vice versa. Actually, a low value of χ indicates good compatibility and a high value indicates poor compatibility.

There are equations for calculation of χ derived from; stress-strain of swollen polymers, osmotic pressure, equilibrium swelling, vapour pressure, viscosity, and depression of the melting point.

Equilibrium swelling of very lightly crosslinked PVC was used by Doty and Zable¹²⁴ to evaluate the interaction parameters of various solvents and plasticizers. According to Flory and Rehner¹²⁶ the amount of swelling of a crosslinked polymer in a given solvent, depends on the degree of crosslinking, but also depends on the interaction between solvent and polymer, as indicated by:

$$\chi v_2^2 = - \ln(1-v_2) - v_2 - \rho_2 V_1 v_2^{1/3} / Mc \quad (1.14)$$

where v_2 is the volume fraction of polymer at equilibrium swelling, ρ_2 is the density of the pure polymer, V_1 is the molar volume of solvent, Mc is the average molecular weight of the polymer between crosslink points, and χ is the interaction parameter between solvent and polymer, which indicates whether or not a given liquid will be a solvent or a non solvent.

Thus, using PVC samples of known Mc , Doty and Zable were able to obtain a series of χ values by simple swelling measurements.

Depression of the PVC melting temperature, in the presence of excess plasticizer, was used by Anagnostopoulos et al¹²⁷⁻¹²⁹ to evaluate the interaction parameter of various solvents and plasticizers. According to Flory¹²³ the depression of the melting temperature is related to the interaction between solvent and polymer by:

$$1/T_m - 1/T_m^0 = RV_2 / (\Delta H_2 V_1) (v_1 - \chi v_1^2) \quad (1.15)$$

where T_m^0 and T_m are the melting temperature of the pure polymer and the depressed melting temperature respectively, R is the gas constant, ΔH_2 is the heat of fusion per mol of polymer repeat unit, V_2 is the molar volume of polymer repeat unit, V_1 is the molar volume of solvent, v_1 is the volume fraction of solvent at T_m , and χ is again the Flory-Huggins interaction parameter.

This equation was adapted by Anagnostopoulos et al to the PVC/plasticizer system. They introduced: $\Delta H_2 = 656$ cal/mol and $V_2 = 44.6$ ml/mol as the average values, and $T_m^0 = 176$ C (449 K) as the extrapolated fusion temperature of PVC. They also assumed that $v_1 = 1$ at complete dissolution. This led to the very simple equation:

$$1/T_m = 1/449 + 0.1351(1 - \chi)/V_1 \quad (1.16)$$

This permits the determination of χ from a single determination of the depressed melting temperature.

For a given plasticizer, the values of χ obtained by Anagnostopoulos et al are very similar to the values of χ obtained by Doty and Zable.

The concept of depressed melting temperature was used by Schreiber^{130,131} for the calculation of χ values directly from processing data.

Using a Brabender torque rheometer, first he obtained the fusion temperatures (fusion peaks) of a PVC/DIOP (di-iso-octyl phthalate) compound at different rotor speeds (25, 14, 6, and 3 rpm), and extrapolated to obtain the fusion temperature at zero rpm, i.e. zero shear. Figure 1.12 A. Then he repeated the experiment at different plasticizer concentrations (70, 60, 50, 40, 30, 25, and 15 phr), to obtain the corresponding fusion temperatures. Finally, he plotted the variation of the fusion temperature (at zero shear) versus the plasticizer volume concentration and found a straight line that could easily be extrapolated to zero plasticizer concentration, i.e. to pure PVC. Figure 1.12 B.

He repeated the complete experiment with other plasticizers, and found that the average fusion temperature of PVC was 205 C (478 K). This value was then introduced by Schreiber into the equation previously used by Anagnostopoulos et al to give:

$$1/T_m = 1/478 + 0.1351(v_1 - \chi v_1^2)/V_1 \quad (1.17)$$

By assuming a higher melting temperature for pure PVC, (higher T_m^0), he calculated lower values of χ , therefore indicating greater compatibility than previously reported. He also calculated the variation of χ with temperature and with plasticizer concentration.

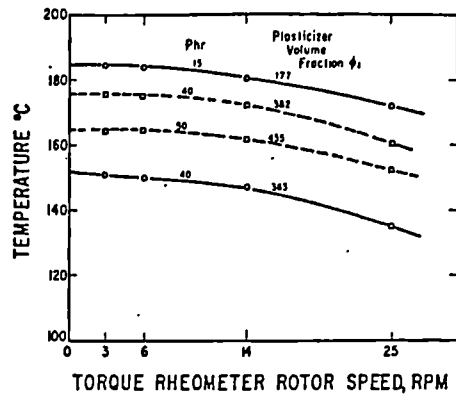


Fig.1.12. Fusion temperature of PVC compounds as a function of rotor speed, showing extrapolation to a depressed melting point, t_m , at zero shear. Solid curves are for DIOP and broken curves are for 6-10 adipate blends, each at the concentration shown. (130)

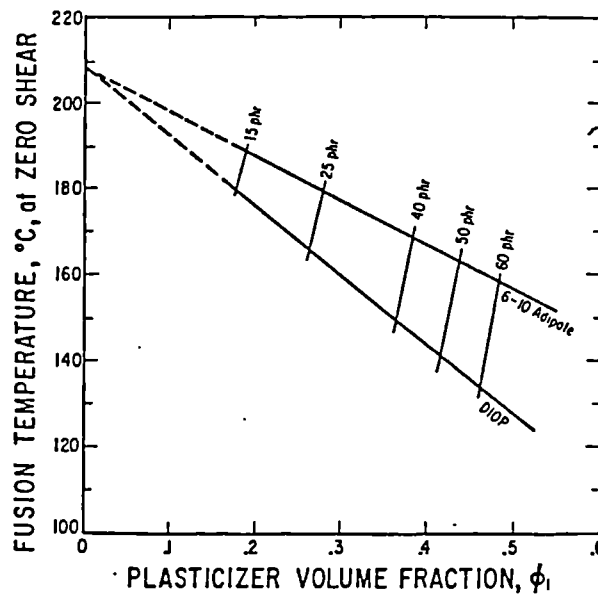


Fig.1.12. Fusion temperature, t_m , (see Fig. 4.14) as a function of plasticizer concentration, with extrapolation to t_m at zero plasticizer content. For the PVC used $t_m = 209^\circ\text{C}$. (130)

1.8.5.6 Activity Parameter

Equation 1.16 (derived from the Flory-Huggins equation) suggests a linear relationship between the degree of PVC/plasticizer interaction, represented by $1/T_m$, and $(1 - \chi)/V_1$. However, the molar volume of the plasticizer at the depressed melting temperature, represented by V_1 , is not a readily accessible figure.

Based on this, Bigg^{132,133} suggested an activity parameter α , where V_1 is replaced by the molecular weight of the plasticizer, and is defined by:

$$\alpha = (1 - \chi) / MW \times 1000 \quad (1.18)$$

where the factor "1000" is used only to produce numbers in a convenient scale.

He demonstrated the agreement between the calculated values of α and the order of plasticizer activity, as indicated by the depressed melting temperatures and by equilibrium swelling.

1.9 Processing

The varied ease of fusion that plasticizers impart to PVC, resulting from the different compatibility of plasticizers, and reflected in the solubility parameter, the solid-gel transition temperature, and the interaction parameter, helps dictate the processing conditions needed for good physical properties of the final product.

Two of the more basic processing operations in plasticized PVC are dry blending and mixing. Dry blending is the production of a homogeneous mixture of PVC and additives, that remains a free flowing powder, which may be used to feed a fabricating process, or alternatively to feed a compounding (mixing) machine to produce fully fused pelletized PVC feedstock. Mixing (or compounding) is the production of a fully fused homogeneous mixture of PVC and additives which is normally used to feed a fabricating process.

1.9.1 Dry Blending

Dry blending is usually carried out in high speed mixers (up to 3000 rpm) at temperatures between 90 to 130 C, after which the mix is cooled down to ca 50 C. The resultant mixture is a free flowing dry powder blend that includes all the liquid and solid additives homogeneously distributed in the PVC grains.

After dry blending, the distribution of solid additives between grains is homogeneous. On individual grains however, the additives tend to concentrate in some areas, for example, in the hollow parts of the grain surface. The distribution of liquid additives that are used in small amounts, on the other hand, tends to concentrate in the small fraction of the grains that first come in contact with the liquid additives, and extended dry blending does not alter this distribution. However, once the dry blend is subjected to the high shear processing conditions, fusion starts and the dispersion of additives greatly improves.

During PVC/plasticizer dry blending, the plasticizer is absorbed by the amorphous phase of the PVC^{101,102}. The ordered regions remain intact until the temperature becomes high enough for fusion.

It has been found that the rate of plasticizer absorption depends on both temperature and plasticizer type^{102,134,135}. The rate of plasticizer absorption increases with increasing temperature and with decreasing plasticizer viscosity. The rate of absorption also increases with increasing plasticizer compatibility.

1.9.2 Mixing (Internal Mixer)

An internal mixer is an enclosed chamber with two rotor blades that mix and fuse the materials which are then discharged for further processing. External heat is supplied to start the process, but the mechanical work (or shear) thereafter supplies much of the required heat for complete fusion and adequate mixing. The torque, time, and temperature required for complete fusion of a given plasticized PVC compound will depend on the PVC molecular weight, but even more on the type and concentration of plasticizer.

During mixing in a Banbury internal mixer, the power and the time required to attain fusion, depend strongly on the plasticizer used^{136,137}, as shown in Figure 1.13. With the more active BBP (butyl benzyl phthalate), fusion is very rapid (indicated by the arrows on the X axis) and the power peak is high. But with the less active and highly lubricating DOS, (dioctyl sebacate), fusion is much slower and the power peak is low.

During mixing for a constant period of time, the total work increased with the compatibility of the plasticizer. But during mixing just until adequate fusion is achieved, the work required decreased with the compatibility of the plasticizer¹³⁶.

It was also noted¹³⁷ that the power peak decreased with plasticizer concentration, but the time and total power required for adequate fusion increased. Therefore, increasing the concentration of plasticizer has the same effect as shifting from a more active to a less active and more lubricating plasticizer.

Bergen and Darby¹³⁷ noted an apparent correlation between the fusion time obtained in an internal mixer, and the Flory-Huggins interaction parameter. Less active plasticizers with χ greater than 0.40 gave longer fusion times, whereas more active plasticizers with χ less than 0.40 gave shorter fusion times.

Also, Derby et al^{120,138,139} observed that after several minutes of mixing in a Brabender torque rheometer, the torque suddenly started to increase. The temperature at this point they designated as "the relative fusion temperature". It was identified as the point at which solvation of the PVC grains had occurred to an extent sufficient to cause the observed increase in torque. Though this process involves only the amorphous phase, the location of this point depends on the ability of the plasticizer to promote fusion. They noted an almost linear relationship between the relative fusion temperature and the solid-gel transition temperature.

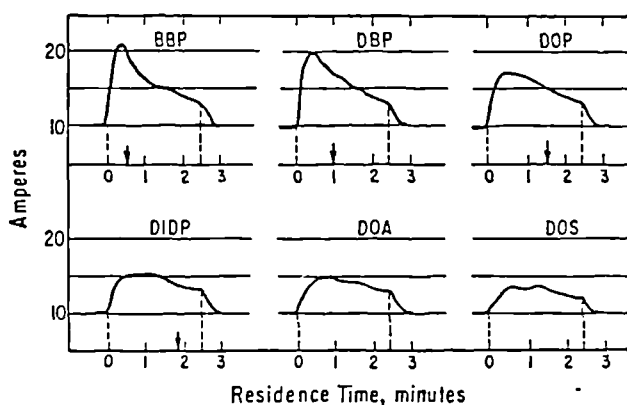


Fig.1.13. Profiles of power requirement during fusion and mixing of PVC-plasticizer blends in a Banbury mixer, as shown by change in amperage. (136)

1.10 Dynamic Mechanical Properties

Clash and Berg¹⁴⁰ and Aiken et al¹⁴¹ reported in the 1940s that the modulus-temperature curve for PVC shifted to lower temperatures with the addition of plasticizer, i.e. T_g decreased. This effect increased with plasticizer concentration, and also was affected by plasticizer type. Apparently, the more aliphatic the plasticizer, the more effective it is in shifting the modulus-temperature curve to lower temperatures.

According to Hata and Tobolsky¹⁴², the elastic modulus G' of plasticized PVC, above T_g , is governed by the nature of the PVC, the viscosity of the plasticizer, and the activity of the plasticizer. Due to the crystallinity of PVC, it appears that plasticizers affect the viscoelastic properties of the PVC compound, first by affecting its T_g and second through the solvent-solute interaction with the PVC.

Nakajima et al¹⁴³ reported the continuous measurement of the apparent viscosity and the elastic modulus of a PVC plastisol, during heating, and showed that both increase rapidly by about 3 decades during fusion. After reaching a maximum at ca 150 C, both viscosity and elastic modulus decrease with increasing temperature. They commented that G' at the maximum is ca 10^5 Pa, which is similar to that of unfilled elastomers, and suggested that the crystallites are possibly acting as the crosslink points of the rubber-like network. The decrease in viscosity, which is larger than expected from temperature dependency only, is attributed to the melting of the crystallites. At about 180 C, the curves of G' and G'' crossover,

indicating that the viscous response (G'') is becoming relatively more important than the elastic response (G'), i.e. the material progressively behaves more like a true melt.

It has also been reported¹⁴⁴ that plots of elastic modulus versus temperature, for rigid PVC samples moulded at 180 C, show a clear change in slope at a point which coincides with the annealing temperature of the sample. For example, the elastic modulus G' of two samples, one annealed at 160 C and one at 180 C, shows no differences below 160 degrees, Figure 1.14. Above 160 C however, two distinct break point are observed (at 160 C and 180 C) and consequently two distinct curves arise. Finally, above ca 210 C, where fusion is almost complete, the two distinct curves rejoin and again no differences are observed. The same behaviour was observed with the dynamic viscosity.

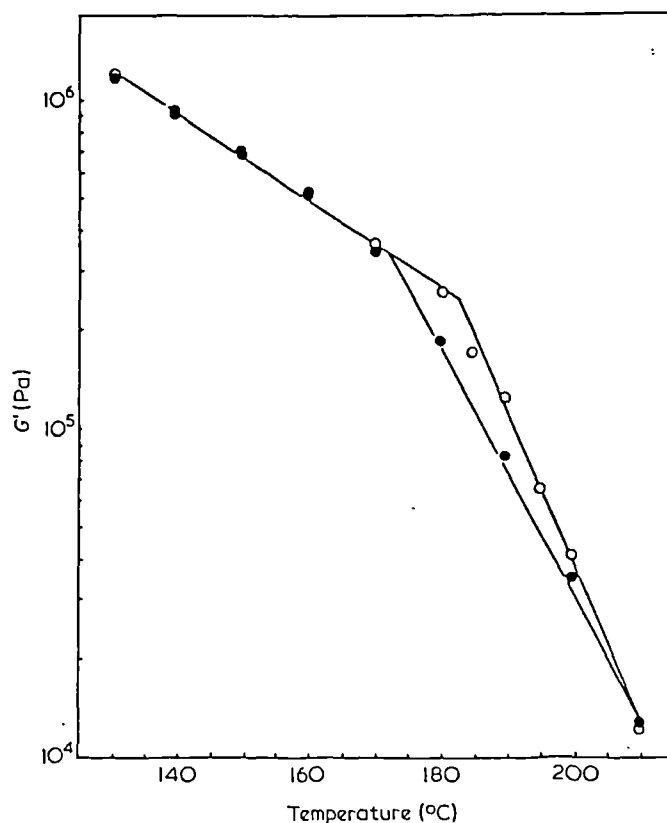


Fig. 1.14 Storage modulus vs. temperature at 1 rad s⁻¹ for samples annealed at ● = 160°C and ○ = 180°C. (144)

1.11 Tensile Properties

Tensile properties of PVC are highly modified by the addition of plasticizers.

Not considering antiplasticization, modulus and tensile strength decrease and elongation increases with increasing plasticizer concentration.

Also, tensile properties are affected by the degree of fusion. It has been reported that the tensile strength of plasticized PVC¹⁴⁵ and the elongation at break of unplasticized PVC¹⁴⁶ increase markedly with processing temperature, i.e. with the degree of fusion.

It has also been reported¹³⁹ that the elongation at break of PVC plastisols increases and reaches a maximum with increasing time at 150 C, i.e. with the degree of fusion. The time needed to attain this maximum decreases with increasing compatibility (or activity) of plasticizer.

In a more recent work, Patel and Gilbert^{77,78} found that the tensile strength and elongation at break of plasticized PVC increase with the degree of fusion up to a maximum, which is reached asymptotically.

Finally, as with many other polymers, the tensile properties of PVC increase with molecular weight¹⁴⁷.

1.12 Antecedent and Objective

In previous work¹⁴⁸, the process of fusion of plasticized PVC was investigated. That work concentrated on assessing the level of fusion and studying the effect of fusion on the processing characteristics of the plasticized PVC compound. The effect of fusion on the tensile properties was also investigated. [Seven plasticizers were included in that study^a].

However, little work was done on studying the interaction between PVC and plasticizer, in terms of compatibility, at a fundamental level.

It was felt therefore, that more experimental work was still required to attain a better understanding of the PVC/plasticizer compatibility and its effect on the processing characteristics of the plasticized PVC. [In addition, more plasticizers should be included to extend this understanding to other plasticizer families].

^abutyl benzyl phthalate

diisooctyl phthalate

diisononyl phthalate

ditridecyl phthalate

trialphanol trimellitate

50/50 mix, diisodecyl phthalate/diisodecyl nylonate

50/50 mix, diisooctyl phthalate/diisooctyl nylonate

Alphanol; mix of linear alcohols of 7-9 C atoms.

Nylonate; mix of adipic, succinic, and glutaric acids.

The objective of this work was therefore to study and determine the compatibility of PVC with a series of plasticizers and to relate this compatibility with the processing characteristics and the mechanical properties of the plasticized PVC compounds.

The work was divided into four goals: first, to determine the PVC/plasticizer compatibility; second, to study the effect of compatibility on the processing characteristics of the plasticized PVC compounds; third, to study the effect of compatibility and type of processing on the level of fusion attained by the plasticized PVC compounds; and fourth, to study the effect of compatibility and fusion level on the mechanical properties of the plasticized PVC compounds.

Chapter 2

EXPERIMENTAL

2.1 Materials Used

2.1.1 PVC Polymer

Polymer.- Two commercial grade suspension PVC homopolymers were used. These were "Corvic S68/173" supplied by ICI Ltd., UK and "Primex p-225-2" supplied by PRIMEX S.A., Mexico. The main characteristics of the polymers are presented in Table 2.1.

TABLE 2.1

Properties of PVC Polymers

	S68/173	p-225-2
K value [Fikentscher] ^a	68	68
ISO viscosity number ^b	117	118
Apparent density [g/cm ³]	0.57	0.55
Molecular weight Mw ^c	166000	167000
Molecular weight Mn ^c	59000	59800

^a DIN 53 726

^b ISO 174

^c Estimated after the K value, from Ref. 122
page 44, Table 2.1.

2.1.2 Plasticizer

Plasticizer.- Twelve different commercial grade plasticizers were used. These included 4 phthalates, 2 adipates, 1 sebacate, 2 trimellitates, 2 polymeric, and 1 phosphate. Figure 2.1 and Table 2.2 present their characteristics. [The plasticizers were provided by PRIMEX, Mexico and by CIBA GEIGY, UK].

2.1.3 Stabilizer

Stabilizer.- Two commercial grade tin stabilizers were used. These were a dibutyl tin mercaptide (Stanclere 135) from Akzo Chemicals, UK and a dibutyl tin mercaptide (Irgastab 17) from CIBA GEIGY, Mexico, both in liquid form.

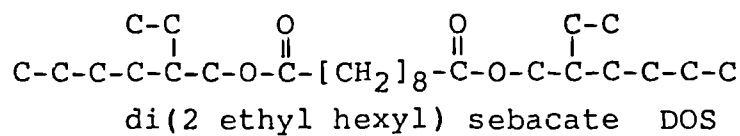
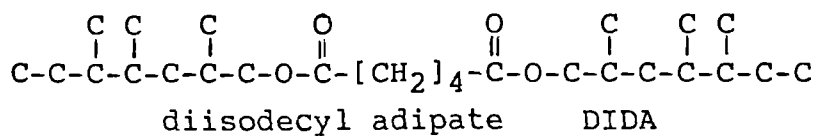
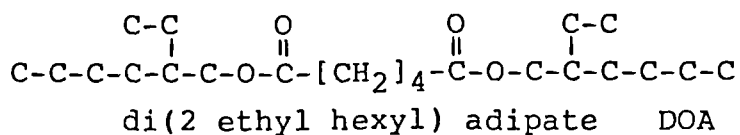
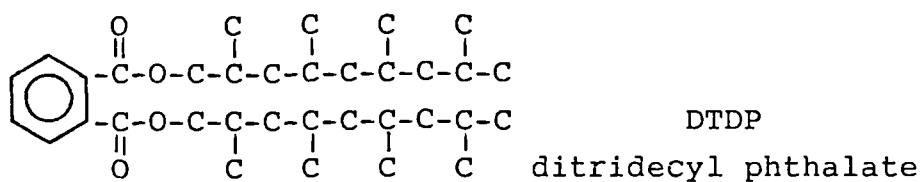
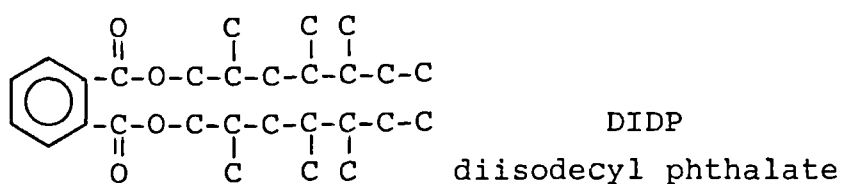
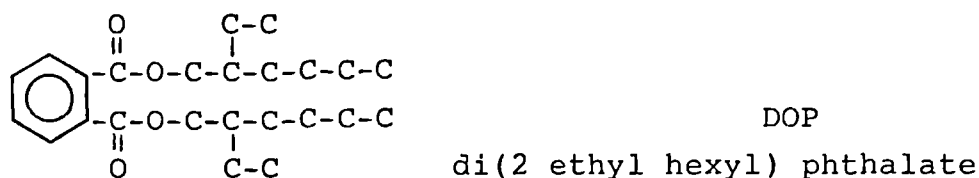
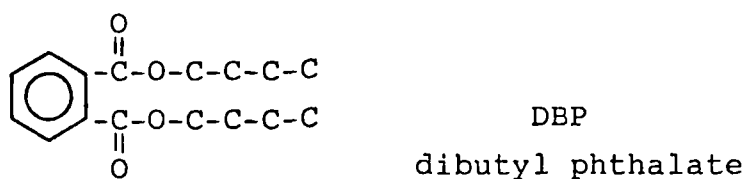


Fig.2.1: Chemical formulae of plasticizers (continues).

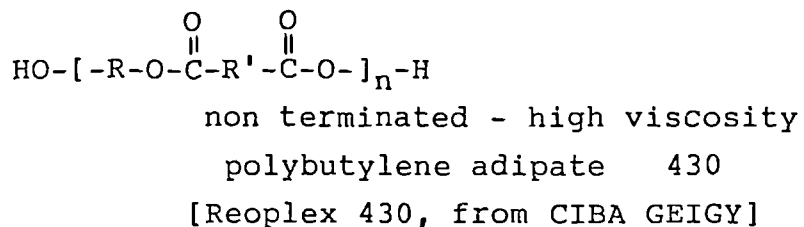
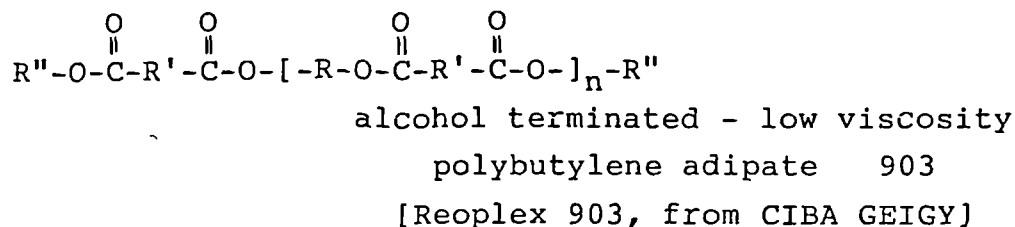
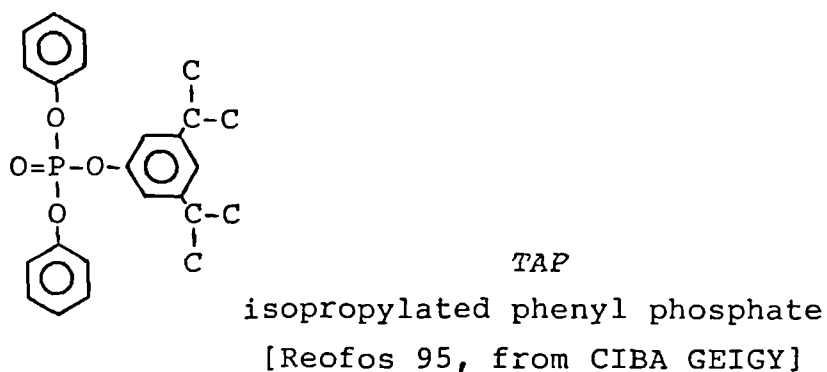
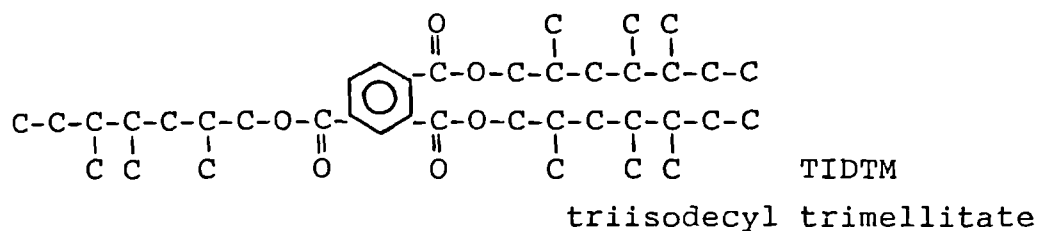
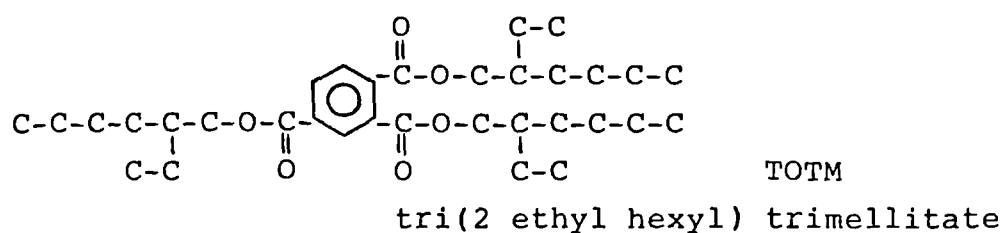


Fig.2.1: Chemical formulae of the plasticizers studied.
Hydrogens on C atoms have been omitted for simplicity.

TABLE 2.2

Reported Properties of the Plasticizers Studied^a

	Molecular Weight	Density g/cm ³	Viscosity mPa.s	Ap/Po	Solubility Parameter	Dielectric Constant	Solid-gel trans. C
DBP	278	1.046	17	8/2	9.41	6.42	86
DOP	390	0.986	60	16/2	8.83	5.18	117
DIDP	446	0.962	103	20/2	8.56	4.44	139
DTDP	530	0.948	190	26/2	8.45	4.05	151
DOA	370	0.920	11	20/2	8.46	4.13	138
DOS	426	0.913	18	24/2	8.43	3.88	151
DIDA	426	0.915	20	24/2	8.25	3.74	156
TOTM	547	0.987	200	24/3	9.00	4.65	142
TIDTM	630	0.968	---	30/3	8.67	4.20	---
903	2250	1.090	3800	92/22	9.20	6.03	150
430	2250	1.125	9000	88/22	9.40	6.16	163
TAP	380	1.137	80	6/3	9.50	6.65	110

^a From Ref. 109, Appendix and Ref. 122, Ch. 5,6, and 7.

2.2 Measurements Related to the Determination of Plasticizer Compatibility

2.2.1 Solid-Gel Transition Temperature (T_m)

This is the temperature at which a PVC grain embedded in excess plasticizer passes from an opaque solid material to a transparent gel.

The solid-gel transition temperatures were determined using the hot stage of a Fisher-Johns melting point apparatus attached to an optical microscope. The procedure was as follows: A drop of plasticizer was placed onto the hot stage and a few grains of PVC were immersed in it; the temperature in the hot stage was then increased at a rate of 1 C/min (starting at a point ca 20 C below the T_m previously determined at a rate of 5 C/min), and the transition from an opaque solid to a transparent gel was taken as the solid-gel transition temperature. Each temperature was determined after examination, through the microscope, of 3-5 different PVC grains. Each temperature is the average of 3 determinations.

2.2.2 Plasticizer Density at T_m

These were determined as follows: Using a graduated test tube, 10 cm³ of plasticizer were weighed, at 23 C, to obtain w_1 [g]. These 10 cm³ were then heated up to the solid-gel transition temperature, at which temperature the volume of plasticizer was measured to obtain v_2 .

The density of the plasticizers at the solid-gel transition temperature was calculated as:

$$\rho = w_1 / v_2 \quad (2.1)$$

each density is the average of 3 determinations.

2.2.3 Flory-Huggins Interaction Parameter

Calculated from [Refer to section 1.8.5.5]:

$$1/T_m = 0.002226 + 0.1351(1 - \chi)/V_1 \quad (2.2)$$

where T_m is the depressed melting temperature of PVC, V_1 is the molar volume of plasticizer at T_m , and χ is the Flory-Huggins interaction parameter.

2.2.4 Activity Parameter

Calculated from [Refer to section 1.8.5.6]:

$$\alpha = (1 - \chi)/MW \times 1000 \quad (2.3)$$

where χ is the Flory-Huggins interaction parameter, MW is the molecular weight of plasticizer, and α is the activity parameter.

2.3 Sample Preparation

2.3.1 Formulations

All formulations used throughout this work, except when specified otherwise, were:

PVC	100 phr
plasticizer	50 phr
stabilizer	1 phr

where "phr" means, parts of additive per hundred parts of resin, (by weight).

2.3.2 Dry Blending

Two different techniques were used for preparing the dry blends.

a).- Dry blends were prepared in a Fielder laboratory high speed mixer, at 3000 rpm, as follows: With the temperature at 80C, the PVC was introduced and preheated for about 4 min. Thereafter, the temperature controls were re-set at 120 C, the plasticizer plus stabilizer were added and the ingredients allowed to mix until they reached 120 C (i.e. allowed to mix for approximately 11 min), at which point the mix is discharged and cooled.

b).- Dry blends were prepared in a Z type blades mixing chamber of 300 cm³ capacity, attached to a Brabender torque rheometer, at 67 rpm and 92C, as follows: With the temperature at 92 C, the chamber was preheated for 10 min. The PVC was then introduced and preheated for 5 min. (from a to b in Fig 2.2), after which the plasticizer plus stabilizer were added.

At this point the torque increases rapidly due to the increased stickiness of the wet PVC grains. But after a short time, (from b to c in Fig 2.2), the plasticizer is absorbed into the PVC grains and the torque decreases. The wet mix has changed to a free flowing dry powder blend. The time from b to c is called the "dry blend time". The total mixing time was always maintained at 20 min. (in all cases the dry blend time was less than 20 min.).

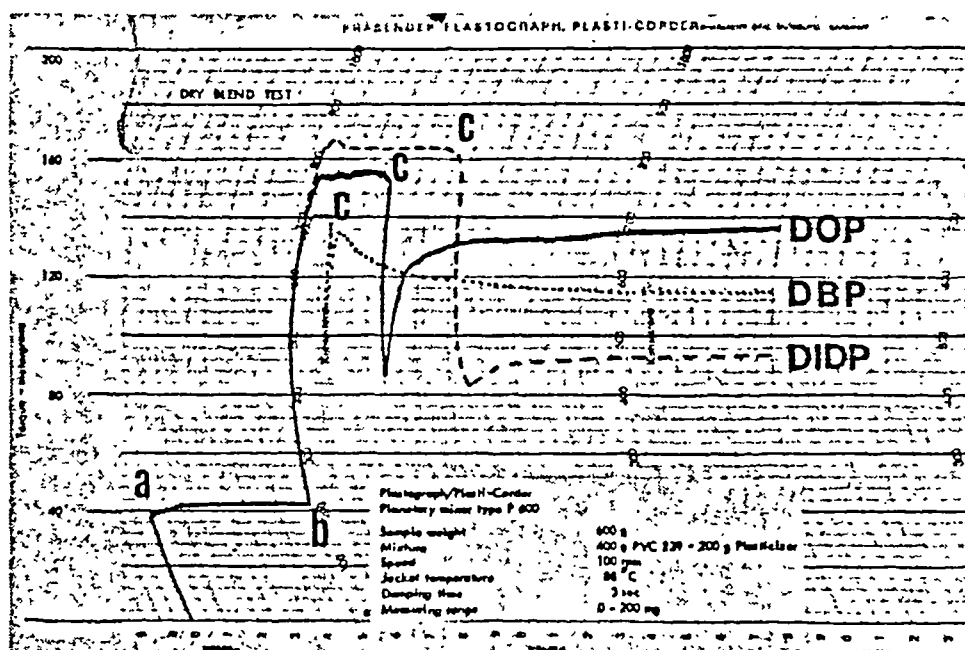


Fig. 2.2: Typical variation of torque versus time during dry blending of a PVC/plasticizer mix in a Brabender torque rheometer.

