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RESILIENCE PROPERTY IMPROVEMENT
OF RIGID PVC THIN SHEET

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                               RIGID PVC THIN SHEET

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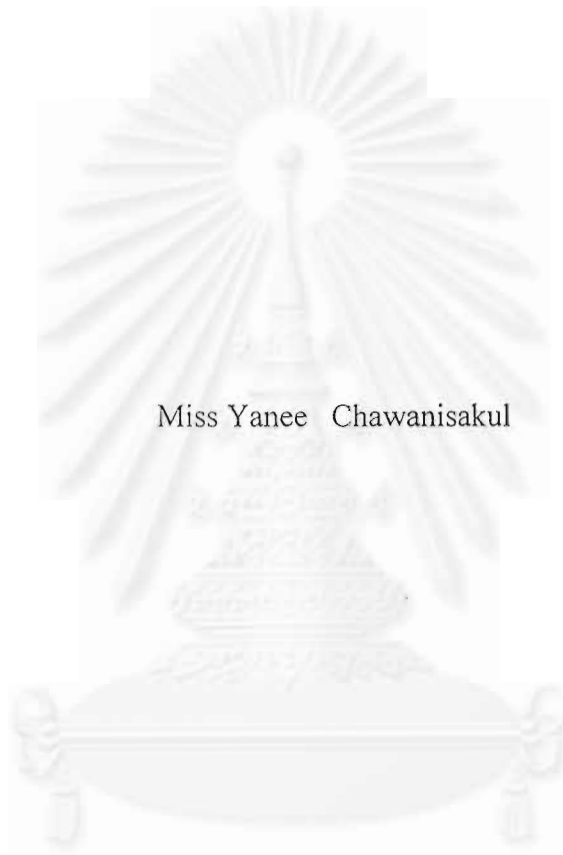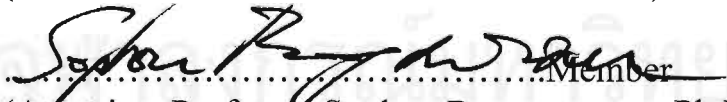
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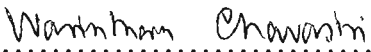
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ได้มีการศึกษาผลของปริมาณ และชนิดของสารเติมแต่ง ต่อปัญหาการคืนตัวใน พอลิ(ไวนิล คลอไรด์) (พีวีซี) แผ่นบางชนิดแข็ง ที่ใช้ในผลิตภัณฑ์ ต้นคริสต์มาสเทียม สารเติมแต่งที่ใช้ในการวิจัยนี้ได้แก่ เมทิล เมทาคริเลต บิวทาไดอีน สไตรีน (เอ็มบีเอส), อะคริโลไนทริล, บิวทาไดอีน สไตรีน (เอบีเอส), คลอริเนตเต็ด พอลิเอทิลีน (ซีพีอี), โพร เซสซิ่ง เอดส์, อินเทอร์นอล ลูบริแคนท์, แคลเซียมคาร์บอเนต และ ทัลค์ พบว่าสารเติม แต่งที่ดีที่สุดในการปรับปรุงสมบัติการคืนตัว คือ เอบีเอส ปริมาณที่เหมาะสมสำหรับ ผลิตภัณฑ์คริสต์มาสเทียม คือ 10 พีเอชอาร์ ได้สมบัติการคืนตัว ของสูตรใหม่ดีกว่าของ ผลิตภัณฑ์ที่จำหน่ายเชิงพาณิชย์ทั่วไป 2 ชนิด เป็นสองเท่า เมื่อเพิ่มปริมาณ เอ็มบีเอส, ซี พีอี, อินเทอร์นอล ลูบริแคนท์, แคลเซียมคาร์บอเนต และ ทัลค์ สมบัติการคืนตัวลดลง ส่วนปริมาณโพรเซสซิ่ง เอดส์ ไม่มีผลในการปรับปรุงสมบัติการคืนตัวอย่างมีนัยสำคัญ เมื่อทำการศึกษาสมบัติต่าง ๆ ได้แก่ การทนแรงดึง, การทนแรงฉีกขาด, ความแข็ง, อุณหภูมิการเสียรูป และอุณหภูมิคล้ายแก้ว พบว่าสมบัติการคืนตัวมีความสัมพันธ์โดยตรง กับความแข็งและการทนแรงดึงของของผสม

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....
หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา ....
ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม ....

The effects of type and quantity of additives on the resilience property of rigid poly(vinyl chloride) (PVC) thin sheet for Christmas tree products were studied. The additives studied in this research are methyl methacrylate butadiene styrene (MBS), acrylonitrile butadiene styrene (ABS), chlorinated polyethylene (CPE), processing aid, internal lubricant, calcium carbonate and talc. It was found that the best additive to improve the resilience property is ABS. The optimum amount of ABS for Christmas tree material is 10 phr. The resilience property of the new PVC formula is 2 times better than that of two commercial products. Increasing MBS, CPE, internal lubricant, calcium carbonate and talc decrease the resilience property. Processing aid dose not significantly improve the resilience property. Properties such as tensile strength, tear strength, hardness, heat distortion temperature (HDT) and glass transition temperature (Tg) were studied and it was found that the resilience property related to both hardness and tensile strength of blends.

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา

ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม

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Chapter I

Introduction

1.1 Statement of problem

One use of Rigid PVC thin sheet products is Christmas tree leaves. They are produced by an injection process that has some disadvantages, i.e. high weight, high waste levels and have an unnatural appearance. Recently, a new process was developed to make PVC thin sheets which are slited and wound around wire. The new products have low weight and look more natural. The injection process was replaced by calendering thin sheet process. Properties were tested such as tear strength, product shade and one of the important properties, resilience property. The finished product of Christmas trees was packed in the boxes and shiped to customer in containers. When the products were put on display, the appearance was poor due to a lack of resilience. This problem caused complaints from the customers.

This problem may be an effect caused by additives such as fillers, processing aid, internal lubricant, and impact modifiers. Various compounds were prepared by mixing and milling to thin sheets. Finally, mechanical properties and thermal properties were measured to choose suitable formulas to improve Christmas tree products.

1.2 Purpose of the research

The purpose of this research is to study mechanical properties such as tensile strength, tear strength, hardness, and thermal properties such as heat distortion temperature and glass transition temperature, of PVC blends with

various additives such as MBS, ABS, CPE, internal lubricant, processing aid, calcium carbonate in order to improve resilience property.

(a)   (b)

Figure 1.1 The appearance of artificial Christmas tree
(a) good product (b) the product with resilience problem

1.3 Scope of the research

In this research, different levels of additives such as calcium carbonate, talc, processing aid, ABS, MBS, CPE and internal lubricant were blended with PVC by two-roll mill. The effects of those additives and their levels were studied by measuring mechanical properties such as tensile strength, tear strength, hardness and thermal properties, heat distortion temperature, glass transition temperature, and resilience property.

Chapter II

Theory and literature reviews

Poly(vinyl chloride) (PVC) is manufactured on a large scale because of its versatile properties in relation to its low price. The natural, characteristic of PVC is noncrystalline. There are still many difficulties associated with its use. Its low heat distortion temperature (HDT) prevents more demanding use. Other limitations of PVC are its poor processability and impact resistance. PVC has enjoyed considerable commercial success in the packaging field over the past few decades. Because PVC exhibits a good balance between mechanical and optical properties, it has been used widely in bottles and films. The polymer is often oriented during the fabrication of these packaging products to achieve improved mechanical toughness and other physical properties. The aim and advantages of blending polymers are as follows : higher performance at a reasonable price, quick modification of performance, reuse of plastic scrap. Various economic and property advantages, accomplished via polyblending of two polymers, are decreasing in density, lower cost, extended service range, light weight, improved extrusion rate, easy processability, lowest die swell, improved dimensional stability and weathering, increased toughening, improved low-temperature properties, enhanced ozone resistance, extenders in engineering plastics , increased flame retardance, increased heat distortion temperature.

Compounding PVC essentially involves adding to the base PVC resin, the components will allow it to be processed into a finished rigid product with the desired properties.

1. Impact modifiers

2. Processing aids

3. Lubricant

4. Fillers

2.1 Impact modifiers

Blending of thermoplastics with elastomers gives polyblends with improved properties such as modulus, hardness, flame retardance, impact resistance, and environmental stress-cracking resistance. On the other hand, blending of elastomers with thermoplastics gives polyblends having enhanced tensile strength, modulus, tear strength, and abrasion resistance. In both cases, a reinforcement of polyblend structure takes place, which leads to property enhancement. The rubber component of the modifier is usually insoluble and incompatible with PVC and forms a distinct, dispersed phase with a low glass transition temperature. Tg. In order to increase ductility and processability of PVC, polymer modifiers are often added. Toughened plastics consist of rigid matrix and an elastomeric dispersed phase. Blends of PVC with an elastomer were shown in Figure 2.1. The dispersed phase(rubber) should be broken down into small particles without becoming too finely dispersed to be effective in toughening the rigid polymer. Optimum rubber particle sizes for toughening to the polyblend matrix vary in the range from 0.1 μ to 2.0 μ. However, in PVC polyblends, toughening occurs, not due to rubber particles,

but due to the network structure of the dispersed elastomeric phase. Once this network structure of the dispersed elastomeric phase is destroyed, phase inversion into rubber particles occurs and the impact resistance is totally lost. For blends of PVC with an elastomer, the morphology and phase structure are controlled by method of blending, compatibility at mechanical blending, and processing temperature [1].
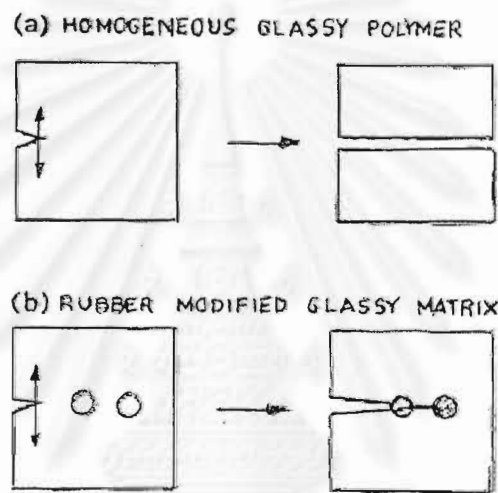
Figure 2.1 Effect of rubber particles on crack propagation in a brittle polymer.

2.1.1 Methacrylate-Butadiene-Styrene (MBS)

Modifiers are graft polymers prepared by polymerizing methyl methacrylate or mixer of methyl methacrylate with other monomers in the presence of polybutadiene or polybutadiene-styrene rubber. These polymers are blended and melt-mixed with PVC resins to improve impact toughness, which is usually measured by notched Izod impact or falling dart impact testing. However, MBS modifiers also accelerate PVC resin fluxing and generally facilitate PVC processing.

The smaller particle size MBS modifier is used for clear PVC bottles and film with high clarity and sparkle. The larger particle size MBS is used for high-impact applications with good clarity control, such as blow-molded bottles with high drop height impact performance.

MBS and all acrylic modifiers are typical core-shell modifiers. The core-shell multipolymers are made via emulsion polymerization to specific sizes and compositions. Transmission electron photomicrograph of well-dispersed MBS impact modifier in PVC is shown in Figure 2.2.

Figure 2.2 Transmission electron photomicrograph of well-dispersed MBS impact modifier in PVC, using OsO_5 for staining the rubber particles.

The core can either be hard or soft and it is surrounded by a shell consisting of a polymer made from one or more monomers. CPE is amorphous polymer that have a relatively high degree of compatibility with PVC.

2.1.2 Acrylonitrile-Butadiene-Styrene (ABS)

A range of ABS resins are available in the free-flowing white powder for blending and compounding with PVC. Some grades of ABS are designed to give clear PVC compounds with improved toughness, rigidity retention, and good chemical resistance. Other grades give opaque PVC compounds with improved toughness and processing. ABS resins facilitate fluxing of PVC resins, improve hot melt strength, and reduce melt elastic strain recovery or die swell. [2]

ABS graft copolymers are prepared by chemically grafting styrene and acrylonitrile monomers onto potybutadiene or styrene-butadiene rubber substrates in emulsion. The diene emulsion is prepared as a precursor to the grafting polymerization. The composition, particle size. and particle size distribution of the rubber emulsion are carefully controlled to ensure consistent impact-modifying performance and optical properties of the grafted rubber modifiers in PVC. Other factors controlled in the final dried resin are residual monomer and moisture content. [1]

ABS plastics comprise a broad, versatile family of engineering thermoplastic materials offering a balance in rigidity, toughness, processability, cost, and chemical resistance. Each monomer is an important component of ABS. Styrene contributes to processability, rigidity. and strength. while acrylonitrile provides surface hardness and chemical resistance. The butadiene rubber contributes toughness, but at the expense of rigidity.

The broad family of different ABS grades results from the many compositional and structural variables that can be selected to achieve a desired property balance. Some of these variables are listed as follows:

Elastomeric phase

- Type and/or composition of rubber
- Cross-link density of rubber
- Size and morphology of rubber particles
- Relative size distribution of rubber particles

Graft phase

- Amount of rubber
- Amount or extent of grafting upon the rubber particles
- Ratio of styrene to acrylonitrile(AN) and/or other monomer(s)
- Core shell versus nodular graft structure
- Molecular weight and polydispersity of the poly (styrene acrylonitrile) (PSAN)
- Choice and level of cross-linking monomer
- Percent of ungrafted rigid present

Rigid phase

- Ratio of styrene to AN and/or other monomer(s)
- Molecular weight and polydispersity of the PSAN rigid

As one can see the ABS chemist is provided with great versatility and flexibility in product development. By polymerizing the ABS as a high rubber graft concentrate or impact modifier and by producing the rigid PSAN phase as an independent material, additional flexibility, product performance, and economy can be realized [2].

Types of ABS Modifier: ABS modifier resins are generally classified according to the tensile modulus of the modifiers themselves. This roughly corresponds to rubber level in the modifier:

- Polymers with a high tensile modulus ($3 * 10^5$ psi) and the lowest rubber level are used primarily as processing aids for opaque applications with some impact modification and hot strength improvement; these modifiers have the least effect on the physical properties of rigid PVC.

- ABS polymers with intermediate tensile modulus ($2 * 10^5$ to $3 * 10^5$ psi) and rubber content are used for opaque PVC applications where hot melt strength and embossing retention are essential and plastic flow and impact performance are required.

- Polymers with a low tensile modulus ($2*10^5$ psi) and the highest rubber content are the most efficient as impact modifiers but are also very important in melt processing. It is noteworthy that modifiers for opaque and clear PVC fall in this grouping and applications include extrusion, calendering, and injection molding.

The morphology of a typical emulsion-prepared rubber is illustrated in Figure 2.3. This type morphology permits the production of high-gloss ABS with excellent Izod and Dart impact performance at room and low temperatures. This morphology generally produces ABS

with inherently low gloss and the ability more effectively to use poly-butadiene to achieve a better balance of toughness and rigidity. Miscibility may also be determined by observing the creation of an immediate glass-transition temperature (Tg) between the two individual
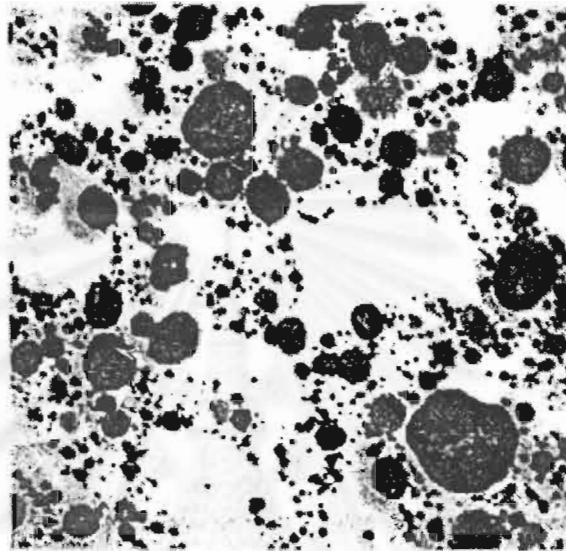
Figure 2.3 Electron photomicrograph of an emulsion ABS rubber.

polymers as measured by either dynamic mechanical analysis (DMA) or differential thermal calorimetry (DSC).

Variables that are critical when blending ABS with other resins include :

- The quantity and relative compatibility of the rigid matrices involved

- Whether the rigid matrices are amorphous/amorphous or crystalline/amorphous

- The amount(s) and/or type(s) of rubbery ABS graft or graft phase(s) used

The one property of importance is the material's behavior at elevated temperature. One of the critical performance properties is deflection temperature under load (DTUL), simply identified as heat-deflection temperature (HDT). Generally, the higher DTUL, the more difficult it will be to process the material. The DTUL properties, on the other hand, are controlled principally by the rigidity of the resin's back bone structure, which correlates well with its high-temperature glass-transition point (Tg). For PSAN and simple ABS formulations, the amount of rubber determines the material's modulus, rigidity, and hardness, which, in turn, also influences DTUL properties and melt flow. [2]

2.1.3 Chlorinated Polyethylene (CPE)

CPE are prepared by chlorinating high-density polyethylene. The properties of CPE polymers and CPE-modified PVC depend on molecular weight, degree of crystallinity, chlorine content, and distribution of chlorine atoms in the polymer chain. CPE with 30 to 40 wt % chlorine exhibits the low glass transition temperature of HDPE and low crystallinity. The level of compatibility with PVC is largely controlled by the chlorine content and distribution of chlorine atoms on the polyethylene backbone. Polymers containing 25 to 40% chlorine with a random distribution of chlorine atoms are the best impact modifiers for PVC; they have sufficient compatibility for adhesion to the PVC matrix without losing particulates and dispersibility. Polymers containing less than about 25% chlorine are incompatible with PVC and do not confer any property enhancement. Polymers with more than about 48% chlorine are highly compatible with PVC and become solubilized, acting

as plasticizer. See the Appendix for available commercial grades, recommended uses, and special features. Blending can also be performed in a high-speed mixer. Care must be taken to minimize heat buildup and avoid "caking" of the modifier. Low-speed operation of the mixer and a minimum cycle time should be used. [1]

It is in this instance that the amorphous chlorinated polyethylene (CPE) polymer is more readily deformed than the rigid PVC with which it is intensively mixed and blended. The CPE impact modifier substantially elongates before it breaks. In addition, it has excellent low-temperature elongation and very low crystallinity, and thus absorbs the energy of impact before its transmittance to the rigid PVC.

CPEs are basically produced in three ranges of chlorine levels. A low chlorine series has about 25%. High-level CPEs are produced with levels of chlorine in the area of 42%. For impact modification, the chlorine content is intermediate, usually about 36%. The low levels are incompatible with PVC, because they are too dominant in the polyethylene-molecule properties. The highest levels are too compatible, and because of this fact, those CPEs function as inefficient, but highly permanent plasticizers. It is significant that the chlorination levels of choice, about 36%, reflect a compatibility that allows the CPE to be dispersed in the PVC matrix, permitting the energy absorption to take place during impact.

While there are other impact modifiers such as the terpolymer acrylonitrile butadiene styrene (ABS) and methacrylate butadiene styrene (MBS), the CPE products have a niche of their own in the impact

modification of rigid PVC. The CPE modifiers have some advantages in processability and cost, as well as in weatherability, specifically in combination with low-temperature applications.