2.3.3 Moulding and Mixing

Two different fusion processes were selected for sample preparation. One was compression moulding, a very low shear process where heating for fusion comes only from the electrically heated press plattens. The other was Brabender mixing, a high shear process where heating for fusion comes from both, the heated walls of the mixer and the mechanical shear exerted upon the sample.

a).- Dry blends were compression moulded at 35 MPa (350 Kg/cm²) for 5 min. at "T_c", and then cooled while still in the mould. T_c was 140, 155, 170, 185, and 200 C. The mould dimensions were 150x150x2.3 mm. This technique produced samples moulded at 5 different temperatures for each of the 12 plasticizers studied. These are referred to as "Moulded Samples".

b).- Dry blends were processed in a roller type blades mixing chamber of 70 cm³ capacity, attached to a Brabender torque rheometer, at 32 rpm, as follows: With the temperature at 80 C, the dry blend was introduced into the chamber, and the temperature controls then set at 200 C. The processing (mixing) was then started and continued until a temperature "T_b" was reached. At this point, the sample was discharged and let to cool at room temperature. T_b was 140, 155, 170, 185, and 200 C. During this processing, the heating rate was approximately 3 C/min. Figure 2.3 illustrates the typical torque-temperature plot for this process. This technique produced samples mixed to 5 different temperatures for each of the 12 plasticizers studied. These are referred to as "Brabender Samples".

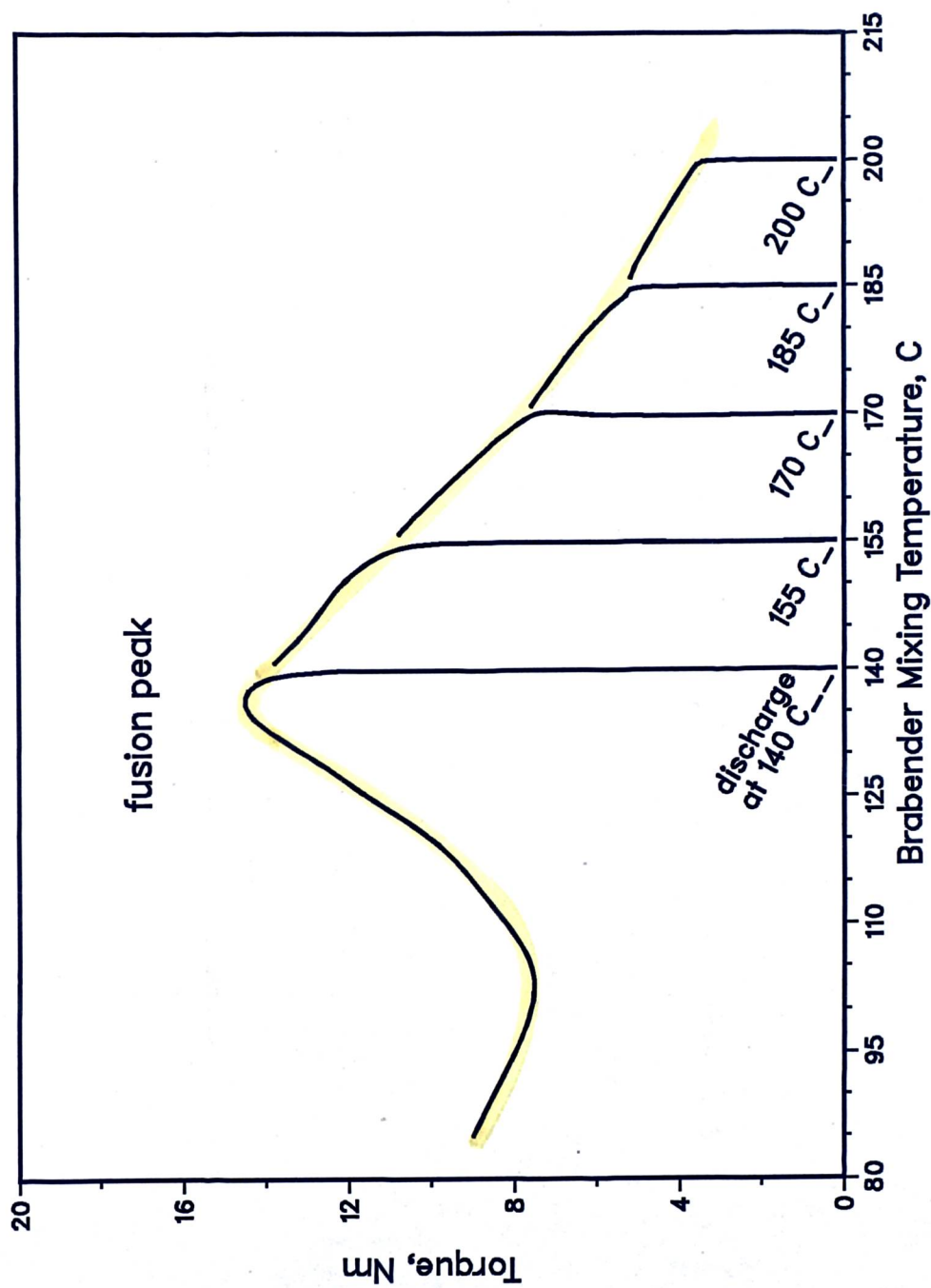


Fig. 2.3: Typical torque – temperature plot during mixing in a Brabender torque rheometer.

2.4 Thermomechanical Analysis

A Dupont TMA was used for determining the T_g 's of the plasticized PVC compounds studied.

The penetration of an indenter into the sample, as it passed from glassy state to elastomeric state, was used to determine T_g .

T_g 's were determined on samples 2.3 mm thick, moulded at 185 C/200 C. The temperature scanning was from -100 C to 100 C, at 5 C/min., and the load weight upon the indenter was 20 g.

T_g 's were determined as indicated in Figure 2.4.

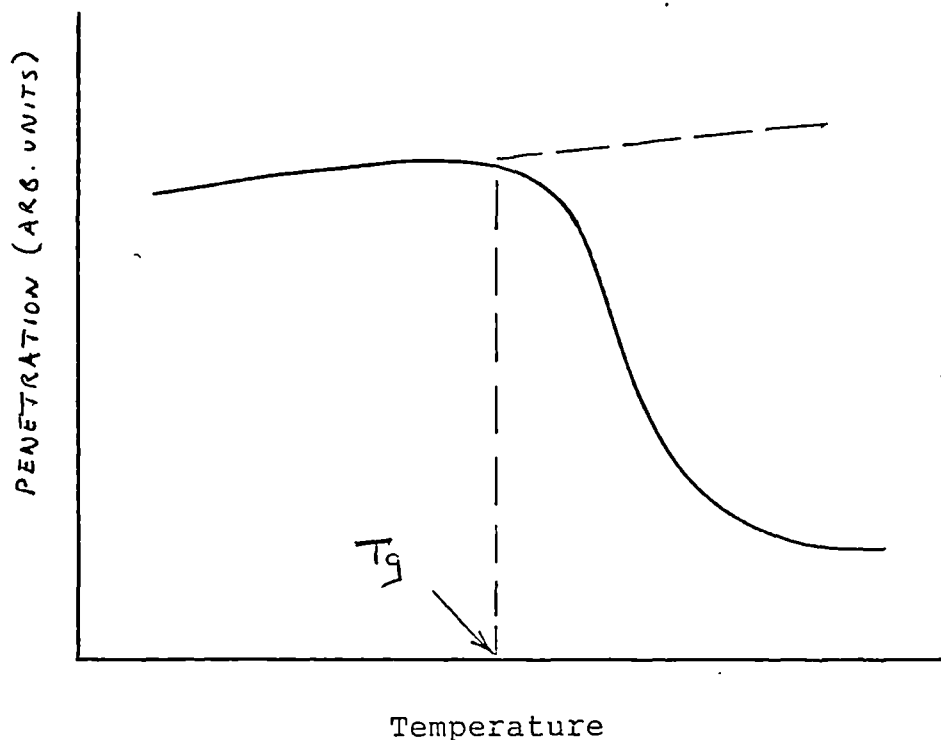


Fig. 2.4: Determination of T_g from TMA.

2.5 Assessment of Fusion

2.5.1 Optical Microscopy (OM)

Solvent swollen Brabender samples were examined through a Carl Zeiss optical microscope. Pieces of approximately 10 mg were first immersed in acetone for one week. These pieces were then taken out and sheared between glass slides, with finger pressure, while still wet. Optical microscopic analysis was then carried out through the glass slides, maintaining the finger pressure on the glass slides during examination. [Refer to section 1.6.3].

2.5.2 Electron Microscopy (EM)

Moulded and Brabender samples were examined through a Jeol transmission electron microscope. Samples were first microtomed, either as such or alternatively after embedding in epoxy resin, after which each sample was examined at magnifications of X 5K and X 10K.

2.5.3 Capillary Rheometry

Moulded and Brabender samples were tested in an Instron capillary rheometer to obtain the extrusion pressure loss at the entrance of the capillary, which is related to the degree of fusion of the PVC sample. [Refer to section 1.6.4]. The test conditions were; temperature of 130 C, Newtonian shear rate of 121 sec^{-1} , and a die with L/R ratio of 2.1 and a diameter of 1.0 mm. Prior to testing, each sample was preheated for 10 min. in the barrel of the capillary rheometer.

2.5.4 Extrudate Distortion or Melt Fracture

During the Capillary rheometry experiment, all extrudates were examined for surface roughness and compared to a set of standards previously prepared for the purpose. A qualification was then given to each sample according to the severity of distortion it showed, i.e. from 1 for very low distortion, to 5 for very high. [Refer to section 1.6.5].

2.5.5 Thermal Analysis

Moulded and Brabender samples were analysed in a Dupont 990 thermal analyzer with a DSC cell, to obtain the enthalpy of the endotherm A and the temperature for the onset of the endotherm B, which are both function of the processing history of the sample. [Refer to section 1.6.8]. The test conditions were; range 10 C/cm, heating rate 20C/min, sensitivity 1 mV/cm, and nitrogen flow rate of ca 60 cm³/min. The mass of the sample used for analysis was ca 15 mg, and the scanning was done over the range 20 to 220 C.

The equation for calculation of enthalpy was:

$$\Delta H = (A/m) (60BE \Delta q) \quad (2.4)$$

where:

A = area of endotherm

m = mass of sample

B = time base setting (range/heating rate)

E = cell calibration coefficient

Δq = Y axis range (sensitivity)

and 60 represents sec/min

2.6 Dynamic Mechanical Analysis

Moulded samples were analysed in a Rheometrics mechanical spectrometer to obtain viscosity and modulus data, using the eccentric rotating disc geometry shown in Figure 2.5. The test temperature was 140 C. The frequencies used ranged from 0.1 to 100 rad/sec. The equations are:

$$G' = F_y / (\pi R^2 \gamma) \quad (2.5)$$

$$G'' = F_x / (\pi R^2 \gamma) \quad (2.6)$$

$$\eta = [G'^2 + G''^2]^{1/2} / \omega \quad (2.7)$$

where:

R = radius of moulded sample disks (1.25 cm)

γ = shear strain imposed on the sample (0.1)

ω = frequency

F_y = force in Y direction

F_x = force in X direction

G' = storage (elastic) modulus

G'' = loss (viscous) modulus

η = dynamic shear viscosity

2.7 Tensile Properties

Moulded samples were tested in an Instron tensile testing machine. Tensile specimens were die cut from the moulded sheets and were as in Figure 2.6. Test conditions were: temperature 23C and rate of stretching 50 mm/min. Tensile strength and elongation were determined at the point of rupture.

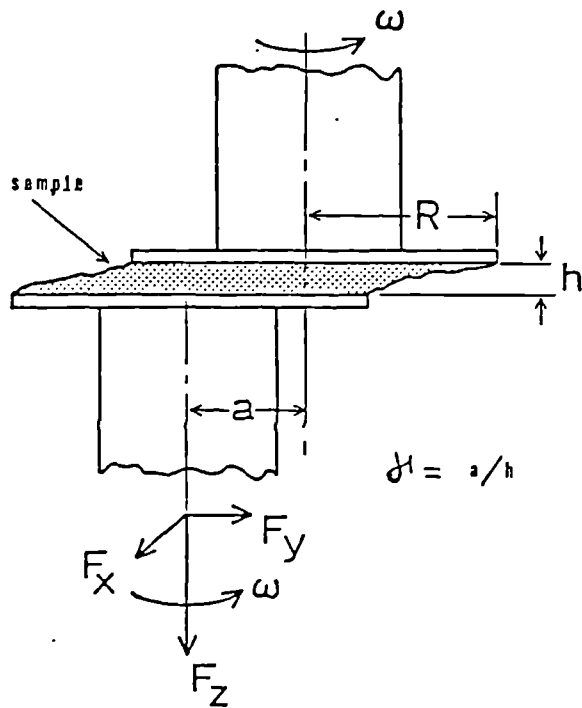


Fig. 2.5: Illustration of the eccentric rotating disk geometry (ERD) used in the Rheometrics mechanical spectrometer.- a is the eccentricity of the disks and h is the separation between disks.

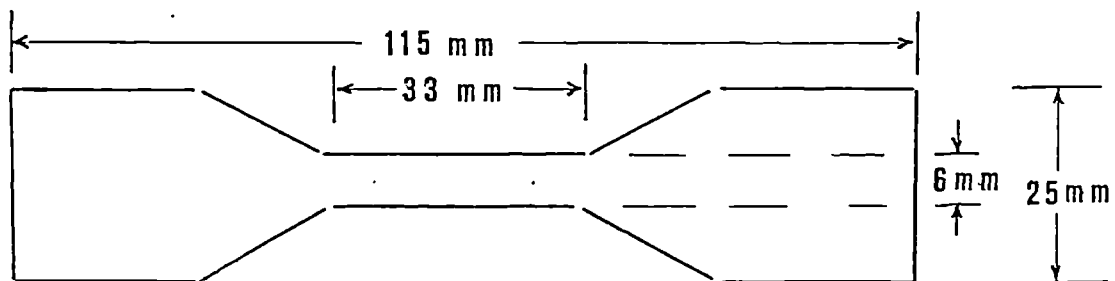


Fig. 2.6: Dimensions of the tensile test specimens.

Chapter 3

RESULTS AND DISCUSSION: PVC/PLASTICIZER COMPATIBILITY

3.1 Compatibility Predictors (δ and ϕ)

Tables 3.1 and 3.2 present the Hildebrand solubility parameter of plasticizers, as compared to that of PVC, as well as the polarity parameter of plasticizers respectively, both arranged in order of increasing magnitude, i.e. in order of decreasing compatibility.

Table 3.1

($\delta_{\text{PVC}} - \delta_{\text{Plasticizer}}$)	
TAP	0.10
DBP	0.19
430	0.20
903	0.40
TOTM	0.60
DOP	0.77
TIDTM	0.93
DIDP	1.04
DOA	1.14
DTDP	1.15
DOS	1.17
DIDA	1.35

Table 3.2

polarity parameter	

TAP	0.76
DBP	1.11
DOP	3.12
DOA	3.71
TOTM	4.38
DIDP	4.47
DOS	5.12
DIDA	5.12
TIDTM	6.30
DTDP	6.90
430	9.00
903	9.40

It is observed that the ordering of plasticizer Compatibility is quite different according to these two compatibility predictors, especially if applied to polymeric plasticizers. It should be noticed however, that if the two polymeric (903 and 430) are excluded from these Tables, the ordering of plasticizers becomes acceptably similar. Therefore, the solubility parameter as well as the polarity parameter of polymeric plasticizers should be used with caution as compatibility predictors for PVC.

3.2 Compatibility Measurements (T_m , χ , α)

Table 3.3 presents the solid-gel transition temperature (T_m) of the plasticizers studied, arranged in order of increasing magnitude, i.e. in order of decreasing compatibility.

Table 3.3

----- solid-gel transition temp. (T_m) -----		
DBP	92 C	365 K
TAP	112	385
DOP	118	391
DIDP	136	409
DOA	138	411
TOTM	139	412
DOS	152	425
903	152	425
DTDP	154	427
DIDA	158	431
430	163	436
TIDTM	164	437

The techniques used to obtain T_m vary, and there is therefore a variation in the reported values. However, the relative ordering of plasticizers is fairly consistent.

According to the values of T_m , The ordering of the plasticizers studied is consistent with those reported in the literature^{122,124,127}.

Figure 3.1 shows the variation of the solid-gel transition temperature with the solubility parameter. It is seen that T_m tends to decrease as the solubility parameter of the plasticizer becomes closer to that of PVC. However, not all plasticizers fall in the same curve. One reason could be that the solubility parameters presented here were determined at 25 C, i.e. they predict compatibility at 25C, whereas T_m measures compatibility precisely at the solid-gel transition temperature. In addition, the solubility parameter decreases with temperature and the variation of δ with temperature is different for each plasticizer.

Figure 3.2 shows the variation of the solid-gel transition temperature with the polarity of the plasticizers. It is seen that T_m decreases with increasing plasticizer polarity, i.e. compatibility increases with polarity of plasticizer (within the plasticizers studied). A least squares fit, excluding the polymeric, gives:

$$T_m[C] = 93.23 + 10.5 \times \phi \quad (3.1)$$

with a low correlation coefficient of 0.9223.

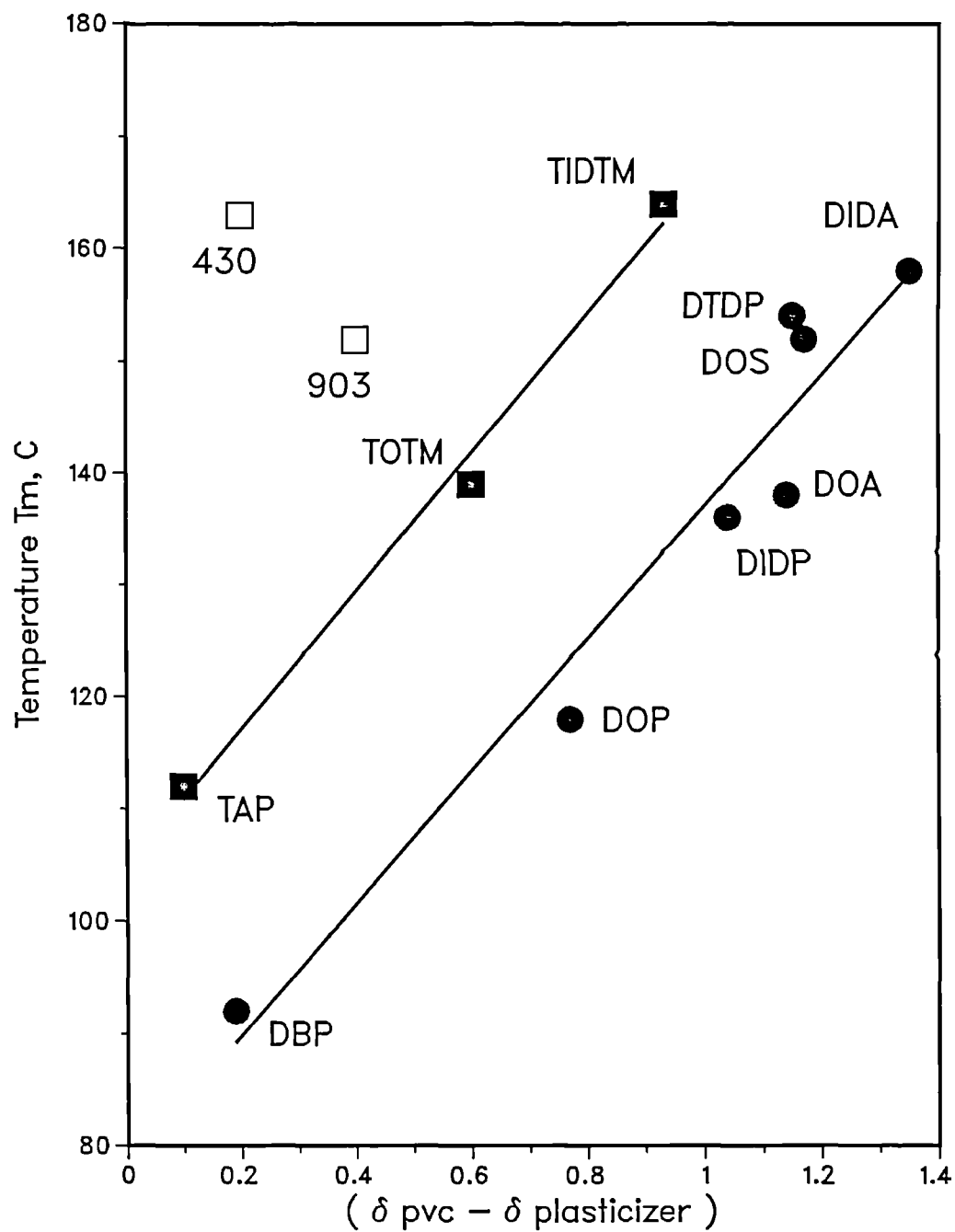


Fig. 3.1: Variation of the solid_{gel} transition temp. with the Hildebrand solubility parameter difference.

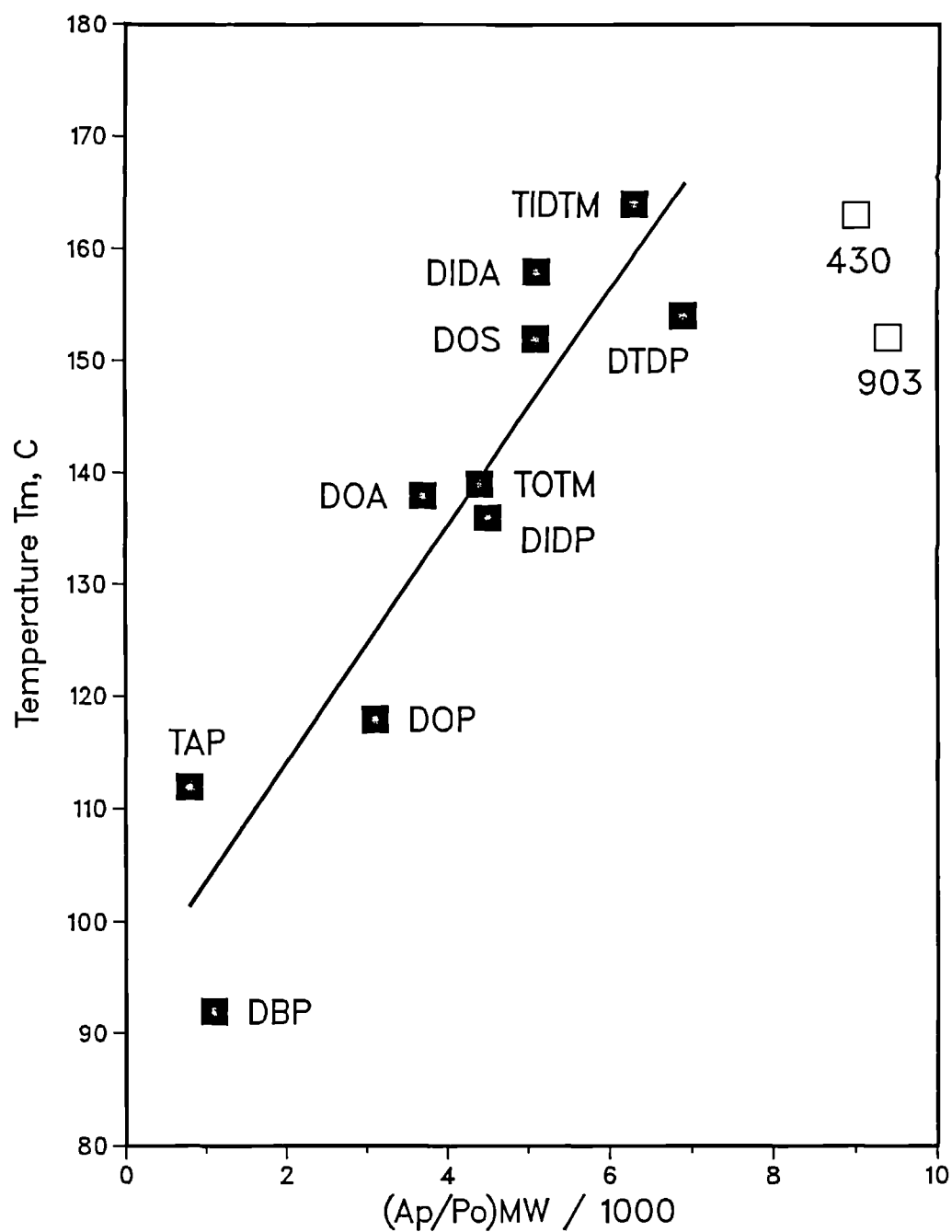


Fig. 3.2: Variation of the solid_{gel} transition temp. with the polarity parameter of plasticizers " φ ".

Table 3.4 presents the Flory-Huggins interaction parameter of the plasticizers studied, calculated from equation 2.2, arranged in order of increasing magnitude, i.e. in order of decreasing compatibility.

Excluding the polymerics, the ordering of plasticizer compatibility given by the interaction parameter is very similar to the ordering given by T_m .

Table 3.4

interaction parameter	
903	-1.08
430	-0.10
DBP	-0.06
TAP	-0.05
DOP	-0.04
TOTM	0.14
DIDP	0.20
DOA	0.33
DTDP	0.48
DOS	0.52
DIDA	0.65
TIDTM	0.67

Figure 3.3 shows the variation of χ with T_m . A least squares fit, excluding the polymerics, gives:

$$\chi = 1.59 - 0.0346xT_m + 0.000179xT_m^2 \quad (3.2)$$

[T_m in C] with a standard deviation of 0.06 between the estimated and the experimental values of χ .

NOTE: Tables 3.5 and 3.6 present the density of plasticizers at T_m , and the molar volume of plasticizers at T_m (V_1) respectively. These are not measurements of compatibility, but V_1 is needed to calculate the Flory-Huggins interaction parameter and V_1 is determined as the ratio of the molecular weight of plasticizer and its density at T_m .

Table 3.5

Table 3.6

density at T_m [g/cm ³]		molar volume at T_m [cm ³ /mol]	
DBP	1.001	DBP	278
DOP	0.919	DOP	424
DIDP	0.893	DIDP	499
DTDP	0.874	DTDP	606
DOA	0.856	DOA	433
DIDA	0.835	DIDA	510
DOS	0.832	DOS	512
TOTM	0.919	TOTM	595
TIDTM	0.890	TIDTM	708
903	1.018	903	2210
430	1.032	430	2180
TAP	1.090	TAP	349

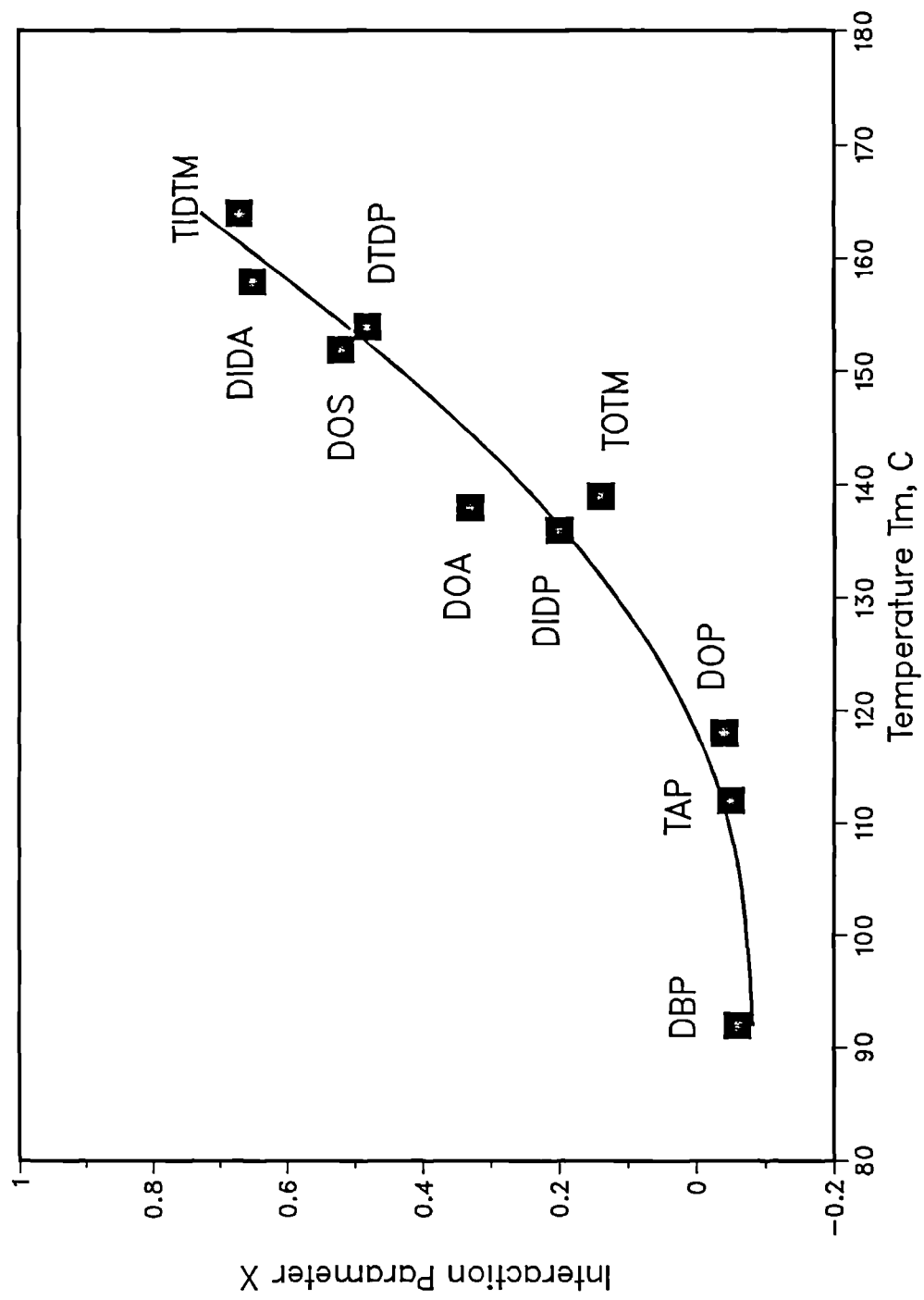


Fig. 3.3: Variation of the Flory Huggins interaction parameter with the solid_gel transition temperature of plasticizers.

Table 3.7 presents the activity parameter of the plasticizers studied, calculated from equation 2.3, in order of decreasing magnitude, i.e. in order of decreasing compatibility.

Including the polymerics, the ordering of plasticizer compatibility given by the activity parameter is identical to the ordering given by T_m . Excluding the polymerics, on the other hand, the ordering given by the activity parameter is very similar to the ordering given by the Flory-Huggins interaction parameter, (and also by the ordering given by T_m).

Table 3.7

activity parameter	
DBP	3.8
TAP	2.8
DOP	2.7
DIDP	1.8
DOA	1.8
TOTM	1.6
DOS	1.1
DTDP	1.0
903	0.9
DIDA	0.8
TIDTM	0.5
430	0.5

Figure 3.4 shows that the activity parameter increases with the polarity of plasticizers. A least squares fit, excluding the polymeric, gives:

$$\alpha = 3.73 - 0.47 \times \phi \quad (3.3)$$

with a low correlation coefficient of 0.9138.

A linear relationship between the activity parameter " α " and the polarity parameter " ϕ " has also been recently reported by Patel and Gilbert⁷⁸. [The plasticizers involved in that study are those listed above in section 1.12].

In addition, Figure 3.5 shows that the activity parameter varies linearly with $1/T_m$. A least squares fit gives:

$$\alpha = -16.42 + 7.42 \times 1000/T_m \text{ [K]} \quad (3.4)$$

with a high correlation coefficient of 0.9956.

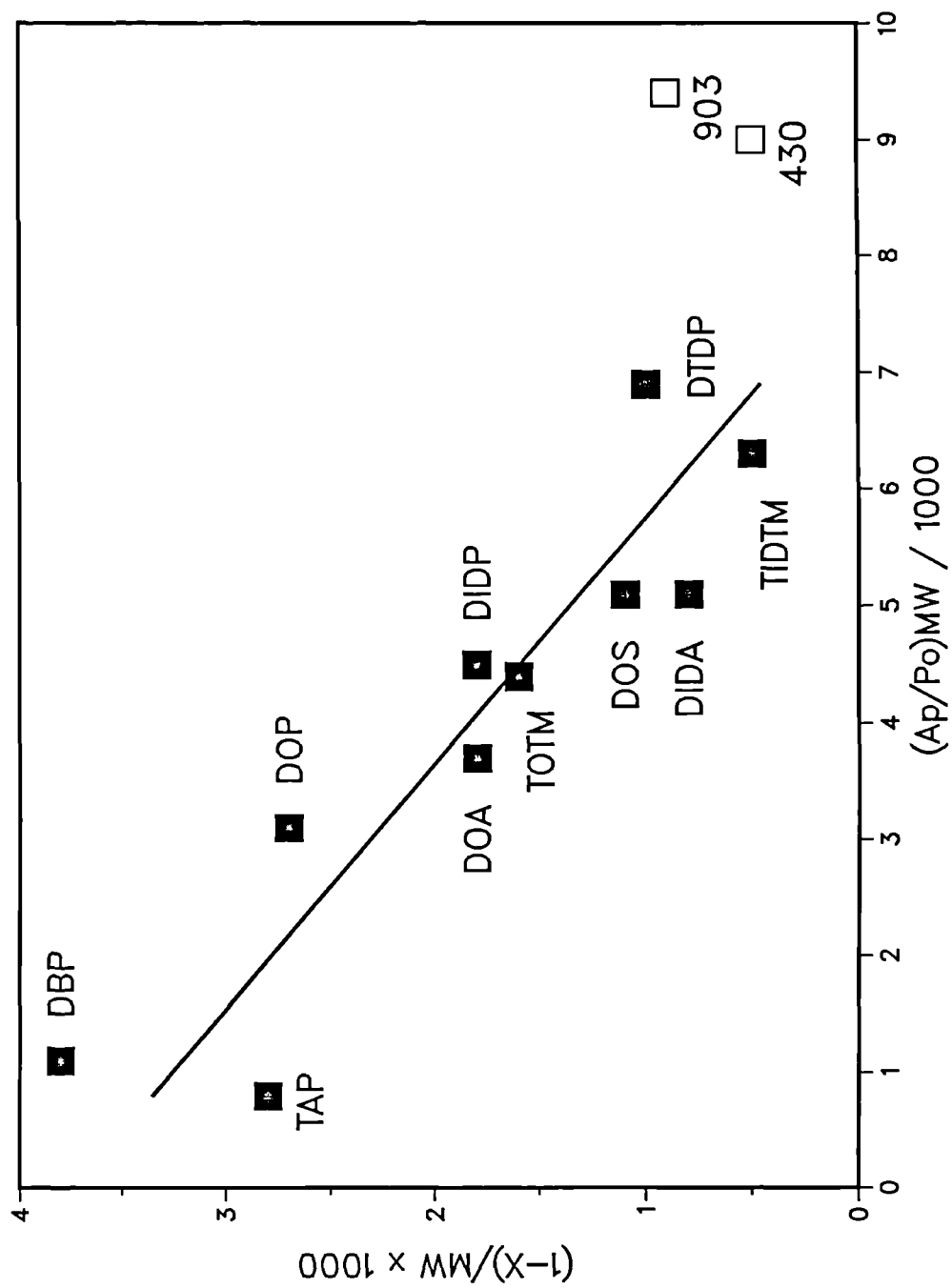


Fig. 3.4: Variation of the activity parameter $\alpha \propto \frac{(1-X)}{MW} \times 1000$ with the polarity parameter of plasticizers $\varphi \propto \frac{(Ap/Po)MW}{1000}$.

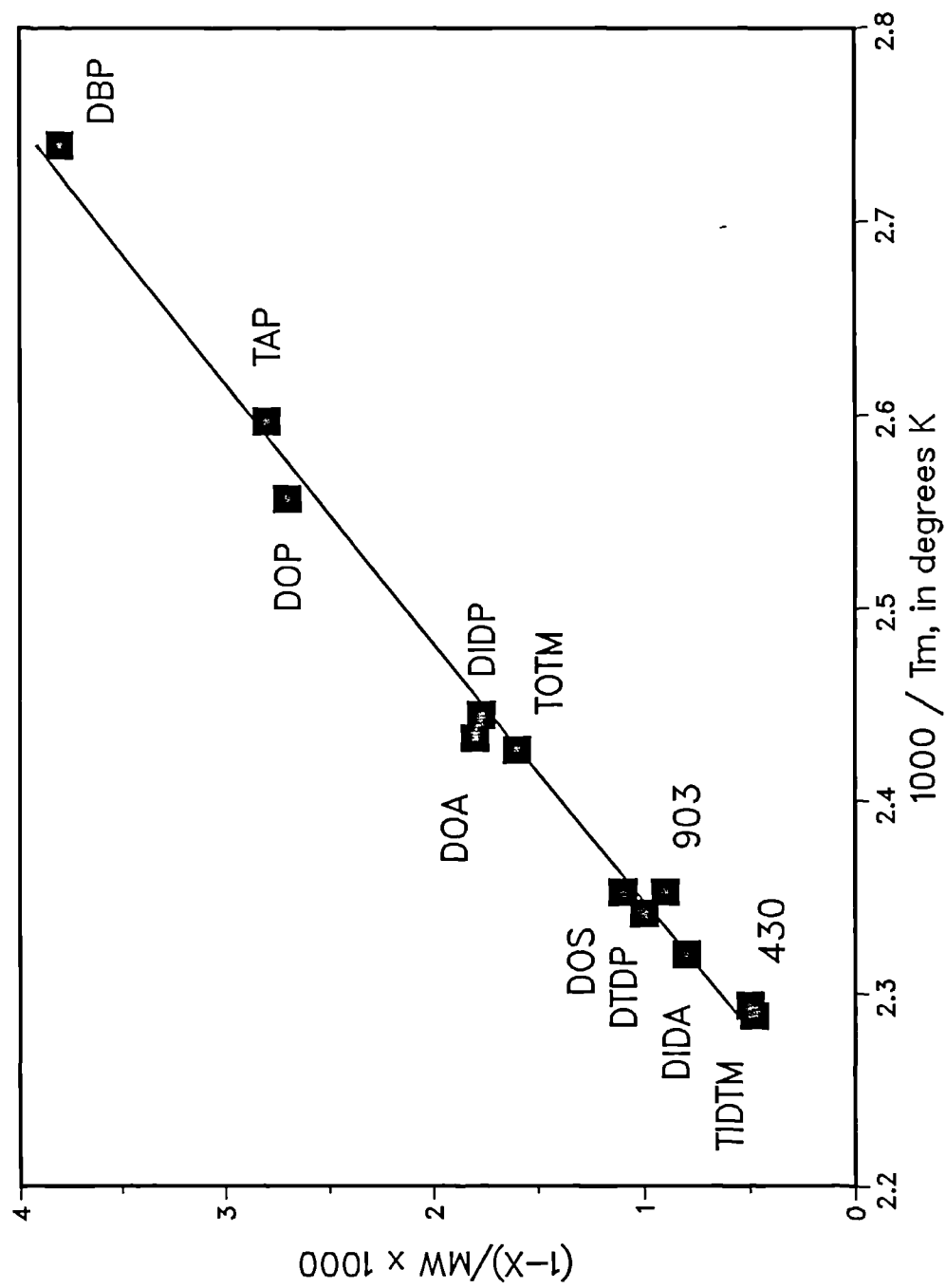


Fig. 3.5: Variation of the activity parameter $\propto \frac{(1-X)}{MW} \times 1000$ with the inverse of the solid_gel transition temp. of plasticizers.

3.3 Remarks and Conclusions

First, the PVC/plasticizer compatibility predicted by the solubility parameters and presented in Table 3.1, applies at 25 C. Yet, even after applying the temperature correction proposed by Fedors¹¹⁸, the modified solubility parameters produce the same ordering of the relative plasticizer compatibilities.

Note: The correction proposed by Fedors is given by:

$$\delta_2 = \delta_1 (V_1 / V_2)^{1.13} \quad (3.5)$$

where V_1 and V_2 are the molar volumes of plasticizer at the temperatures T_1 (25 C) and T_2 , and δ_1 and δ_2 are the solubility parameters at T_1 and T_2 .

Second, it is recommended that compatibility predictors, such as δ and ϕ , should not be used alone as the sole indicators of compatibility. Though they predict the relative compatibilities of plasticizers belonging to the same family, e.g. phthalates, they fail to predict the relative compatibilities of plasticizers of different families.

On the other hand, compatibility measurements, such as T_m , χ , and α , give a much more consistent, and therefore more reliable indication of the relative compatibilities of plasticizers of even very different families, with the exception of χ when applied to polymeric plasticizers. In addition, these compatibility measurements are relatively easy to carry out in the laboratory.

Third, according to T_m and α , the compatibility of PVC with the polymeric plasticizers (903 and 430) is relatively low. However, according to χ , the compatibility of these polymerics is much higher, (the highest of all the plasticizers studied), which is difficult to believe. One possible explanation could be the following: The equation used to obtain the Flory-Huggins interaction parameter (equation 1.16 or 2.5) considers as V_2 , (i.e. the volume of the polymer molecule that interacts with the plasticizer), the molar volume of the polymer repeat unit. Whereas it considers as V_1 , (i.e. the volume of the plasticizer molecule that interacts with the polymer repeat unit), the molar volume of the plasticizer. However, it is suggested that when applied to polymeric plasticizers, V_1 should be equal, not to the molar volume of the plasticizer, but to some smaller volume that might be the one that interacts with the molar volume of the polymer repeat unit.

For example, considering this smaller volume as the molar volume divided by 3 or by 4, the interaction parameter of the two polymerics becomes:

molar volume/3	molar volume/4
$\chi_{903} = 0.35$	$\chi_{903} = 0.50$
$\chi_{430} = 0.66$	$\chi_{430} = 0.72$

In doing so, the ordering of plasticizer compatibility, according to the interaction parameter, (including the polymerics this time), becomes very similar to that obtained by T_m and α .

It may be assumed, that the volume of plasticizer that interacts with the volume of the PVC repeat unit should be below a critical limit. If the molar volume of plasticizer were higher, then the plasticizer molecule can either become progressively less efficient (the molar volume becoming higher than the necessary to effect plasticization), or alternatively, divide itself into units that will act as separate plasticizer molecules. Possibly, the molecules of polymeric plasticizers are long enough as to act as several separate units, as depicted in Figure 3.6.

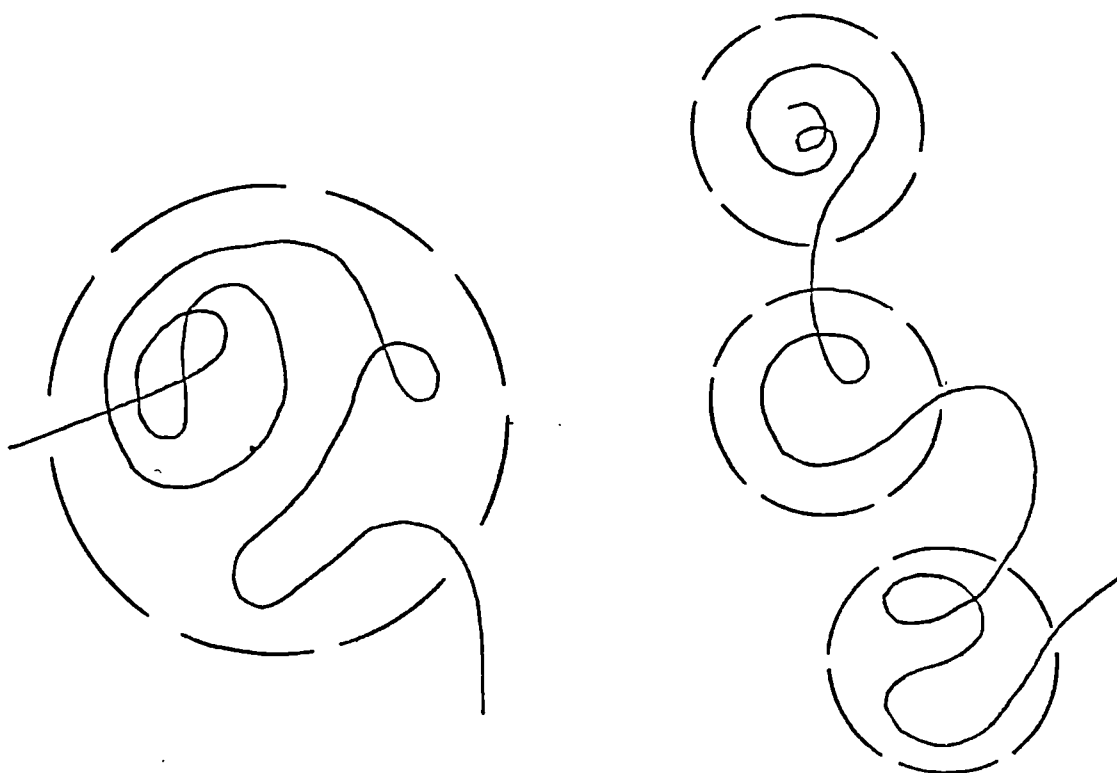


Fig. 3.6: Representation of the polymeric plasticizer molecule arranging itself into one unit the size of the molar volume, or alternatively, into three units each one approximately one third of the molar volume.

Fourth, the only difference between the two polymeric plasticizers (similar molecular weight and similar main chain constituents) is the chain termination. It has been reported¹²² that end termination, e.g. alcohol termination, reduces the viscosity of polymeric plasticizers by reducing the hydrogen bonding capability of the terminal hydroxyl or carboxyl groups. Furthermore however, it is also noticed that the lower viscosity tends to increase the plasticizer compatibility with PVC. (e.g. 903 being more compatible than 430).

Fifth, several equations were obtained that relate the different compatibility parameters.

Chapter 4

RESULTS AND DISCUSSION: PROCESSING

4.1 Compression Moulding

The dry blends were compression moulded at temperatures ranging from 140 to 200C, to produce moulded sheets of different degrees of fusion.

In addition, compression moulding was also used to produce moulded disks of 25 mm in diameter and 2.3 mm thick, at temperatures ranging from 140 to 200C, which were later used in the Rheometrics mechanical spectrometer.

4.2 Brabender Mixing

The dry blends were processed in a roller type blades mixing chamber attached to a Brabender torque rheometer. The Brabender mixing was carried out as follows: With the (chamber) temperature at 80C, a batch of dry blend (e.g. PVC/DOP) was introduced into the chamber. The temperature controls were then set at 200 C, and the mixing and heating up started. The mix was discharged at 140 C and allowed to cool at room temperature (referred to as Brabender sample DOP/140). Again at 80C, another batch of dry blend was introduced into the chamber, the temperature controls were set at 200 C and the mixing and heating up started. The mix was discharged at 155 C and allowed

to cool at room temperature (referred to as Brabender sample DOP/155). The procedure was repeated to obtain the Brabender samples DOP/170, DOP/185, and DOP/200.

The torque - temperature curve for the PVC/DOP compound in Figure 4.1, is the result of superimposing the 5 different curves previously described for the PVC/DOP samples.

The whole procedure was repeated with each one of the 12 different plasticizer.

Figures 4.1 to 4.4 present the torque-temperature variation of the PVC/plasticizer compositions studied, and Table 4.1 presents the time, temperature, and torque at the fusion peak, [Refer to section 2.3.3], arranged in order of increasing fusion temperature T_f , i.e. in order of decreasing plasticizer compatibility.

It is observed that the temperature at the fusion peak increases with decreasing PVC/plasticizer compatibility. Also, the ordering of plasticizers in Table 4.1 is very similar to that obtained according to the physical-chemical parameters that measure their compatibility with PVC, such as the solid-gel transition temperature, the Flory-Huggins interaction parameter, and the activity parameter, described in chapter 3. This suggests a clear relationship between the Brabender data at the fusion peak and the above mentioned physical-chemical parameters.

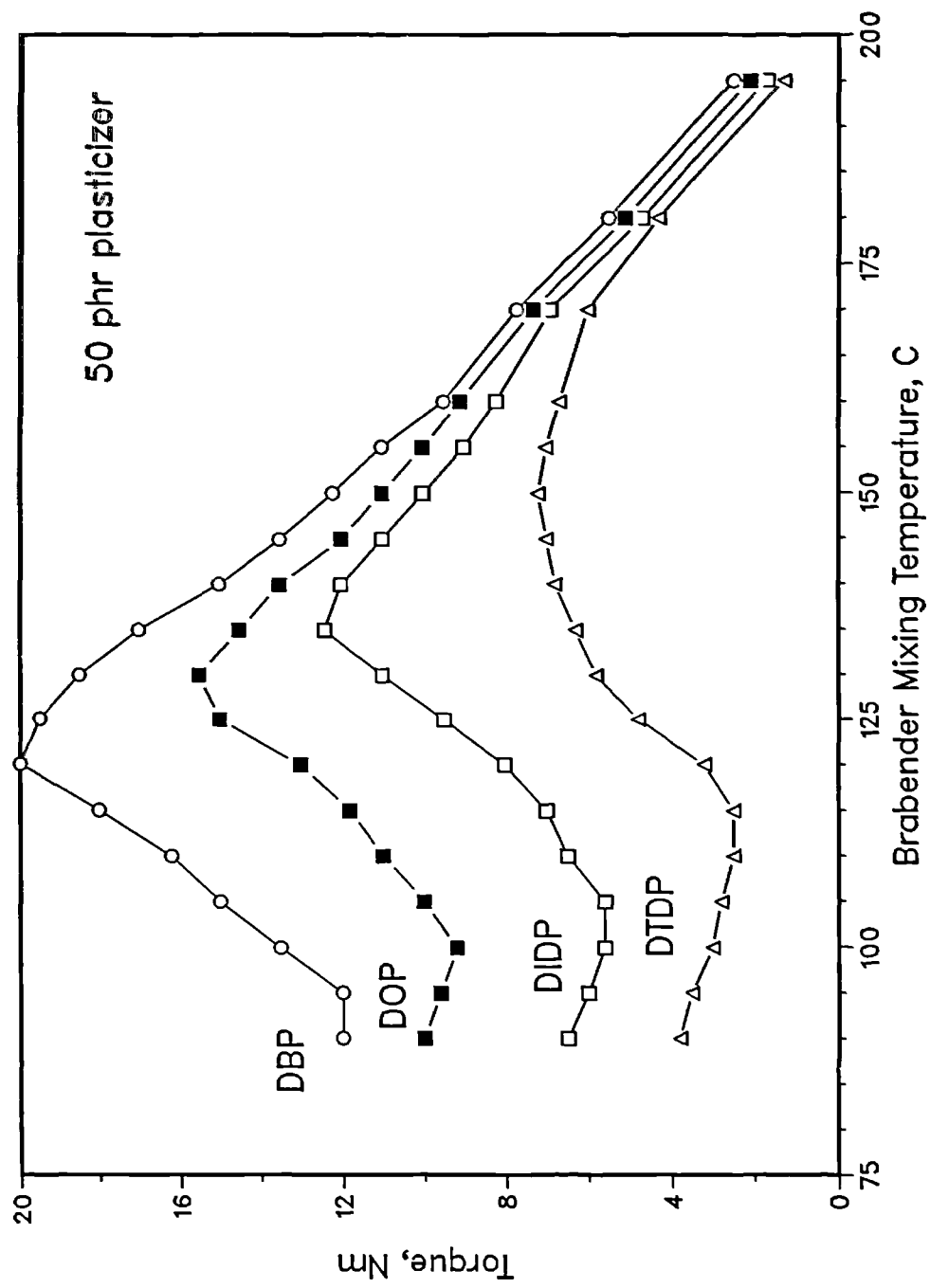


Fig. 4.1: Variation of torque with temperature of plasticized PVC, during mixing in a Brabender torque rheometer.

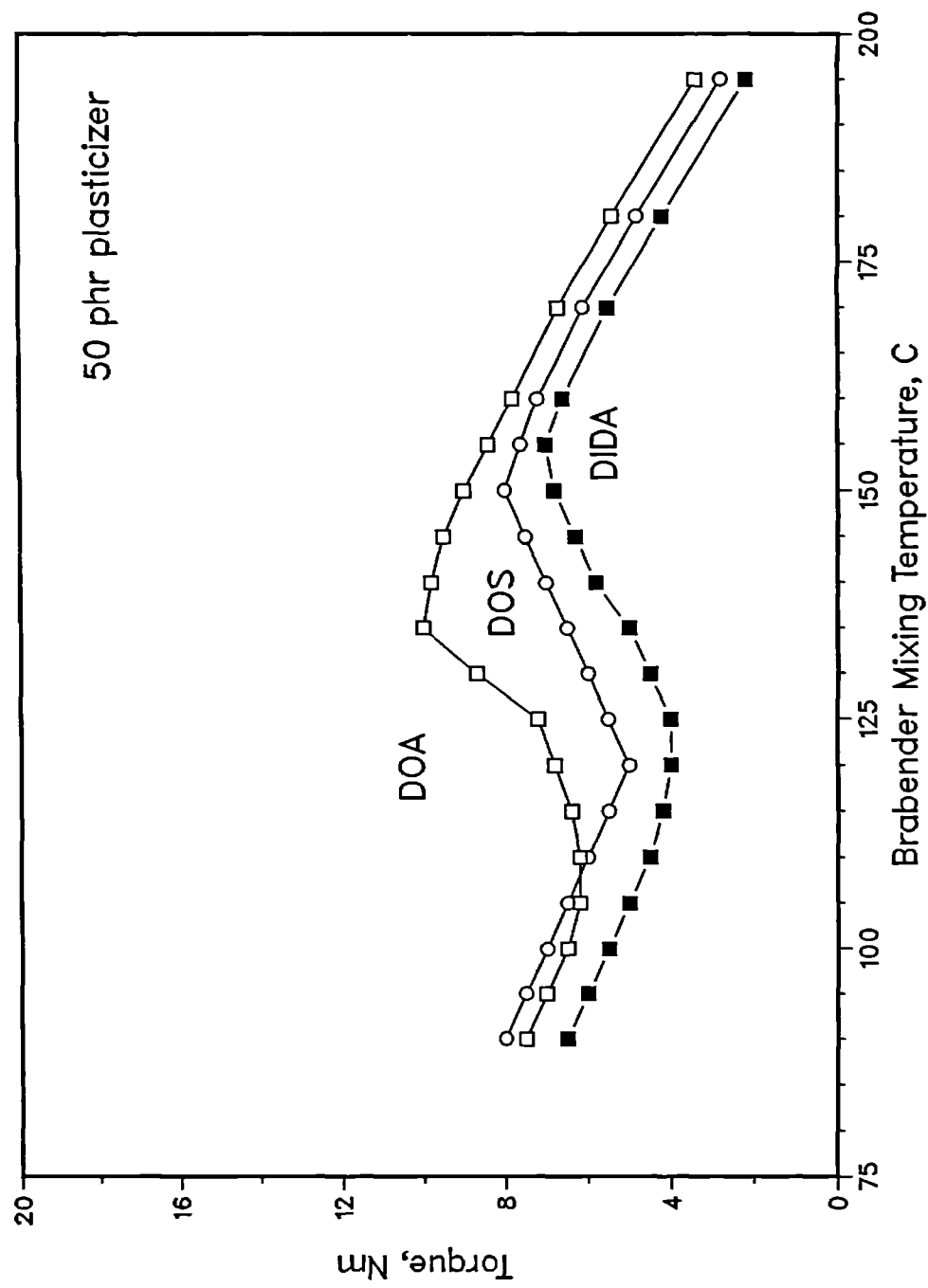


Fig. 4.2: Variation of torque with temperature of plasticized PVC, during mixing in a Brabender torque rheometer.

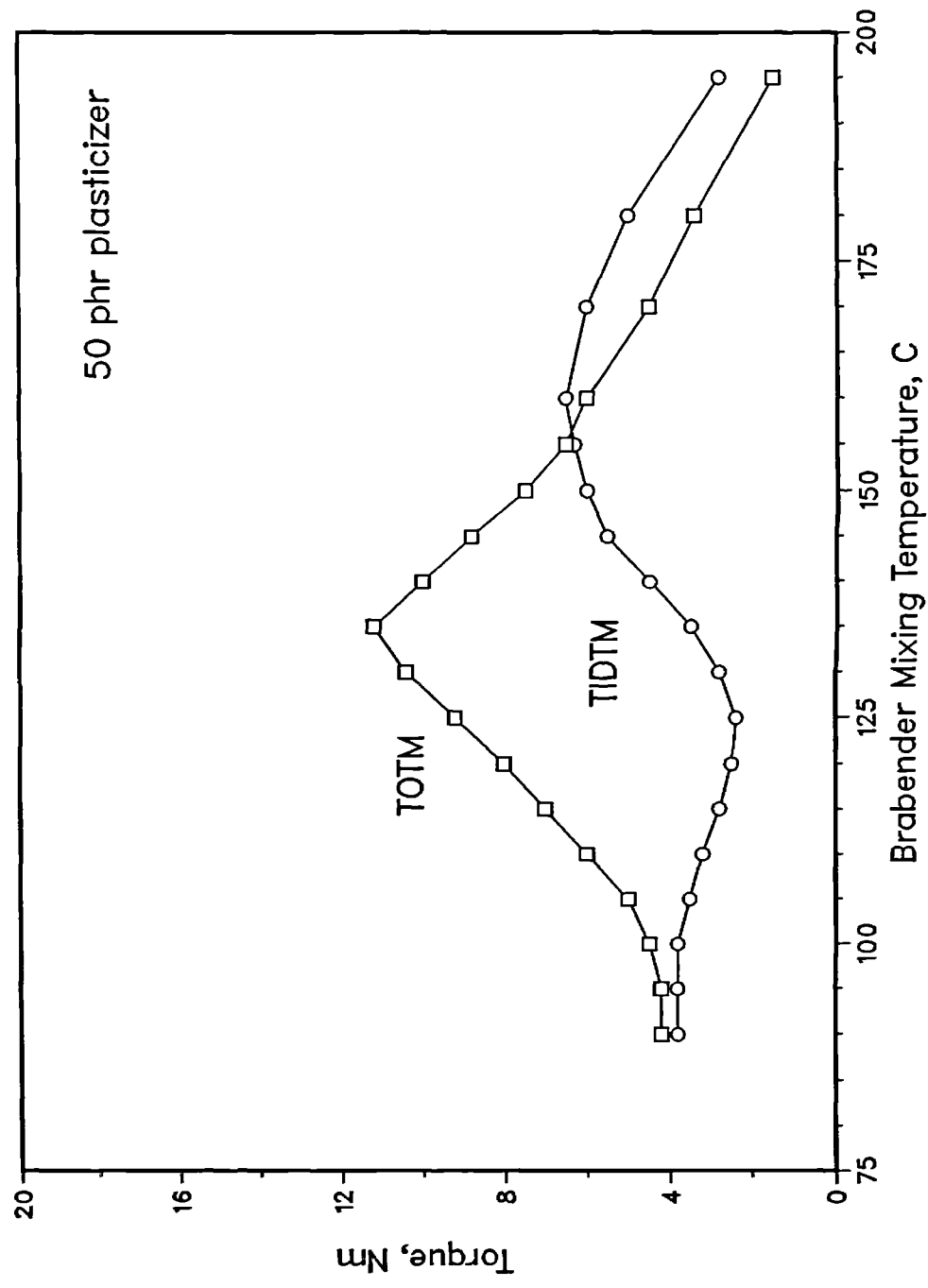


Fig. 4.3: Variation of torque with temperature of plasticized PVC, during mixing in a Brabender torque rheometer.

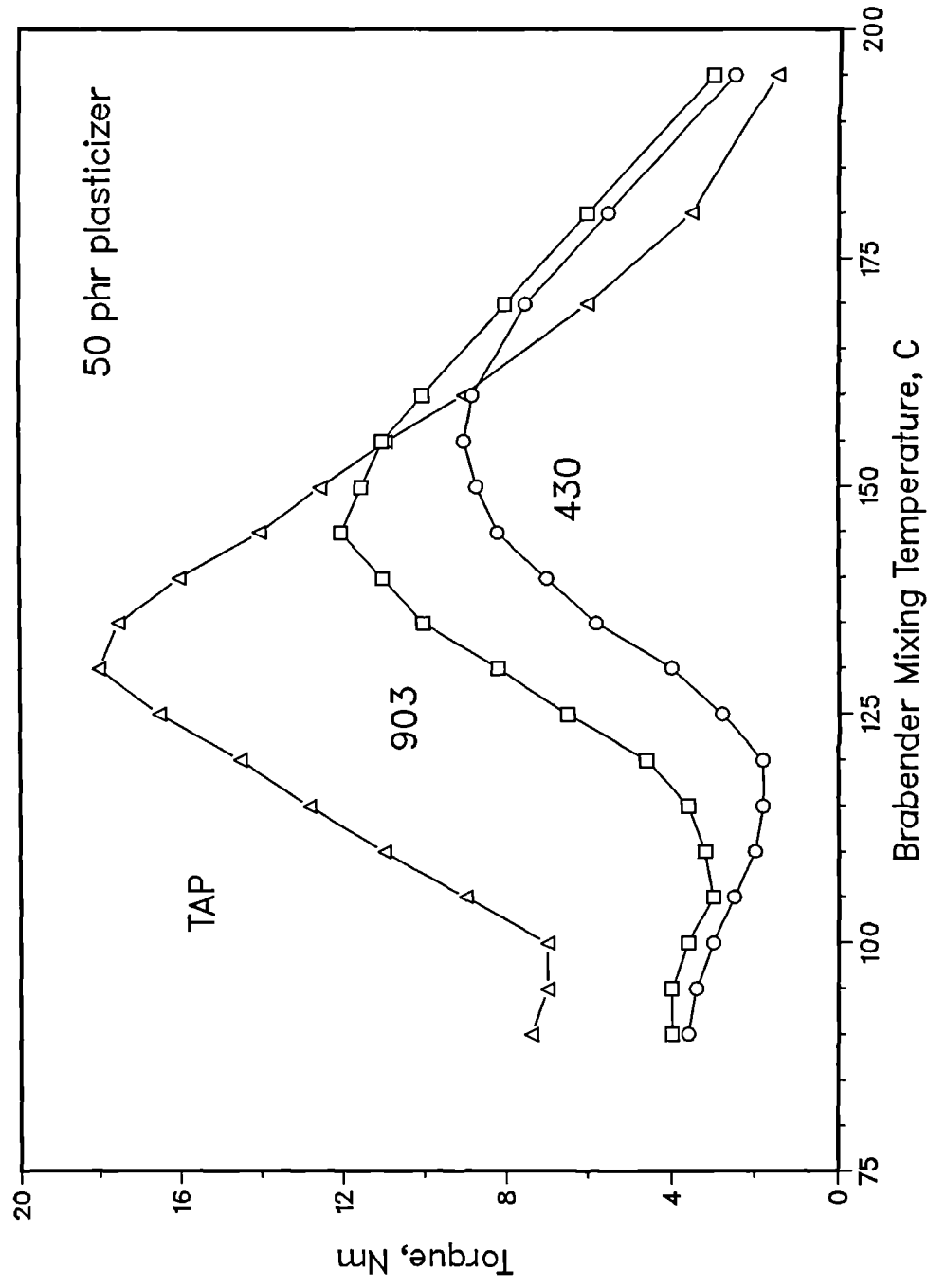


Fig. 4.4: Variation of torque with temperature of plasticized PVC, during mixing in a Brabender torque rheometer.

Table 4.1

Time, Temperature "Tf", and Torque at the Fusion
Peak in the Brabender Torque Rheometer

	Time, min	Tf, C	Torque, Nm
DBP	10	118	20.5
TAP	12	126	18.0
DOP	14	127	16.0
DIDP	18	134	12.5
DOA	19	136	10.0
TOTM	17	137	11.5
903	19	145	12.0
DOS	22	148	8.0
DTDP	27	149	7.2
DIDA	25	153	7.0
430	22	155	9.0
TIDTM	28	160	6.5

Figures 4.1 to 4.4 and Table 4.1 also show that the higher the compatibility of the plasticizer, the shorter the time needed to attain the fusion peak, but the higher is the torque at that fusion peak. This is in accordance with the work reported by Bargellini¹³⁶. During Banbury mixing, he showed that the higher the PVC/plasticizer compatibility, the higher the power peak but the shorter the time at which it occurred.

It may be concluded that the time needed to attain fusion and the temperature at the fusion peak are mainly dictated by the PVC/plasticizer compatibility, but the torque at the fusion peak (or

the power consumption) is jointly affected by: a) the viscosity of the compound, b) the temperature at the fusion peak, and c) the plasticizer viscosity and "lubricity".

a) The viscosity of the compound will depend on its degree of fusion. The higher the degree of fusion the higher the viscosity. But once a certain level of fusion is achieved, (e.g. the fusion peak), the viscosity of the compound will decrease with temperature, as all thermoplastic melts do.

b) The higher the temperature at which this certain level of fusion is achieved, the lower the viscosity of the compound at this point, simply because the melt viscosity decreases with temperature.

c) The viscosity of the compound will tend to decrease, as the viscosity of the plasticizer decreases. Also, the viscosity of the compound will decrease with the external "lubricity" of the plasticizer, i.e. with increasing chain length of the non polar aliphatic alcohol of the ester, or with shifting from an aromatic to an aliphatic ester.