2.2 Processing aid

Processing aids accelerate and control the fusion process in PVC compounds, they strongly affect the rheological characteristics of the fully fused PVC melt. The mechanism by which processing aids improve the fusion characteristics of PVC powder blends, is generally accepted that they accelerate the process by increasing the interactions between the PVC grains. Figure 2.4 is shown electron microphotograph of mass polymerized PVC.
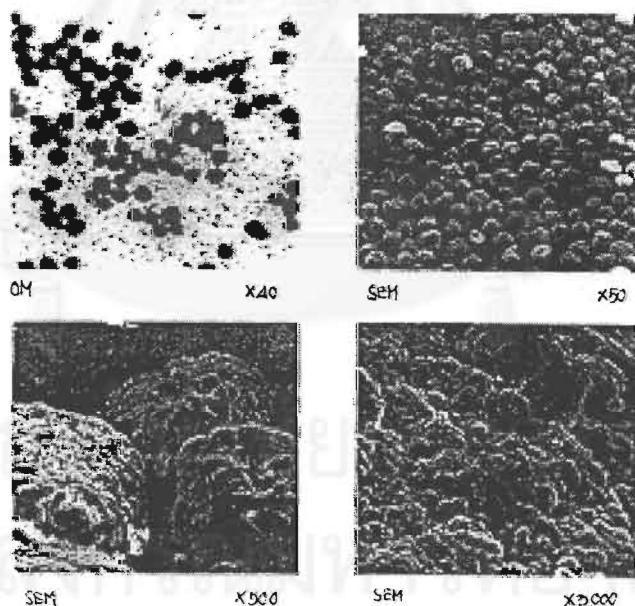
Fig. 2.4 Electron microphotograph of mass polymerized PVC

Processing aids are used in PVC formulations for many reasons, but they can all be grouped into two general categories of effects:

1. They accelerate and control the fusion process in PVC compounds.

2. They strongly affect the rheological characteristics of the fully fused PVC melt.

Processing aids improve the fusion process by increasing particle-to-particle friction, hastening the breakdown of the PVC grains and the ultimate exchange of chains between particles. They also suggest that the processing aid molecules improve the heat transfer during this process by virtue of increasing contacts between grains. Gould and Player attribute the particular effectiveness of acrylic processing aids in increasing interparticle friction to their high surface hardness. On the other hand, bases his explanation of acrylic processing aid performance other ability to increase the coefficient of friction between the PVC melt and the metal surfaces of processing machinery.

Notwithstanding the fusion and homogenization effects discussed above, the most important reason for adding processing aids to rigid PVC compounds is to improve the elasticity and extensibility of the melt. This effect can be observed even in simple laboratory experiments such as milling. An experienced operator can easily sense by hand the improvement in tear strength and extensibility which occurs when a processing aid is added to the formulation.

In addition to conventional processing aids, many materials have been conceived. The most successful of these has been a class of lubricating

processing aids, which combine very strong external lubrication effects with the conventional rheological improvements of acrylic processing aids. Besides such commercial additives, similar principles have been applied to internal modification of PVC resins during their production to give "easy processing" lubricated resins [3]. Other experimental multipurpose processing aids have been tested but without extensive commercial use to date. These include processing aids which reduce the viscosity of the PVC compound. Lastly, the possibility of raising the heat distortion temperature of PVC compositions has been suggested through the use of processing aids incorporating methacrylate copolymers with bicyclic side chains or styrene/acrylonitrile/acrylamide terpolymers.

The polymers used as processing aids generally have fairly good physical properties themselves, related to their high molecular weight and high-Tg compositions. In addition, the compatibility of most processing aids with PVC avoids problems of inhomogeneities in the product, which could serve as initiation sites for failure.

Physical properties of compounds containing normal use levels of processing aids normally are within experimental error of the properties of control samples without processing aid. In fact, in many cases the physical properties of fabricated PVC products containing processing aids are better than those of unmodifier controls due to the better fusion in compounds containing processing aid. Likewise, the optical properties of PVC compounds are not greatly changed by the addition of processing aids, and the improvements in surface quality, gloss, and so forth usually outweigh any changes in the actual clarity of the

product. The heat stability of rigid PVC compounds containing processing aids, specially the most popular commercial acrylic processing aids, is at least as good as that of unmodified control compounds. Overall, the effect of commercial processing aids on properties other than processibility can generally be assumed to be neutral.

2.3 Lubricants

The lubricant does not fully encompass the role a lubricant plays in PVC, but if the interpretation of the key words "reducing friction of surfaces" is expanded to include intramolecular effects, a more complete picture of the function of lubricants in PVC is seen. It is important to realize that in the context of the use of these materials in PVC, controlled application and controlled release are the key words. Lubricant level must be adjusted for optimum performance. Overuse of lubricants can lead to problems as severe as those experienced with insufficient lubrication.

A lubricant must be only partially soluble in the PVC polymer. If the material has zero solubility, it will bloom to the surface. If it has too much compatibility, it will become a plasticizer and adversely affect the flexibility, hardness, or rigidity of the product. The materials most often used are long-chain hydrocarbons with a few polar groups to make them compatible. Some examples of these materials are natural waxes, low-molecular-weight polyolefins, paraffin waxes, oils, fatty esters, fatty amides, and metal soaps, usually based on fatty acids and alkaline earth metals.

Lubricant additives are usually used in rigid PVC, where they are necessary to reduce mely viscosity and allow the machinery to process at high shear rates. Because they reduce frictional heat buildup and often contain costabilizing functional groups, lubricants can significantly improve the stability of a compound. Lubricants function as processing aids. Because of the multitude of possible ingredients and the wide variety of processing equipment, there is no one universal lubricant that can provide all the needed properties for all formulations. Care must be taken to select lubricants and levels thereof which provide a proper combination of flow, metal release, and cost effectiveness. The best philosophy is to keep lubricant concentrations to a minimum. Overlubrication is a problem that results in scorching, low output, surging, poor impact strength, and poor surface.

The mechanism of lubrication can be discussed in terms of two general classes of lubricants based on function. These are external lubricants and internal lubricants. They are very broad classifications and no one material functions entirely as an internal or external lubricant, but usually exhibits a combination of the properties of the two with one being predominant.

2.3.1 External lubricants

These are responsible for two phenomena; metal release and particulate flow in the melt. The mechanism by which metal release is obtained is twofold. Some lubricants have a high affinity for metal surfaces and form a lubricant film, while others have low compatibility with the polymer and form a film at the interface between the polymer melt and the metal as they exude. Two types of lubricants, metal soaps and organic acids, appear to belong to the first group. Because of their polar nature, they have

an affinity for metal and coat the metal surfaces. The polar ends of the molecules are attracted to the metal and the polymer, while the organic ends are attracted to themselves, forming a reduced-friction surface over which the polymer will slide. Esters of low polarity, polyethylenes, and aliphatic organic waxes represent the second group, which is incompatible with the polymer and will form a film on the polymer surface

They reduce friction and adhesion between resin particles in the polymer mass. If one thinks of resin particles as ball bearings lubricated by machine oil and tries to extrude them, the lubricated ball bearings would offer less resistance than unlubricated ones because frictional forces would be reduced to allow sliding as well as rolling (Figure 2.5).
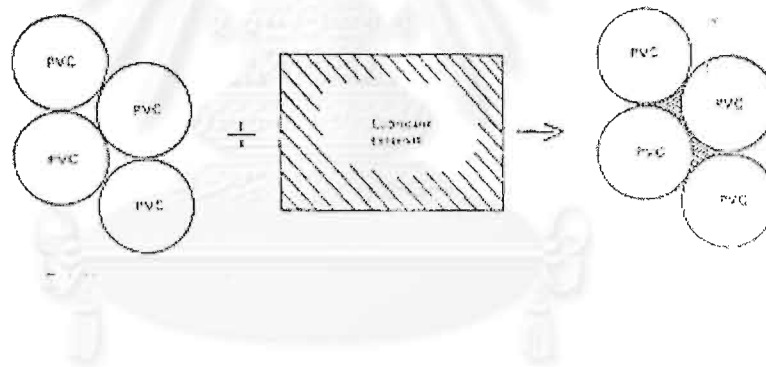
Figure 2.5 External luricant

The total effect in extrusion is that lubrication of the resin particles slows fusion, which increases powder conveying over melt conveying. This phenomenon reduces the amperage demand on the machine and reduces temperature over-ride problems in processing due to high viscosity.

2.3.2 Internal Lubricants

These materials promote intermolecular flow via a chain slippage mechanism. Such materials are characterizer by being some what polar and semicompatible. They are usually lower in molecular weight than the externals and demonstrate pseudoplasticizing effects. A plasticizer causes embrittlement at very low concentrations, but internal lubricants are not polar enough to change flexibility or hardness at room temperature. Internal lubricants function at processing temperatures is shown in Figure 2.6. The polar nature of these materials allows them to be accepted into the polymer matrix at high temperature. The van der Waals forces between chains are reduced by the polar lubricant,
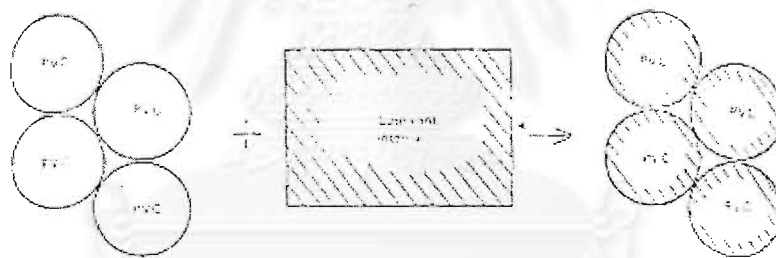
Figure 2.6 Internal lubricant

which slips in between the polymer chains. This allows the chains greater ease of movement because it decreases attraction between molecules. As rigid PVC cools, internal lubricant precipitates and becomes nonfunctional at room temperature. The clarity is only slightly reduced because the lubricant is very finely divided in the polymer matrix. On the other hand, external lubricants adversely affect the clarity because of incompatibility and organize themselves into large droplets. These

pseudoplasticizers can adversely affect the heat distortion temperature by lowering the glass transition temperature of the polymer.

In real terms, internal lubricants reduce internal friction, which reduces shear burn in injection molding applications, back pressure in extrusion, and roll-parting forces in calendering. They give better gauge control in films, sheets, and pipes, shorten cycles, and promote better mold filling. Internal lubricants at typical concentrations have minimal adverse effects on fusion time, nor do they contribute significantly to metal release. If the concentration of the internal lubricant exceeds its solubility constant in the polymer, the internal will act as an external. [1]

2.4 Fillers

Fillers will always modify the mechanical properties of the final composite, often improving such properties as flexural modulus, temperature resistance, and warpage. For this reason, they are more properly called functional fillers, mineral additives, or reinforcing agents.

Although resins are usually homogeneous materials, in which bulk mechanical properties can be fairly well predicted based on intrinsic chemical properties and stress-strain relationships, a composite is heterogeneous in nature and usually will not involve the same relationships. A mineral-resin composite is made up of two very dissimilar materials, The resin is organic in nature, consisting of covalent bonds between atoms. The mineral is inorganic with ionic interactions between atoms. Resin surfaces are hydrophobic; mineral

surfaces are hydrophilic. Other differences also exist, as in surface tension, coefficient of linear expansion, elasticity, and so on. In general, the following properties of mineral additives have the greatest influence on the final mechanical properties of a composite: average particle size, particle-size distribution, particle shape, particle integrity (friability), and surface properties.

Particles come in a variety of shapes and sizes. Very fine particles (less than 5 microns), when properly dispersed in a resin, generally provide the best mechanical properties, since the composite is more uniform. However, fine particles have higher surface areas and are, therefore, harder to disperse. As a consequence, they have a greater influence in increasing melt viscosity than do coarser particles. Often this can pose processing difficulties and limit the amount of loading obtainable with very fine materials. Particle size and shape are very important with respect to packing phenomena.

The shape of an individual particle has a great influence on the flexural modulus of a composite. Usually, shape is discussed in terms of aspect ratio. Aspect ratio is defined as the ratio of the longest length of a particle to its thickness. Some examples of general ranges of aspect ratios for various particle shapes are given in Figure 2.7.

SPHERE	CUBE	BLOCK	PLATE	FLAKE	FIDER

ASPECT RATIO

1	-1	1-4	4-30	80-200	20-?
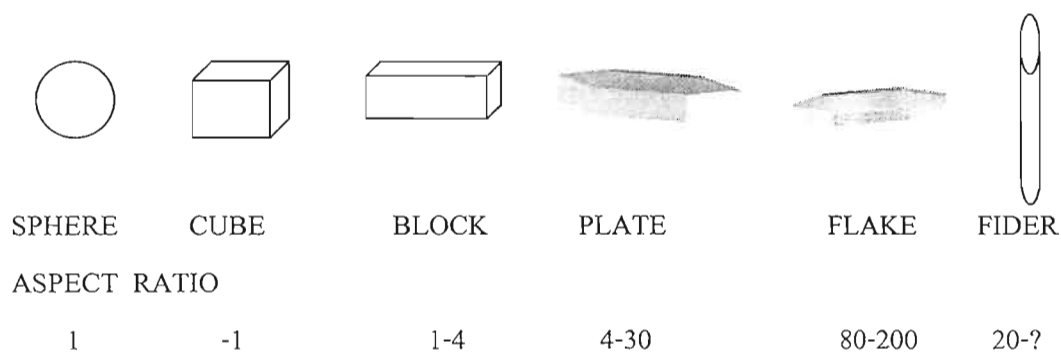
Fig. 2.7 Aspect ratios for particle shapes.

Melt viscosity is dependent on loading level, surface area, and the aspect ratio of a filler. Viscosity will increase with increasing aspect ratio at equal loading levels. Glass spheres therefore, give good processing rheology, but poor stiffness. Glass fiber, with its high aspect ratio, provides the opposite. The narrower the distribution of similarly shaped particles, the higher will be the melt viscosity; and the wider the distribution, the lower will be the viscosity. Also, the particle shape can influence the flow patterns of a composite melt.

2.4.1 Calcium carbonate

Calcium carbonate is known by many names, including marble, limestone, calcite, chalk, aragonite, dolomite, coral shell, and whiting. Carbonate is probably one of the most widely used mineral additives because of its whiteness, low abrasion, availability in wide particle-size ranges, and low cost. The solid-state structures of the two forms are composed of alternating calcium cations and trigonal planer carbonate anions, as shown in Figure 2.8

Three major commercial grades of calcium carbonate are used by the plastics industry – coarsely ground, finely ground, and precipitated.

The low-purity, coarse-particle calcium carbonate (larger than 12 microns) is processed by dry grinding techniques.
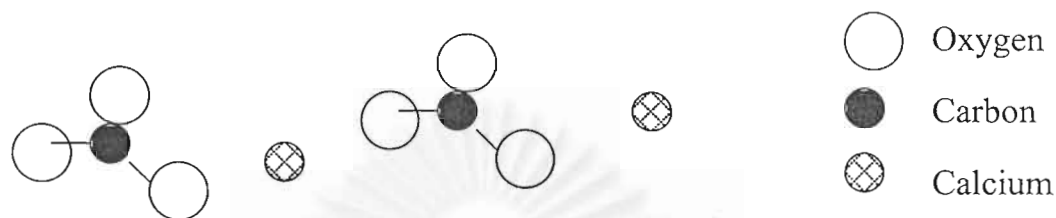
Fig. 2.8 Calcium carbonate $CaCO_3$

Surface-treated grades of calcium carbonate are commercially available. Since standard silanes are not very effective with carbonates, stearates or metallic stearates usually are the surface treatment of choice. The stearate allows for improved dispersion and, therefore, reduction of agglomeration, especially with respect to the very-fine-particle-size grades. The stearate treatment renders the mineral's surface more hydrophobic, thus aiding wetout. The stearate, however, will not interact strongly with the resin, and so increased physical strength, as is often obtained with coupling agents, usually does not result.

Ground calcium carbonate will improve rigidity and density, as well as act as a processing aid in PVC; however, most mechanical properties of the plastic will be reduced. Moreover, the loading level of finely ground calcium carbonate improved properties of other polymer such as polypropylene is shown in table 2.1.

Property	Homopolymer			Copolymer		
	Unfilled	40% Talc	40% Calcium Carbonate	40% Mica[b]	40% Talc	4% Calcium Carbonate
Melting temperature, °C (crystalline)	168–175	164	168	168	—	—
Processing temperature range						
Injection	500–550	350–550	375–525	350–470	350–470	350–470
Extrusion	400–500	—	—	—	425–475	—
Molding pressure range, 10^3 psi	10–20	10–20	8–20	—	15–20	15–20
Compression ratio	2.0–2.4	—	—	—	2–2.5	2–2.5
Mold shrinkage	0.01–0.025	0.008–0.015	0.007–0.014	0.007–0.008	0.009–0.012	0.006–0.012
Tensile strength at break, psi	4500–6000	4300–5000	3400–3560	4500	3500	2700
Compressive strength, psi	5500–8000	7500	3000–7200	—	—	—
Flexural strength, psi	6000–8000	7000–9200	5500–7000	7000	5100	4300–6500
Tensile modulus, kpsi	165–225	450–575	375–500	700	—	3500
Flexural modulus, kpsi, 73°F	170–250	450–625	360–450	600	340–400	300–370
Notched Izod impact, ft-lb/in.	0.4–1.2	0.4–0.6	0.6–1.0	0.7	0.8–4.0	0.7–1.0
Hardness (Rockwell)	R80–102	R94–110	F78–99	—	R83	R81
Coefficient of linear expansion, 10^{-6} in./in./°C	81–100	42–80	28–50	—	—	—
Deflection temperature under flexural load, °F	120–140	175–180	150–170	205	150–165	150–155
Thermal conductivity	2.8	7.6	6.9	—	—	—
Specific gravity	0.9–0.91	1.23–1.27	1.22–1.25	1.23	1.23–1.24	1.24
Water absorption,						
% 24 hours	0.01–0.03	0.01–0.03	0.02–0.05	—	0.02	0.02
Dielectric strength, short time, V/mil	600	500	410–500	—	—	—

Table 2.1 Mineral-Filled Polypropylene and Polypropylene Copolymers [2]

2.4.2 Talc

Talc is a white to a pale green hydrate magnesium silicate. Although different, talc is often associated with soapstone and pyrophyllite. The mineral is made up of neutral layers consisting of a center brucite plane chemically boned by bridging oxygen atoms to two tetrahedral silica planes. The individual layers are held together by weak van der Waals forces This differs form other minerals such as mica, in which the layers are held together by ionic forces, or kaolin, where hydrogen bonding forces hold the alumio-silicate layers together. Because of this weak interaction, talc can easily be delaminated and usually is processed to particles retaining a relatively high aspect ratio of up to 20:1. This weak interaction is also the major reason why talc is such a soft mineral. The outer layers easily peel off, providing the lubricity characteristics associated with talc. Figure 2.9 shows the talc structure.
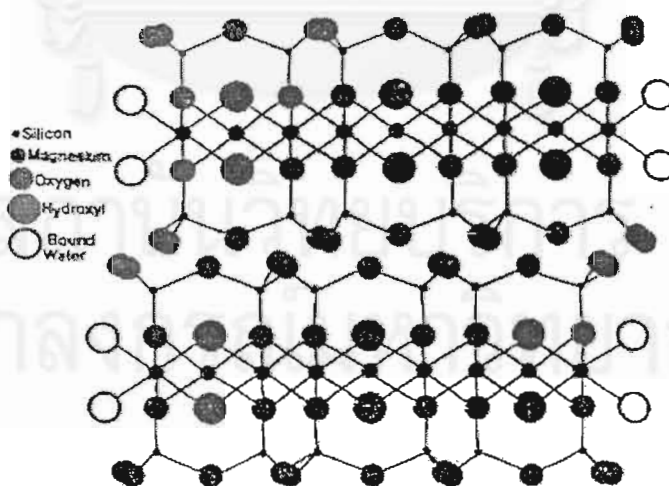
Figure 2.9 Structure of talc

The purity of talc is particularly important to the thermal properties. The presence of low levels of metal ions can catalyze degradation of the plastic, which will decrease the long-term thermal stability of the composite. Surface-treated grades do not affect the thermal properties as adversely. Apparently, the surface impurity sites are covered by the treatment, thus reducing their deleterious affect.

As with other minerals, efforts to improve the mineral-polyolefin interface by modifying the resin have been attempted. Acrylic-acid-grafted polypropylene has been shown to improve tensile strength, flexural modulus, and heat-deflection temperature of talc-filled polypropylene.

Talcs with high impurities require beneficiation by flotation, magnetic separation, bleaching, and so forth to attain a brighter and chemically purer product. In plastic processing, the platy particles align in the machine direction. In general platy talcs improve hot strength, increased modulus, and tensile strength and are generally used in plasticized PVC applications. especially vinyl flooring. The fibrous New York talcs have also been used in this application in the past.

The talc surface is highly active. Talc can be surface-treated to achieve a wide variety of useful properties. The most common surface-treating agents are properties and polyols, which give the talc improved properties for a variety of applications [2]. Because of the silicate surface, talc also reacts with silanes. In PVC such products show improved dispersibility.

2.5 Literature reviews

W. Yang. [4] studied the effects of styrene-co-acrylonitrile resin (AS) on the mechanical properties, morphology, and plasticizing and rheological behaviors of poly(vinyl chloride)/chlorinated polyethylene (PVC/CPE) blends. The results show that the tensile strength decreases, elongation at break increases, and impact strength varies in an S-type curve with the increase in the amount of CPE, which indicate a typical property of plastics toughened with elastomers. Some impact modifiers with linear structure (e.g., ethylene vinyl acetate, nitrile butadiene rubber, CPE etc.) can form a continuous network embedding the primary particles of PVC when the amount of impact modifiers and processing conditions are proper, and the formation and improvement of this special structure favorably affects the impact strength.