Figure 4.5 presents the relationship between the temperature at the Brabender fusion peak (T_f) and the solid-gel transition temperature (T_m). A least squares fit on the curve for 50 phr plasticizer gives:

$$T_m = - 738 + 11 \times T_f - 0.0334 \times T_f^2 \quad (4.1)$$

[T_f in C] with a standard deviation of 1.77 between the estimated and the experimental values of T_m .

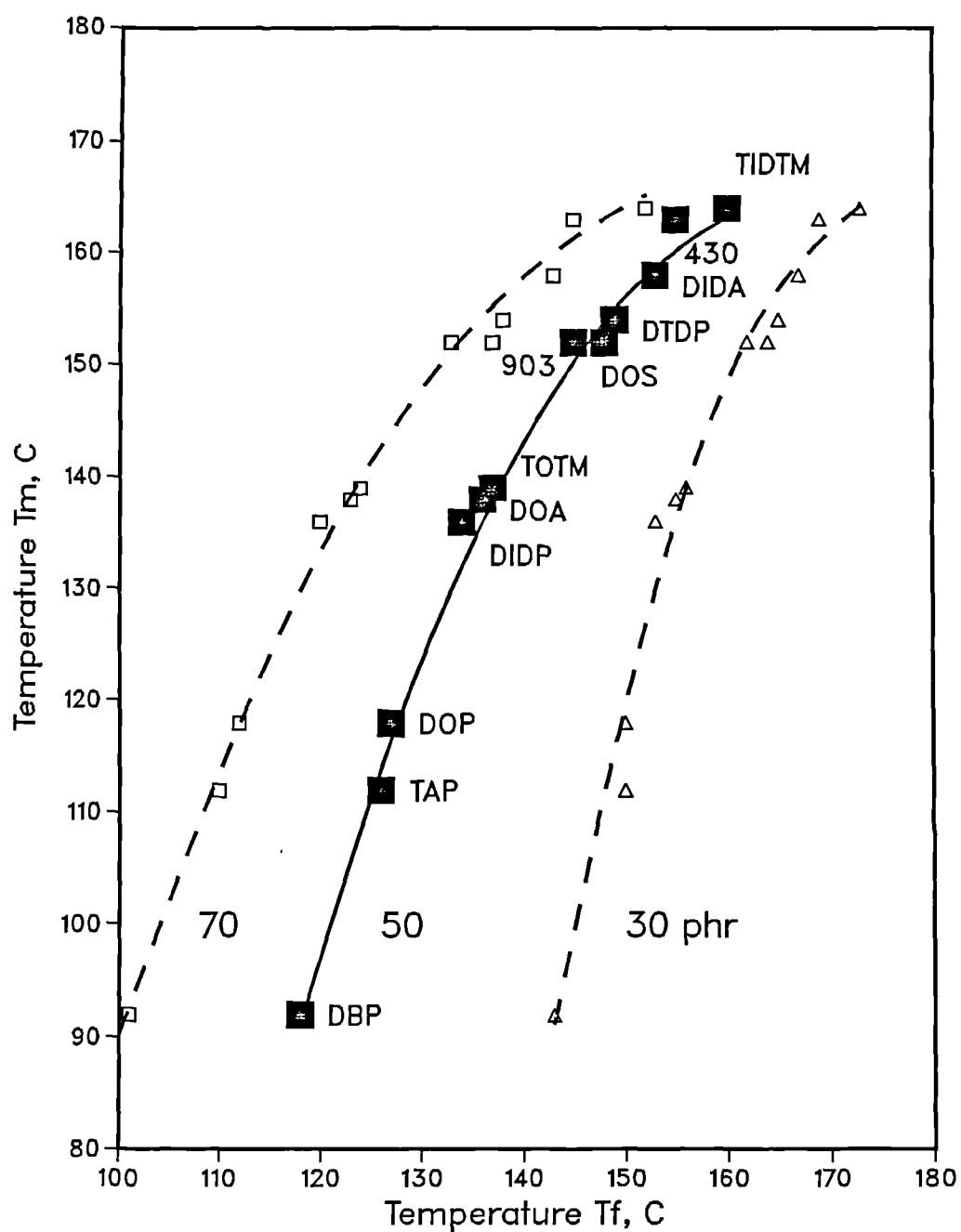


Fig. 4.5: Variation of the solid_gel transition temp. (T_m) with the Brabender fusion temp. (T_f) of plasticized PVC.

It must be mentioned that the curves for 30 and 70 phr were estimated according to a procedure somewhat similar to that described by Schreiber^{130,131}, [Refer to section 1.8.5.5], and described below.

First, the plasticizer volume concentration corresponding to 30, 50, and 70 phr was determined, and is shown in Table 4.2.

Table 4.2

Plasticizer Concentration in Volume %,
Corresponding to 30, 50, and 70 phr.

	30 phr	50 phr	70 phr
DBP	28.7	40.1	48.4
TAP	27.0	38.1	46.3
DOP	29.7	41.2	49.9
DIDP	30.4	42.1	50.5
DOA	31.3	43.2	51.6
TOTM	29.9	41.5	49.5
903	27.8	39.1	47.4
DOS	31.5	43.4	51.8
DTDP	30.7	42.5	50.8
DIDA	31.5	43.3	51.7
430	27.2	38.3	46.6
TIDTM	30.3	42.8	50.3

Second, the variation of the Brabender fusion temperature with the volume concentration of DOP was plotted, and the data (from Figure 4.9) was fitted into a straight line with a high correlation coefficient of 0.9998, and is shown in Figure 4.6.

Third, a straight line was fitted for each plasticizer between the point corresponding to 50 phr and T_f and the point corresponding to zero phr and 205C, (as shown for DBP, DIDP, and DTDP in Figure 4.6).

Fourth, the Brabender fusion temperatures (T_f) of each plasticizer, corresponding to 30 and 70 phr, were determined by interpolation and extrapolation of these straight lines. These fusion temperatures are presented in Table 4.3.

Table 4.3

Brabender Fusion Temperatures [T_f C] of
PVC Compounds with Varying Amounts of Plasticizer

	30 phr	50 phr	70 phr
DBP	143	118	101
TAP	150	126	110
DOP	150	127	112
DIDP	153	134	120
DOA	155	136	123
TOTM	156	137	124
903	162	145	133
DOS	164	148	137
DTDP	165	149	138
DIDA	167	153	143
430	169	155	145
TIDTM	173	160	152

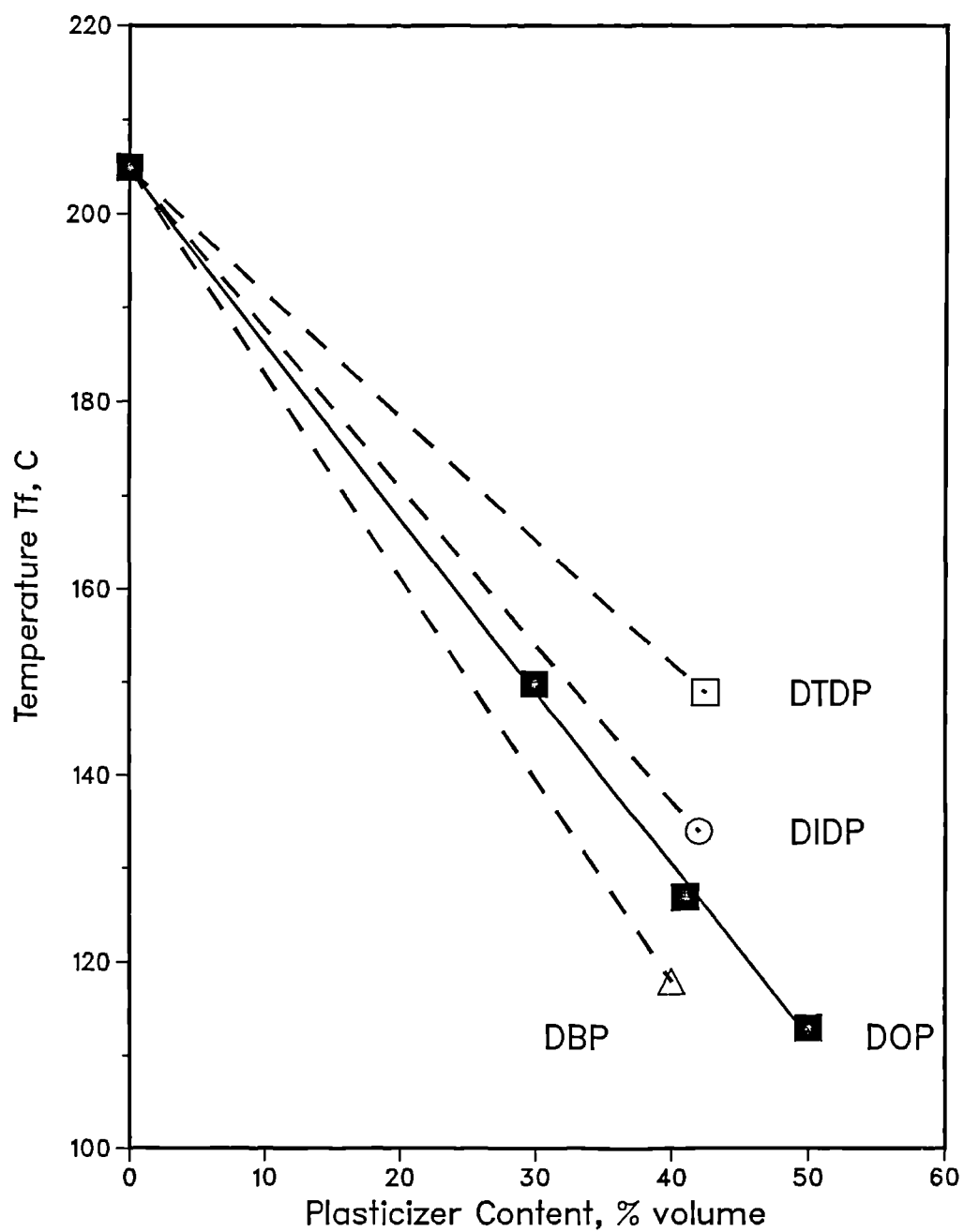


Fig. 4.6: Variation of the Brabender fusion temp. of PVC with the plasticizer volume content, and extrapolation to zero plasticizer content, i.e. pure PVC.

It is observed in Figure 4.5 and Table 4.3 that:

- 1) The fusion temperature decreases as the plasticizer concentration increases. However, this decrease in T_f is less each time the amount of plasticizer is further increased, e.g. T_f decreases by 23 C as the DOP content increases from 30 to 50 phr, but it only decreases by 15 C as the DOP content increases from 50 to 70 phr.
- 2) The effect of plasticizer concentration on T_f is more pronounced as the PVC/plasticizer compatibility increases, e.g. T_f decreases by 23 C as the DOP content increases from 30 to 50 phr, but it only decreases by 14 C in the case of 430. and
- 3) It is easy to estimate the amount of plasticizer needed to achieve any given fusion temperature. Also, it is possible to estimate the amount of plasticizer No.2 "that will produce the same fusion temperature" as plasticizer No.1. (From Fig. 4.5, 30 phr DOP will produce the same T_f as 50 phr DTDP, i.e. 150 C).

Figure 4.7 presents the relationship between the Brabender fusion temperature and the Flory-Huggins interaction parameter. A least squares fit gives:

$$\chi = -2.7 + 0.0215 \times T_f \quad (4.2)$$

[T_f in C] with a correlation coefficient of 0.9672. (χ for 903 and 430 were calculated from equation 3.2).

Figure 4.8 presents the relationship between T_f and the activity parameter. A least squares fit gives:

$$\alpha = 40.4 - 0.483 \times T_f + 0.00147 \times T_f^2 \quad (4.3)$$

[T_f in C] with a standard deviation of 0.082 between the estimated and the experimental values of α .

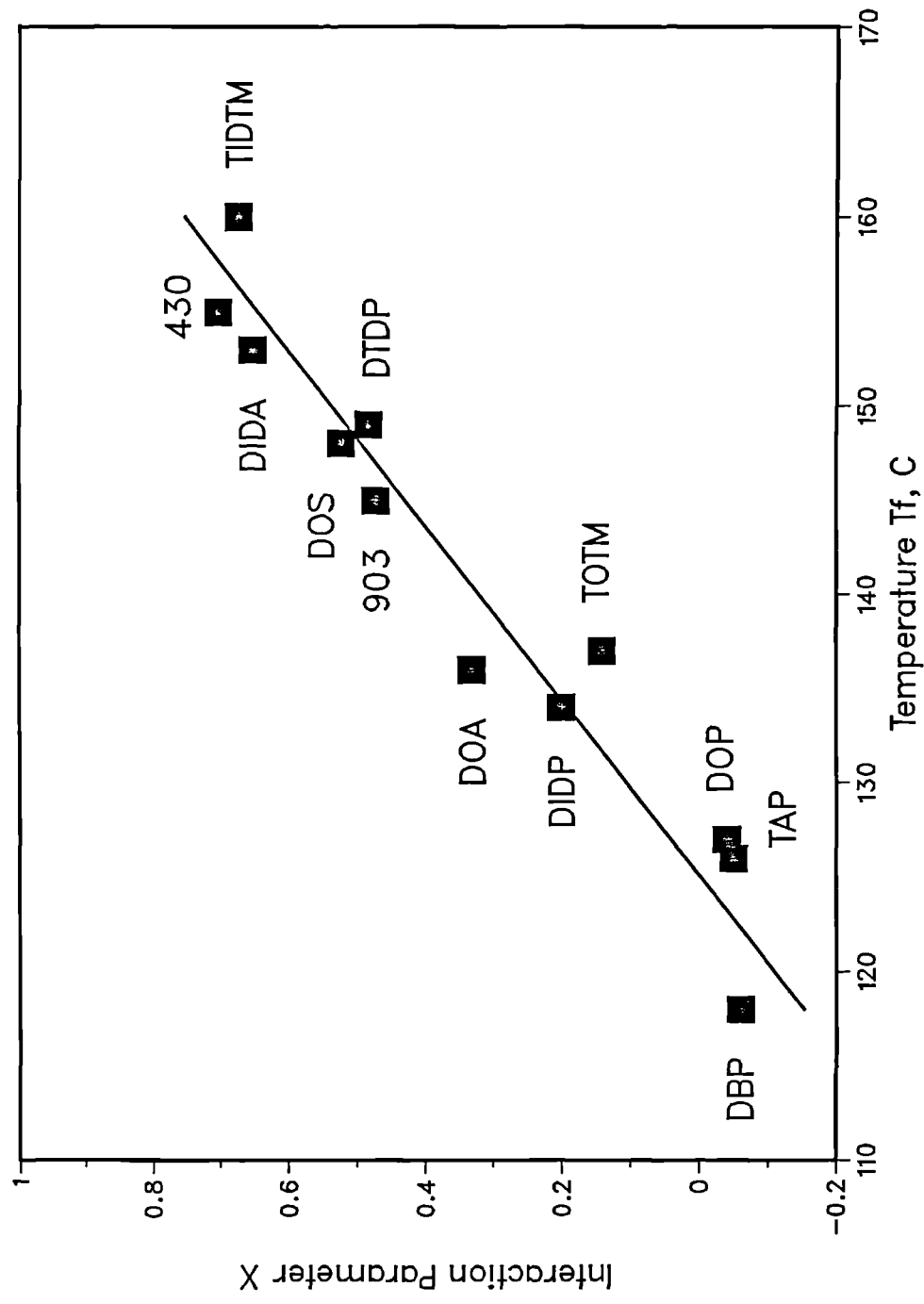


Fig. 4.7: Variation of the Flory Huggins interaction parameter with the Brabender fusion temperature of PVC with 50 phr plasticizer.

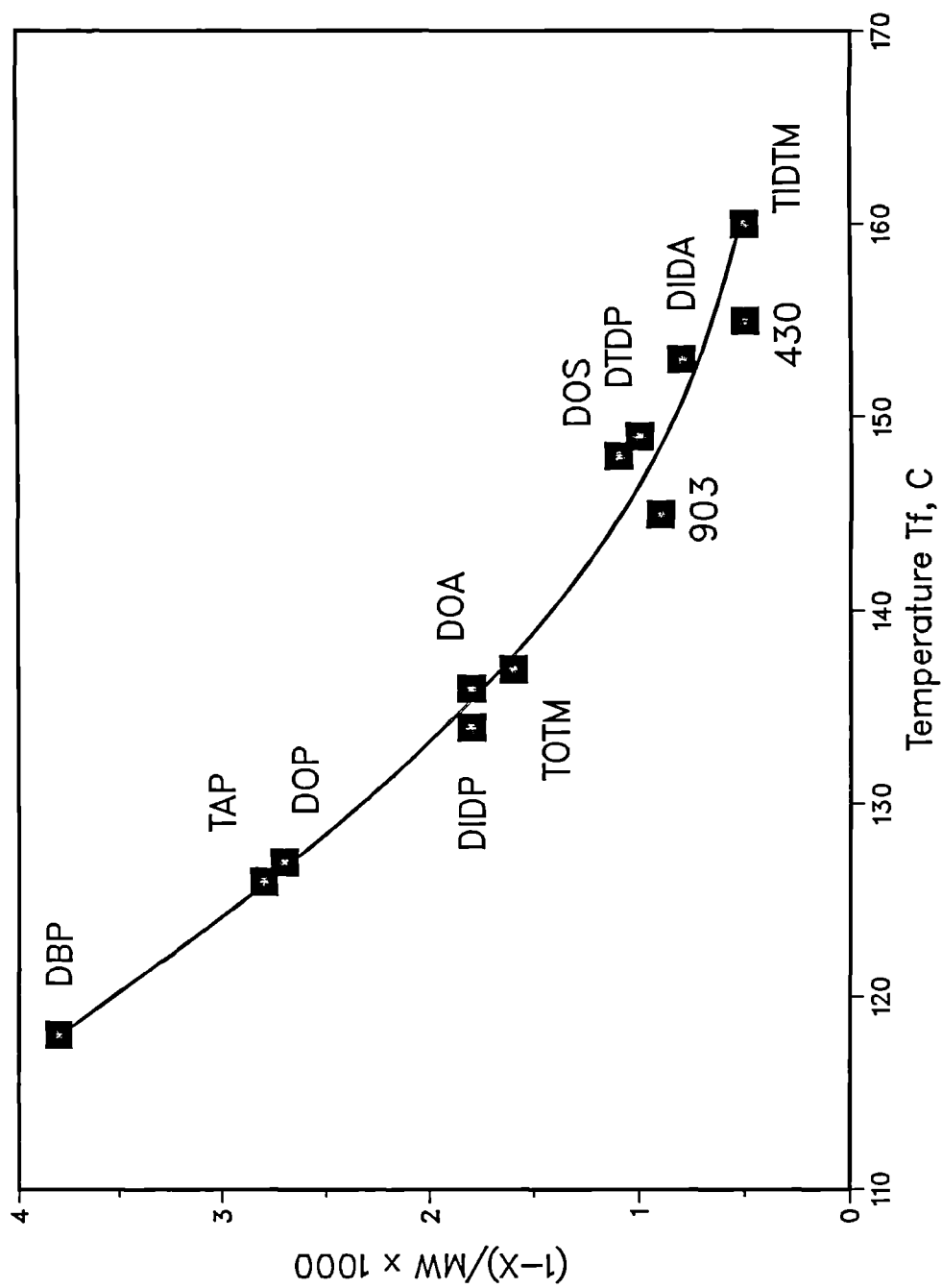


Fig. 4.8: Variation of the activity parameter $\alpha''(1-X)/MW \times 1000$ with the Brabender fusion temperature of PVC with 50 phr plasticizer.

Figure 4.9 presents the torque-temperature variation for PVC with different concentrations of DOP. It is observed that the temperature, as well as the torque at the fusion peak, both decrease with increasing DOP concentration.

This variation of torque (at the fusion peak) with concentration for DOP, may also be extended to all plasticizers. The magnitude of change however, should be different for each plasticizer.

During mixing in the Brabender torque rheometer, the heat for fusion comes from both, the heated walls of the mixing chamber and the mechanical shear exerted upon the sample. However, the mechanical shear will be different for each PVC/plasticizer composition. Figure 4.10 shows the variation of temperature with time, during Brabender mixing of plasticized PVC compositions with phthalate plasticizers. Within the registered interval, it can be observed that; 1) the variation of temperature with time can be divided into two regions (region 1 and region 2), 2) the dividing point between these two regions lies around the Brabender fusion temperature, 3) the heating rate in region 1 is in each case greater than that in region 2, 4) the heating rate in region 2 appears to be similar between all different plasticizers, and 5) the heating rate in region 1 increases with the PVC/plasticizer compatibility. Region 1 in Figure 4.10, corresponds to that region in Figures 4.1 to 4.4, in which torque is increasing up to the fusion peak.

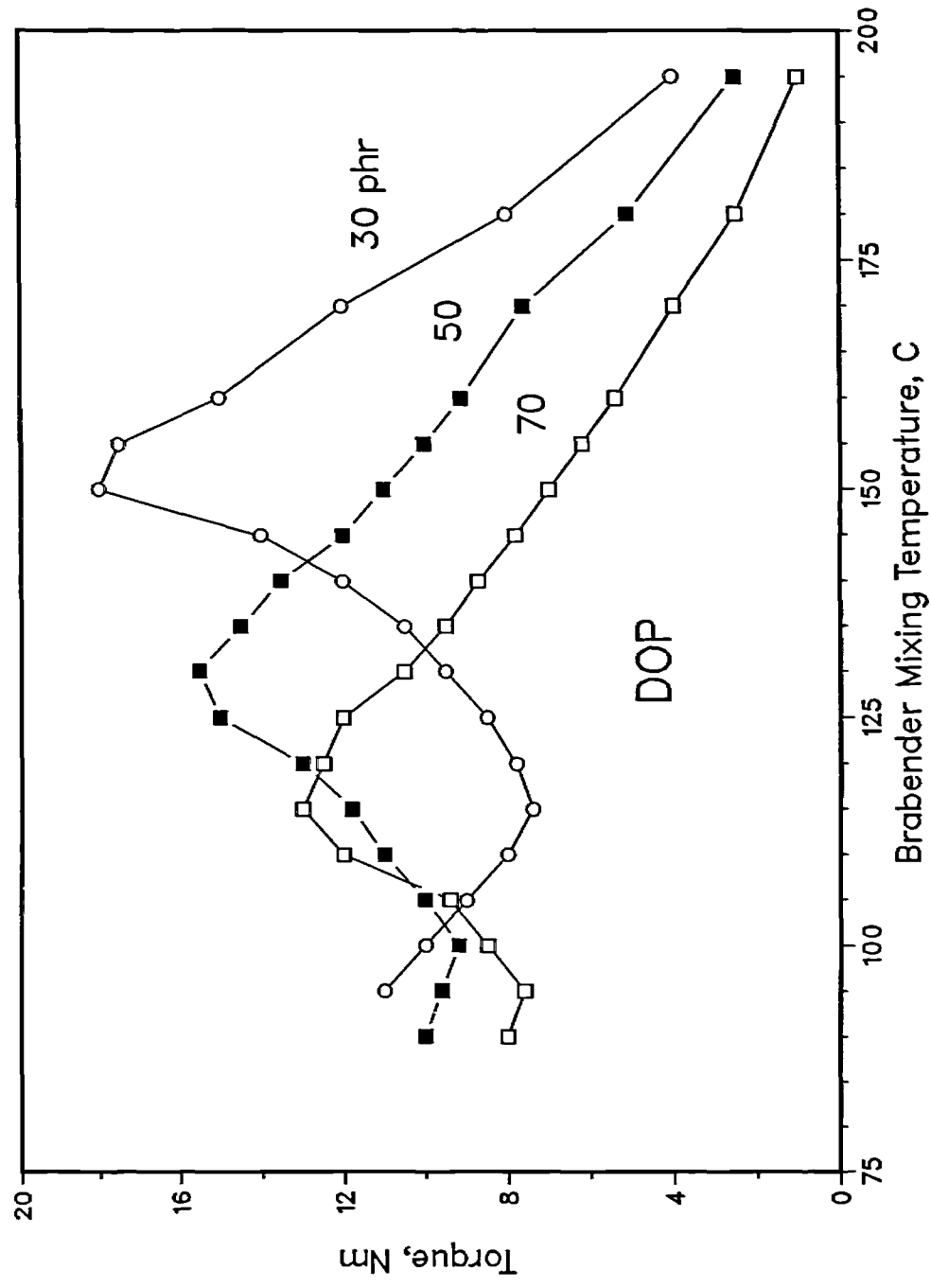


Fig. 4.9: Variation of torque with temperature of plasticized PVC, during mixing in a Brabender torque rheometer.

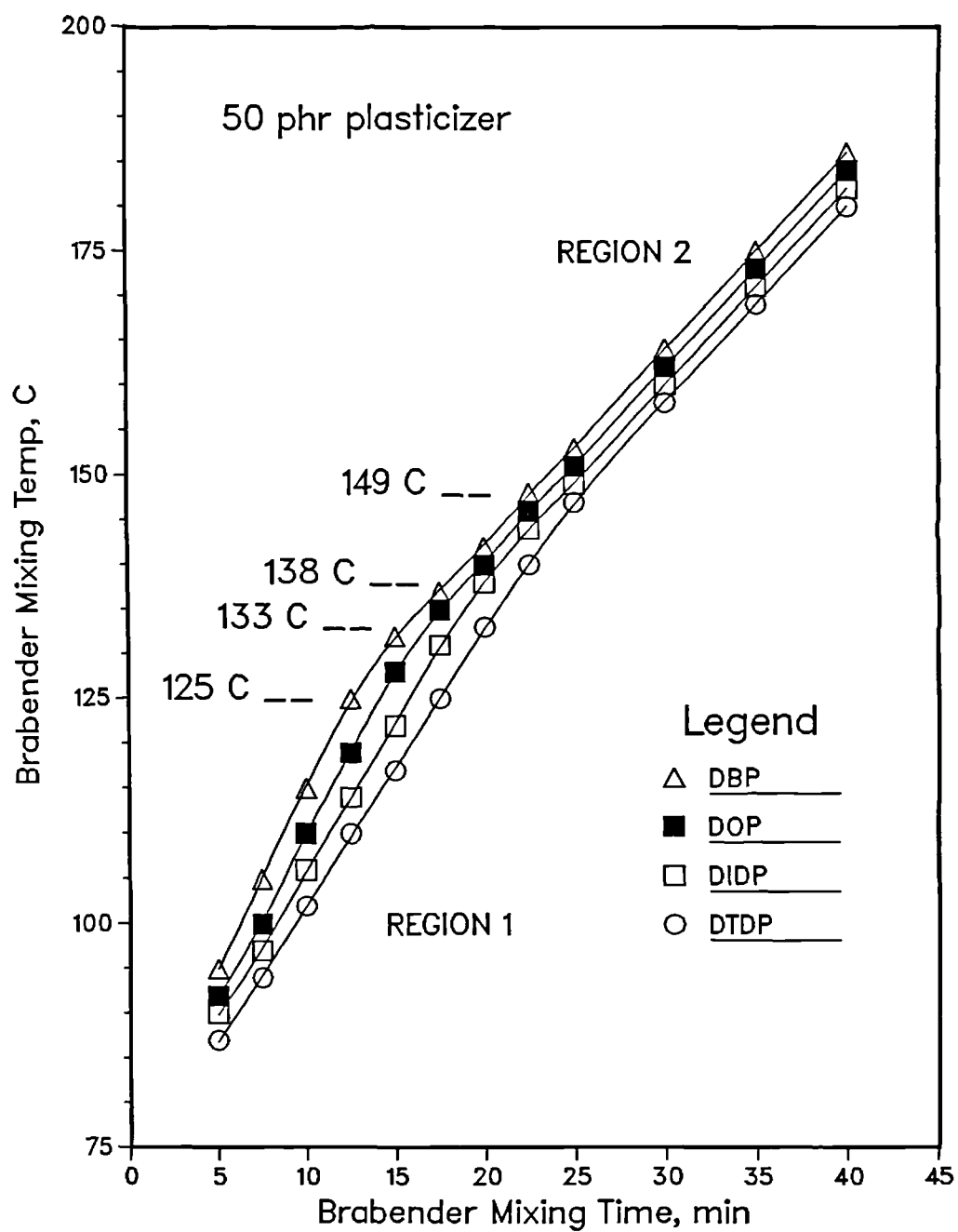


Fig. 4.10: Variation of temperature with time for pPVC, during mixing in a Brabender torque rheometer.

4.3 Remarks and Conclusions

First, there is a clear relationship between the PVC/plasticizer compatibility, determined by T_m , χ , or α , and the processing characteristics encountered in the Brabender torque rheometer.

Table 4.4 lists the plasticizers studied in order of decreasing compatibility, according to such compatibility parameters as T_m , χ , and α , as well as the Brabender fusion temperature T_f .

Table 4.4

T_m , χ , α , and T_f of the Plasticizers Studied

	T_m , C	χ	α	T_f , C
DBP	92	-0.06	3.8	118
TAP	112	-0.05	2.8	126
DOP	118	-0.04	2.7	127
DIDP	136	0.20	1.8	134
TOIM	139	0.14	1.6	137
DOA	138	0.33	1.8	136
903	152	0.47 ^a	0.9	145
DOS	152	0.52	1.1	148
DTDP	154	0.48	1.0	149
DIDA	158	0.65	0.8	153
430	163	0.71 ^a	0.5	155
TIDTM	164	0.67	0.5	160

^aFrom equation 3.2, Chapter 3.

In addition, it was found that the greater the PVC/plasticizer compatibility, the lower the temperature and the shorter the time needed to attain fusion, but the greater the torque (or power peak) at that fusion point. This relationship can be extended to other processes, e.g. extrusion, in which case, it is presumed that the higher the compatibility, the lower the temperature and the shorter the residence time needed to attain fusion, but the greater the electricity consumption per unit time, by the motor of the extruder.

Second, the variation of the Brabender fusion temperature with the plasticizer concentration can be estimated by simple interpolation or extrapolation between two single points, (one point at zero plasticizer concentration and 205 C, and the other point at some other plasticizer concentration and its corresponding Brabender fusion temperature).

Third, three different equations were obtained that relate the Brabender fusion temperature " T_f " with such compatibility parameters as the solid-gel transition temperature, the Flory-Huggins interaction parameter, and the activity parameter. Thus, the processing temperature required to process a given plasticized PVC composition can be estimated from a single determination of compatibility, such as the solid-gel transition temperature, and the subsequent application of the equation that relates T_m with T_f .

Fourth, it is clear from the previous chapters, that the PVC/plasticizer compatibility (as determined by δ , ϕ , T_m , α , χ , and T_f) is a function of the plasticizer chemical make up. For example:

a) Within the same family:

An increase in the alkyl chain length (e.g. DBP-DOP-DIDP-DTDP) will tend to decrease the plasticizer compatibility with PVC. Also, an increase in the alkyl chain length will tend to increase the viscosity of the plasticizer.

b) Between different plasticizer families:

An increase in the number of alkyl chains (e.g. phthalate-trimellitate) will tend to decrease the plasticizer compatibility with PVC. Also, an increase in the number of alkyl chains will tend to increase the viscosity of the plasticizer.

A change from aromatic to aliphatic type (e.g. phthalate-adipate) will tend to decrease the plasticizer compatibility with PVC. Also, a change from aromatic to aliphatic will tend to decrease the viscosity of the plasticizer.

c) Between polymeric plasticizers:

Alcohol termination, as compared to non termination, decreases the viscosity of the plasticizer, which in turn tends to increase the plasticizer compatibility with PVC.

Chapter 5

RESULTS AND DISCUSSION: ASSESSMENT OF FUSION

5.1 Electron Microscopy

Figure 5.1 presents the TEM photomicrographs of PVC/DOP Brabender samples. The progressive transition of the particulate structure into a continuous fused mass can be observed.

At 125 C, there is no apparent sign of the PVC grains, the primary particles are already visible. That is, comminution of the PVC grains has already started to occur. It is observed nevertheless, that the primary particles are separated from one another, showing no fusion amongst themselves. As the processing temperature is increased to 140 and 155 C, the PVC primary particles are still visible. However, fusion of the primary particles (at 140 C) and loss of the primary particle boundaries (at 155C) has already started to occur. At 170 C, the primary particle boundaries are completely lost. The sample nevertheless still appears to be formed of particles, though smaller than the primary particles observed at the two previous processing temperatures. At 185 C, the particulate structure is completely lost and the sample appears to be formed of well fused material.

At 170/185 C therefore, the PVC/DOP Brabender sample has passed from a particulate structure to a completely fused structure.