M. Yokouchi, S. Seto, and Y. Kobayashi [5] studied brittle and glassy components in ABS, i.e. polystyrene and polyacrylonitrile which improve the tensile strength while polybutadiene (rubber) contributed to toughness. The mechanical properties have been shown to be affected by the type of ABS due to different polybutadiene content.

J.C. Lim, K.E. Min. [6] studied the mechanical properties of poly (vinyl chloride) and transparent acrylonitrile-butadiene-styrene resin (Tr-ABS) blends which were studied for stress-strain, flexural, and impact behavior. The blends were found to be more ductile than Tr-ABS in general,

and significant stress-whitening behavior owing to the formation of shear band and craze was observed. The impact strength of the blends containing 50 to 60% of Tr-ABS by weight was almost double to the pure Tr-ABS. It was considered that brittle-ductile(B-T) transition in failure occurs at the blends containing above the levels of 30 wt% Tr-ABS resin.

A. Tse, R. Laakso, E. Baer, A. Hiltner [7] studied the effects of CPE chlorine content and chlorine distribution on the morphology, optical clarity, and toughness of blends with PVC. The CPE resins were characterized in terms of the glass transition temperature, residual crystallinity, density, and refractive index. Increasing residual crystallinity and increasing chlorine content both increased the refractive index closer to that of PVC. A linear relationship was observed between the fourth power of the refractive index and the CPE glass transition temperature. With a phase-separated blend morphology in all cases, improved transparency was achieved in this system by reducing the refractive index difference between CPE and PVC. Both haze and transparency showed the predicted linear dependence on the square of the refractive index difference. To a first approximation, modifications of the experimental CPE resins that improved optical transparency of the blends also tended to reduce the toughness enhancement.

K. Marossy [8] studied PVC/CPE blend. They found that the TSD spectra show the structural changes in the PVC-CPE blend well and allow the processes at the phase boundaries to be ascertained. The impact strength values of tested samples can be related to TSD results.

Chlorinated polyethylene is a commonly used impact modifier for PVC. Because the PVC and CPE are not compatible, the structure, and therefore the properties of their blends strongly depend on processing conditions.

S.N. Maiti, U.K. Saroop, and Misra. [9] studied the blending of poly (vinyl chloride) (PVC) and acrylonitrile butadiene styrene (ABS) terpolymer. The blends were prepared in different ratios by a melt blending technique. ABS containing three different levels of rubber content were used. A quantitative assessment of ABS in PVC/ABS blends has been shown by infrared studies. ABS content has been shown as the presence of the characteristic acrylonitrile peak; differential scanning calorimetry (DSC) studies have been carried out to study the glass transition (Tg) behavior of the blends. Two Tg values corresponding to PVC styrene acrylonitrile (SAN) copolymer have been observed. Thermogravimetric analysis (TGA) reveals a significant improvement in thermal stability of these blends as compared to PVC. Mechanical properties show a significant increase in the impact strength which is related to rubber content of the ABS used. Morphological studies have been carried out by scanning electron microscopy which support thew observation that an increase in rubber content results in grater ductility.

When ABS is incorporated in PVC, there is a decrease in the tensile strength and tensile modulus which can be attributed to the presence of ABS in the polyblend. When ABS with 25% rubber content is used there is a decrease in the tensile strength up to 20% ABS. However, at 30% and 40% levels there is an increase in the tensile strength of the polyblend which is

greater than both PVC and ABS. In the case of polyblends containing 30% and 36.5% rubber content there is a constant decrease in the tensile strength with an increase in the ABS level.

S. Havriliak, S.E. Slavin, T.J. Shortridge [10] studied PVC/MBS blends. Tensile yield measurements were made on blends of poly(vinyl chloride) (PVC) with a methyl methacrylate-butadiene-styrene impact modifier (MBS) covering a blend range of 0 to 20 wt% MBS, a temperature range of -50 to 25 $^\circ$C, and a strain rate range of $10^{(-3)}$ to $10^{(0)}$ s^{-1}. Increasing MBS level in PVC reduces the tensile yield stress. The tensile yield stress variation with temperature and strain rate at constant MBS level were represented in terms of the Ree-Eyring-Roetling rate model.

D. Dompas, G. Groenincky, M. Isogawa, T. Hasegawa, M. Kadokura [11] studied on the effect of about different MBS rubber particles to tensile property. Real-time stress-whitening experiments were performed on initially transparent poly(vinyl chloride)/methyl methacrylate-butadiene-styrene graft copolymer (MBS) blends containing very small MBS rubber particles. The chemical composition of the different MBS rubber particles was held constant and it was found that the onset of internal rubber cavitation in the blends during a tensile test depends only on the size of the rubber particles. The real-time, stress-whitening experiments indicate that the resistance against cavitation increases with decreasing rubber particle size. Small particles are unable to cavitate. This is further confirmed

independently on the basis of transmission electron microscopy observations and density measurements on the deformed samples.

V.I. Mandrukova and A.V. Stalbovskaya [12] studied PVC/ABS blends. They found a significant increase in impact strength and heat distortion temperature although there was marginal loss in tensile strength and rigidity.

Chapter III

Experimental

3.1 Materials

Materials used in this research as tabulated in table 3.1 are obtained from various sources.

Table 3.1. Materials and source

Materials	Trade name	Source of Suppliers
Polyvinyl Chloride	SG-610	Thai Plastic Co., Ltd.
Butyltin Stabilizer	JF-50R	Sankyo
Acrylic Copolymer	PA-20	Kaneka
Oleochemical Derivative	G-161	P.P.P. Chemical and Lube
Complex Ester	G-70S	Henkel
Methyl Methacrylate Butadiene Styrene	B-51	Kaneka
Acrylonitrile Butadiene Styrene	ABS	Thai Plastic Co., Ltd.
Calcium Carbonate	CaCO$_3$	Peerash
Talc	Talcum	Polymer Innovation
Chlorinated Polyethylene	CPE	Gredmann Co., Ltd.

3.2 Apparatus

1. Two-Roll Mill : MODELCR820 SER.NO.7182

2. Compression Molding Machine : MODEL : GT7014-10

3. Mixer : MODEL MX-T31GN SER.NO950728

4. Oven : TYPE 1511530000202 NO#T31GN DIN12880

5. Hardness Tester : MATSUZAWA DXT Rockwell ASTM D-785

6. Differential Scanning Calorimeter : DSC 7

7. Universal Tester : TESTROMETRIC MICRO 350

8. Heat Deflection Temperature Tester : ASTM D-648

3.3 Experiment procedure

PVC compounds were prepared by varying the amount of calcium carbonate, talc, processing aid, ABS, MBS, CPE and internal lubricant (table 3.2). The components were prepared in part per hundred by weight of PVC resin. Compounds were mixed by mixer for 3 minutes and blended on two-roll mills at 195 $^\circ$C for 5 minutes in 0.3 mm for tensile test and compressed for heat distortion temperature (HDT), glass transition temperature (Tg), and hardness at 0.09-0.11 mm for the resilience test.

Mechanical properties i.e., HDT, Tg, tensile strength, and hardness of each composition were measured and related to the resilience property.

Table 3.2. Formulation of PVC compounds

Sample	PVC (phr)	Tin Stabilizer (phr)	Processing Aid (phr)	Internal Lubricant (phr)	External Lubricant (phr)	MBS (phr)	ABS (phr)	CPE (phr)	CaCO$_3$ (phr)	TALC (phr)
M1	100	1.80	0.80	1.00	0.85	5.00	-	-	-	-
M2	100	1.80	0.80	1.00	0.85	10.00	-	-	-	-
M3	100	1.80	0.80	1.00	0.85	15.00	-	-	-	-
M4	100	1.80	0.80	1.00	0.85	20.00	-	-	-	-
M5	100	1.80	0.80	1.00	0.85	25.00	-	-	-	-
M6	100	1.80	0.80	1.00	0.85	30.00	-	-	-	-
ABS1	100	1.80	0.80	1.00	0.85	-	5.00	-	-	-
ABS2	100	1.80	0.80	1.00	0.85	-	10.00	-	-	-
ABS3	100	1.80	0.80	1.00	0.85	-	15.00	-	-	-
ABS4	100	1.80	0.80	1.00	0.85	-	20.00	-	-	-
ABS5	100	1.80	0.80	1.00	0.85	-	25.00	-	-	-
ABS6	100	1.80	0.80	1.00	0.85	-	30.00	-	-	-
CPE1	100	1.80	0.80	1.00	0.85	-	-	5.00	-	-
CPE2	100	1.80	0.80	1.00	0.85	-	-	10.00	-	-
CPE3	100	1.80	0.80	1.00	0.85	-	-	15.00	-	-
CPE4	100	1.80	0.80	1.00	0.85	-	-	20.00	-	-
CPE5	100	1.80	0.80	1.00	0.85	-	-	25.00	-	-
CPE6	100	1.80	0.80	1.00	0.85	-	-	30.00	-	-
P1	100	1.80	0.50	1.00	0.85	5.50	-	-	-	-
P2	100	1.80	1.00	1.00	0.85	5.50	-	-	-	-
P3	100	1.80	1.50	1.00	0.85	5.50	-	-	-	-
P4	100	1.80	2.00	1.00	0.85	5.50	-	-	-	-
P5	100	1.80	2.50	1.00	0.85	5.50	-	-	-	-
P6	100	1.80	3.00	1.00	0.85	5.50	-	-	-	-

Table 3.2. Formulation of PVC compounds

(Continued)

Sample	PVC (phr)	Tin Stabilizer (phr)	Processing Aid (phr)	Internal Lubricant (phr)	External Lubricant (phr)	MBS (phr)	ABS (phr)	CPE (phr)	CaCO$_3$ (phr)	TALC (phr)
L1	100	1.80	0.80	0.50	0.85	5.50	-	-	-	-
L2	100	1.80	0.80	1.00	0.85	5.50	-	-	-	-
L3	100	1.80	0.80	1.50	0.85	5.50	-	-	-	-
L4	100	1.80	0.80	2.00	0.85	5.50	-	-	-	-
L5	100	1.80	0.80	2.50	0.85	5.50	-	-	-	-
L6	100	1.80	0.80	3.00	0.85	5.50	-	-	-	-
CA1	100	1.80	0.80	1.00	0.85	5.50	-	-	-	-
CA2	100	1.80	0.80	1.00	0.85	5.50	-	-	5.00	-
CA3	100	1.80	0.80	1.00	0.85	5.50	-	-	10.00	-
CA4	100	1.80	0.80	1.00	0.85	5.50	-	-	15.00	-
CA5	100	1.80	0.80	1.00	0.85	5.50	-	-	20.00	-
CA6	100	1.80	0.80	1.00	0.85	5.50	-	-	25.00	-
CA7	100	1.80	0.80	1.00	0.85	5.50	-	-	30.00	-
TA1	100	1.80	0.80	1.00	0.85	5.50	-	-	-	-
TA2	100	1.80	0.80	1.00	0.85	5.50	-	-	-	5.00
TA3	100	1.80	0.80	1.00	0.85	5.50	-	-	-	10.00
TA4	100	1.80	0.80	1.00	0.85	5.50	-	-	-	15.00
TA5	100	1.80	0.80	1.00	0.85	5.50	-	-	-	20.00
TA6	100	1.80	0.80	1.00	0.85	5.50	-	-	-	25.00
TA7	100	1.80	0.80	1.00	0.85	5.50	-	-	-	30.00
NEW	100	1.80	0.8	1.00	0.85	-	10	-	-	-

3.3.1 Mixing procedure

The compositions were prepared by mixing them in a small high speed mixer for 3 minutes and blending all of the composition on two roll mills at 200 $^{\circ}$C for 5 minutes to make sheets of about 0.09-0.10 mm for the resilience test. The nip between the rolls was adjusted to facilitate mixing. The sheets, 0.30 mm, were molded on a compression molding machine at 200 $^{\circ}$C and 200 kg/cm^2 for 13 minutes to make sheets of about 3 mm in thickness for testing the hardness and HDT in relation to the resilience property.

3.3.2 Resilience property

Samples were prepared by cutting 0.09-0.10 mm thin sheets in 1"x10" sizes for ten samples of a composition. The samples were rolled into small paper cores 2 cm in diameter. After that the samples were placed in paper rolls, baked in the oven at 50 $^{\circ}$C for 30 minutes and kept at room temperature for 1 hour. The samples were brought off the paper rolls and the diameter of sample rolls measured. The percent of resilience of each sample was calculated by comparing them to the paper core diameter.

3.3.3 Mechanical measurement

Mechanical properties such as tensile strength, tear strength and hardness were measured to study the effects of various compounding. The mechanical properties were obtained by using standard size and shape under standard test methods of the American Society for Testing and Materials (ASTM) and were subject to the following measurements:

Tensile Strength   : testing method of ASTM D-638

Tear Strength   : testing method of ASTM D-1938

Hardness   : testing method of ASTM D-785

3.3.4 Heat distortion temperature

The heat distortion temperature (HDT) of each sample was measured to study the effects of various types and dosages of additives according to ASTM D-648.

3.3.5 Differential scanning calorimeter

The 4.0 to 5.0 mg range of samples were put on an aluminium pan with tweezers and then a hole punched in the cover to provide atmosphere before testing. Nitrogen was used as purge gas to control the atmosphere in the sample cells. The temperature range of the analysis was run from 50 to 90 $^{\circ}$C at a heating rate of 10 $^{\circ}$C min^{-1}

3.3.6 The effect of impact modifiers

Various amounts of impact modifiers such as MBS, ABS and CPE at 5, 10, 15, 20, 25 and 30 phr were mixed with PVC and other additives according to table 3.2 and milled to obtain samples to measure the properties, HDT, Tg, and resilience properties.

3.3.7 The effect of processing aid

Various amounts of processing aid at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 phr were mixed with PVC and other exact amounts of additives according to table 3.2 and milled to obtain samples. The properties, HDT, Tg, and resilience properties were measured.

3.3.8 The effect of lubricant

Various amounts of internal lubricant at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 phr were mixed with PVC and other exact amounts of additives according to table 3.2 and milled to obtain samples. The properties, HDT, Tg, and resilience properties were measured.

3.3.9 The effect of fillers, $CaCO_3$, Talc

Various amounts of fillers at 0, 5, 10, 15, 20, 25 and 30 phr were mixed with PVC and other exact amounts of additives according to table 3.2 and milled to obtain samples. The properties, HDT, Tg, and resilience properties were measured.

Chapter IV

Results and discussion

4.1 The effect of the amount of impact modifiers

PVC is a rigid and rather brittle polymer. The incorporation of rubbery materials in PVC results in a decrease of the tensile yield stress property of PVC. In this study the tensile properties of PVC blends with various impact modifiers such as MBS, ABS, CPE were determined.

4.1.1 The effect of MBS

MBS is one of the impact modifiers for PVC compound. It is grafted methyl methacrylate with polybutadiene-styrene rubber. Polybutadiene-styrene rubber is usually insoluble and incompatible with PVC. MBS was used to study the effects on some properties of PVC compounds. (at 5, 10, 15, 20, 25 and 30 phr.) It can be observed from Figure 4.1 that when MBS is incorporated in PVC there is a decrease in the tensile strength which can be attributed to the presence of MBS in the polyblend. The blends will have a rubbery phase of MBS dispersed in the rigid and glassy PVC matrix. A decrease in the tensile strength occurs when the MBS level is increased. The results agreed with the research of S. Havriliak, S.E. Slavin and T.J. Shortrige [10] who studied the blends of PVC with MBS covering a blend range of 0 to 20 wt. % MBS. They found that increasing amount of MBS in PVC reduces the tensile yield stress.

The tear strength of blends used is an average value from the beginning to the end of test. The dispersed phase (rubber) should be broken down into small particles. These rubber particles decrease the average values of tear strength. Figure 4.2 shows that tear strength decreases with the increasing MBS level.

Figure 4.3 shows that the hardness decreases with the increasing amount of MBS. This can be attributed to the rubber phase. As poly (butadiene styrene) rubber is increased, the MBS level is also increased this affects the hardness of blends.

It can be observed from Figure 4.4 and Figure 4.5 that when MBS is incorporated in PVC there was a decrease in the HDT and Tg which could be attributed to the presence of MBS in the polyblend. The rubber component, butadiene styrene rubber, of the modifier is usually insoluble and incompatible with PVC and form a distinct disperse phase with a low Tg and HDT. [1] Figure 4.5 shows that MBS levels do not affect the Tg of PVC blends.

Figure 4.6 shows that the resilience property is decreased by increasing the amount of MBS which could be attributed to the fact that the MBS matrix has a rubber phase of rubber particles that are easily moveable when temperature is increased.

Figure 4.1   Effect of MBS amount on tensile strength

Figure 4.2   Effect of MBS amount on tear strength

Figure 4.3   Effect of MBS amount on hardness

Figure 4.4   Effect of MBS amount on heat distortion temperature

Figure 4.5   Effect of MBS amount on glass transition temperature
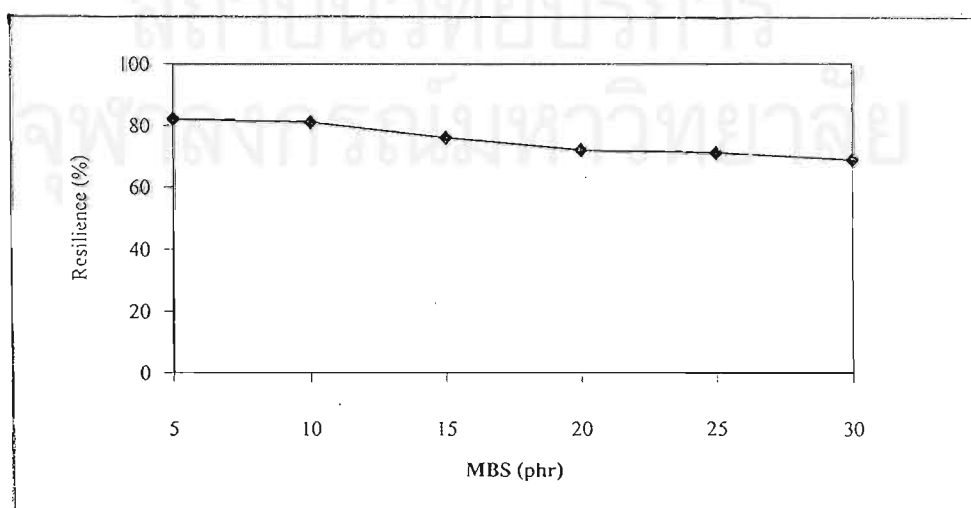
Figure 4.6   Effect of MBS amount on resilience properties .

4.1.2 The effect of ABS

ABS or acrylonitrile butadiene styrene polymers are prepared grafted styrene and acrylonitrile monomers onto polybutadiene or styrene-butadiene rubber which constitute the main polymer chain. The glassy phase is made of styrene and acrylonitrile grafted onto polybutadiene. Thus, it combines the impact strength of rubber and the tensile strength and heat stability of SAN(Styrene acrylonitrile) matrix which is also imparted to PVC/ABS blends. ABS was used in this research in various amounts at 5, 10, 15, 20, 25 and 30 phr.

The decrease in the tensile strength of PVC/ABS can be attributed to the fact that the final blend contains a greater amount of polystyrene and polyacrylonitrile in the form of SAN co-polymer which is a rigid glassy material with high tensile strength thus the ABS was used in this research have rather high rubber content. So the tensile strength and tear strength decrease by increasing ABS amounts as shown in Figure 4.7 and Figure 4.8. The results correspond with research of S.N. Maiti et. al [9]. It was observed from the results that when ABS was incorporated in PVC there was a decrease in the tensile strength.

Each monomer is an important component of ABS. Styrene contributes to processability, rigidity and strength, while acrylonitrile provides surface hardness and chemical resistance. The butadiene rubber contributes toughness, but at the expense of rigidity. Thus the increase of the butadiene rubber level is the cause of a reduction of rigidity and hardness. Those results are shown in Figure 4.9.

V.I. Mandrukova [12], H. Masayanaki [13] reported that PVC/ABS blends had significant increase in impact strength and HDT. In ABS the brittle and glassy components i.e. polystyrene and polyacrylonitrile, improved the HDT while polybutadiene contributed to impact strength depending on the ratio of glassy component and rubber component. Figure 4.10 shows an increase of HDT with increasing the amount of ABS. Figure 4.11 shows that the Tg of the blends are rather constant while increasing the amount of ABS. The increase of the resilience property by increasing the amount of ABS is shown in Figure 4.12, which can be attributed to the fact that an increase of the glassy phase has the effect of increasing the resilience property.
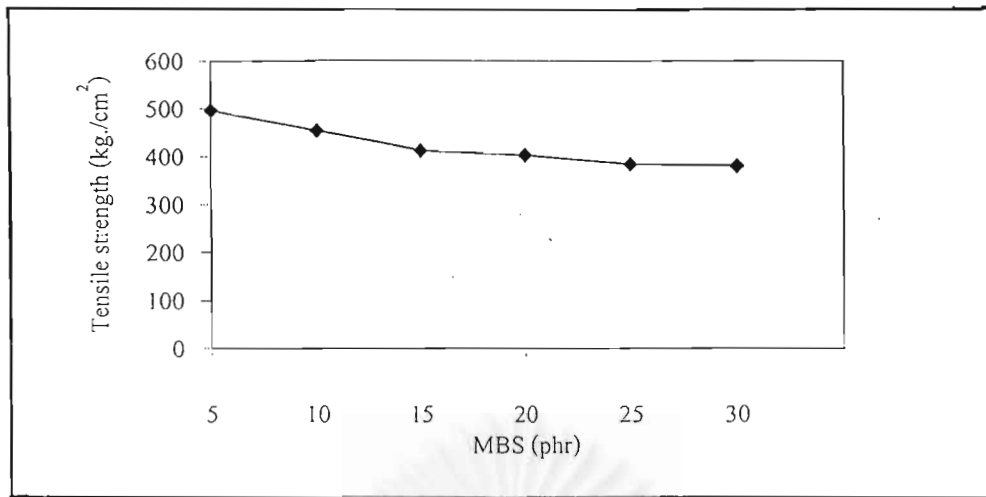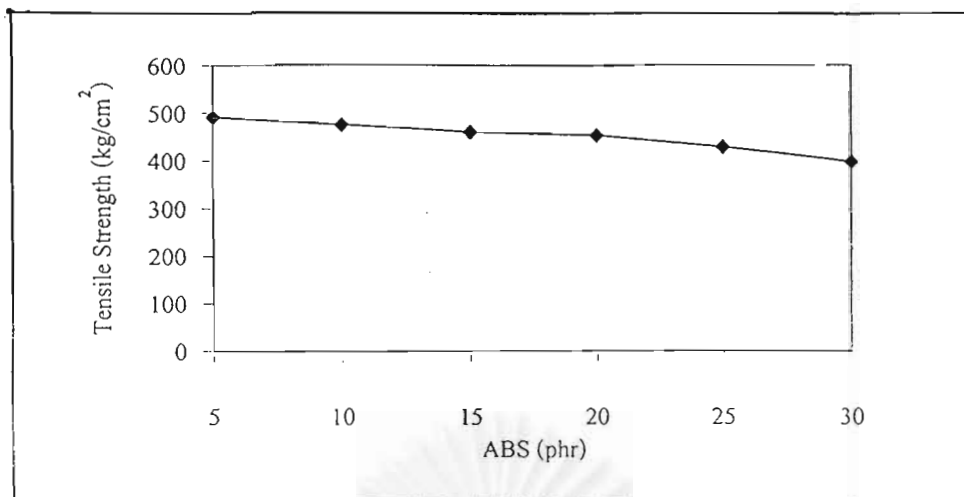
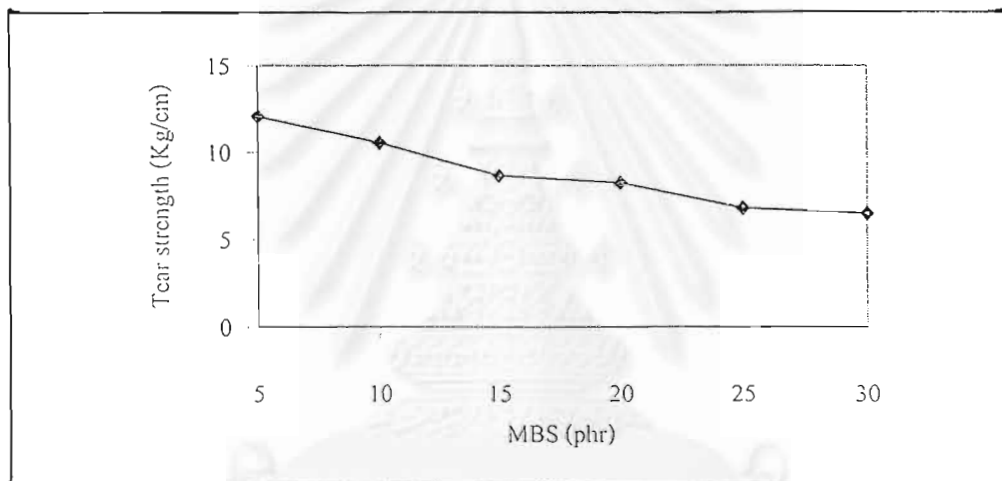Figure 4.7   Effect of ABS amount on tensile strength

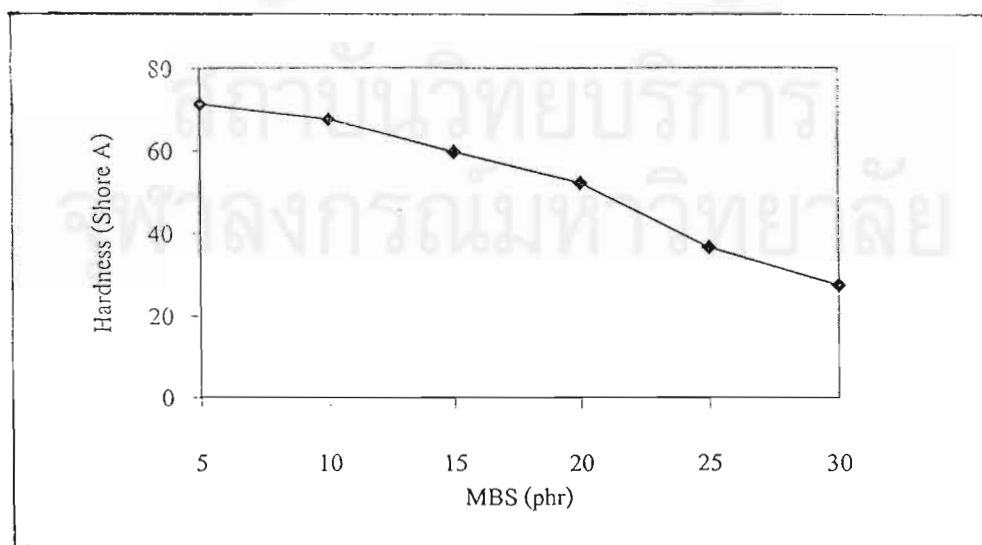Figure 4.8   Effect of ABS amount on tear strength

Figure 4.9   Effect of ABS amount on hardness
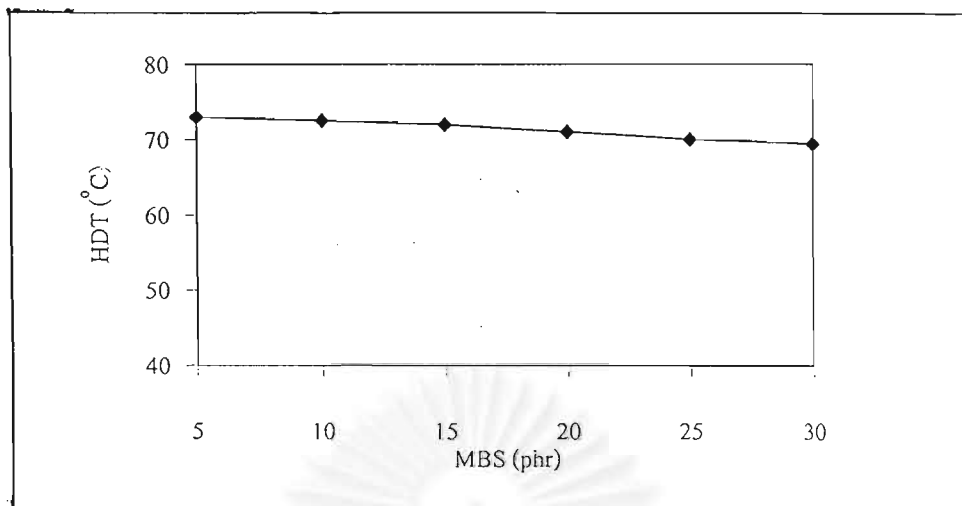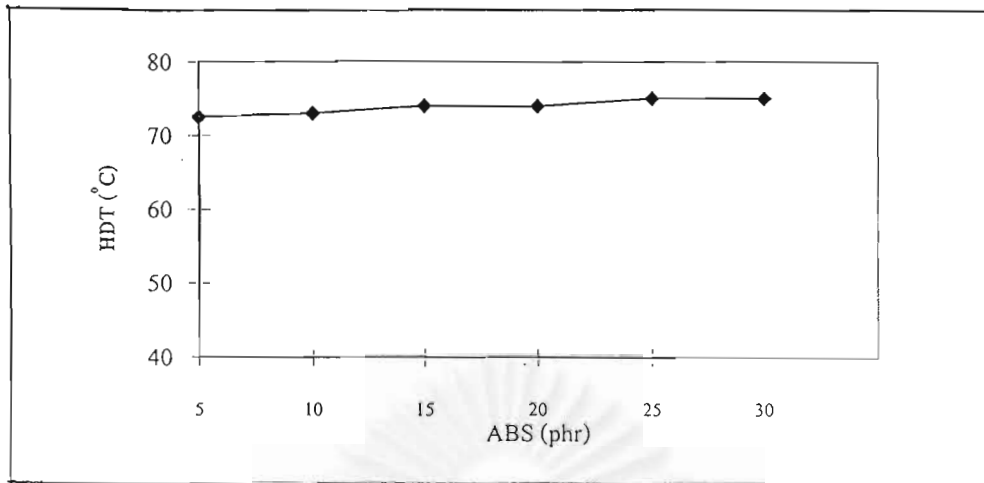
Figure 4.10   Effect of ABS amount on heat distortion temperature
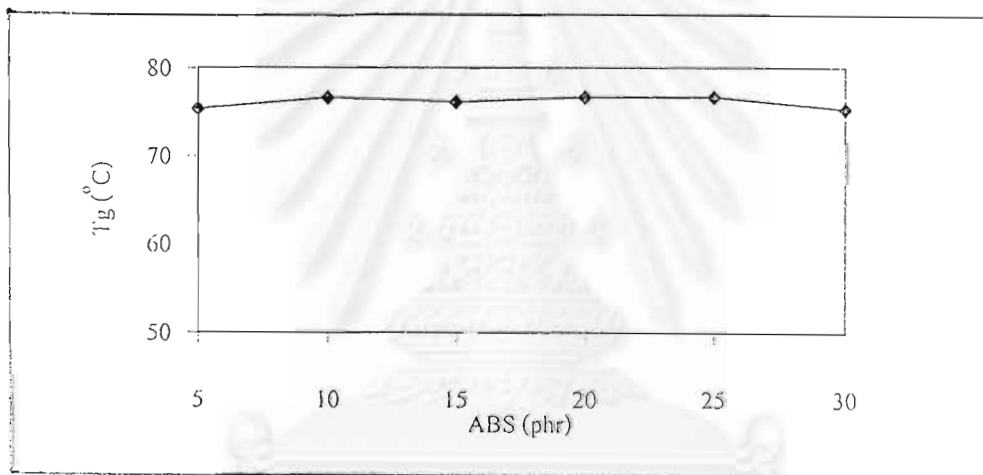
Figure 4.11   Effect of ABS amount on glass transition temperature
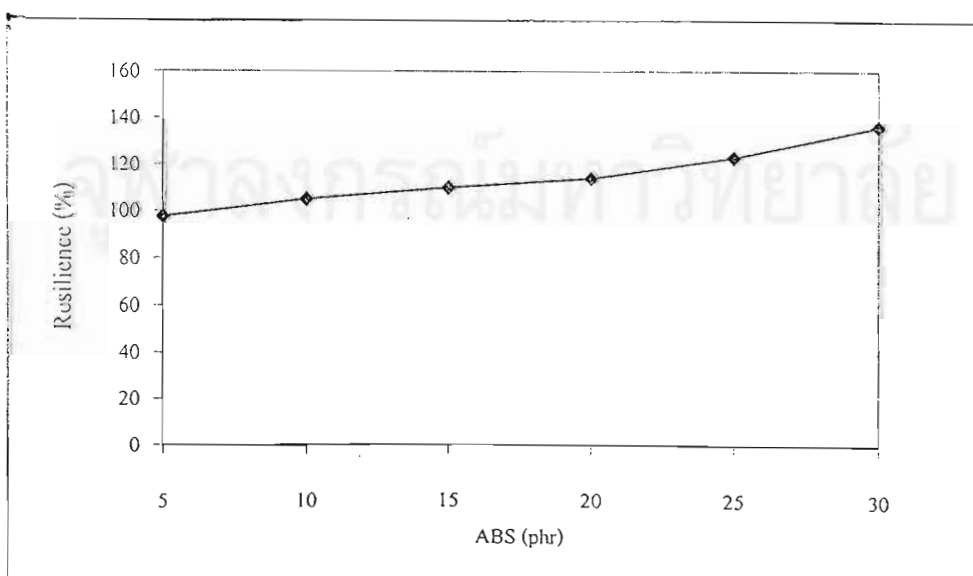
Figure 4.12   Effect of ABS amount on resilience properties

4.1.3 The effect of CPE

There are many other additives that can be used with CPE-modified rigid PVC, many of which are common to all types of rigid PVC. It is significant that the chlorination level of choice, at 36%, reflects a compatibility that allows the CPE to be dispersed in the PVC matrix. Various amounts (at 5, 10, 15, 20, 25 and 30 phr.) of CPE at a 36% Cl content was used in this research.

W. Yang [4] studied the plasticizing and the rheology behaviors of PVC/CPE blends. The results showed that the tensile strength decreases by increasing the amount of CPE.

Figure 4.13 shows that the tensile strength decreases by increasing the CPE level, which can be attributed to the presence of CPE in polyblend. The blends have a rubbery phase of each impact modifier dispersed in the rigid and glassy PVC matrix, which represents a decrease in the tensile strength when increasing the CPE level. The results agree with Yang's study.

The tear strength of blends used is an average value from the beginning to the end of the test. The dispersed phase (rubber) should be broken down into small particles. These rubber particles decrease the average values of tear strength. Figure 4.14 shows that tear strength decreases with the increase of the CPE level.

Figure 4.15 shows that hardness decreases by increasing amounts of CPE. It can be attributed to the fact that CPE is an amorphous polymer that has a relatively high degree of compatibility with PVC [2]. The composition may be used to adjust compatibility with PVC to

allow them to be used as plasticizers for PVC. Thus the hardness of PVC/CPE blends decreases by increasing the CPE level.

In fact, the general effects of the impact-modifier concentration, MBS, ABS and CPE decrease the heat distortion temperature [2]. PVC and CPE structures are not compatible and therefore the properties of their blends strongly depend on the processing condition [14, 15]. The results showed the blend morphology and are related to the mixing conditions used during the blending process. The molecular weight, crystallinity, chlorine content, and chlorine distribution of the CPE, as well as the ultimate CPE loading in the PVC, have a significant effect on the mixing requirements and the resulting blend morphology. Thus from the results of this research, CPE levels have no effect on HDT and Tg of the blend as shown in Figures 4.16 and 4.17.

It can be observed from Figure 4.18 that when CPE is incorporated in PVC there is a decrease in the resilience property which can be attributed to the presence of CPE in the polyblend. When CPE with 36% chlorine content was used, there was a dominant effect in properties. The increase of the CPE level increases the softness of the blend resulting in the decrease of resilience property.
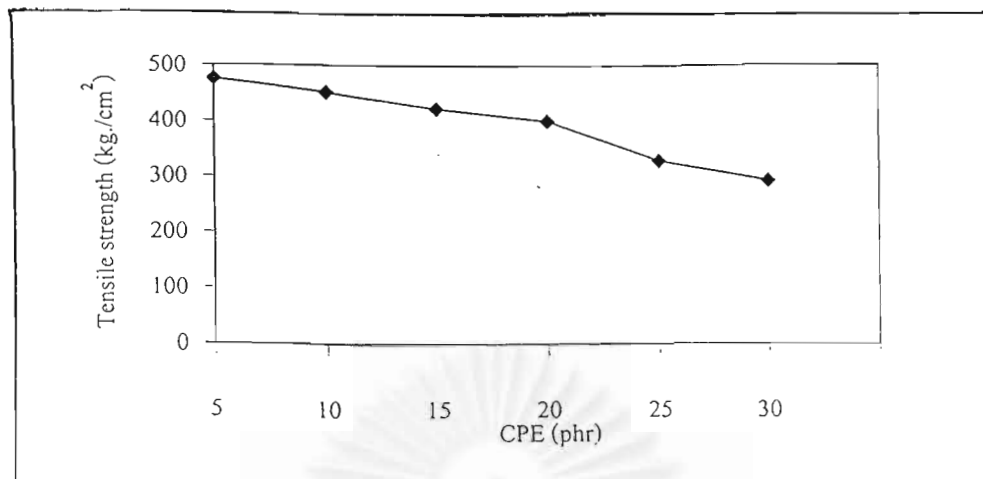
Figure 4.13   Effect of CPE amount on tensile strength
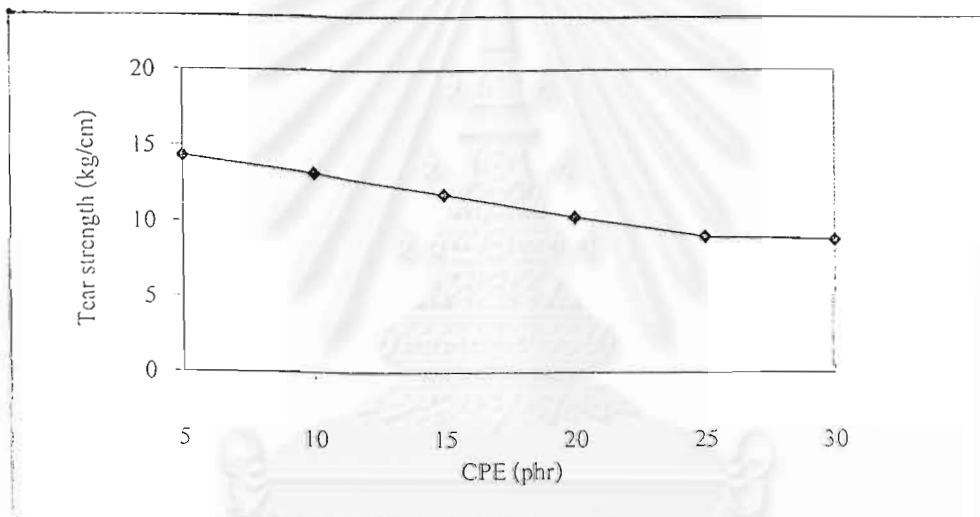
Figure 4.14   Effect of CPE amount on tear strength
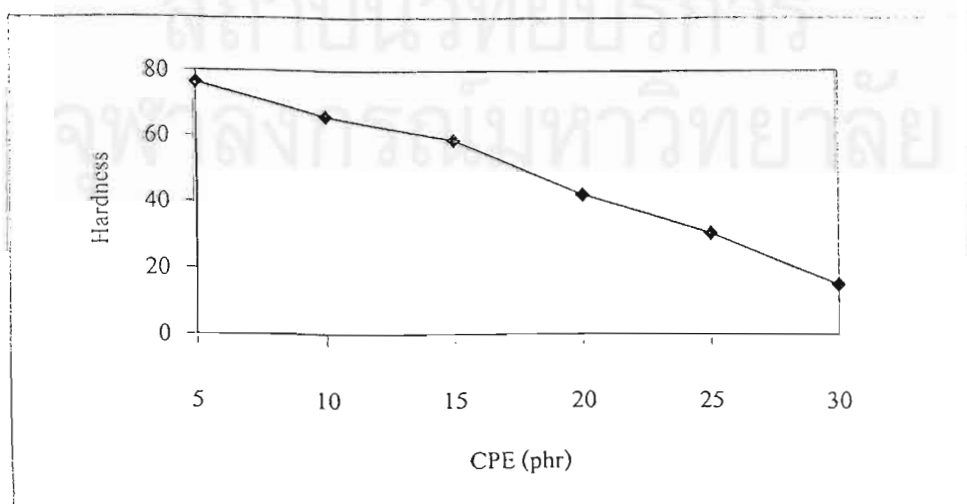
Figure 4.15   Effect of CPE amount on hardness
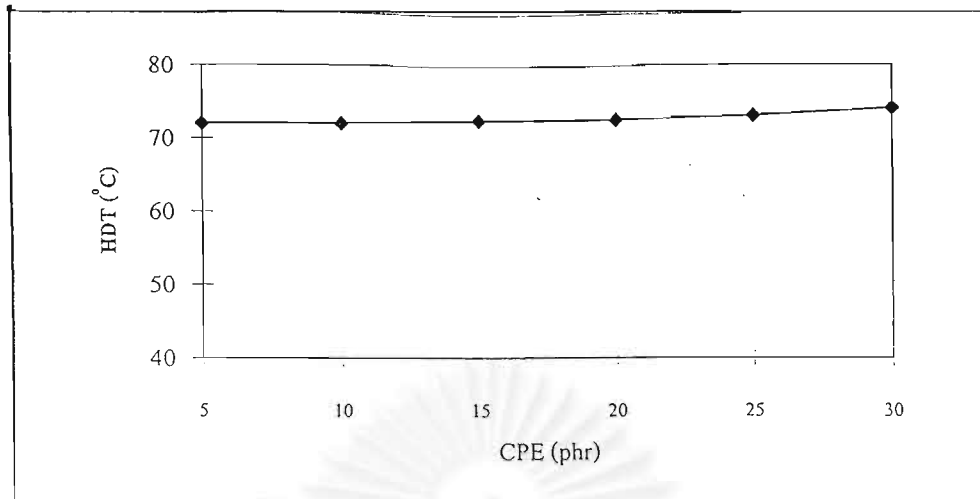
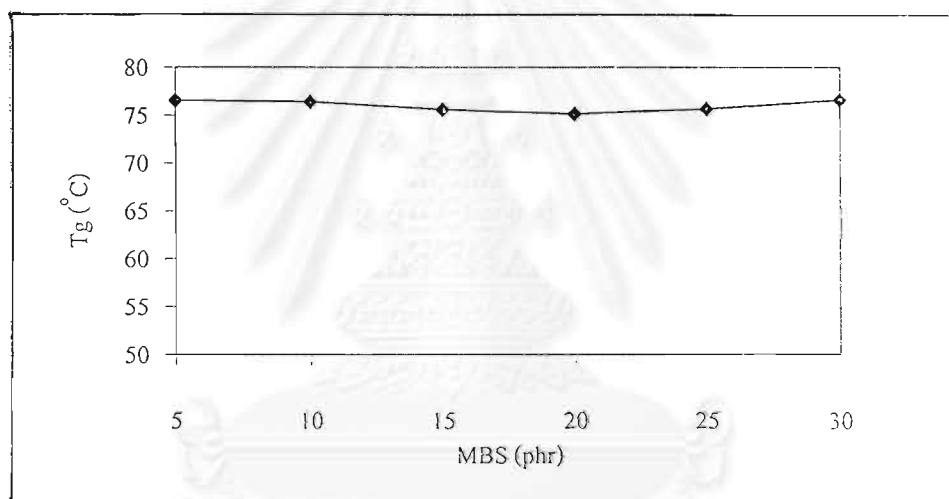Figure 4.16   Effect of CPE amount on heat distortion temperature