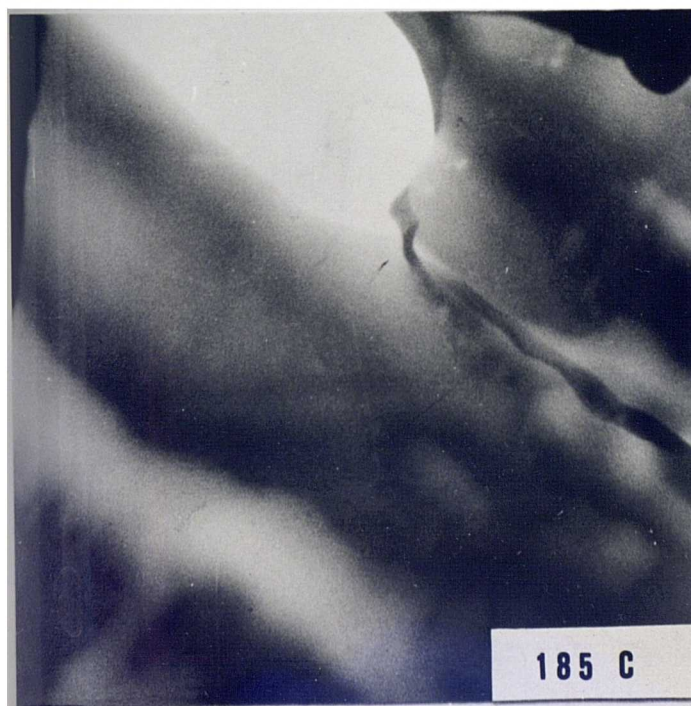
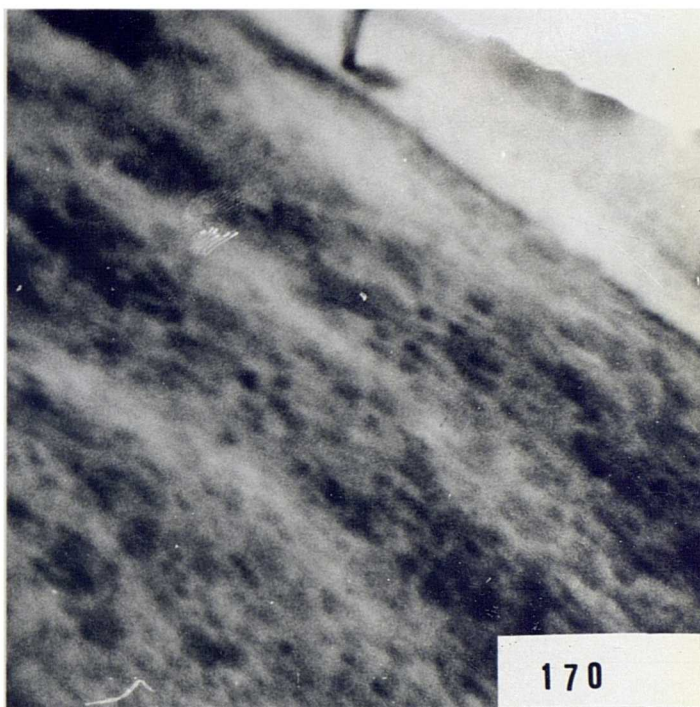
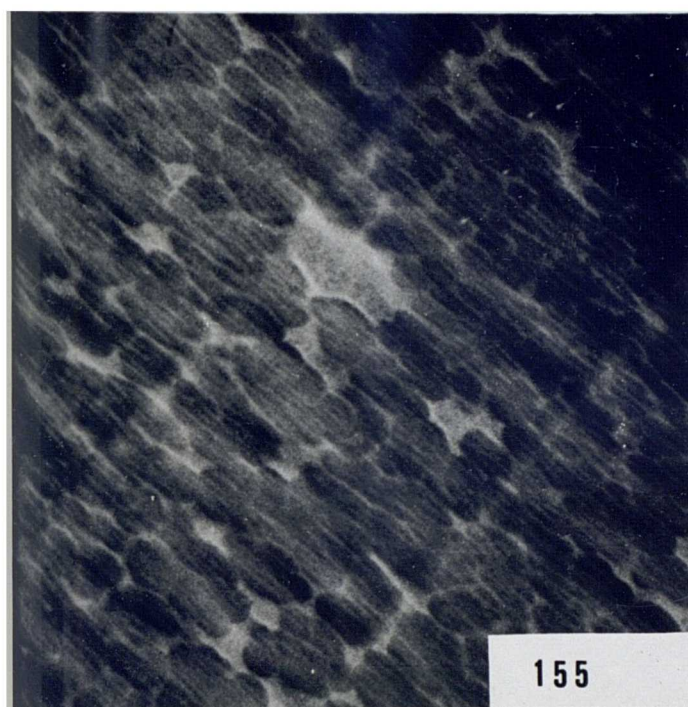
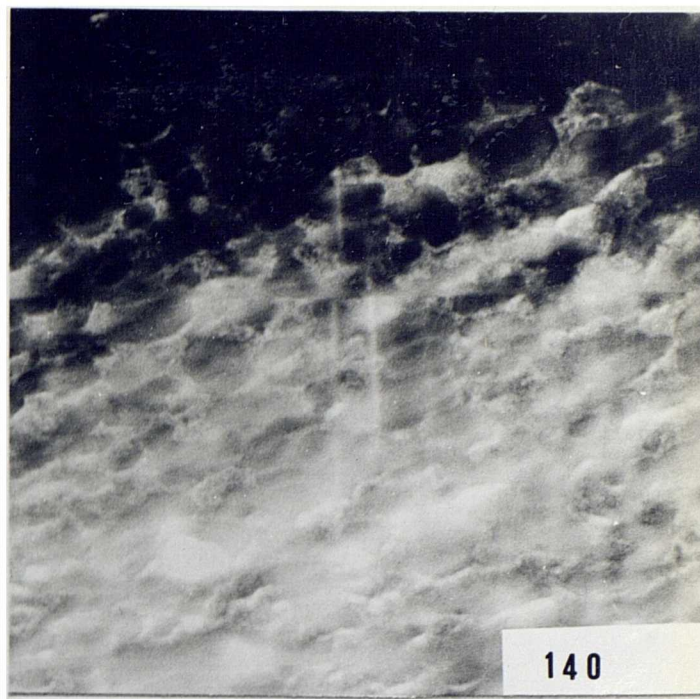
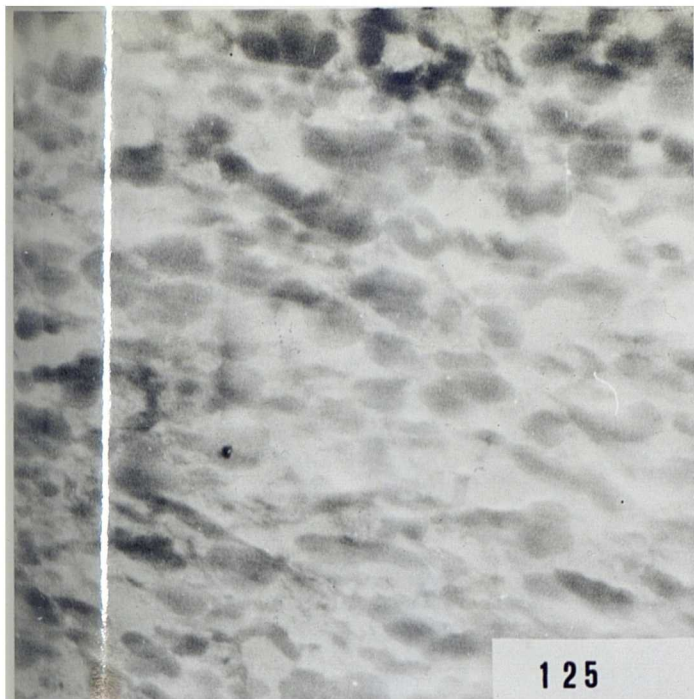


Fig.5.1
 TEM micrographs of PVC/DOP
 Brabender samples (50 phr).
 Processed at indicated temp.
 1 cm = 2 um

Figure 5.2 shows the TEM photomicrographs of PVC/DOP moulded samples. In contrast to the Brabender samples described above, it is observed that the primary particles are still visible at 170 C. However, fusion of the primary particles and loss of the primary particle boundaries have started to occur. At 185 and 200 C, the primary particles are completely lost and the sample appears as a mass of well fused material.

At 185/200 C therefore, the PVC/DOP moulded sample has passed from a particulate structure to a well fused structure.

That is, due to the mechanical shear involved, Brabender mixing makes fusion occur at lower temperatures than compression moulding.

[At 140 and 155 C, the micrographs simply present a thin slice of a PVC grain, where the black areas represent the PVC and the white areas represent the embedded epoxy resin used to prepare the samples].

Figures 5.3 and 5.4 present the TEM micrographs of PVC/903 and PVC/DOP (30 phr) Brabender samples. In both cases, a well fused structure is obtained only after processing at temperatures between 185 and 200 C.

Finally, comparing Figures 5.1 to 5.4, it is observed that the temperature needed to obtain an apparently well fused structure, increases with: 1) decreasing the applied mechanical shear during processing (from Brabender mixing to compression moulding), 2) with decreasing plasticizer compatibility (from DOP to 903), and 3) with decreasing plasticizer concentration (from 50 to 30 phr).

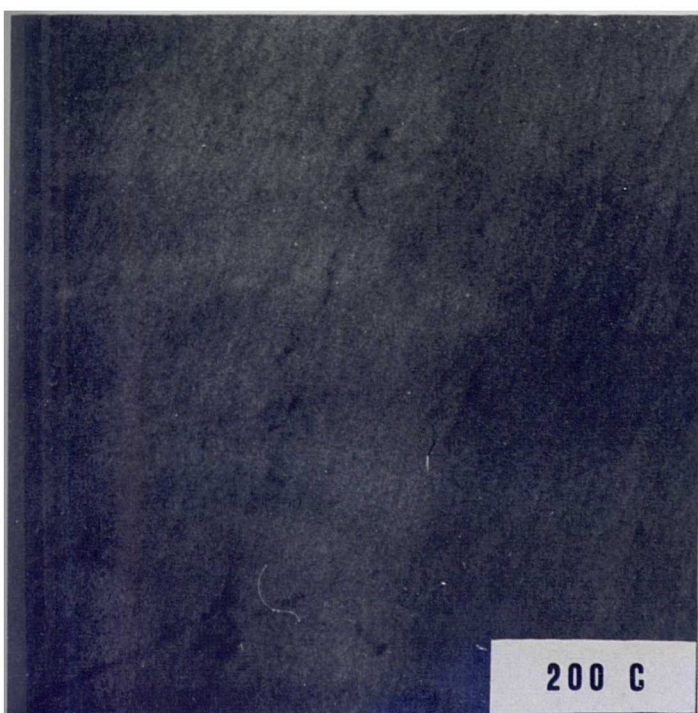
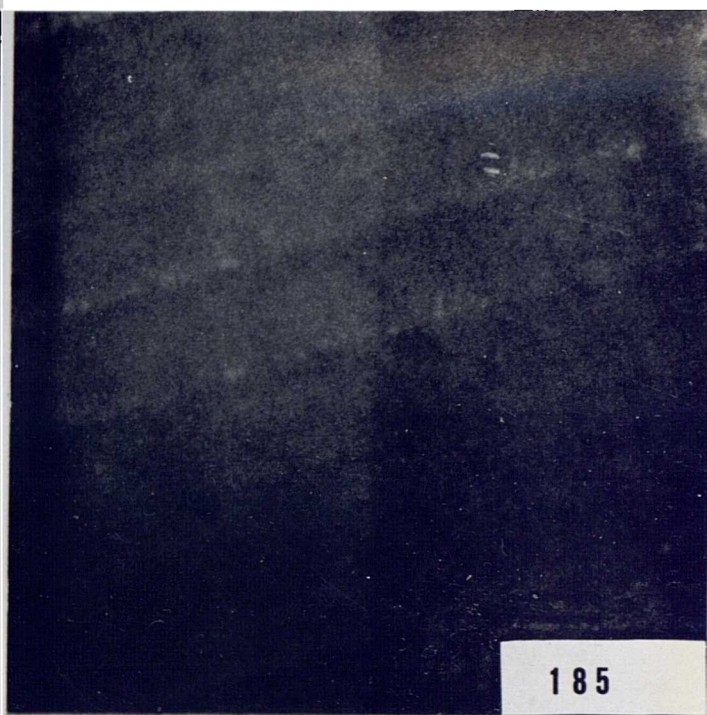
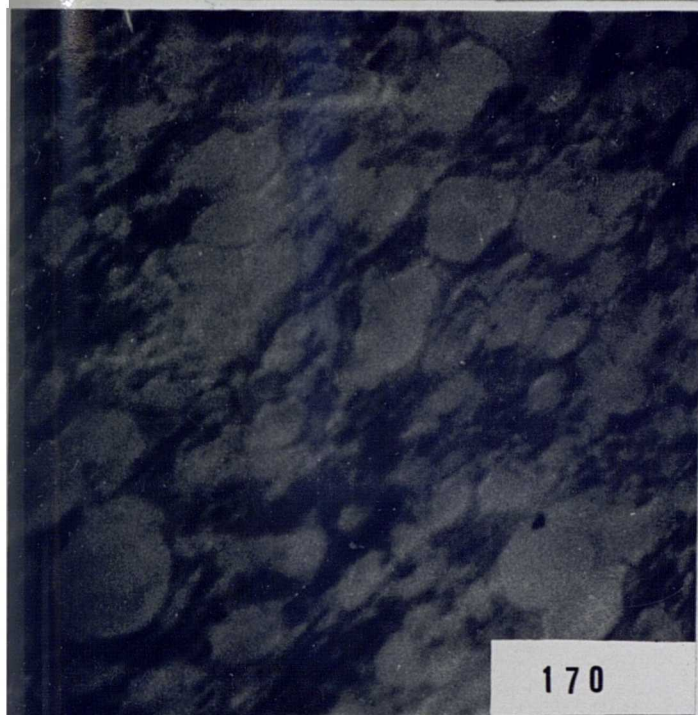
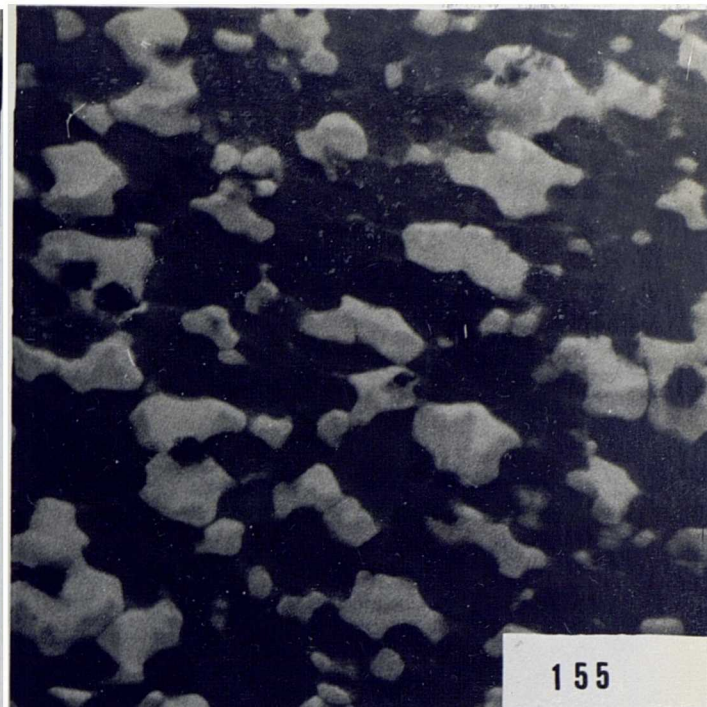
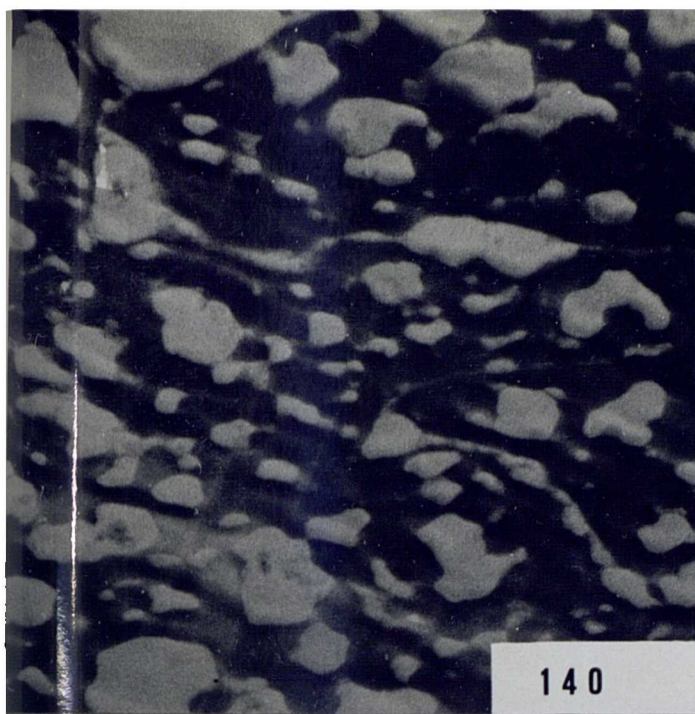


Fig.5.2
TEM micrographs of PVC/DOP
moulded samples (50 phr).
Moulded at indicated temp.
1 cm = 2 um

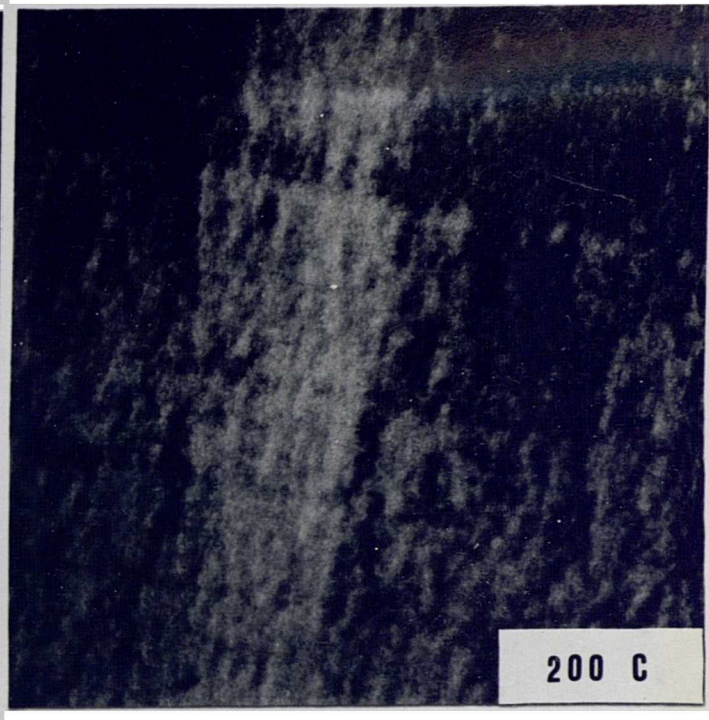
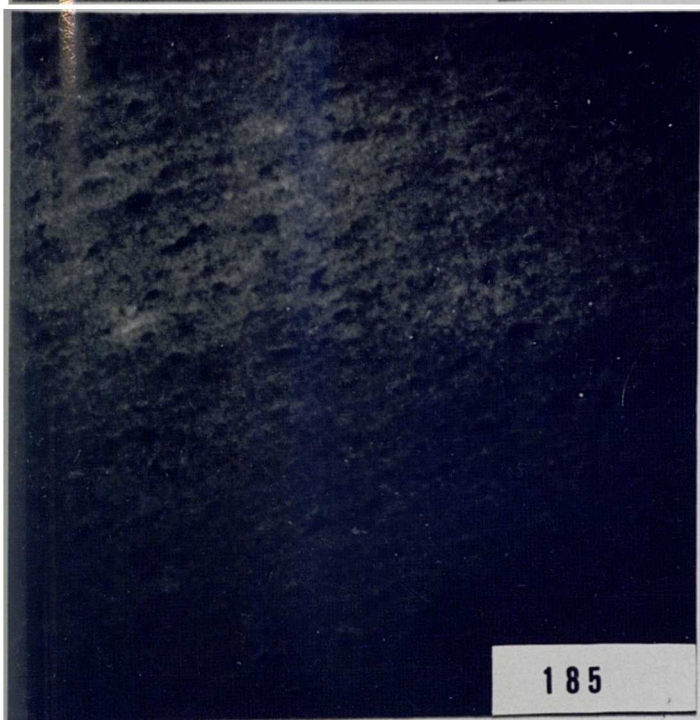
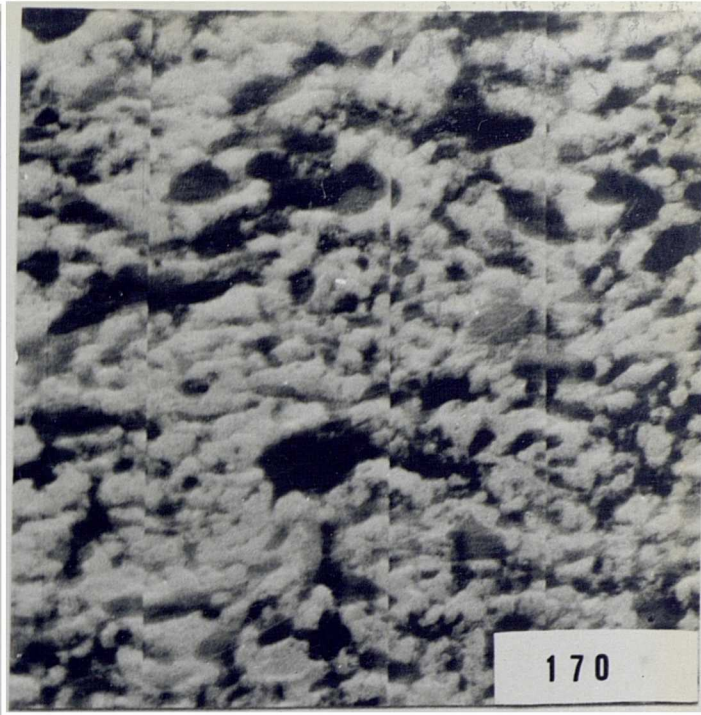
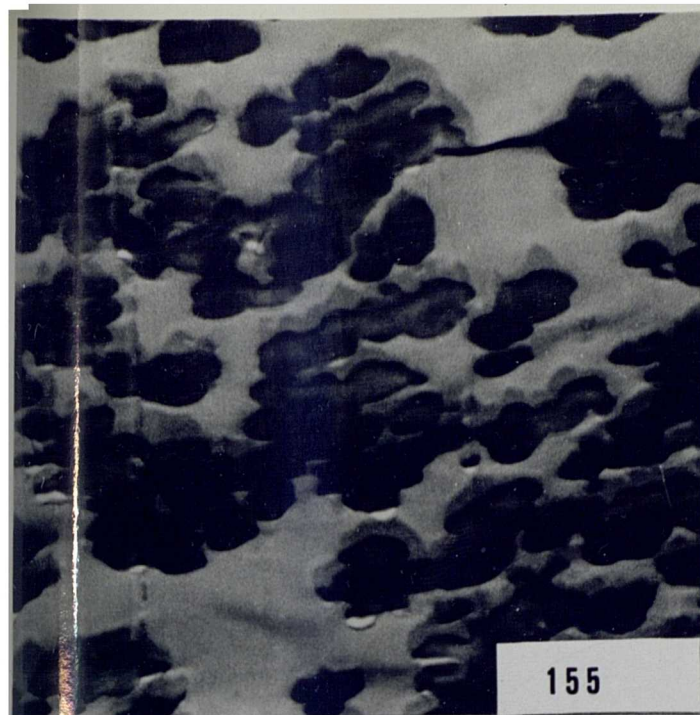


Fig.5.3
 TEM micrographs of PVC/903
 Brabender samples (50 phr).
 Processed at indicated temp.
 1 cm = 2 um

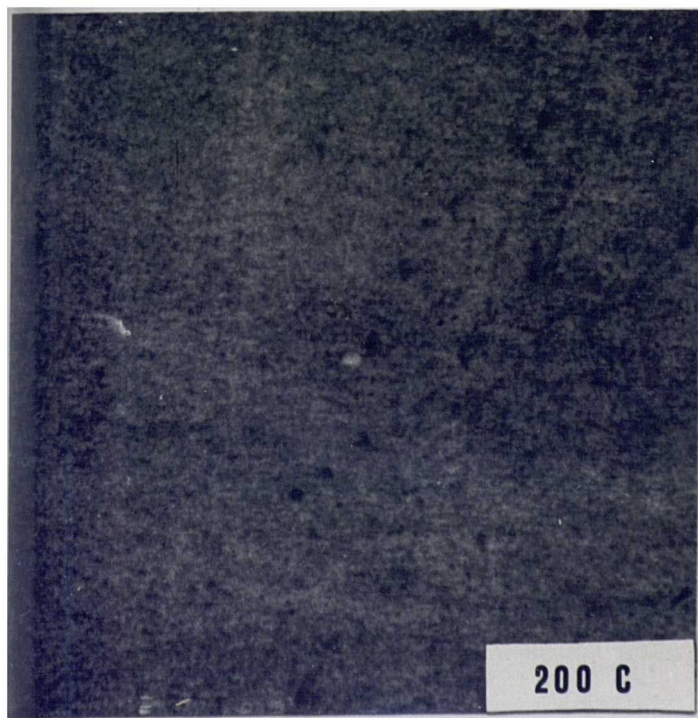
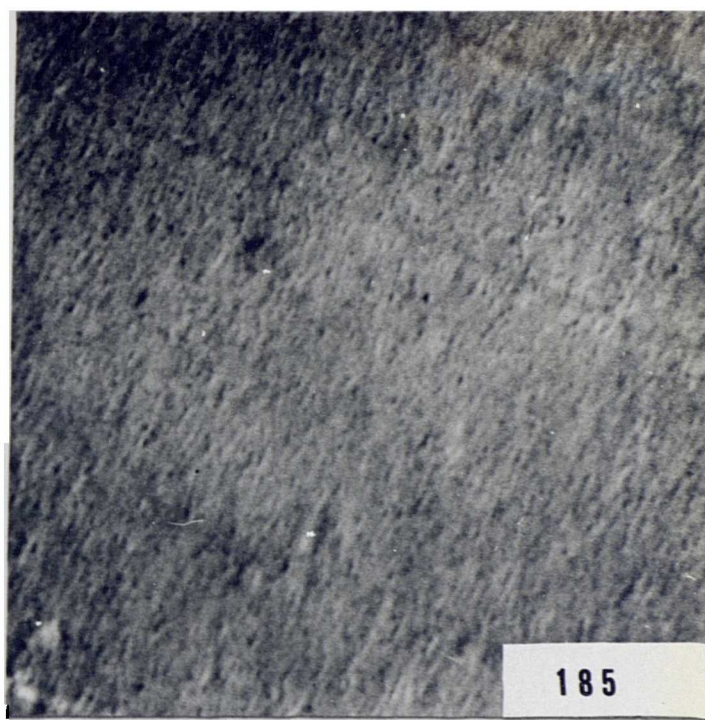
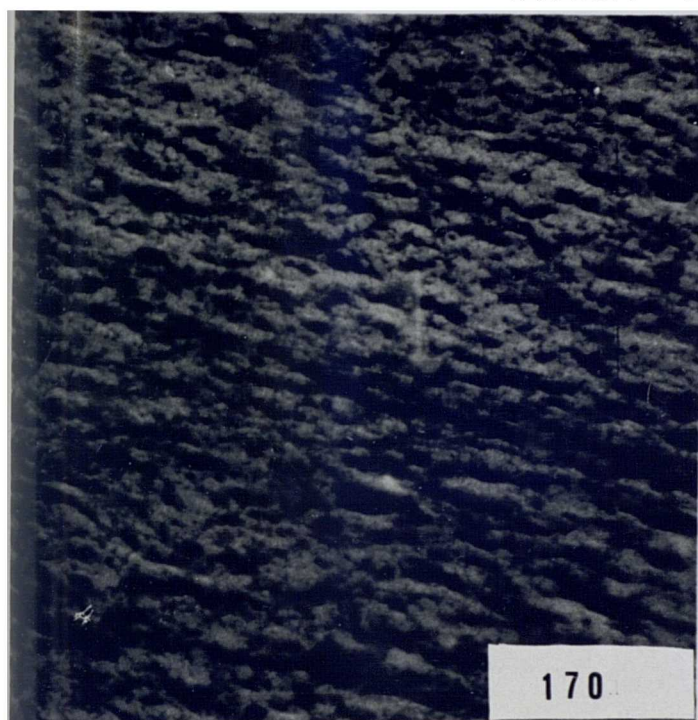
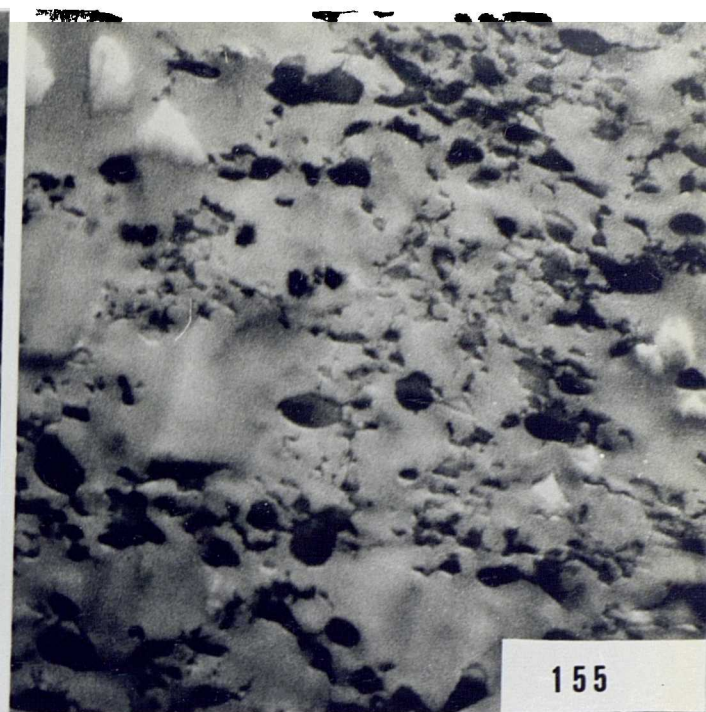
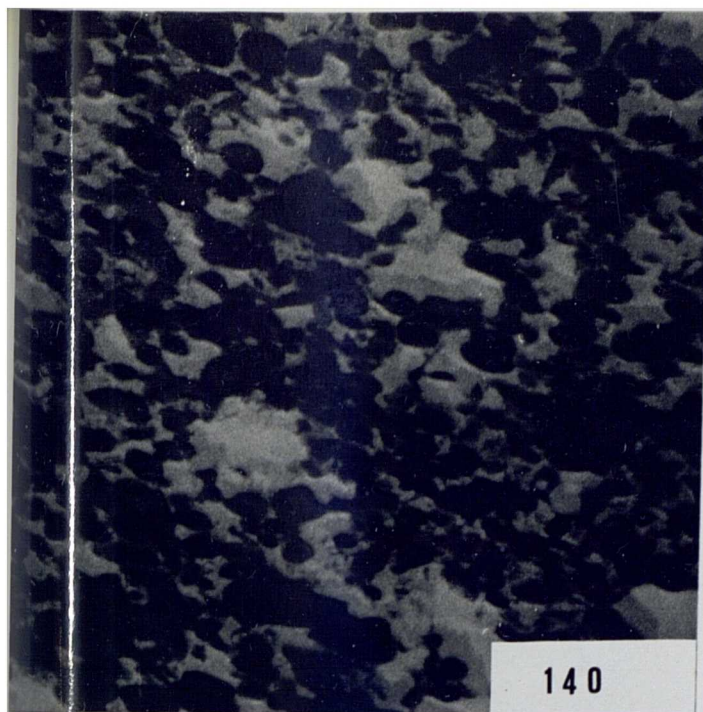


Fig.5.4
 TEM micrographs of PVC/DOP
 Brabender samples (30 phr).
 Processed at indicated temp.
 1 cm = 2 um

5.2 Optical Microscopy

Figure 5.5 presents the OM photomicrographs of PVC/DOP Brabender samples. It is observed that at 140 C, the plasticized PVC remains unfused, with the grains apparently broken down into primary particles. As the processing temperature is increased to 155 and 170 C, the primary particle boundaries start to disappear and the majority of the primary particles are now fused into larger structures. These larger structures nevertheless, are readily broken down upon shearing under the glass slides. As the processing temperature is further increased to 185 C, the primary particle boundaries have disappeared completely and the sample appears to be one large structure of very well fused material. This structure is not broken down easily, but stretches and deforms upon shearing under the glass slides.

The same comments can be applied to the PVC/DTDP Brabender sample presented in Figure 5.6, after shifting the whole description to higher temperatures.

That is, optical microscopy as well as electron microscopy, both show the effect of plasticizer type (plasticizer compatibility) on the fusion of PVC.

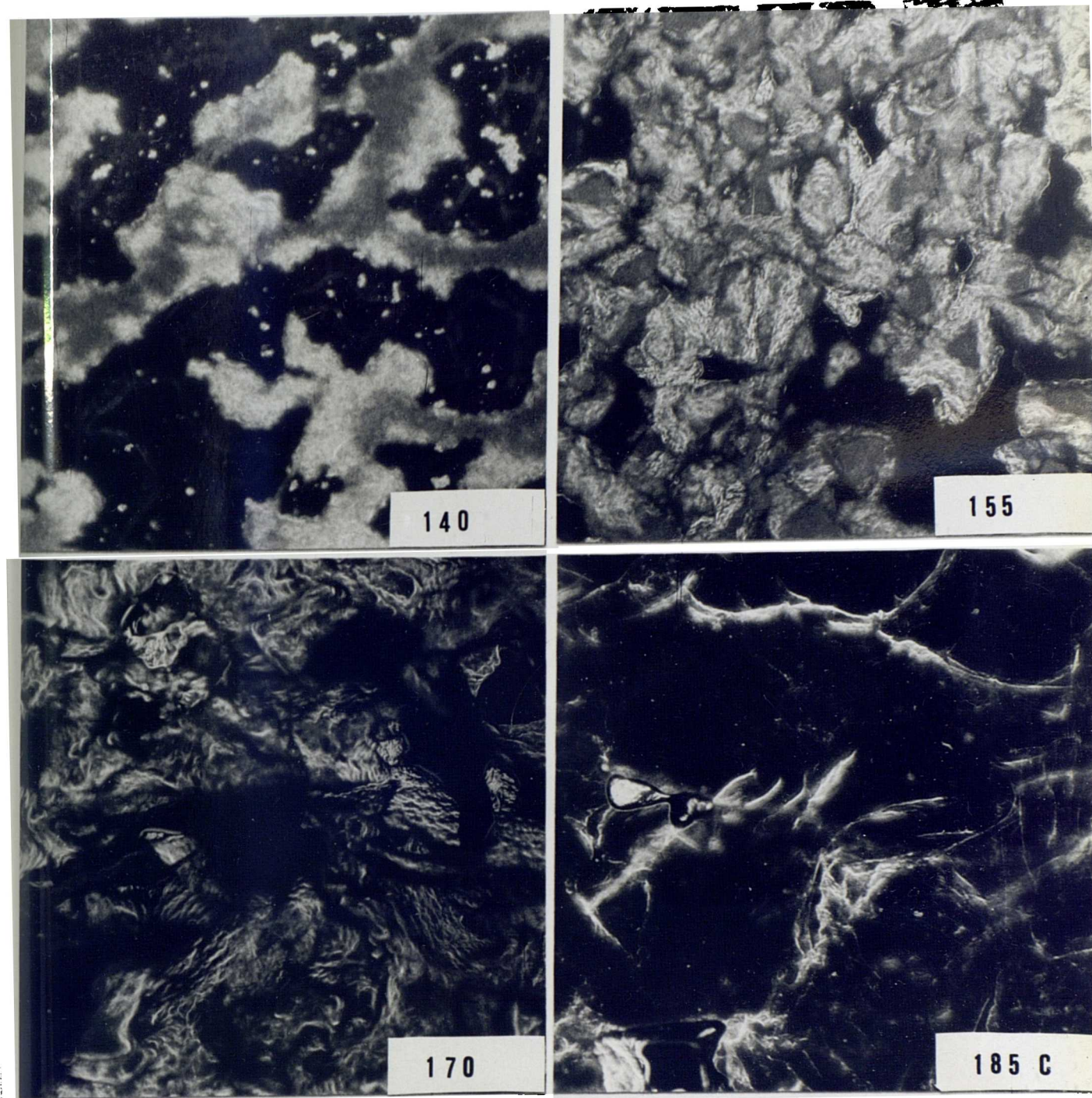


Fig. 5.5 OM micrographs of PVC/DOP
Brabender samples (50 phr).
Processed at indicated temp.
and then swollen in acetone.
1 cm = 100 um

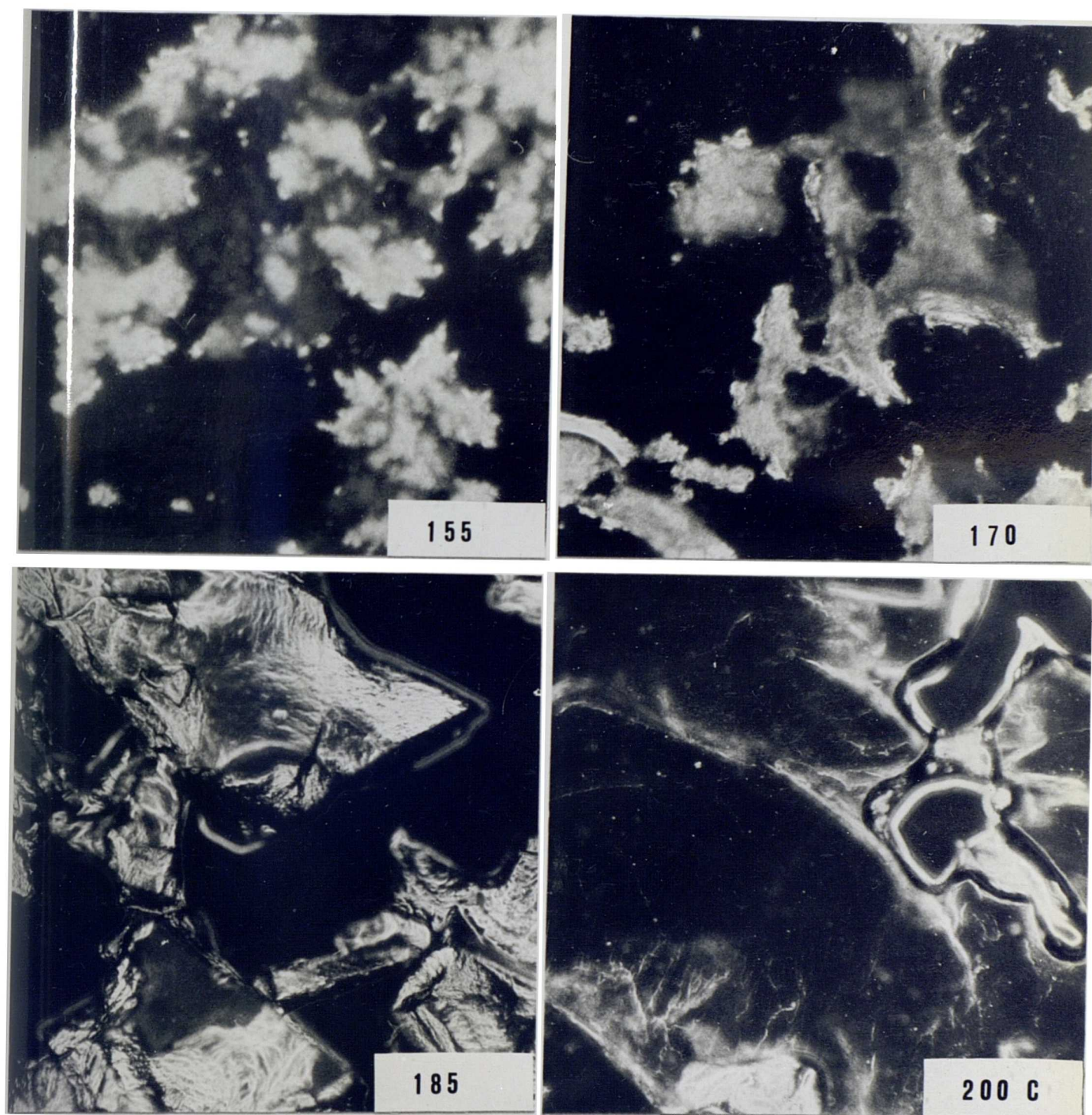


Fig.5.6 OM micrographs of PVC/DTDP
Brabender samples (50 phr).
Processed at indicated temp.
and then swollen in acetone.

1 cm = 100 um

5.3 Capillary Rheometry

This test is designed to monitor the gross increase in the elasticity of the compound, which is due to the formation of entanglements that occur during fusion (as the elasticity increases, the extrusion pressure also increases).

Figures 5.7 to 5.10 present the variation of the extrusion pressure with the processing temperature, for the moulded samples as well as the Brabender samples.

It is observed that the extrusion pressure increases with the processing temperature, irrespective of the plasticizer type or the type of processing. However, the temperature at which the extrusion pressure reaches the maximum or the magnitude of increase in pressure, do depend on the plasticizer type. The temperature at which the pressure reaches the maximum, decreases with increasing PVC/plasticizer compatibility. Table 5.1 presents the processing temperatures at which each compound reaches the maximum extrusion pressure, arranged in order of increasing magnitude, i.e. in order of decreasing plasticizer compatibility. The magnitude of increase in pressure on the other hand, is apparently more related with the plasticizer viscosity and its relative efficiency. Table 5.2 presents the viscosities and the relative efficiencies of the plasticizers studied, arranged in order of increasing magnitude, and their corresponding maximum pressures obtained in the capillary rheometry experiment.

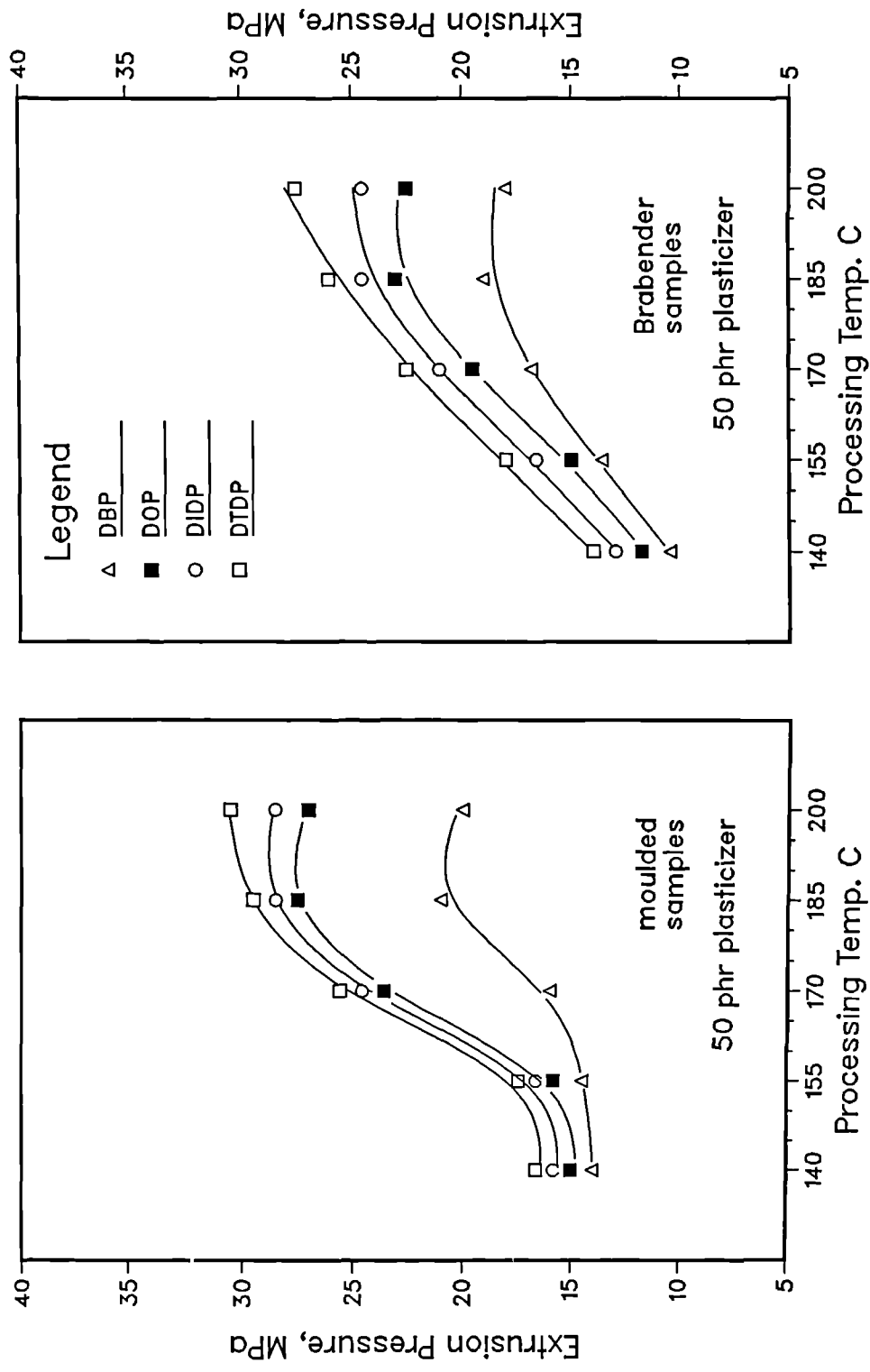


Fig. 5.7: Variation of the extrusion pressure with the processing temperature. Capillary rheometry test at 130 C.

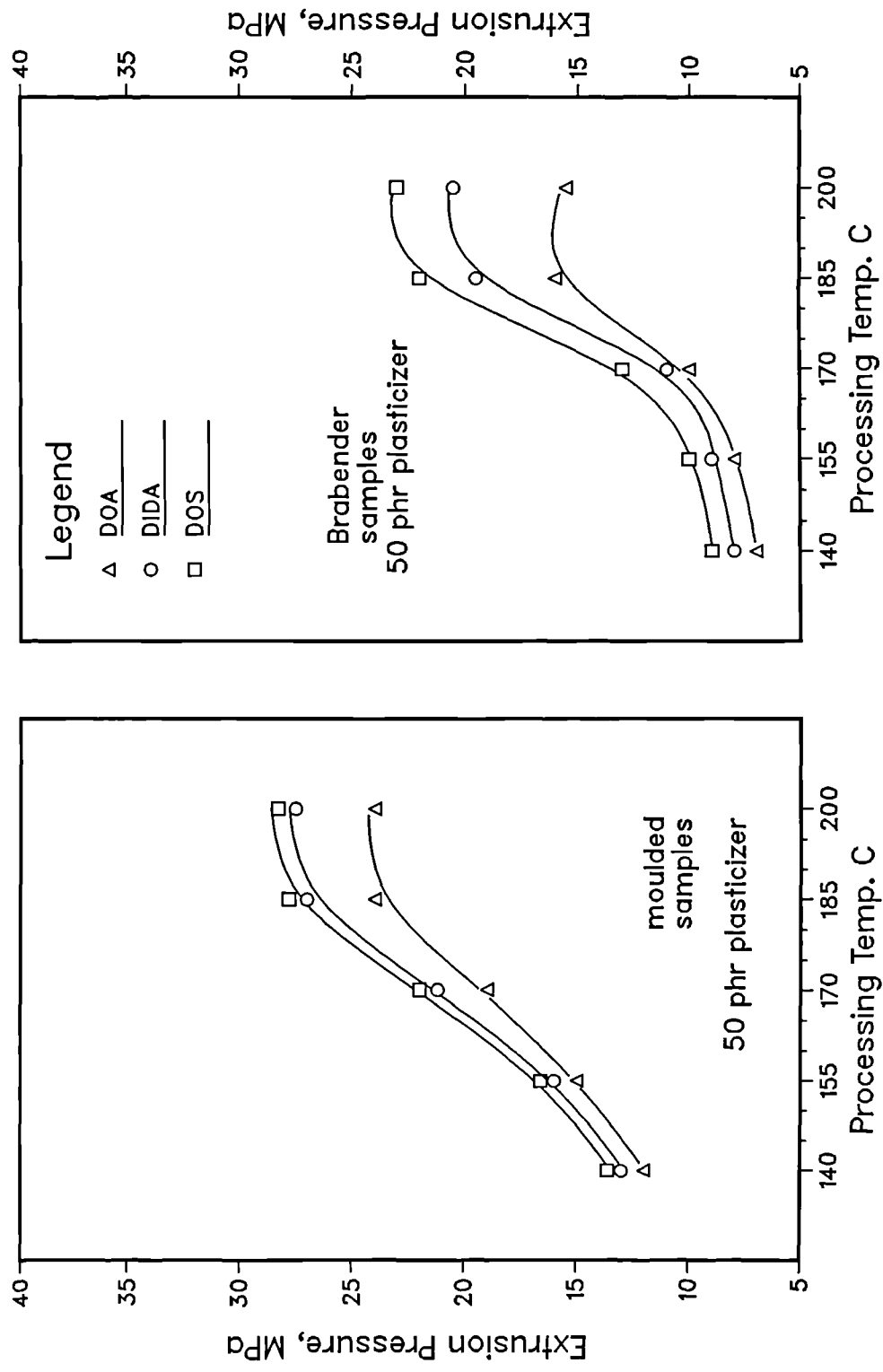


Fig. 5.8: Variation of the extrusion pressure with the processing temperature.
Capillary rheometry test at 130 C.

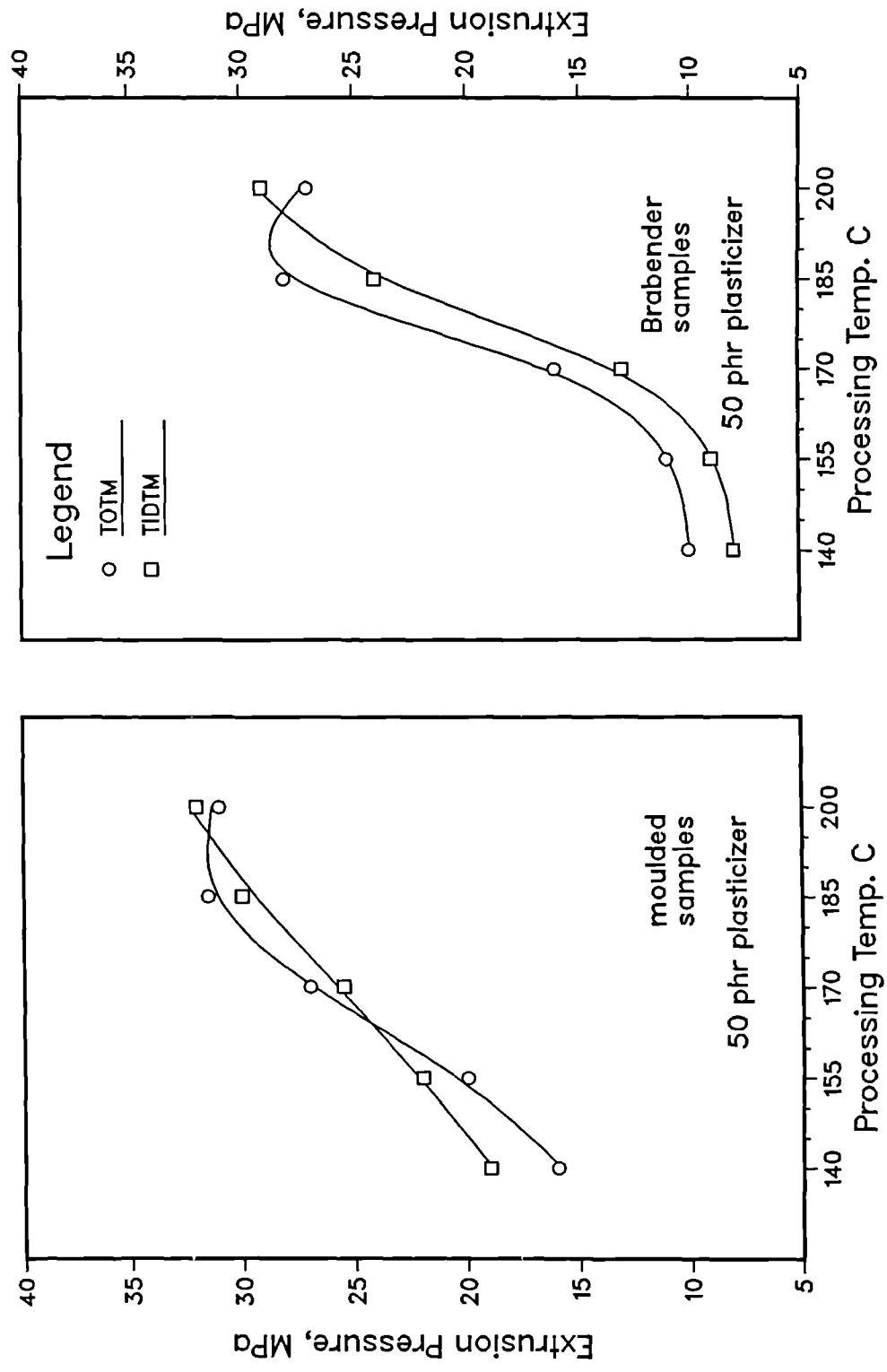


Fig. 5.9: Variation of the extrusion pressure with the processing temperature.
Capillary rheometry test at 130 C.

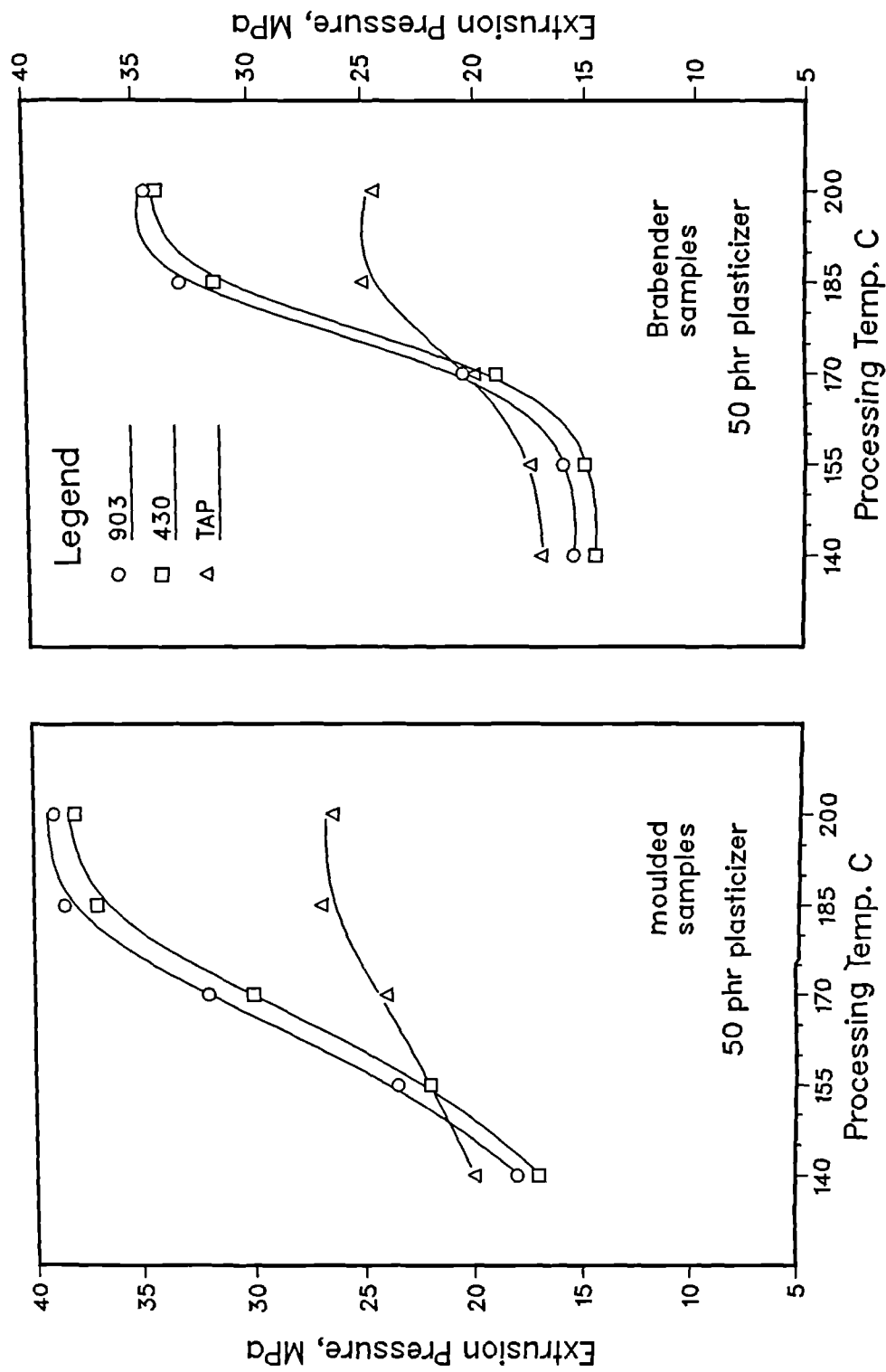


Fig. 5.10: Variation of the extrusion pressure with the processing temperature.
Capillary rheometry test at 130 C.

It is evident from the capillary rheometry experiment, as well as from TEM and OM analysis, that the process of fusion is affected by the plasticizer. The higher the PVC/plasticizer compatibility, the lower the temperature at which fusion commences, and therefore the lower the temperature at which fusion is apparently completed (as indicated by the temperature at which the extrusion pressure reaches the maximum).

Table 5.1

Temperature at Which the Extrusion Pressure
Reaches the Maximum in the CR Experiment.

DBP	185 C
TAP	185
DOP	190
DIDP	195
DOA	195
TOTM	195
903	200
DOS	200
DIDA	200
DTDP	> 200
430	> 200
TIDTM	> 200

It can also be observed in Figures 5.7 to 5.10, that the extrusion pressure is in all cases greater in the moulded samples than in the Brabender samples.

Since the increase in the extrusion pressure is due to an increase in the elasticity of the compound, which in turn is due to the formation of entanglements. The difference between the moulded and the Brabender samples is possibly due to the "combing out effect"⁸⁰, which tends to occur whenever shear on a preferred direction is applied on a polymer melt. This opposes the formation of entanglements and tends to reduce therefore the elasticity of the compound.

Table 5.2

Viscosity and Relative Efficiency of Plasticizers
and Their Corresponding Maximum Extrusion Pressure

	Viscosity ^a mPa.s	Relative ^b Efficiency	Pmax, MPa moulded	Pmax, MPa Brabender
DOA	11	0.84	24.0	16.5
DBP	17	0.85	21.0	18.5
DOS	18	0.89	28.0	22.5
DIDA	20	0.90	27.5	21.5
DOP	60	1.00	27.5	23.0
TAP	100	1.15	27.5	25.0
DIDP	103	1.10	28.5	25.0
DTDP	190	1.18	31.0	27.5
TOTM	202	1.16	31.5	28.0
TIDTM	---	1.19	34.0	30.0
903	4000 ^c	1.22 ^c	39.0	35.0
430	11000 ^c	1.25 ^c	38.0	34.0

^a At 25 C. From Ref. 109, Appendix. [1 mPa.s = 1 cps].

^b Stress at 100% = 7.7 MPa. From Ref. 109. Appendix.

^c From Ref. 122.

Figure 5.11 presents the variation of the extrusion pressure with the processing temperature, for PVC/DOP compounds with varying concentration of DOP. It is observed that the temperature at which the extrusion pressure reaches the maximum decreases with plasticizer concentration. The magnitude of the extrusion pressure also decreases with plasticizer concentration.

The curve from the CR experiment, tends to be an S shaped curve. The maximum in this curve "Pmax" has been referred to as the point where 100% fusion is attained. Having therefore a reference S shaped curve, and assigning 100% degree of fusion to the maximum and zero % to the minimum, the degree of fusion of a given sample can then be determined by comparing its extrusion pressure with the reference curve. Nevertheless, a given reference curve is only valid for the given formulation used to obtain the reference curve. In addition, a given reference curve will only be valid if the reference, as well as the sample, were both processed in the same type of equipment.

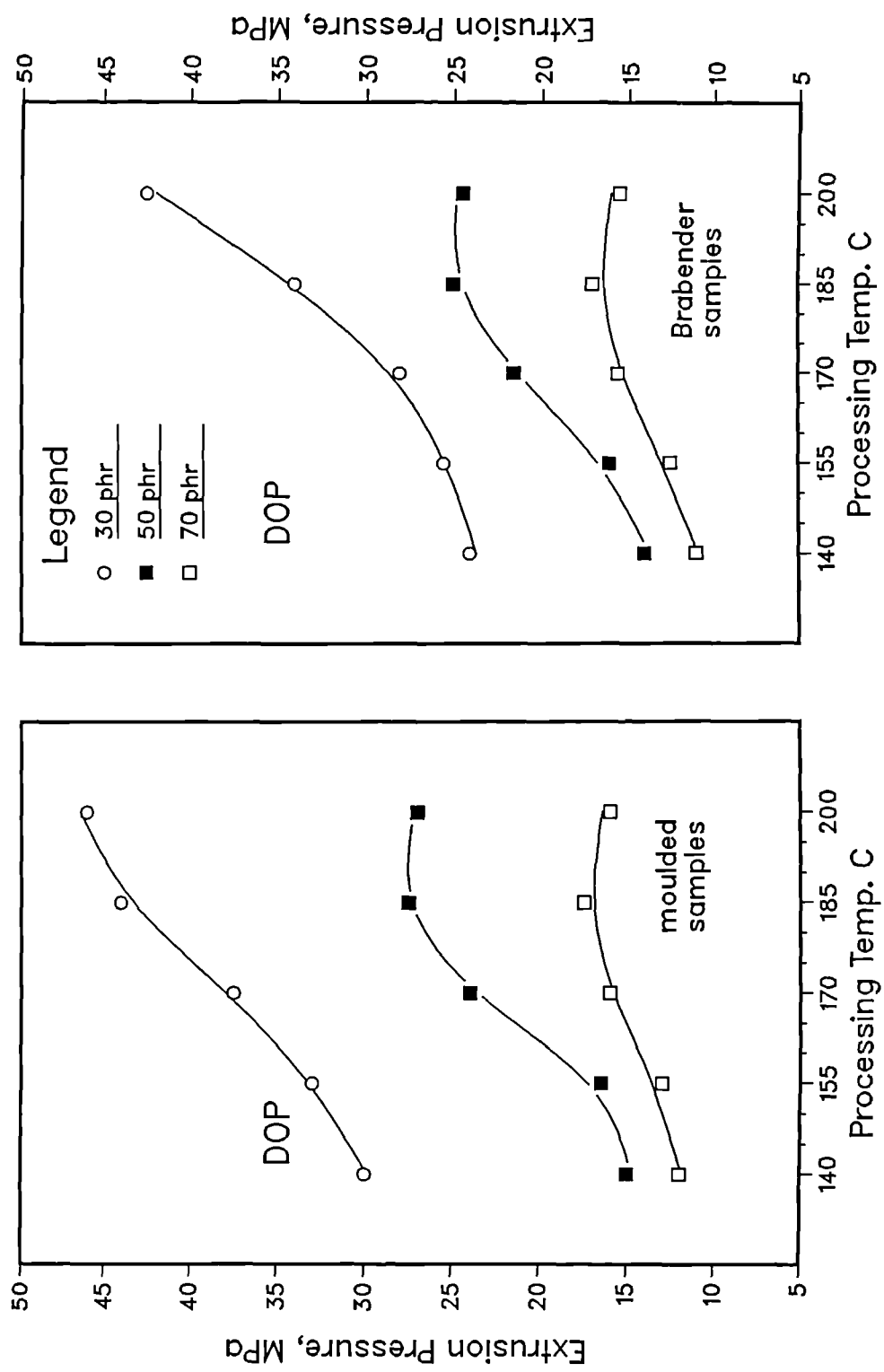


Fig. 5.11: Variation of the extrusion pressure with the processing temperature. Capillary rheometry test at 130 C.

5.4 Extrudate Distortion or Melt Fracture

It has been established that the elasticity of a PVC compound increases with the processing temperature. This increase in elasticity will also manifest itself as variations in the surface appearance of the extrudates (in the capillary rheometry experiment). It is known that melt fracture largely depends on the elasticity of the compound, i.e. as elasticity increases, melt fracture increases. Thus, the severity of melt fracture can be used to evaluate the level of fusion of a PVC sample.

Table 5.3 indicates the severity of melt fracture observed on the PVC/plasticizer compositions studied. The plasticizers are arranged in order of decreasing compatibility. Each result is the average of various observations. The difference between the moulded and the Brabender samples was not considered, i.e. the PVC/DOP moulded and Brabender samples for example, were treated as one set. The severity of melt fracture was determined in accordance with the qualifications given in Figure 5.12.

It is observed in Table 5.3, that the higher the PVC/plasticizer compatibility, the lower the processing temperature at which melt fracture appears. That is, the formation of entanglements that produce the progressive increase in elasticity, (i.e. fusion), is facilitated by the increasing solvating power (compatibility) of the plasticizer.