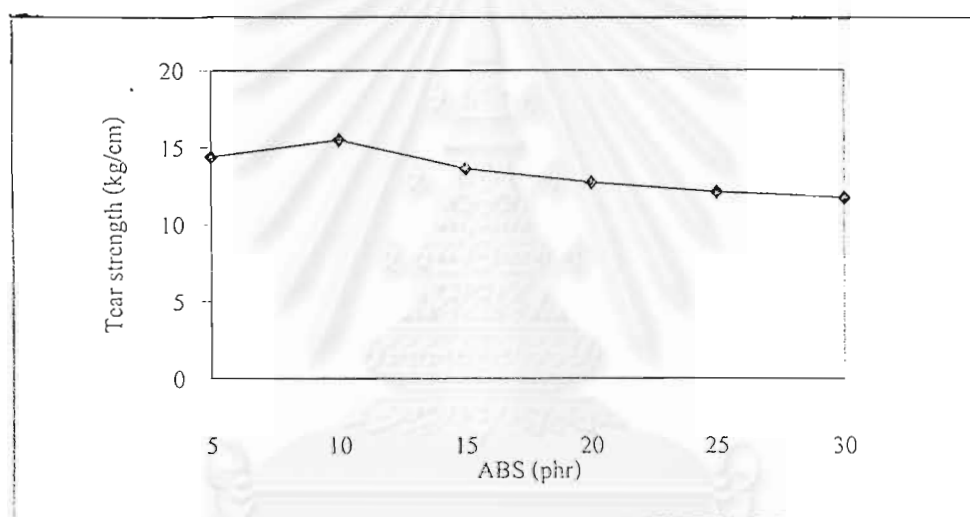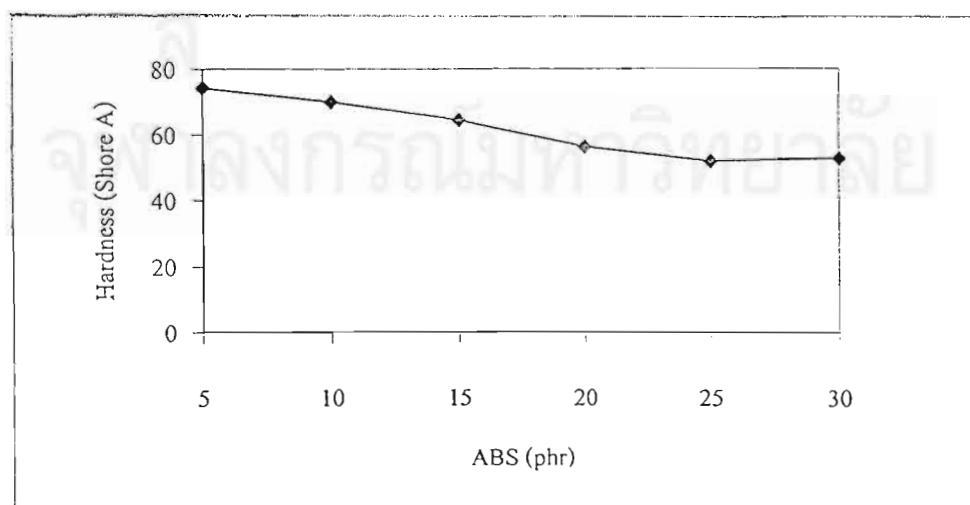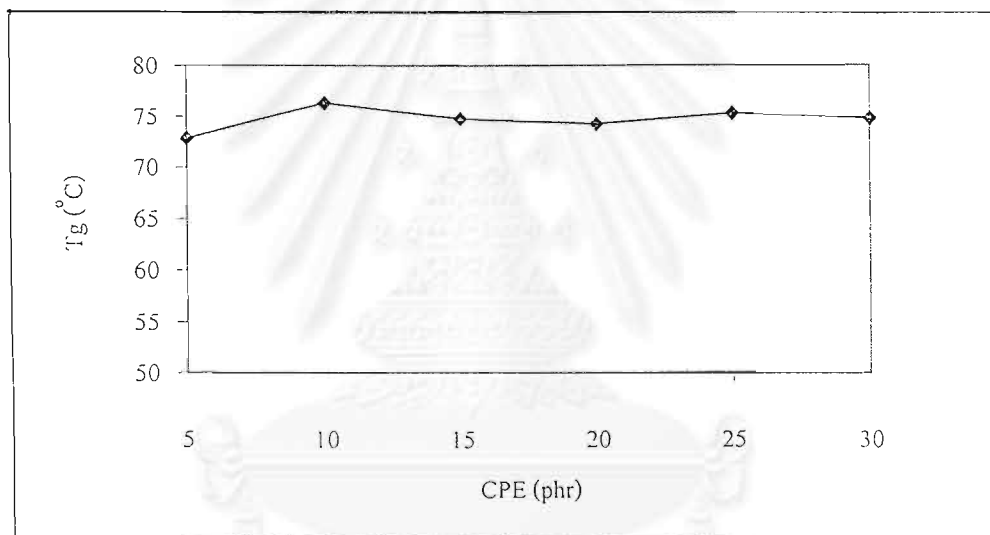Figure 4.17   Effect of CPE amount on glass transition temperature
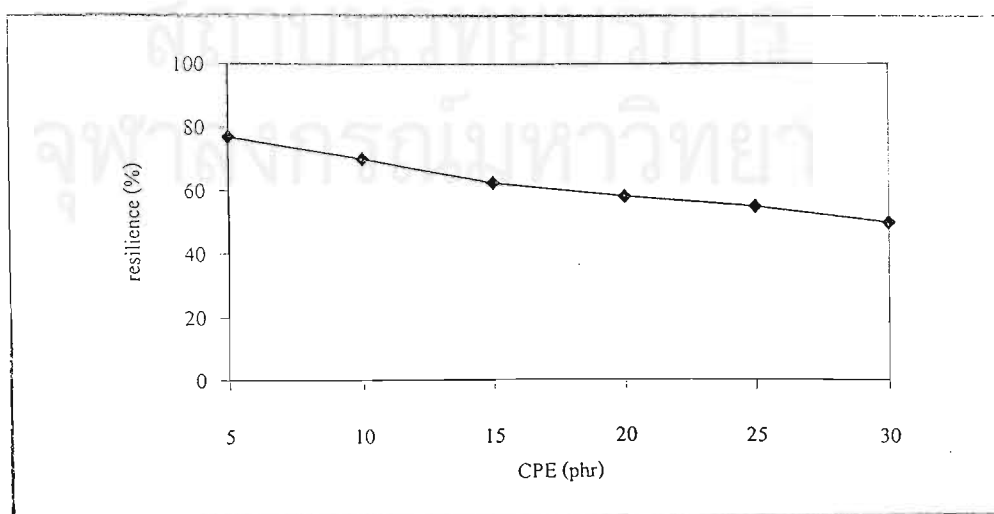
Figure 4.18   Effect of CPE amount on resilience properties

4.2 Effect of processing aid level

The polymers used as processing aids generally have fairly good physical properties themselves on their high molecular weight and high-Tg compositions. The products containing processing aids are better than those of unmodified controls due to the better fusion in compounding. In this study, PVC compounds were prepared by various amounts of processing aid at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 phr.

The tensile strength is almost unchanged with the increasing amount of processing aid as shown in Figure 4.19.

Figure 4.20 is the graph of tear strength versus the amount of processing aid which showed a maximum at 1.5 phr and then gradually dropped down with increasing processing aid level. This indicates that 1.5 phr of processing aid level is the best to improve the tear strength of blends.

The particular effectiveness of acrylic processing aids increases interparticle friction to their high surface hardness [1]. Figure 4.21 shows that the hardness of blends are almost unchanged with increasing the amount of processing aid, which can be attributed to the fact that very little amount of processing aid has no effect on the hardness of the compound.

The dominant commercial processing aid compositions are high-molecular-weight copolymer of methyl methacrylate (MMA) and alkyl acrylates, where MMA is the major component. The glass-transition temperature (Tg) of the copolymer is generally greater than that of PVC [2]. The addition of processing aids improved the heat distortion temperature of

the compounds [16]. Figure 4.23 and 4.22 show that Tg and HDT increase with increasing the amount of the processing aid.

The relatively unchanged resilience property with increasing processing aid amount is shown in Figure 4.23. That means, too small amount of processing aid has no effect on the resilience property.
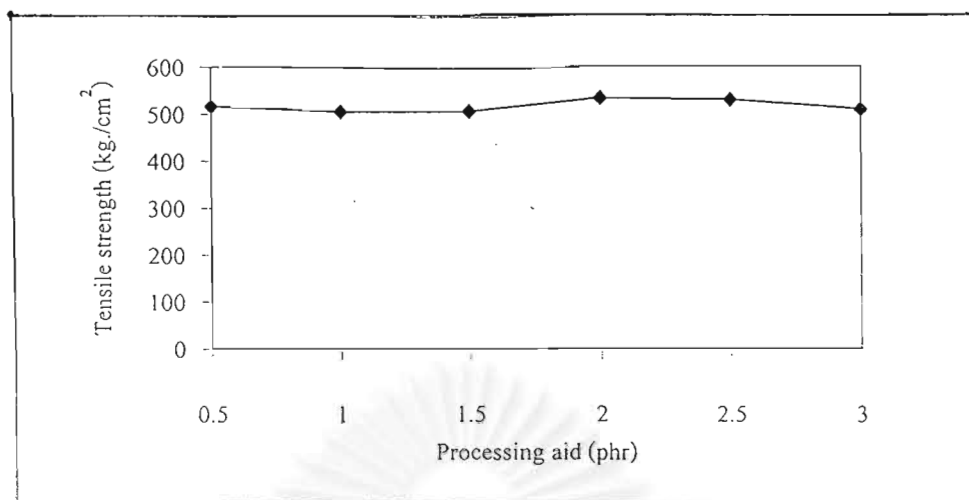
Figure 4.19 Effect of processing aid amount on tensile strength
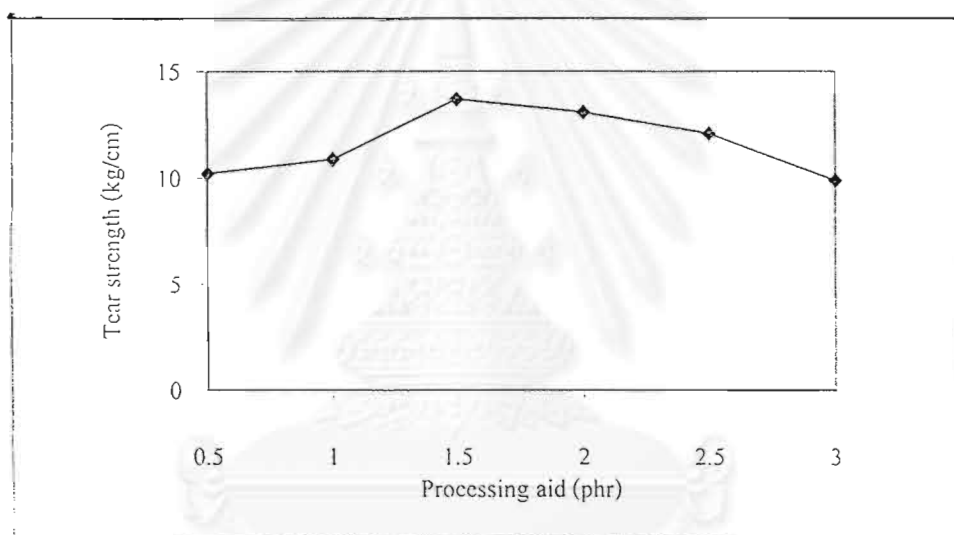
Figure 4.20 Effect of processing aid amount on tear strength
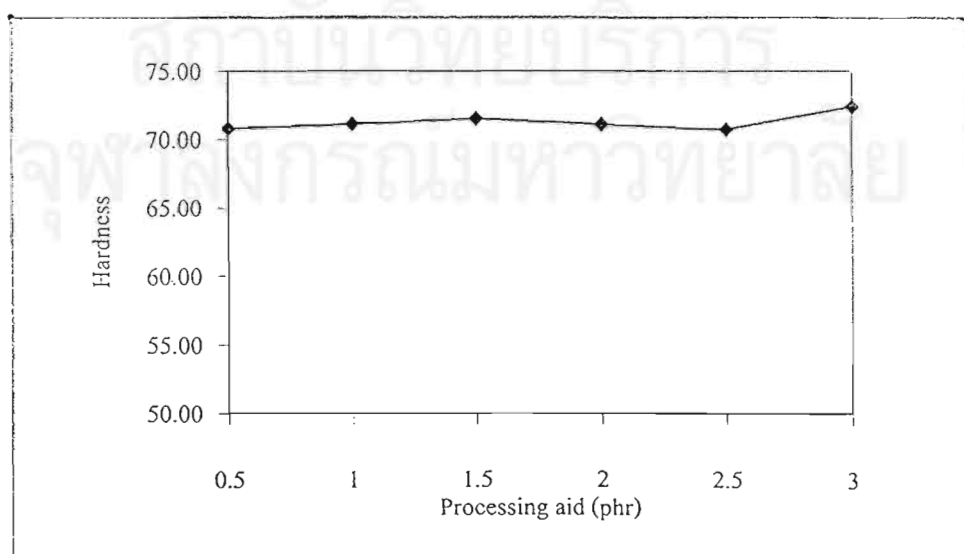
Figure 4.21 Effect of processing aid amount on hardness
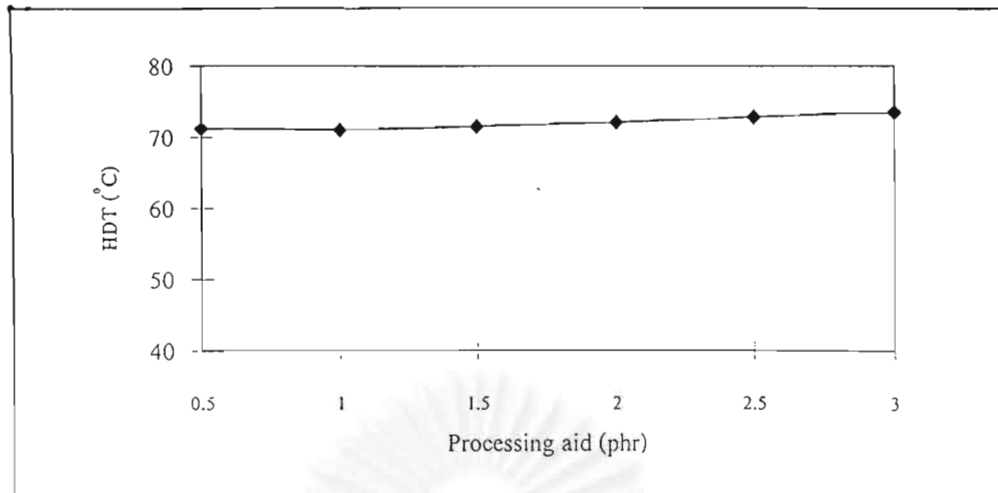
Figure 4.22 Effect of processing aid amount on heat distortion temperature

Figure 4.23 Effect of processing aid amount on glass transition temperature
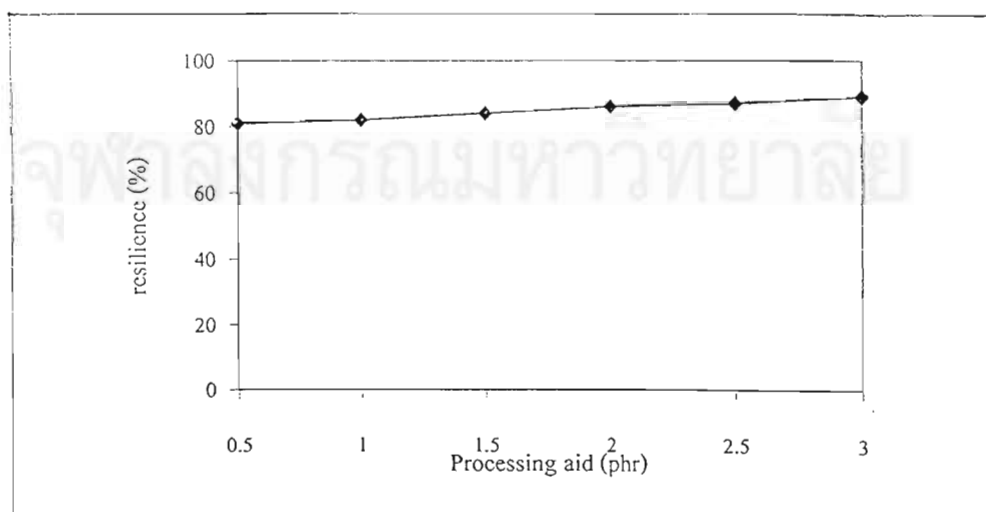
Figure 4.24 Effect of processing aid amount on resilience properties

4.3 The effect of internal lubricant level

Various amounts of internal lubricant (at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 phr) were blended with PVC and other additives. The properties of blends were measured to study the effects of internal lubricant levels.