Table 5.3

Variation of the Severity of Melt Fracture
with the Processing Temperature

	140 C	155 C	170 C	185 C	200 C
DBP	1	2	3	4	5
TAP	0	2	4	5	5
DOP	0	1	3	5	6
DIDP	0	1	3	4	6
DOA	0	1	3	4	5
TOTM	0	1	3	4	6
903	0	0	3	4	6
DOS	0	0	4	4	5
DTDP	0	0	2	4	5
DIDA	0	0	1	3	4
430	0	0	2	4	5
TIDTM	0	0	1	3	4

Severity of melt fracture:

0	no melt fracture	4	high
1	very low	5	very high
2	low	6	extremely high
3	medium		

TAP

DOS

903



Fig.5.12 Variation of extrudate distortion with processing temperature (samples extruded at 140 C).

5.5 Thermal Analysis

Figures 5.13 and 5.14 show the effect of processing temperature on the enthalpy of endotherm A, for the moulded and the Brabender samples respectively.

It is observed that the enthalpy of endotherm A increases with the processing temperature. However, no apparent difference can be appreciated due to plasticizer type. In addition, comparison of Figures 5.13 and 5.14 indicates no apparent difference due to the effect of different types of processing.

Figure 5.15 on the other hand, shows the variation of the enthalpy of endotherm A with the processing temperature, for samples plasticized with varying concentrations of DOP. Again, the enthalpy of endotherm A increases with the processing temperature, but no difference can be appreciated due to the effect of plasticizer concentration.

It has been reported¹⁴⁸ nevertheless, that the enthalpy of endotherm A, apparently does depend on the plasticizer type and concentration and on the type of processing. However, the data reported is not conclusive as to how these variables affect the enthalpy of endotherm A.

The fact is that the enthalpy of endotherm A does increase with the processing temperature, and it can be used therefore to establish the degree of fusion of a given PVC sample.

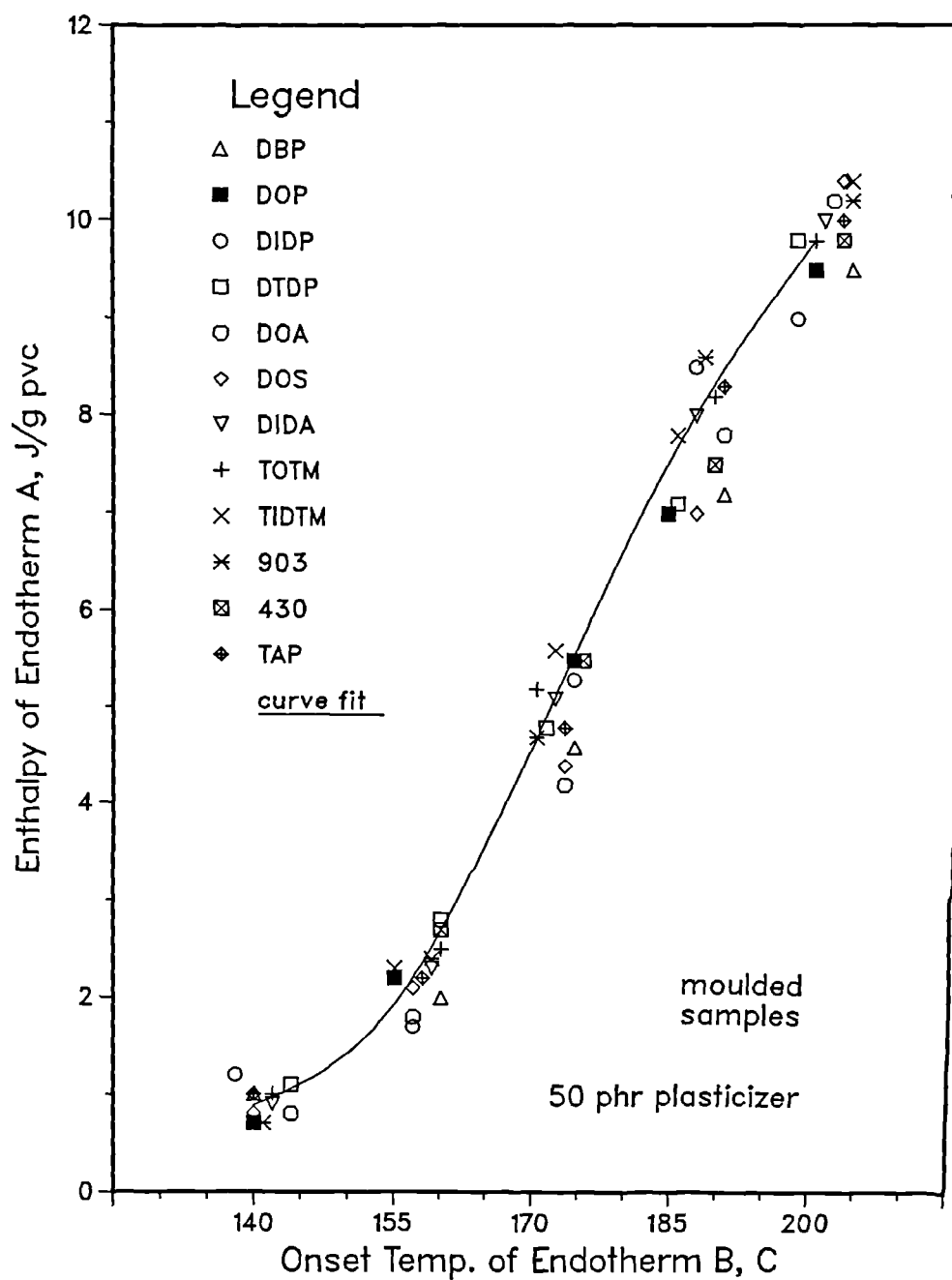


Fig. 5.13: Variation of the enthalpy of endotherm A with the onset temperature of endotherm B, i.e. with the processing temperature.

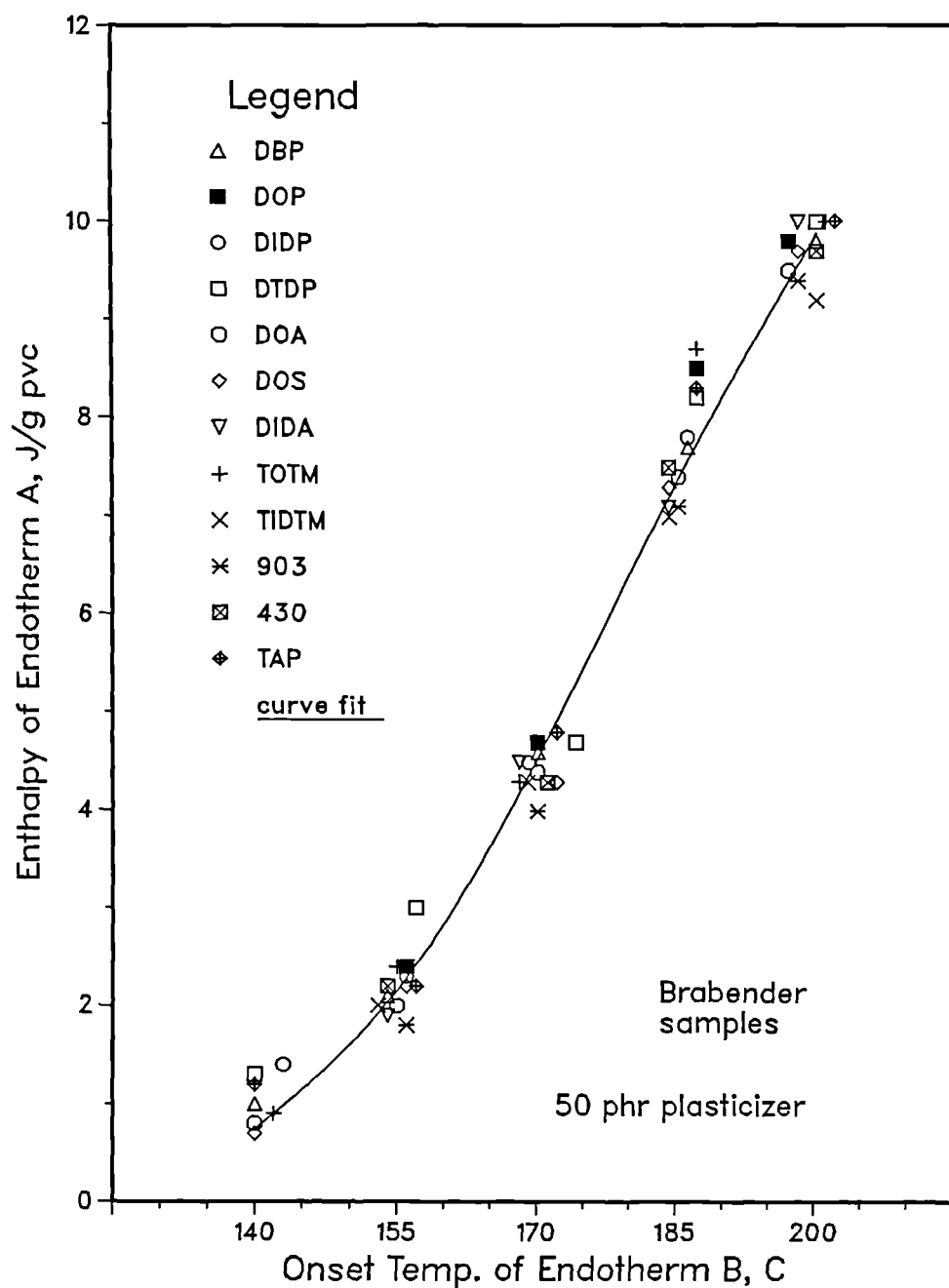


Fig. 5.14: Variation of the enthalpy of endotherm A with the onset temperature of endotherm B, i.e. with the processing temperature.

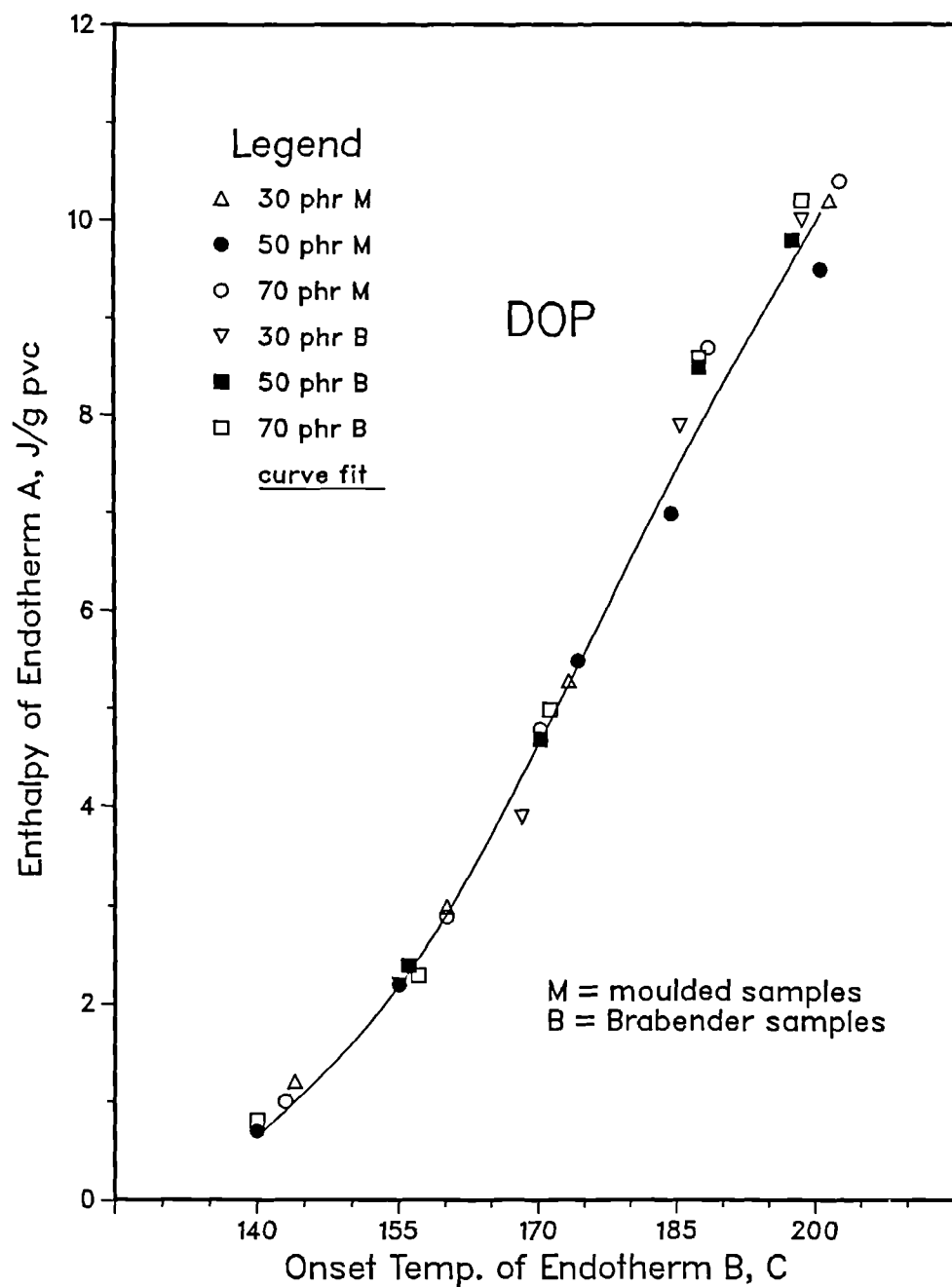


Fig. 5.15: Variation of the enthalpy of endotherm A with the onset temperature of endotherm B, i.e. with the processing temperature.

5.6 Remarks and Conclusions

First, with the exception of thermal analysis, all other techniques used to assess the degree of fusion, such as microscopy (electron and optical microscopy) and capillary rheometry (extrusion pressure and melt fracture), were able to establish the effect of plasticizer type upon the fusion characteristics of PVC.

Second, apart from thermal analysis, the capillary rheometry extrusion pressure seems to be the only one that determines the degree of fusion as a simple and objective number. The limitation is nevertheless, that the reference curve needed to assess the degree of fusion of a PVC sample will only be valid for a sample having a similar formulation and having being processed in a similar equipment as the reference. [Different formulations and different processings will need different reference curves, as noticed in Figures 5.7 to 5.11].

Microscopy, on the other hand, gives a very good estimate of the degree of fusion, irrespective of the formulation or the type of processing. The result however, is subjective, and may depend on the person who examines the micrograph. [Unless the micrographs are compared to a standard set of micrographs showing the changes that occur with the progression of fusion, as the standard set of micrographs in ASTM D2663, used to establish the degree of carbon black dispersion in rubbers].

Third, it is observed that fusion of plasticized PVC is highly dependent on the plasticizer type (i.e. plasticizer compatibility) and concentration. The higher the PVC/plasticizer compatibility, the lower the temperature at which fusion is apparently completed. That is, the higher the plasticizer compatibility, the lower the processing temperature or the shorter the processing (or residence) time required to attain the best mechanical properties characteristic of a well fused PVC compound.

Fourth, thermal analysis did not establish any difference in the enthalpy of endotherm A, arising from the effect of different plasticizer types and concentration, or from different types of processing. Nevertheless, it has been reported otherwise¹⁴⁸. One important difference between the results reported in section 5.5 and the results in Ref. 148 was the time elapsed between the preparation of the samples and the subsequent determination of the enthalpy of endotherm A. This time was no more than 1 month in Ref. 148, whereas it was around 5 months in this study.

If endotherm A is due to the formation of imperfect ordered regions⁸³, then, the formation of these imperfect ordered regions should be time/temperature dependent.

A very simple experiment was devised to examine the effect of the time elapsed between sample preparation and the determination of the enthalpy of endotherm A.

Figure 5.16 shows the variation of the enthalpy of endotherm A with time, for two plasticized PVC compositions with 50 phr DOP and 50 phr DTDP. It is observed that: 1) the enthalpy of endotherm A first increases slightly and then decreases with time to a constant and steady value, and 2) the DOP and DTDP compounds show initially a difference in the enthalpy of endotherm A, but this difference tends to disappear with time.

It is assumed therefore, that the enthalpy of endotherm A will always tend to reach a constant and steady value. However, the time needed to attain this value may depend on the plasticizer type (and concentration) and on the ageing temperature.

This is why when the samples (in section 5.5) were tested 5 months after preparation, no variation in endotherm A with plasticizer type was observed.

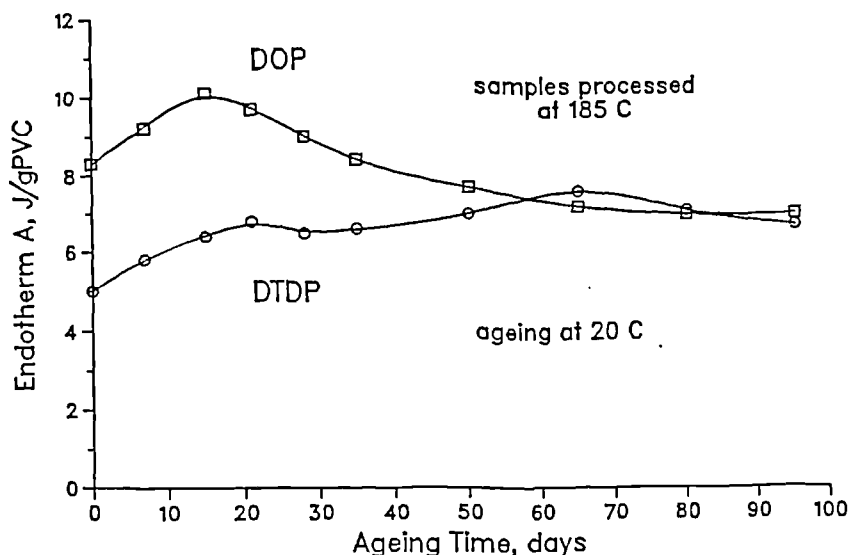


Fig.5.16: Variation of endotherm A with ageing time.

Chapter 6

RESULTS AND DISCUSSION: MECHANICAL PROPERTIES

6.1 Dynamic Mechanical (Rheological) Properties

PVC shows a marked change in elasticity as the level of fusion increases. For example, the pressure loss at the capillary entrance, as well as the extrudate appearance and the die swell, which are largely dependent on the elasticity of the compound, are all affected by the level of fusion of the PVC. It is to be expected therefore, that the dynamic mechanical properties also be affected by the level of fusion of the PVC.

Figures 6.1 to 6.4 present the variation of the elastic modulus with the processing temperature, for the plasticized PVC compounds studied. It is observed that the elastic modulus first decreases, reaches a minimum, and then increases with increasing moulding temperature. Figure 6.5 on the other hand, shows the variation of the dynamic shear viscosity with the processing temperature. The viscosity also, first decreases, reaches a minimum, and then increases with the moulding temperature.

This may be explained as follows: At low moulding temperatures, (140-155 C, Fig. 5.2), the particulate structure largely consists of spongy and irregularly shaped grains ca 100 μm in size. But as the moulding temperature is increased, (170C, Fig. 5.2), the

particulate structure now consists entirely of the more compact and regularly shaped primary particles ca 1 μ m in size. At the same time, the increase in temperature causes the less perfect crystallites start to melt.

It is this transition, from the irregularly shaped and large grains to the somewhat spherical and small primary particles, and the onset of fusion of the less perfect crystallites, that causes the observed decrease in viscosity and elasticity.

As the moulding temperature is further increased, the primary particle boundaries disappear. This permits molecules from different primary particles to interact between each other, and facilitates the formation of entanglements. These in turn will increase the viscosity and the elasticity of the compound.

This minima in viscosity (torque in the Brabender torque rheometer) and elasticity (extrusion pressure in the CR experiment) have been observed elsewhere. Smith¹⁴⁹ found that the extrusion pressure of suspension PVC, first reaches a minimum and then increases with increasing moulding time, i.e. with increasing fusion. This minimum was not observed with emulsion PVC. Gonze⁷² and Grey⁷⁴ found that, under certain conditions of testing and for compounds of a certain formulation or processed under certain conditions, the extrusion pressure also shows a minimum just before the normal increase that occurs with increasing processing temperature. During Brabender mixing, Sieglaf⁵⁷ and Rabinovitch and Summers⁷¹ found that the torque shows a minimum just before the normal increase that occurs with increasing time of mixing.

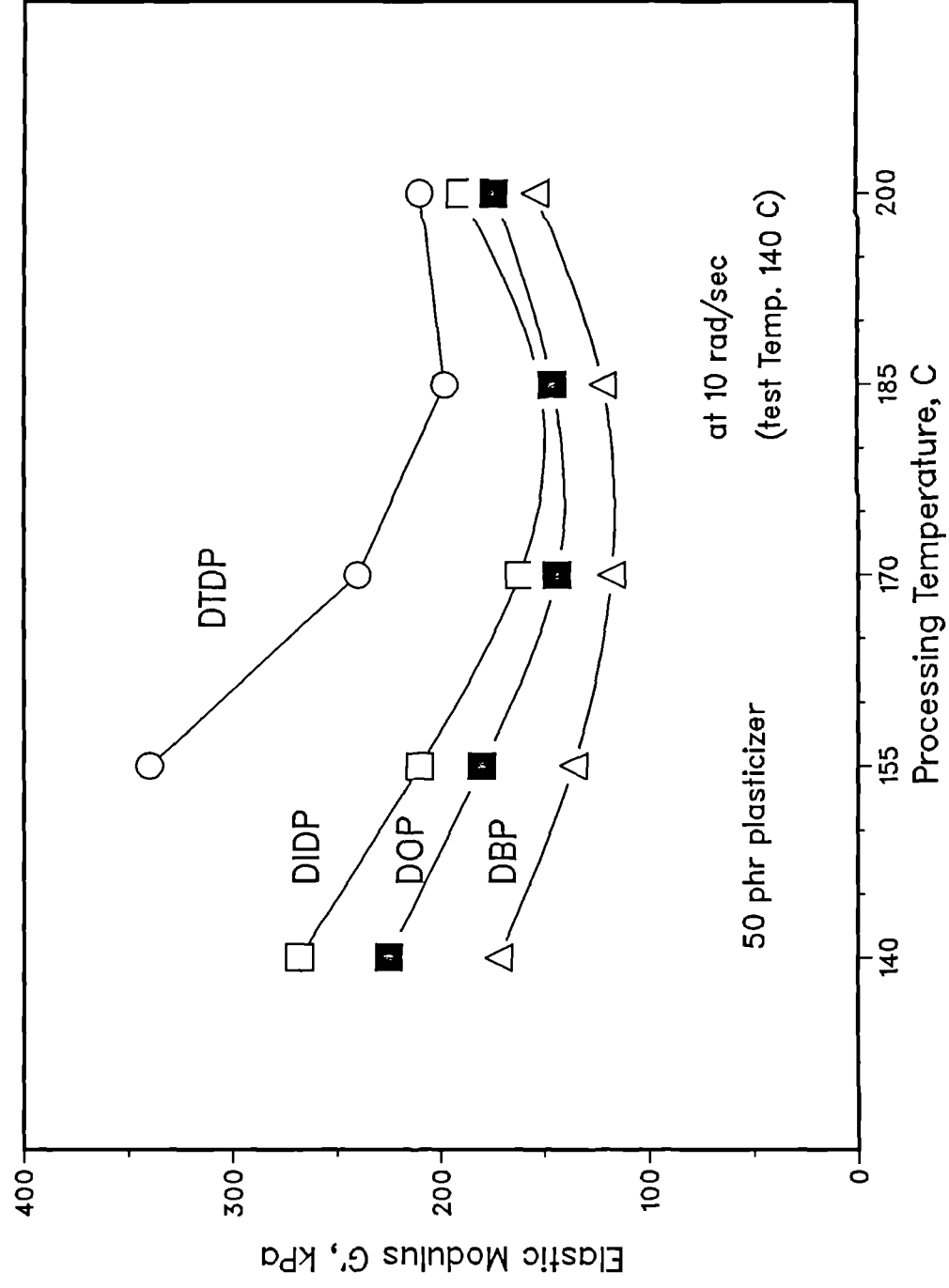


Fig. 6.1: Variation of the elastic modulus with the processing temperature.

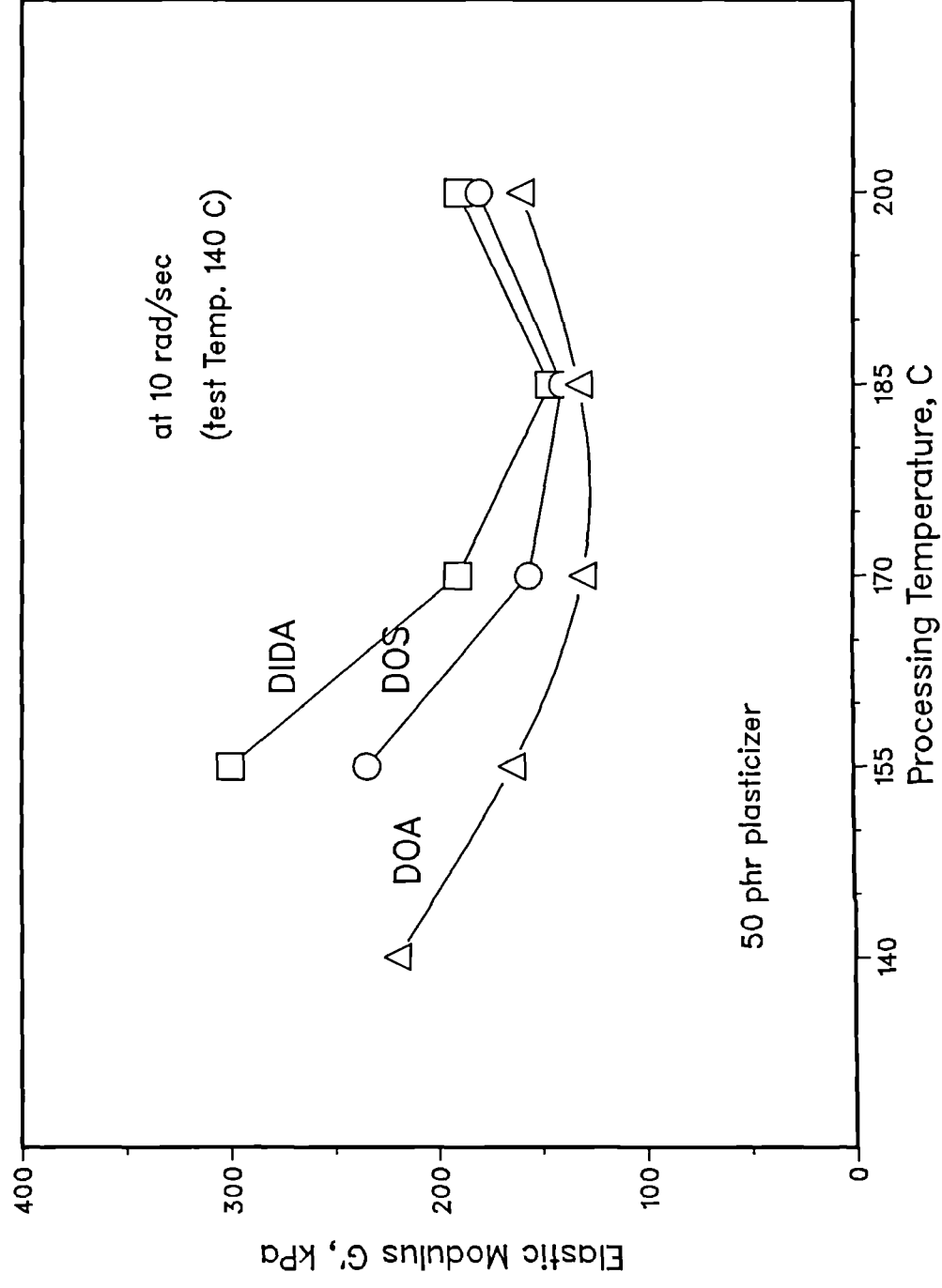


Fig. 6.2: Variation of the elastic modulus with the processing temperature.

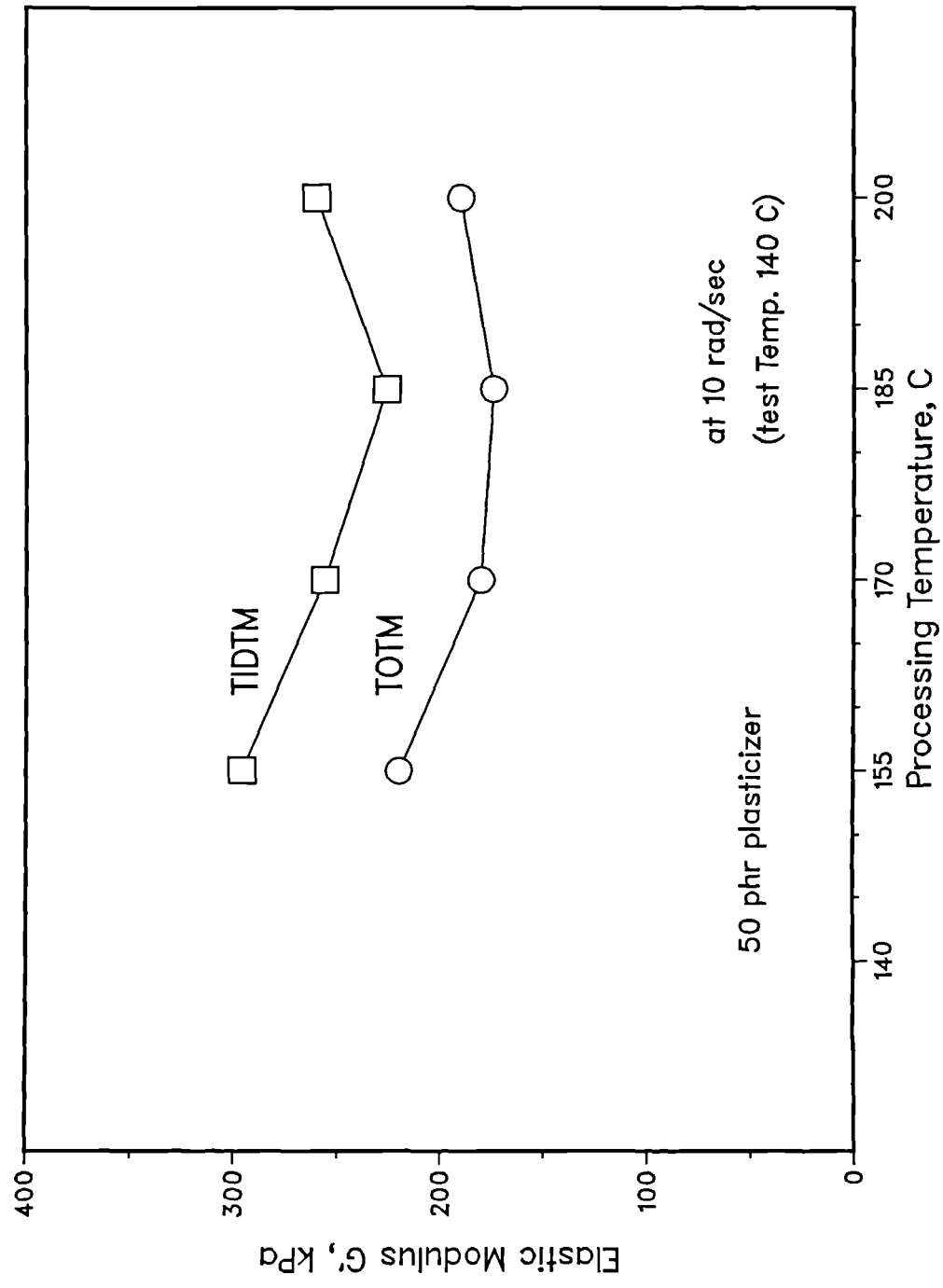


Fig. 6.3: Variation of the elastic modulus with the processing temperature.