Internal lubricants promote intermolecular flow via a chain slippage mechanism. Their molecular weight is usually lower than the external lubricant which demonstrates pseudoplasticizing effects. So tensile strength and tear strength decrease with the increase of internal lubricant levels. (Figures 4.25 and 4.26)

Internal lubricants are not polar enough to change flexibility or hardness at room temperature. The polar nature of these materials allows them to be accepted into the polymer matrix at high temperatures. The van der Waals forces between chains are reduced by the polar lubricant which slips in between the polymer chain. This allows the chains greater ease of movement because it decreases attraction between molecules. As rigid PVC cools, internal lubricant precipitates and becomes nonfunctional at room temperature. This component is not soluble in PVC at room temperature. They have no effect on the ambient temperature flexibility of the products and they do not act as plasticizers [2]. These pseudoplasticizers can adversely affect the HDT by lowering the Tg. Figure 4.27 shows that the internal lubricant levels have no effect on the hardness of blends. The magnitude of the difference between the polymer's Tg and the compound's HDT is directly related to the degree of solubility of the additive in the polymer. Lubricants that depress the HDT most are the most soluble and the most compatible, and

are thus classified as internal lubricants or plasticizers. The internal lubricant was used in the research which is slightly soluble in PVC, so it has very little effect on HDT and Tg. (Figures 4.28 and 4.29) Internal lubricant levels had no effect on the resilience property to 2.5 phr and then gradually dropped down with increasing internal levels at 3 phr, which can be attributed to the fact that this level is the highest solubility of internal lubricant in the PVC matrix. More softness of blend results in reduction of the resilience property.
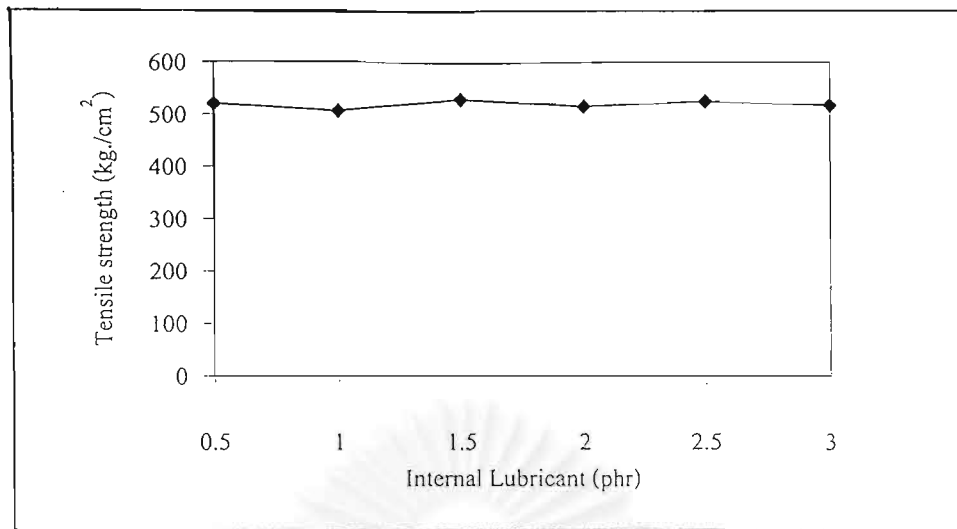
Figure 4.25 Effect of internal lubricant amount on tensile strength
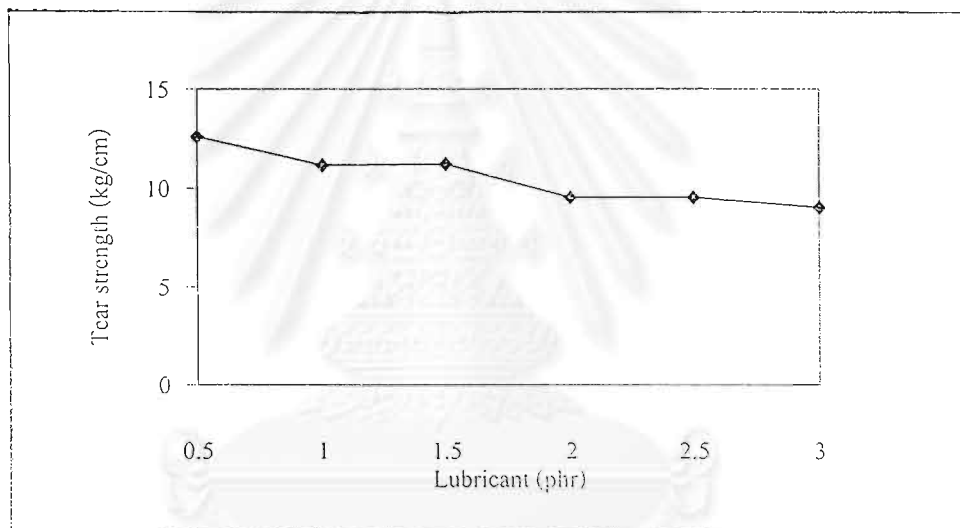
Figure 4.26 Effect of internal lubricant amount on tear strength
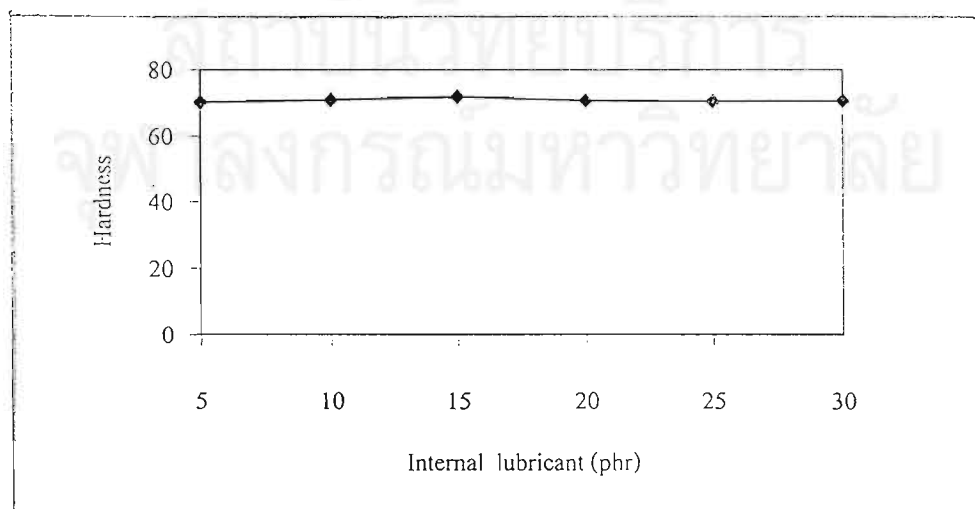
Figure 4.27 Effect of internal lubricant amount on hardness
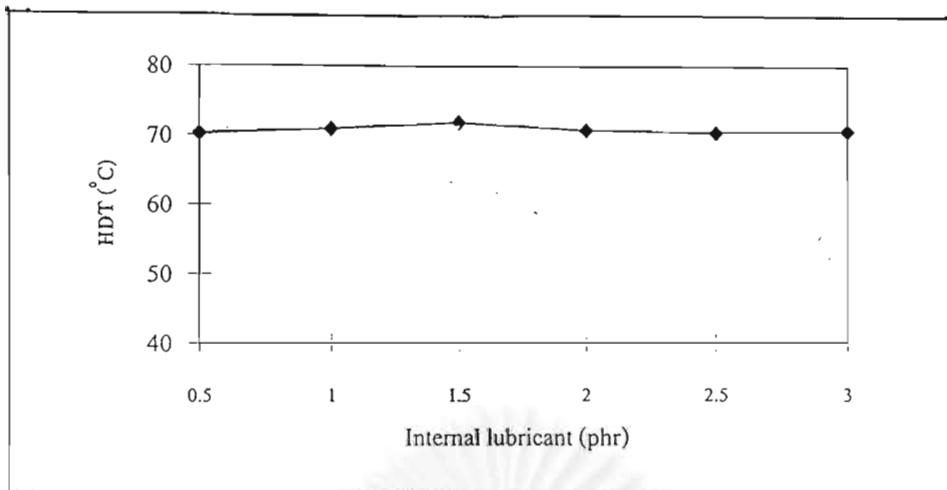
Figure 4.28 Effect of internal lubricant amount on heat distortion temperature
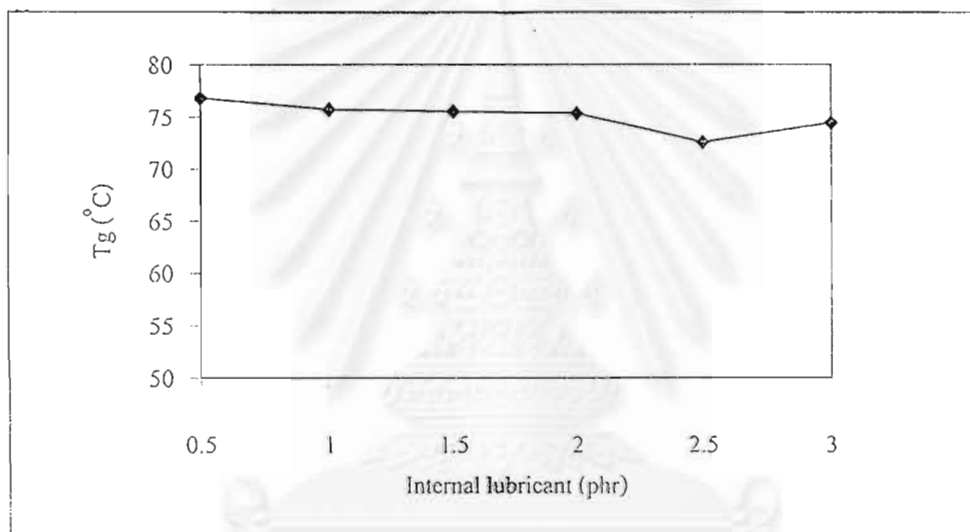
Figure 4.29 Effect of internal lubricant amount on glass transition temperature.
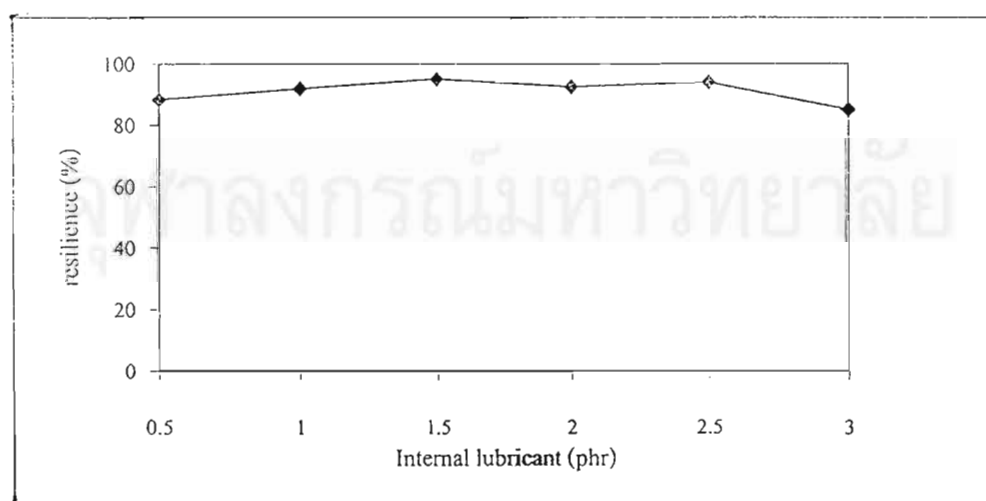
Figure 4.30 Effect of internal lubricant amount on resilience properties

4.4 The effect of fillers

In PVC, these filler properties strongly influence the mechanical properties (tensile strength, impact strength, modulus and hardness), shrinkage, creep, surface glass, fire resistance and permeability. This research used sphere (calcium carbonate) and platy (talc) fillers. The fillers at 0, 5, 10, 15, 20, 25 and 30 phr were blended with PVC and other additives.

4.4.1 The effect of calcium carbonate

Physico-mechanical properties of blends or composites are better when the particle diameter of the filler is smaller. The smaller the particle size of the dispersed filler for its fixed concentration the higher the strength of the composite. The strength of the composite with dispersed particles is lower than that of the matrix. The strength versus the particle size curve gradually rises to a limit. As in most resin systems, the carbonate, because of its low aspect ratio, generally reduces the mechanical properties [16, 17, 18]. The coarse particles of calcium carbonate used in this research are the reason for the decrease of tensile strength as shown in Figure 4.31.

It can be observed from Figure 4.32 that about 10 phr of calcium carbonate resulted in the maximum improvement in the tear strength. With further increase in the amount of calcium carbonate, the tear strength gradually decreased.

Surface-treated grades of calcium carbonate are commercially available. The stearate allows for improved dispersion and therefore,

Surface-treated grades of calcium carbonate are commercially available. The stearate allows for improved dispersion and therefore, reduction of agglomeration, especially with respect to the very-fine-particle-sized grades. The large stearic acid level is used to treat the calcium carbonate surface which effects the hardness of the composite. Figure 4.33 shows the hardness decreases with increasing calcium carbonate levels. Figure 4.34 and Figure 4.35 show that calcium carbonate has no effect on HDT and Tg of the composite.

Resilience property decreases with increasing amount of calcium carbonate as shown in Figure 4.36.
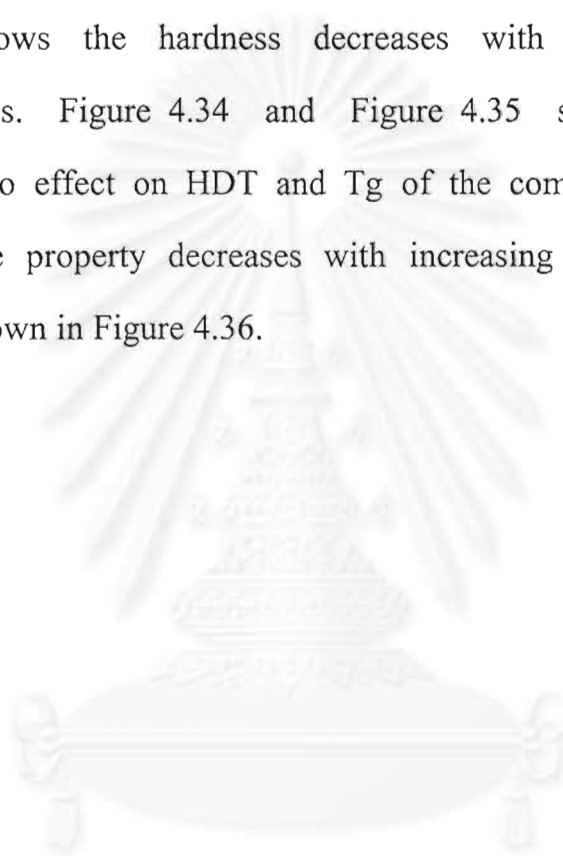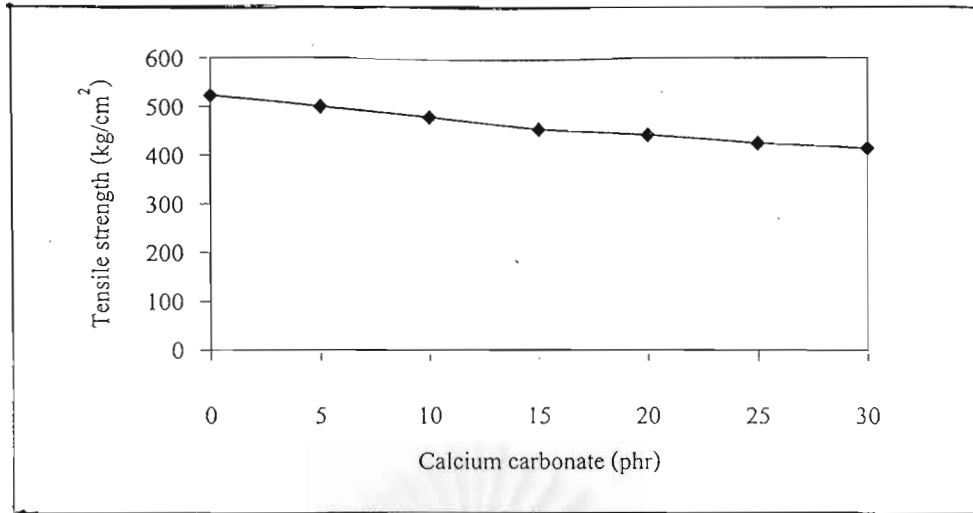
Figure 4.31   Effect of calcium carbonate amount on tensile strength
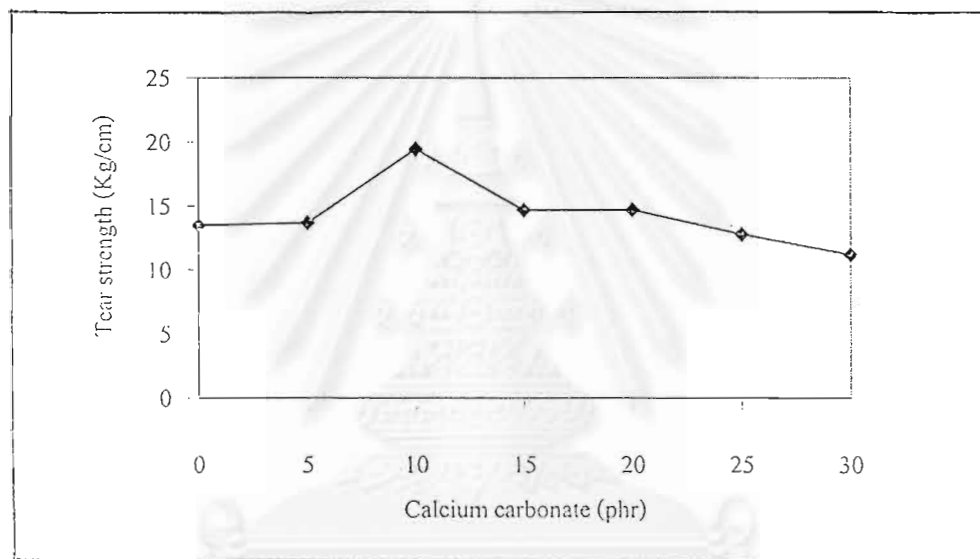
Figure 4.32   Effect of calcium carbonate amount on tear strength
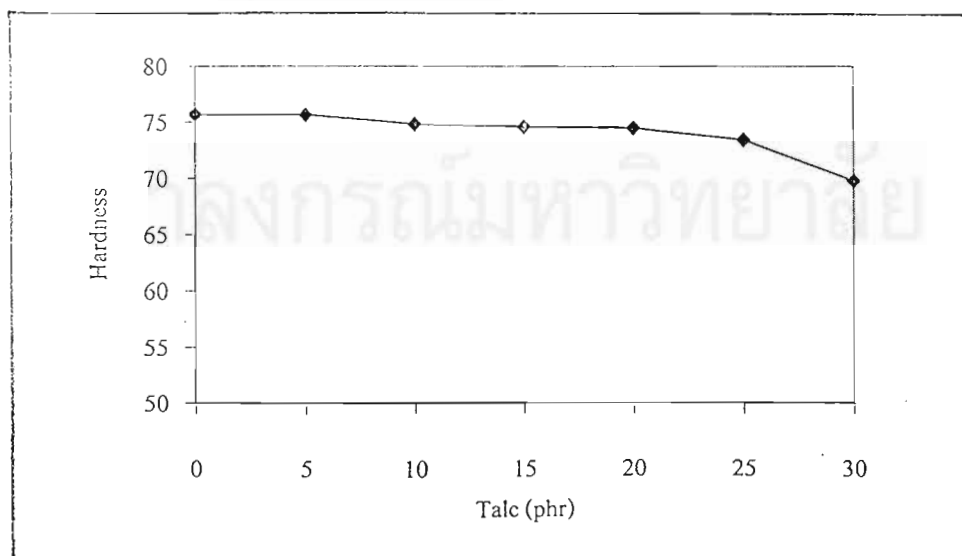
Figure 4.33   Effect of calcium carbonate amount on hardness
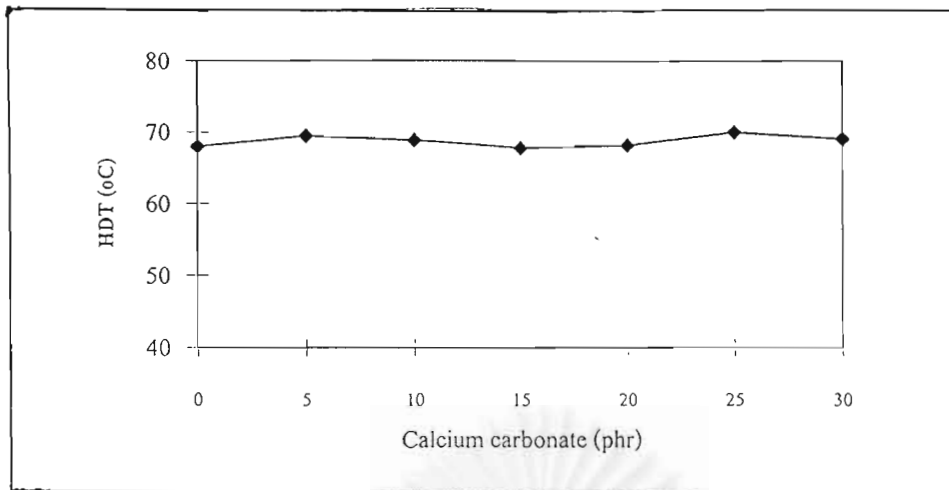
Figure 4.34 Effect of calcium carbonate amount on heat distortion temperature
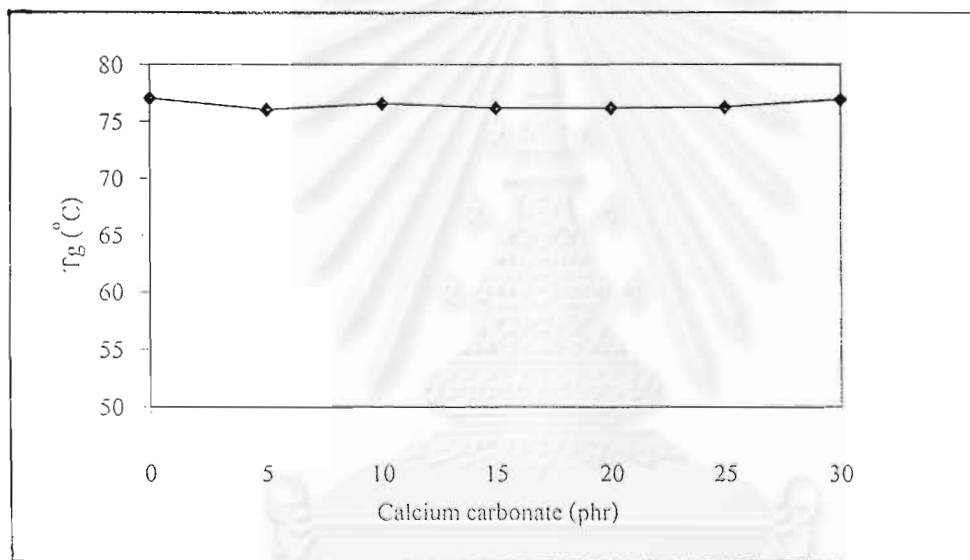
Figure 4.35 Effect of calcium carbonate amount on glass transition temperature
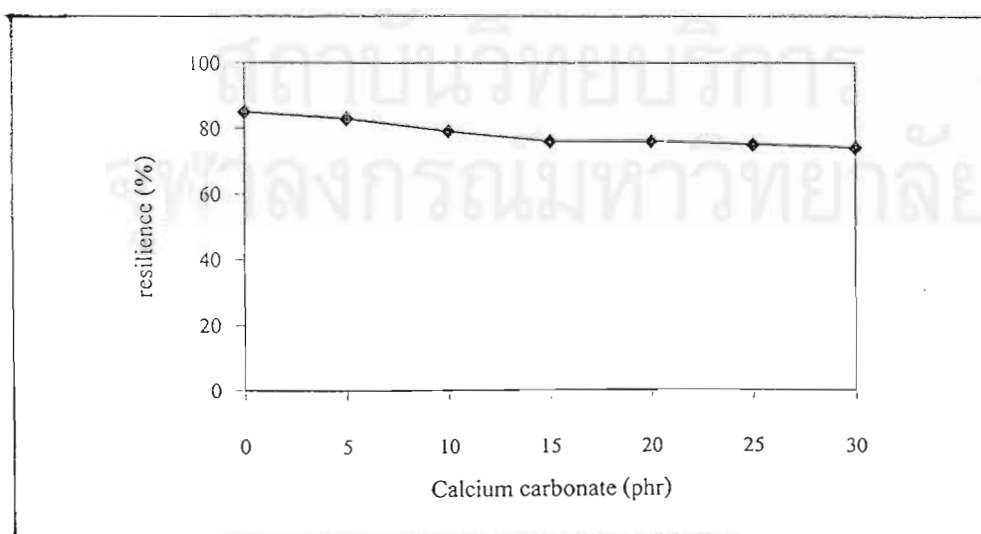
Figure 4.36 Effect of calcium carbonate amount on resilience properties