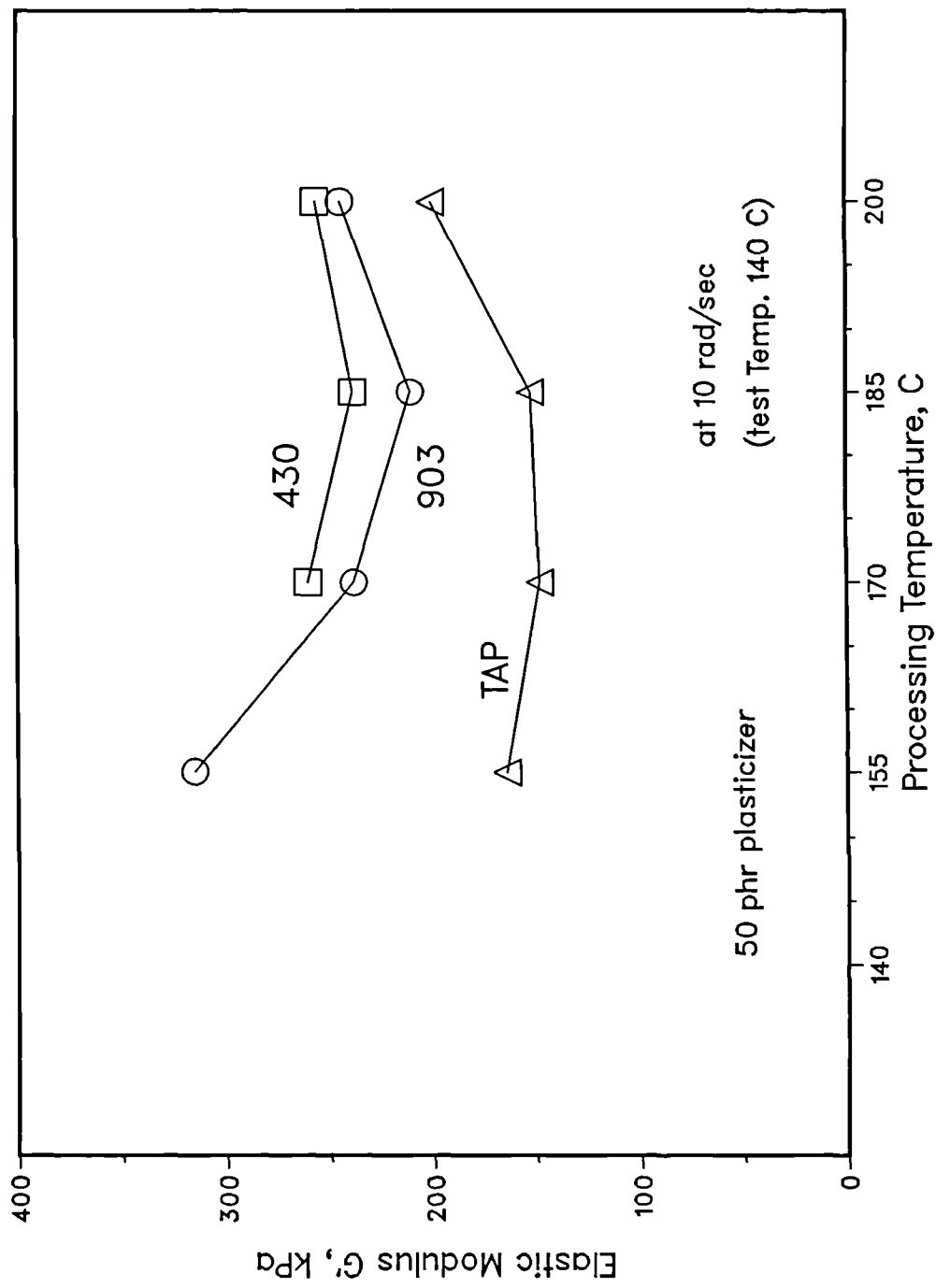


Fig. 6.4: Variation of the elastic modulus with the processing temperature.

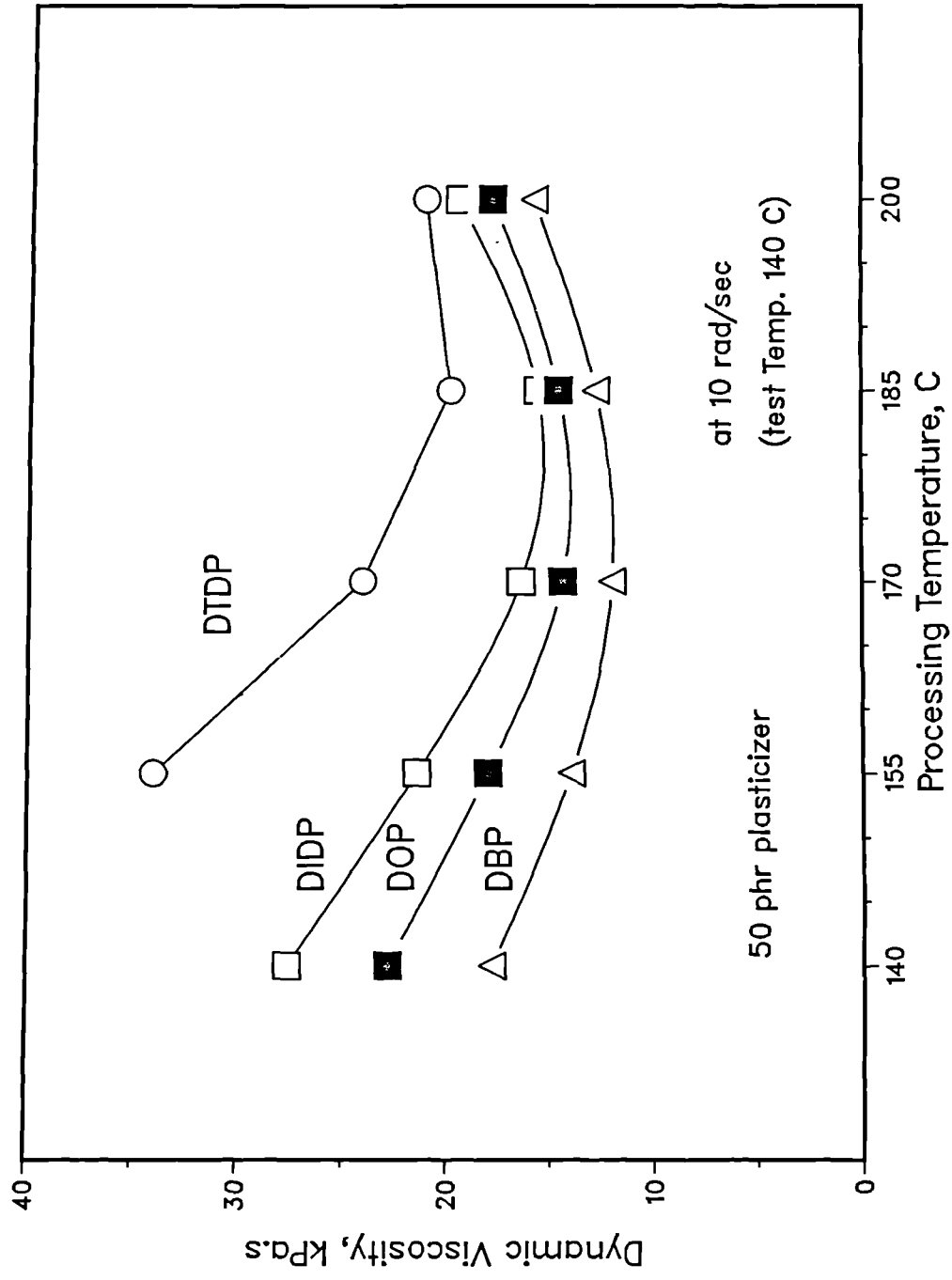


Fig. 6.5: Variation of the dynamic viscosity with the processing temperature.

Assuming the variations in elastic modulus and dynamic viscosity presented above, are due to the structural changes that occur during the process of fusion, these variations should be affected by the PVC/plasticizer compatibility. This is demonstrated in Table 6.1, which presents the moulding temperature at which each compound reaches the minimum elastic modulus and dynamic viscosity, arranged in order of increasing magnitude. It is noticed that the higher the plasticizer compatibility, the lower the temperature at which the minimum occurs. [The ordering of plasticizers in Table 6.1 coincides with the ordering of plasticizer compatibility].

Table 6.1

Moulding Temperature at Which Each Compound^a
Shows the Minimum Elastic Modulus and Viscosity

DBP	171 C
TAP	171
DOP	176
DOA	179
TOTM	180
DIDP	181
DOS	183
903	184
DIDA	186
DTDP	187
430	188
TIDTM	188

^a PVC with 50 phr plasticizer.

Figure 6.6 shows the variation of viscosity with shear rate, for PVC/DOP compounds. It is observed that viscosity decreases with shear rate (as in all pseudoplastic polymers), irrespective of the structure of the sample, i.e. particulate structure (in samples processed at low temperatures) or molecular network structure (in samples processed at high temperatures). However, the effect of the structure is observed in comparing the viscosities, at each shear rate, of the samples processed at different temperatures. The viscosity first decreases with increasing moulding temperature (from 140 to 170 C). This is associated with the breakdown of the 100 μm PVC grains into the 1 μm primary particles. Thereafter, the viscosity increases with the moulding temperature (from 170 to 200 C). This is associated with the progressive fusion of the primary particles and the resulting formation of entanglements.

Figure 6.7 shows the variation of viscosity with shear rate, for several plasticized PVC compositions. Plotted in this graph, are the viscosities obtained at the minimum in plots similar to Fig. 6.5, i.e. at the point where flow dependency is changing from particulate to molecular deformational. Therefore, the viscosities plotted in Fig. 6.7 correspond to compounds having similar fusion levels.

Table 6.2 lists the plasticized PVC compounds studied, in order of increasing viscosity. [Viscosities at the minimum, from plots similar to Fig. 6.7]. It is observed that the ordering corresponds with that of plasticizer viscosity, as shown in Table 5.2. That is, the viscosity of plasticized PVC will tend to increase with the viscosity of the plasticizer.

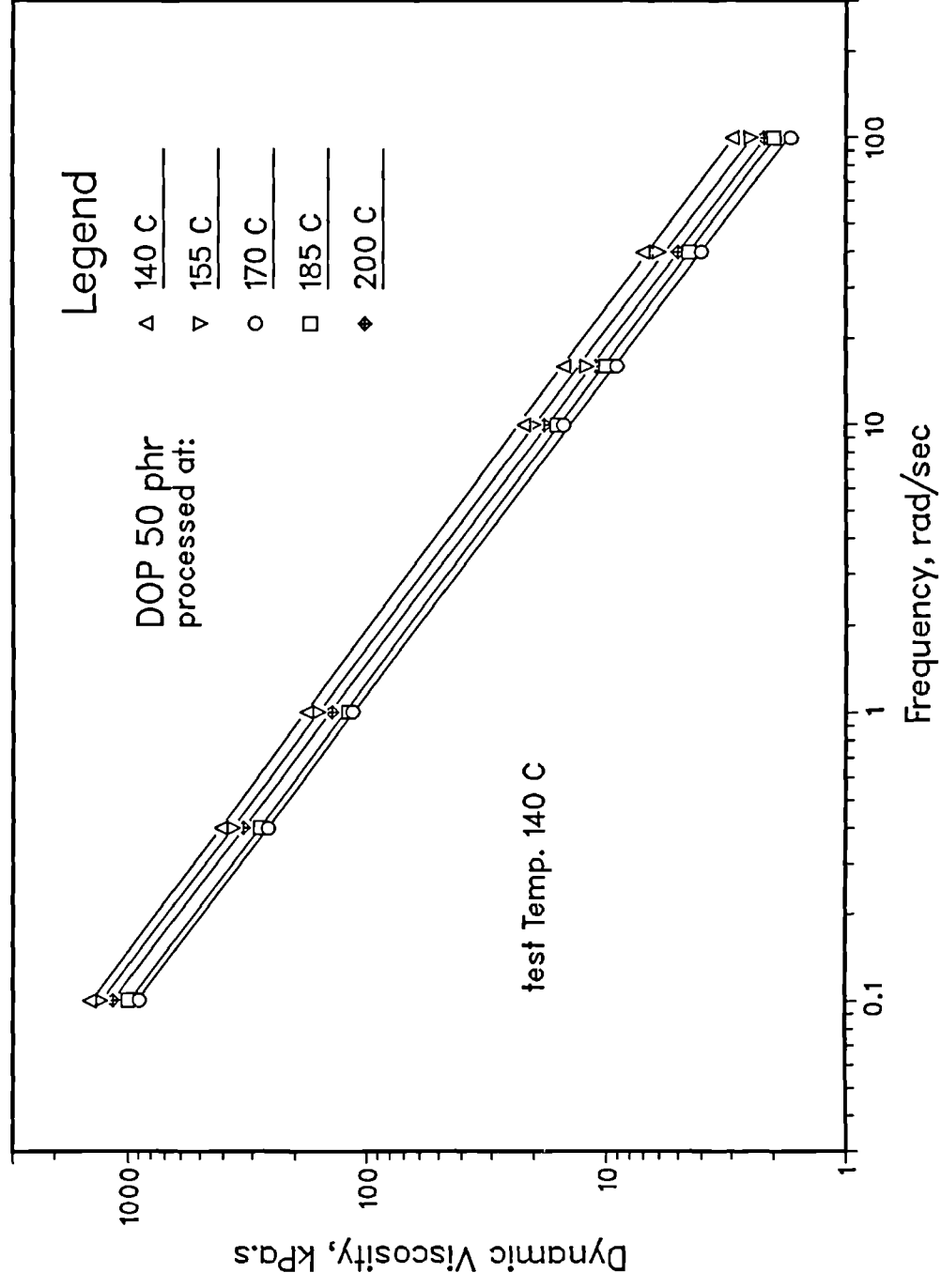


Fig. 6.6: Variation of the dynamic viscosity with shear rate, for PVC/DOP processed at different temperatures.

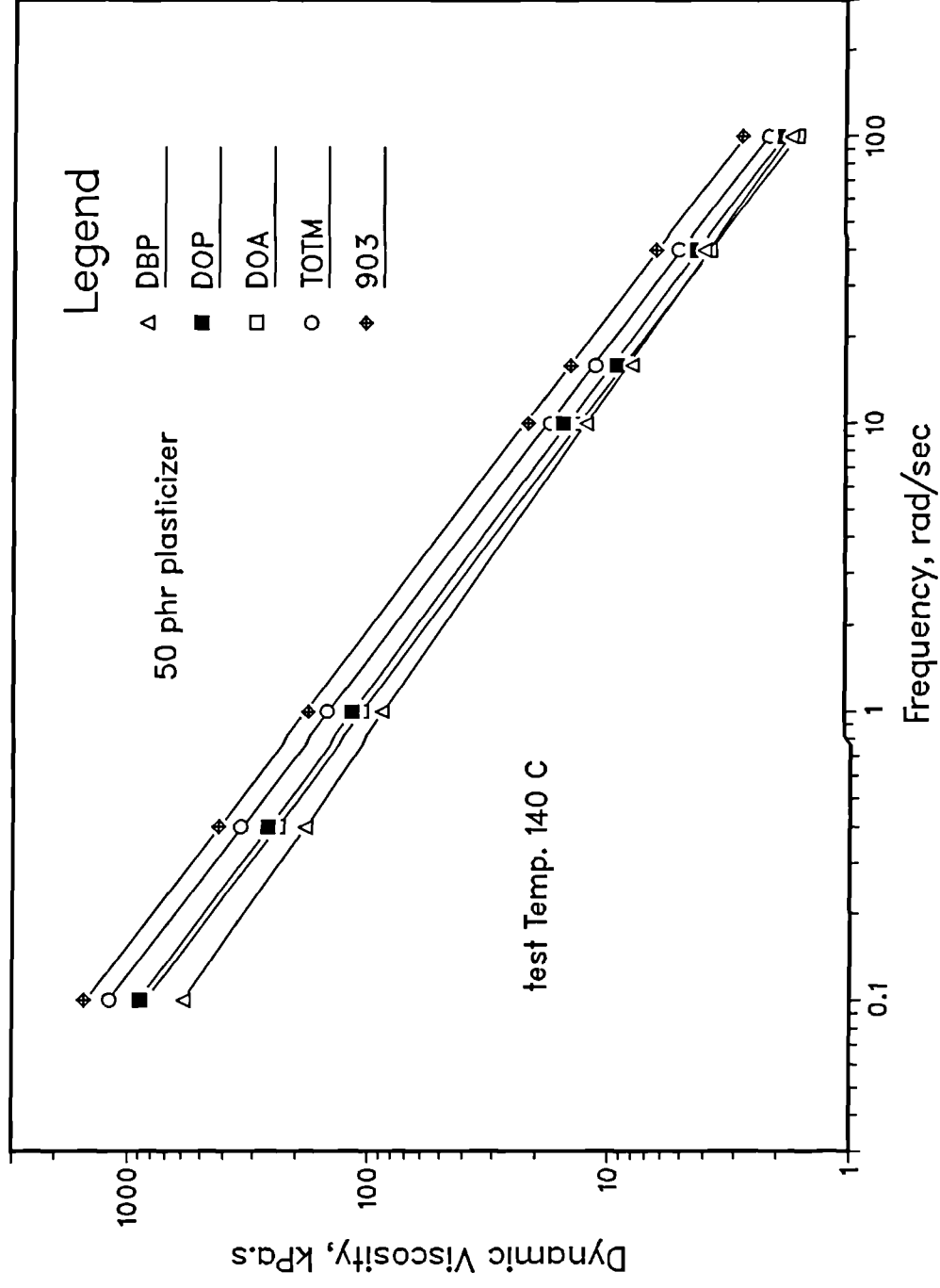


Fig. 6.7: Variation of the dynamic viscosity with shear rate. Samples processed at 170 C (dbp, dop, doa) and 185 C (totm, 903).

Table 6.2

Viscosity^a of Plasticized PVC Compounds,
(50 phr plasticizer), At Similar Fusion Levels

DBP	12	kPa.s
DOA	13	
DOS	13.5	
DOP	14	
DIDA	14	
TAP	14.5	
DIDP	15	
TOTM	17	
DTDP	20	
903	22	
TIDTM	23	
430	25	

^a Determined at 10 rad/sec

6.2 Tensile Properties

Figure 6.8 presents the variation of tensile strength and elongation at break with the processing temperature, for several plasticized PVC compositions. Tensile strength and elongation at break, both increase with the processing temperature, up to a maximum which is reached asymptotically. In addition, it is observed that the processing temperature required to attain the maximum tensile, (or elongation), decreases with the PVC/plasticizer compatibility. But the magnitude of that maximum tensile (or elongation) on the other hand, shows no relationship with that compatibility.

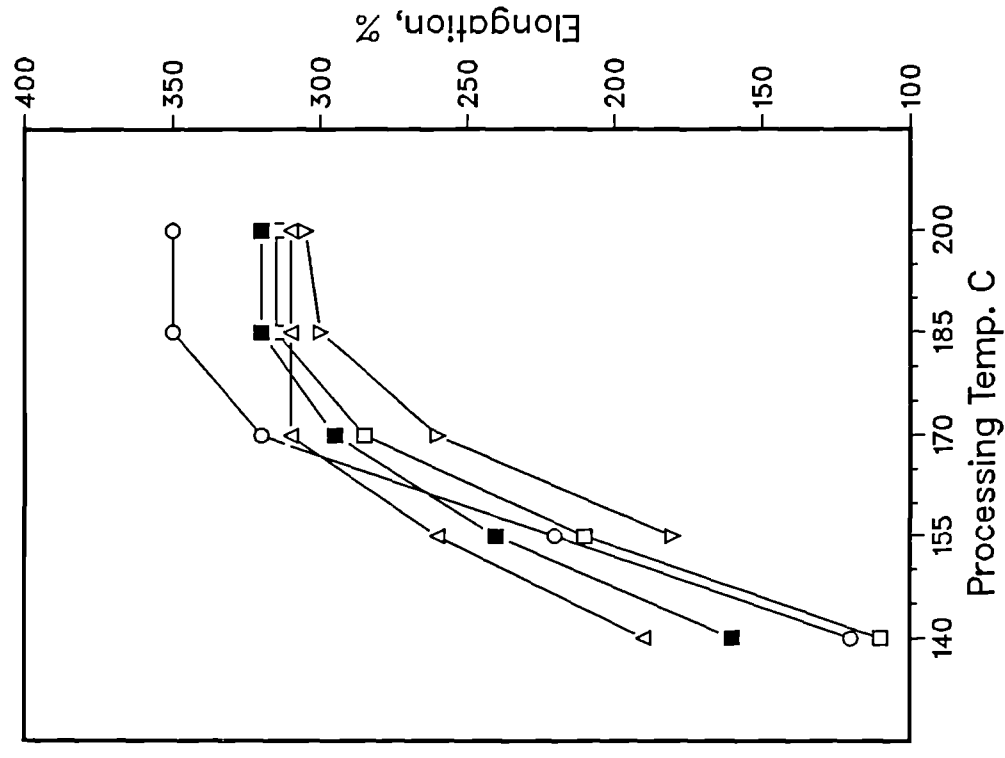
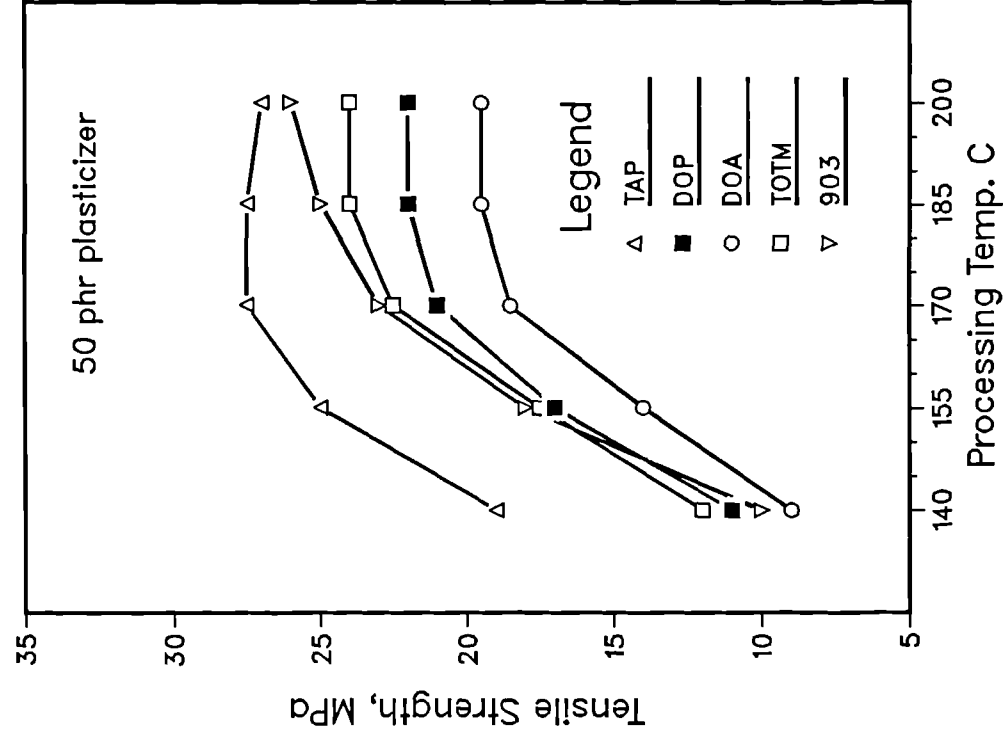


Fig. 6.8: Variation of tensile strength and elongation with the processing temperature.

Tables 6.3 and 6.4 present the tensile strength and the elongation at break, as a function of the processing temperature, for the plasticized PVC compounds studied. [Compounds are presented in order of increasing maximum tensile or decreasing maximum elongation]. Within a given plasticizer family, (e.g. phthalates, adipates, or trimellitates), the maximum tensile increases with the plasticizer molecular weight. However, the more significant feature is the fact that the ordering of plasticized PVC compounds in Table 6.3, (in order of increasing maximum tensile), coincides with the ordering of plasticized PVC compounds in Table 6.5, (in order of increasing glass transition temperature).

Table 6.3

Tensile Strength of Plasticized PVC, MPa.

	Moulded at: 140	155	170	185	200 C
DOA	9.5	13.9	18.5	19.5	19.5
DOS	8.5	14.5	19.2	20.2	20.4
DIDA	8.0	15.0	19.5	20.3	20.5
DBP	12.3	18.5	21.0	21.0	20.5
DOP	11.3	17.2	21.0	22.0	22.0
TOTM	11.4	17.3	22.5	24.0	24.0
DIDP	11.5	18.4	22.4	24.0	24.0
DTDP	--	16.2	22.3	24.6	25.5
903	10.0	17.8	23.0	25.0	25.8
430	7.6	17.1	22.9	25.0	26.0
TAP	19.0	25.0	27.5	27.5	27.5
TIDTM	--	17.5	23.0	26.0	27.5

PVC/50 phr plasticizer. Moulded for 5 min at 27 MPa.

Table 6.4

Elongation at Break of Plasticized PVC, %.					
	Moulded at; 140	155	170	185	200 C
DOA	120	220	330	350	345
DOS	---	190	305	330	340
DIDA	---	180	280	320	340
DOP	160	235	295	320	320
DBP	210	275	315	315	315
TOTM	110	210	290	315	315
DIDP	125	210	270	310	315
DTDP	---	---	230	270	310
903	---	180	260	300	305
TAP	190	260	305	305	305
430	---	160	240	285	300
TIDTM	---	---	200	275	295
PVC/50 phr plasticizer. Moulded for 5 min at 27 MPa.					

Figure 6.9 presents the variation of tensile and elongation with the processing temperature, for PVC compounds with varying plasticizer concentration. Tensile and elongation, both increase with processing temperature, up to a maximum. That maximum will be attained at lower processing temperatures, as the plasticizer concentration increases. In addition, the maximum tensile decreases, whereas the maximum elongation increases with increasing plasticizer concentration.

Table 6.5

"T_g"^a of Plasticized PVC (50 phr)

DOS	-47 C
DOA	-45
DIDA	-40
DOP	-20
DIDP	-18
DTDP	-16
DBP	-15
TOTM	-13
903	0
TAP	5
430	5
TIDTM	8

^a From TMA, as in section 2.4

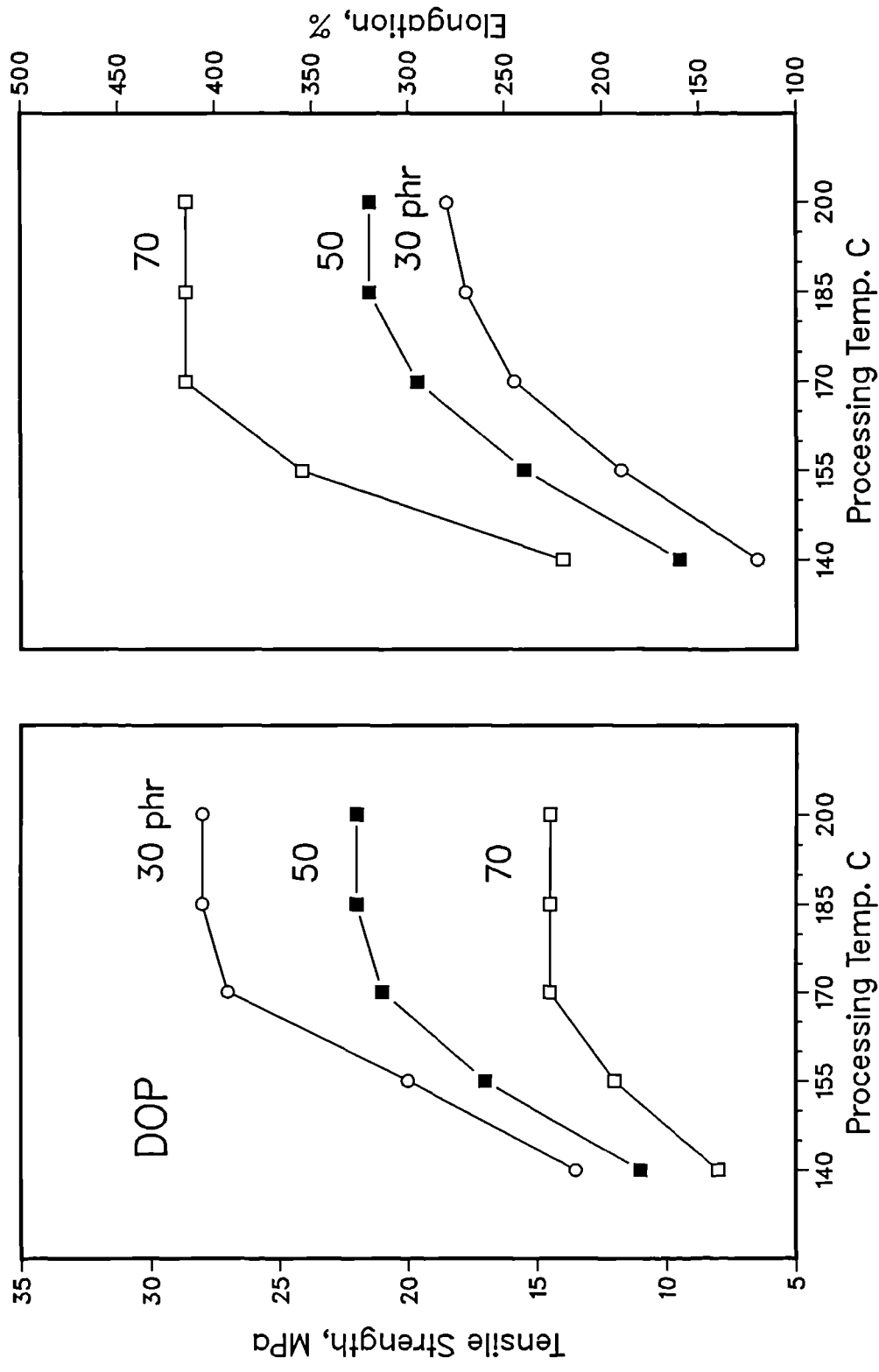


Fig. 6.9: Variation of tensile strength and elongation with the processing temperature.

6.3 Remarks and Conclusions

First, the tensile properties of plasticized PVC depend on the level of fusion. Tensile strength and elongation at break, both increase with the level of fusion up to a maximum. The higher the PVC/plasticizer compatibility, the lower the processing temperature required to attain this maximum. However, the magnitude of this maximum depends on the T_g of the compound; the higher the T_g , the greater the tensile strength and the lower the elongation at break. In addition, the higher the plasticizer concentration, the lower the processing temperature required to attain that maximum.

Second, the elastic modulus G' shows a noticeable dependence on the level of fusion of the plasticized PVC compound. A minimum G' is observed at a point which coincides with the transition from particulate flow dependency to molecular deformational flow dependency. For this minimum G' is observed at lower processing temperatures, the higher the PVC/plasticizer compatibility.

Third, the dynamic viscosity of the plasticized PVC compositions shows the same dependence on the level of fusion, as G' .

Fourth, at a similar fusion level, the dynamic viscosity of plasticized PVC depends on the plasticizer viscosity. The viscosity of plasticized PVC will tend to increase with increasing plasticizer viscosity.

Chapter 7

GENERAL CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 General Conclusions

- Compatibility predictors, such as δ , and ϕ , should not be used alone as the sole indicators of the PVC/plasticizer compatibility. Their reliability is small, especially if applied to polymeric plasticizers.

- Compatibility measurements, such as T_m , χ , and α are highly consistent and reliable indicators of compatibility, with the exception of χ when applied to polymeric plasticizers.

- The Flory-Huggins interaction parameter, calculated from equation 2.2, is an inconsistent indicator of compatibility when applied to polymeric plasticizers.

- Several relationships were obtained between the different compatibility parameters.

- There is a clear relationship between such compatibility parameters as T_m , χ , and α , and the processing characteristics encountered in the Brabender torque rheometer.

- Several relationships were obtained between T_m , χ , and α , and the Brabender fusion temperature (T_f).

- The Brabender fusion temperature can be used as indicator of the PVC/plasticizer compatibility.

- The process of fusion of plasticized PVC is highly dependent on plasticizer compatibility.

- Microscopy and capillary rheometry can be used to establish the effect of plasticizer type upon the process of fusion of PVC.

- The enthalpy of endotherm A increases with the level of fusion of plasticized PVC. However, there is no difference in the enthalpy of endotherm A, arising from the effect of plasticizer type or concentration or from the type of processing, (it must be emphasised that the samples were examined after ca 5 months of ageing at room temperature).

- The tensile properties of plasticized PVC depend on the level of fusion.

- The processing temperature required to attain the maximum tensile properties of plasticized PVC depends on the plasticizer compatibility. The magnitude of the tensile properties however, depends on the glass transition temperature of the plasticized PVC.

- The elastic modulus and the dynamic viscosity of plasticized PVC depend on the level of fusion.

- The magnitude of the dynamic viscosity depends on the viscosity of the plasticizer used in the plasticized PVC compound.

7.2 Suggestions for Further Work

A large discrepancy was found in the estimated compatibility of polymeric plasticizers. Compatibility was high according to χ , whereas it was low according to T_m , α , and T_f . A study of the compatibility of polymeric plasticizers is suggested. The objective should be to establish the volume (V_1) of the polymeric plasticizer that interacts with the molar volume (V_2) of the polymer repeat unit in the Flory-Huggins equation.

It was found that the extrusion pressure, in the capillary rheometry experiment, was always lower for the Brabender samples than for the moulded samples. It was mentioned that this was possibly due to the combing out effect that occurs in samples subjected to shear. A study of the effect of orientation on the capillary rheometry extrusion pressure is suggested.

It was found that the enthalpy of endotherm A tends with time to attain a constant and steady value. Before that is achieved however, the enthalpy of endotherm A is affected, e.g. by the plasticizer type. A study of the enthalpy of endotherm A, and its dependency on such variables as the plasticizer type and concentration, and the time and temperature of aging, is suggested.

It was found during Brabender mixing, that the more compatible the plasticizer, the shorter the time and the lower the temperature needed to attain fusion, but the higher the torque peak. During extrusion, this implies that the more compatible the plasticizer, the shorter the residence time and the lower the temperature needed to attain fusion, but the higher the power consumption per unit time. A study of the effect of plasticizer compatibility and viscosity on the power consumption per unit time and power consumption per unit product, during extrusion, is suggested.

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