4.4.2 The effect of talc

In plastic processing, the platy particles align in the machine direction. In general, platy talc improves hot strength, increased modulus, and tensile strength to composite more than other particulate fillers because of its platelet like structure. [1, 19] Figure 4.37 clearly shows that the tensile strength of the composites increased with increasing amount of talc.

Particle size and shape are very important with respect to packing phenomena and the properties of composite. The platy particles increase in tensile property but decrease in tear dimension. The curve of tear strength versus talc quality showed maximum at 5 phr of talc and then gradually dropped down with increasing amount of talc. (Figure 4.38)

The different particle shape of talc and calcium carbonate has an effect on packing phenomena. Talc is an extremely soft mineral. It is used as a standard in the Mohs hardness scale with the value of 1 but commercial talc is often higher owing to impurities. The level of impurity effects the hardness of talc. Figure 4.39 shows that hardness increases with increasing talc levels, which can be attributed to the packing of talc and the impurities effect on the increase of composite hardness.

Figure 4.40 shows that the HDT increases with an increase amount of talc levels and dropped down at 30 phr, and it reached maximum value at 5 phr. Too high of a talc level (30 phr) decreases

attraction between talc and PVC particles. Figure 4.41 shows that Tg is almost unchanged with the increase amount of talc.

The resilience property decreases with the increasing amount of talc, (Figure 4.42) which can be attributed to the fact that talc has a platelet like structure. Therefore, it has more difficulty to mobilize in the PVC matrix.
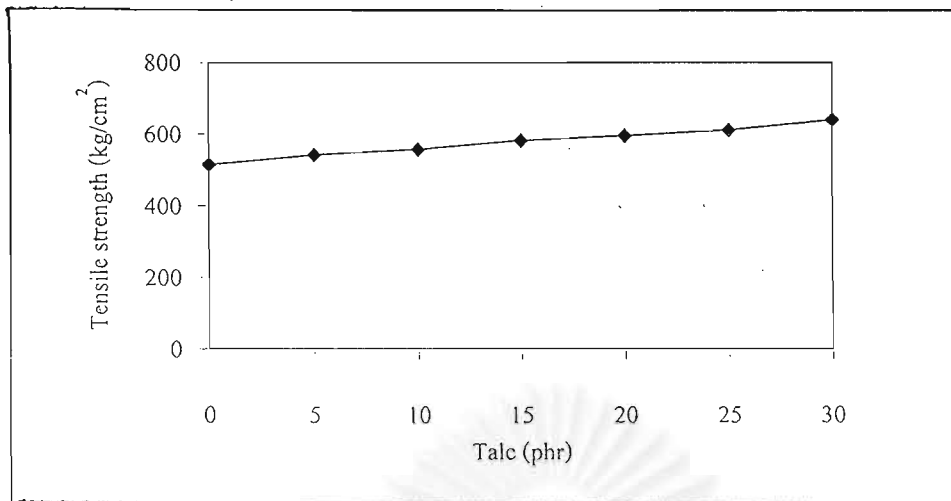
Figure 4.37 Effect of talc amount on tensile strength
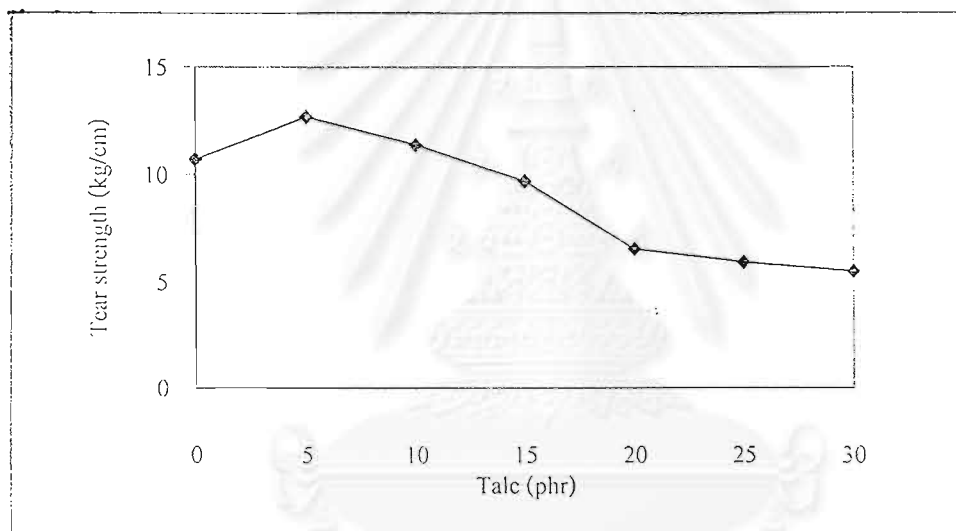
Figure 4.38 Effect of talc amount on tear strength
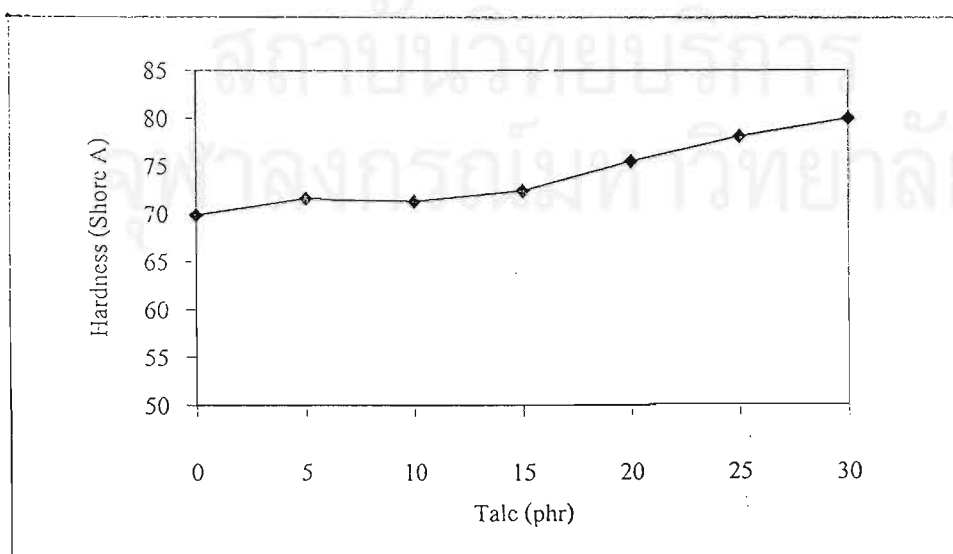
Figure 4.39 Effect of talc amount on hardness
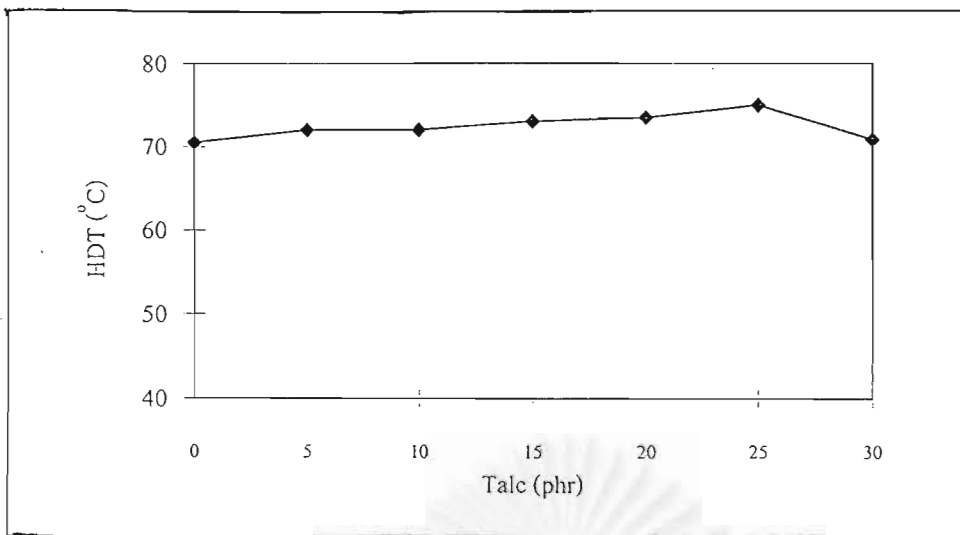
Figure 4.40   Effect of talc amount on heat distortion temperature
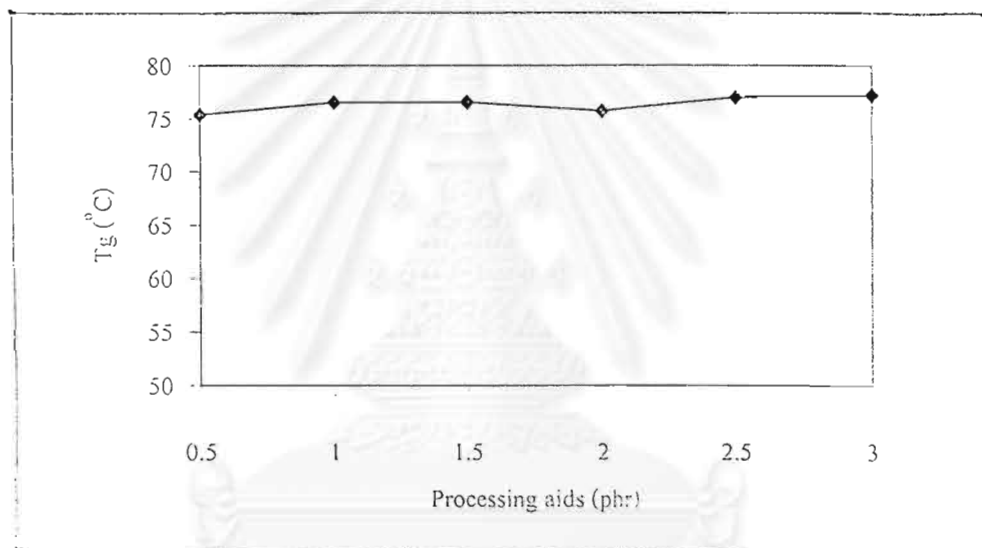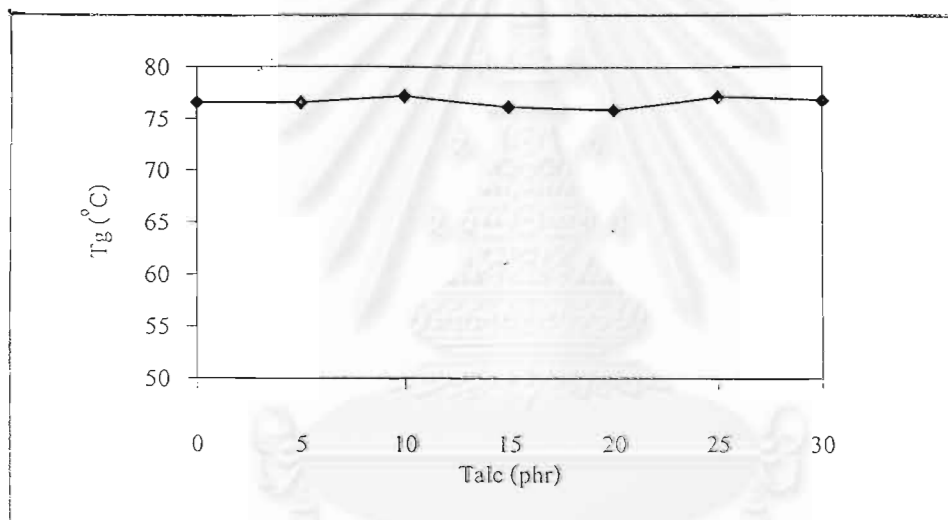

Figure 4.41   Effect of talc amount on glass transition temperature
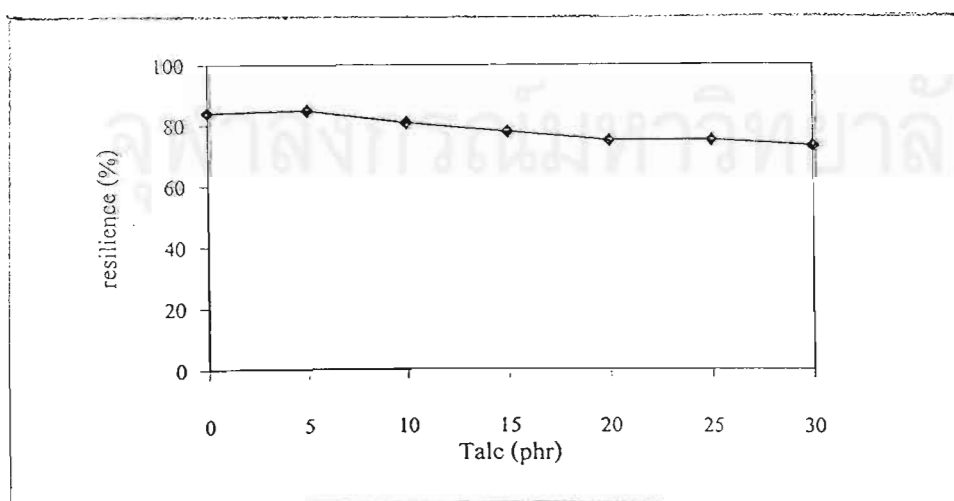
Figure 4.42 Effect of talc amount on resilience properties

4.5 Resilience and other properties

The relations of resilience and other properties of each additive are shown in Table 4.2. The results of this research are observed as the resilience property increases with increasing hardness and tensile strength. Some cases, such as hardness increase with increasing talc quantity while the resilience property decreases. It can be explained by the fact that talc is a platy material so the movement of particles is difficult to the original structure after cooled down to room temperature. The resilience property is related to the hardness and the tensile strength of blends. Thus the additives for hardness and tensile strength improvers may be chosen to blend with PVC in order to improve the resilience property.

Table 4.1 Resilience and other properties of blends

	Tensile strength (kg/cm^2)	Tear strength (kg/cm)	Hardness	HDT ($^\circ$C)	Tg ($^\circ$C)	Resilience (%)
MBS	D	D	D	D	C	D
ABS	D	D	D	I	C	I
CPE	D	D	D	C	C	D
PA	C	I/D	C	I	I	C
INT	C	D	C	C	C	C
CA	D	I/D	D	I	I	D
TA	I	I/D	I	I	C	D

MBS = Methacrylate butadiene styrene, ABS = Acrylonitrile butadiene styrene,

CPE = Chlorinated polyethylene, PA = Processing aid, INT = Internal lubricant,

CA = Calcium carbonate, TA = Talc, D = Decrease, I = Increase, C = Constant
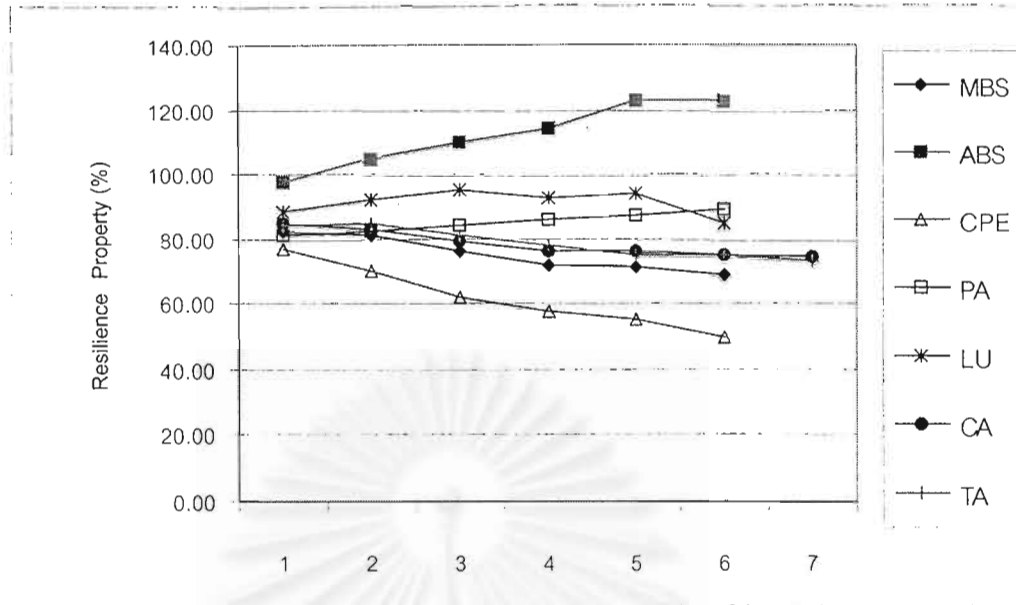
MBS = Methacrylate butadiene styrene, ABS = Acrylonitrile butadiene styrene,

CPE = Chlorinated polyethylene, PA = Processing aid, INT = Internal lubricant,

CA = Calcium carbonate, TA = Talc

Figure 4.43. Resilience property of PVC compounds

From Figure 4.43, it can be observed that the best additive for improvement of the resilience property is ABS. Optimum increase in the resilience property with acceptable cost is 10 phr. Too much of an ABS quantity introduces higher compound costs while too low of an ABS level effects other properties such as impact resistance, and tensile strength. Processing aid was used in normal dosages because it did not significantly affect the resilience property. Other additives such as MBS, CPE, internal lubricants, calcium carbonate and talc reduce the resilience property; MBS and CPE are not chosen to be impact modifiers in Christmas tree products, internal lubricant was used in normal levels. Calcium carbonate and talc are not used in the products to improve the resilience property.

4.6 Properties of new formula and commercial products

The optimum formula to improve the resilience property is shown in Table 4.2. The comparative properties of commercial products with the new formula are shown in table 4.3. It was found that the resilience property of the new formula is 2 times better than commercial products.

Some properties such as tensile strength, hardness, tear strength, heat distortion temperature (HDT), glass transition temperature (Tg) and resilience of commercial rigid PVC thin sheet for Christmas tree leaves were measured.

Table 4.2 The optimum formula to improve resilience property (NEW)

PVC (phr)	Stabilizer (phr)	Processing Aid (phr)	Internal Lubricant (phr)	External Lubricant (phr)	ABS (phr)
100	1.8	0.8	1	0.85	10

The results in Table 4.3 show that the resilience property in new formula (NEW) is better than that of commercial products A and B. So the new formulation is used to improve the resilience property in Christmas tree products.

Table 4.3 Properties of new PVC formulas compared to commercial PVC products.

Sample	Tensile strength (kg/cm^2)	Tear strength (kg/cm)	Hardness	HDT (^{o}C)	Tg (^{o}C)	Resilience (%)
A	466.5	11.3	61.9	73.0	78.8	55.5
B	467.0	8.4	69.3	73.5	79.1	48.0
NEW	474.5	15.5	70.0	73.0	76.6	111.0

4.7 Economic consideration

Table 4.4 shows that new formula has a lower price than commercial products. However, it is noteworthy that this calculation cost excludes operating costs.

Table 4.4 Cost analysis of the new formula

Sample	PVC	MBS	ABS	Processing aid	Stabilizer	Internal Lubricant	External Lubricant	Mixed Compound	Total
Price (B/kg)	32	90	70	100	182	83	175	74	
Commercial	100	6	-	1.3	2.5	0.6	-	2.5	112.9
	3200	540	-	130	455	49.8	-	185	4559.8
									40.4
NEW	100	-	10	0.8	1.8	1	-	0.85	114.5
	3200	-	700	80	327.6	83	-	148.8	4539.4
									39.7

Chapter V

Conclusion and suggestion

5.1 Conclusion

This study described the effects of additives, MBS, ABS, CPE, processing aid, internal lubricant, calcium carbonate and talc in rigid PVC thin sheet for Christmas tree products on tensile strength, tear strength, hardness, HDT and Tg to improve the resilience property with the following conclusions.

Addition of ABS can improve the resilience property but the suitable ABS amount with acceptable economic and other properties in Christmas products is 10 phr. The blend of PVC with 10 phr ABS offers better tensile strength, tear strength and hardness than commercial products. The resilience property of the blend is 2 times better than other products. The price of the new formula is similar to that of commercial products.

The resilience property is related to the hardness and the tensile strength of the blend. In the case of talc addition, hardness is increased but resilience property is not significantly increased. This may be due to talc particle packing.

The effects of increasing the amount of each additives on other properties of PVC compounds were the following.

- The tensile strength of PVC decreases with increasing amount of MBS, ABS, CPE and calcium carbonate but increasing talc amount resulted in increasing tensile strength.

- The tear strength decreases with increasing amount of MBS, ABS, CPE and internal lubricant.

- The hardness decreases with increasing amount of MBS, ABS, CPE and calcium carbonate.

- The HDT decreases with increasing amount of MBS but increasing ABS, processing aid, calcium carbonate and talc amount results in increasing HDT.

- The Tg increases with increasing processing aid and calcium carbonate.

- The resilience property decreases with increasing MBS, CPE, calcium carbonate and talc. On the other hand increasing ABS and processing aid are not significant factors in the increase of the resilience property.

5.2 Suggestion

The following studies are suggested.

The effects of the K-value of PVC on, other additives (e.g. pigment, external lubricant), processing conditions (such as temperature, winding tension) and particle size of filler on resilience and other properties.

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APPENDICES

APPENDIX A

Table A1 Technical data of PVC grade SG-610

Item	Unit	Value	Test Method
K-value	-	61	DIN-53726
Corresponding Polymerization Degree	-	810	JIS-K 6721
Apparent Bulk Density	g/ml	0.53	ISO-1269
Volatile Matters	%	<0.3	ASTM D 1921-63
Sieve Analysis			
- Retained on 60 mesh	%	0	
- Retained on 270 mesh	%	>98	
Ash as Sulfates	%	<0.1	ISO-1270
Impurities and Foreign matters	point	<5	ISO/R-1265

Table A2 Specification of Tin stabilizer grade JF-50R

Item	Specification
Composition	Butyltin containing sulfue complex
Appearance	Amber yellow oily liquid
Specific Gravity (25 $^\circ$C)	1.09-1.50
Refractive Index (25 $^\circ$C)	1.49-1.50

Table A3 Specification of Talc

Typical Chemical Content	Value
SiO_2	60% min.
MgO	30% min.
Whiteness	90% min.
Size	98% min.

Table A4 Specification of internal lubricant grade G-161

Item	Specification
Description	Oleochemical derivative
Appearance	Liquid
Acid value	5 max.
Iodine value	78-90
Specific gravity at 30 ^{o}C	0.920-0.930

Table A5 Specification of processing aid grade PA-20

Item	Unit	KM	KNK
Appearant specific gravity	g/cc	0.5	0.52
Particle size	D50 (um)	175	155
Transparency	T2 (%)	77.8	77.1
	Haze (%)	14.5	15.3
Color	b value	12.2	11.9
Fish eye	p/5000cm^2	93	85

Table A6 Specification of external lubricant grade G 70S

Description	Solid, high molecular, multi-functional fatty acid ester (complex ester)
Appearance	Pale yellow coloured, practically odourless

Item	Value
Drop point	55-58 $^{\circ}$C
Acid value	0 - 15
Sponification value	270 - 280
Lavibond 1"	
yellow	0 - 15
red	0 - 3

Table A7 Specification of impact modifier grade B-51

Description	Methyl metacrylate butadiene styrene copolymer		
Appearance	White powder		

Item	Unit	Value	Method
Volatile Matter	%	0.3 or less	105 oC x 60min
Apparent Specific Gravity	g/cc	0.37 - 0.47	JIS K6721
Particle Size Distribution	%	1.0 or less	Wet Sieve Method
Foreign material	pieces/20g	0 (>500um)or less (<500um)	Sedimentation Mothod

Table A8 Specification of impact modifier grade ABS

Item	Unit	Method	Value
Rubber	%	-	50
Appearance	-	Visual Judgement	White powder
Bulk Density	g/cm^3	TPI's method	>0.34
Volatile Matter	%	105°C x 60min	<0.50
Particle Size	%	Sieve method	<=45

Table A9 Specification of impact modifier grade Tyrin CPE

Item	Unit	Value
Bulk Density	g/cm^3	0.43
Melt Viscosity	poises/1000	26.5
Chlorine Content	%	36
Heat of Fusion	Cai/gram	0.2
Residual Crystallinity	%	2
Volatiles	%max.	0.2
Typical Screen Analysis	% Retained on 20 mesh	0
Tensile Strength	kg/cm^2	105.6
Ultimate Elongation	%	800
100% Modulus	kg/cm^2	10.8
Hardness	shore A	60
Specific Gravity	g/cm^3	1.1

Table A10 Specification of Calcium Carbonate grade PR-89C

Items	Unit	Value
Specific Surface Area	cm^2/g	23,000+-500
Top Cut (d98%)	um	6
Average Particle Size (d50%)	um	0.7
Whiteness	%	94
True Spec. Gravity	g/cm^3	2.8
DOP Absorption Value	cc/100g	21
Moisture	%	0.15

Table A11 Average mechanical analysis data sheet of PVC compounds

Sample	Tensile Strength (kg./cm.^{2})	Tear Strength (kg./cm.)	Hardness	HDT (^{o}C)	Tg (^{o}C)	Resilience (%)
A	467.0	11.30	61.9	73.0	78.8	55.6
B	467.0	8.40	69.3	73.5	79.1	48.0
MBS1	495.9	12.00	71.3	73.0	76.6	82.0
MBS2	453.6	10.54	67.6	72.5	76.4	81.0
MBS3	412.0	8.65	59.7	72.0	75.6	76.0
MBS4	402.5	8.25	52.2	71.0	75.1	72.0
MBS5	382.8	6.79	36.6	70.0	75.6	71.0
MBS6	379.9	6.50	27.3	69.5	76.6	69.0
ABS1	491.3	14.40	74.3	72.5	75.0	97.5
ABS2	474.5	15.50	70.0	73.0	76.6	111.0
ABS3	460.3	13.60	64.5	74.0	76.2	105.0
ABS4	452.7	12.70	56.3	74.0	76.7	114.0
ABS5	427.2	12.10	51.8	75.0	76.7	123.0
ABS6	395.7	11.70	52.7	75.0	75.3	50.0
CPE1	475.6	14.30	76.0	72.0	72.8	77.0
CPE2	452.4	13.20	65.9	72.0	76.3	70.0
CPE3	422.7	11.80	58.7	72.5	74.8	62.0
CPE4	400.6	10.35	42.3	72.5	74.3	58.0
CPE5	328.0	9.01	30.6	73.0	75.3	55.0
CPE6	292.4	8.80	15.3	74.0	74.8	50.0
P1	515.9	10.20	70.8	71.2	75.4	81.0
P2	505.7	10.90	71.1	71.0	76.5	82.0
P3	509.1	13.70	71.5	71.5	76.5	84.0
P4	533.6	13.10	71.1	72.0	75.7	86.0
P5	529.8	12.10	71.7	72.8	77.0	87.0
P6	509.5	9.88	72.4	73.5	77.2	89.0

Table A11 Average mechanical analysis data sheet of PVC compounds (Continued)

Sample	Tensile Strength (kg./cm.^{2})	Tear Strength (kg./cm.)	Hardness	HDT ($^{\circ}$C)	Tg ($^{\circ}$C)	Resilience (%)
L1	520.0	12.60	70.2	73.0	76.8	88.3
L2	506.4	11.20	70.9	71.8	75.7	92.0
L3	529.8	11.20	71.8	71.8	75.5	95.0
L4	515.5	9.52	70.7	71.0	75.3	82.5
L5	524.3	9.52	70.4	69.5	72.5	94.0
L6	517.3	9.02	70.6	69.3	74.4	85.0
CA1	522.7	13.50	75.7	68.0	77.0	85.0
CA2	499.8	13.70	75.7	69.5	76.0	83.0
CA3	480.5	19.45	74.8	68.8	76.6	79.0
CA4	456.1	14.70	74.6	67.8	76.2	76.0
CA5	442.2	14.70	74.5	68.2	76.2	76.0
CA6	424.0	12.80	73.4	70.0	76.3	75.0
CA7	415.1	11.20	69.8	69.0	77.0	74.0
TA1	514.7	10.70	69.8	70.5	76.6	84.0
TA2	541.7	12.70	71.6	72.0	76.6	85.0
TA3	558.5	11.40	71.2	72.0	77.2	81.0
TA4	583.0	9.71	72.4	73.0	76.2	78.0
TA5	593.8	6.53	75.4	73.5	75.9	75.0
TA6	608.7	5.91	78.1	75.0	77.2	75.0
TA7	639.3	5.48	80	76.0	76.8	73.0

Table A12 Mechanical analysis data sheet of PVC compounds

Sample	Analysis No.	Tensile Strength (kg./cm.^{2})	Tear Strength (kg./cm.)	Hardness	HDT ($^\circ$C)
A	1	465.8	11.28	61.4	73.0
	2	460.0	11.35	61.6	73.0
	3	470.5	11.42	62.1	72.5
	Average	465.4	11.35	61.7	72.8
B	1	460.2	8.35	69.4	73.5
	2	465.5	8.30	69.3	74.0
	3	458.3	8.44	70.3	73.2
	Average	461.33	8.36	69.7	73.6
MBS1	1	495.9	12.10	71.4	73.0
	2	498.5	12.48	71.3	73.0
	3	490.8	11.84	71.3	72.8
	Average	495.1	12.14	71.3	72.9
MBS2	1	449.3	10.65	67.2	72.0
	2	461.7	10.55	67.7	72.5
	3	450.9	10.40	67.5	72.5
	Average	454.0	10.53	67.5	72.3
MBS3	1	412.3	8.54	59.5	72.0
	2	412.3	8.53	59.8	71.5
	3	414.9	8.68	59.6	72.0
	Average	413.2	8.58	59.6	71.8
MBS4	1	405.3	8.15	52.2	71.0
	2	408.7	8.20	52.5	71.0
	3	400.5	8.35	52.4	71.5
	Average	404.8	8.23	52.4	71.2
MBS5	1	388.2	6.75	36.4	70.0
	2	375.5	6.78	36.7	69.5
	3	382.6	6.83	36.5	70.0
	Average	382.1	6.79	36.5	69.8
MBS6	1	383.9	7.81	27.6	69.0
	2	379.5	7.79	27.5	69.5
	3	376.5	7.98	27.3	69.5
	Average	380.0	7.86	27.5	69.3
ABS1	1	490.3	14.46	74.0	72.5
	2	492.4	14.32	74.3	72.0
	3	490.1	14.38	74.2	72.5
	Average	490.9	14.39	74.2	72.3

Table A12 Mechanical analysis data sheet of PVC compounds (continued)

Sample	Analysis No.	Tensile Strength (kg./cm.^{2})	Tear Strength (kg./cm.)	Hardness	HDT ($^\circ$C)
ABS2	1	475.3	15.51	69.9	73.0
	2	475.5	15.52	69.5	72.8
	3	472.6	15.46	70.1	73.5
	Average	474.5	15.50	69.8	73.1
ABS3	1	463.2	13.50	64.1	74.0
	2	460.5	13.70	64.6	73.5
	3	458.2	13.60	64.5	74.0
	Average	460.6	13.60	64.4	73.8
ABS4	1	450.2	12.68	56.5	73.5
	2	448.3	12.65	56.2	73.5
	3	453.8	12.59	56.3	74.0
	Average	450.8	12.64	56.3	73.7
ABS5	1	425.5	12.05	51.6	75.0
	2	428.8	12.10	52.1	75.0
	3	428.3	12.20	51.6	75.5
	Average	427.5	12.12	51.8	75.2
ABS6	1	393.3	11.54	52.4	74.5
	2	397.3	11.76	52.6	74.5
	3	395.8	11.74	52.8	75.5
	Average	395.5	11.68	52.6	74.8
CPE1	1	473.0	14.28	75.8	72.0
	2	476.9	14.20	76.3	71.5
	3	474.3	14.34	76.2	72.0
	Average	474.7	14.27	76.1	71.8
CPE2	1	450.2	13.10	66.2	72.0
	2	451.1	13.25	65.6	72.5
	3	453.1	13.21	65.9	72.0
	Average	451.5	13.19	65.9	72.2
CPE3	1	420.2	11.72	58.9	72.5
	2	421.2	11.80	58.7	72.5
	3	421.8	11.70	58.6	72.5
	Average	421.1	11.74	58.7	72.5
CPE4	1	402.3	10.30	42.4	72.0
	2	399.8	10.27	42.2	72.5
	3	401.3	10.55	42.2	72.5
	Average	401.1	10.37	42.3	72.3

Table A12 Mechanical analysis data sheet of PVC compounds (continued)

Sample	Analysis No.	Tensile Strength (kg./cm.²)	Tear Strength (kg./cm.)	Hardness	HDT (°C)
CPE5	1	325.5	8.94	30.4	73.5
	2	328.5	8.90	30.8	73.0
	3	329.8	9.00	30.0	73.0
	Average	327.9	8.95	30.4	73.2
CPE6	1	292.3	8.83	15.3	74.0
	2	291.5	8.70	15.4	73.5
	3	293.5	8.80	15.5	74.0
	Average	292.4	8.78	15.4	73.8
PA1	1	512.5	10.10	71.1	71.5
	2	516.4	10.00	70.6	71.2
	3	515.5	10.25	69.7	71.5
	Average	514.8	10.12	70.5	71.4
PA2	1	503.8	10.95	72.1	70.8
	2	506.5	10.94	69.7	71.0
	3	507.3	10.76	71.1	71.3
	Average	505.9	10.88	71.0	71.0
PA3	1	508.5	13.65	70.6	71.5
	2	509.3	13.80	72.1	71.5
	3	507.3	13.81	71.0	71.0
	Average	508.4	13.75	71.2	71.3
PA4	1	534.3	13.15	71.2	72.0
	2	533.8	13.11	71.3	72.0
	3	533.5	13.13	70.8	71.5
	Average	533.9	13.13	71.1	71.8
PA5	1	528.2	12.11	71.8	72.5
	2	528.9	12.05	71.2	73.0
	3	530.3	12.08	71.6	73.5
	Average	529.1	12.08	71.5	73.0
PA6	1	510.5	9.92	72.5	73.5
	2	510.4	9.91	73.6	73.5
	3	509.6	9.73	72.3	73.0
	Average	510.2	9.85	72.8	73.3
LUB1	1	522.0	12.51	69.4	73.5
	2	521.3	12.55	69.3	73.0
	3	518.2	12.71	70.1	73.0
	Average	520.5	12.59	69.6	73.2

Table A12 Mechanical analysis data sheet of PVC compounds (continued)

Sample	Analysis No.	Tensile Strength (kg./cm.²)	Tear Strength (kg./cm.)	Hardness	HDT (°C)
LUB2	1	504.3	11.18	70.9	71.5
	2	503.8	11.30	70.9	71.0
	3	510.5	11.11	71.1	71.5
	Average	506.2	11.20	71.0	71.3
LUB3	1	528.3	11.35	71.8	72.0
	2	530.5	11.11	72.2	72.0
	3	528.7	11.13	70.3	72.0
	Average	529.2	11.20	71.4	72.0
LUB4	1	517.3	9.43	70.5	70.5
	2	515.2	9.60	70.2	71.0
	3	515.8	9.60	71.3	71.0
	Average	516.1	9.54	70.7	70.8
LUB5	1	525.6	9.45	70.4	69.5
	2	524.3	9.60	69.3	69.5
	3	523.8	9.51	70.8	70.0
	Average	524.6	9.52	70.2	69.7
LUB6	1	515.8	9.10	70.1	69.0
	2	517.6	9.15	70.8	69.5
	3	518.3	8.90	70.2	69.0
	Average	517.2	9.05	70.4	69.2
CA1	1	524.5	13.45	75.5	68.0
	2	522.1	13.51	76.0	67.5
	3	523.3	13.40	75.6	68.0
	Average	523.3	13.45	75.7	67.8
CA2	1	498.3	13.68	75.8	69.5
	2	499.3	13.65	75.5	69.5
	3	498.5	13.78	75.7	69.0
	Average	498.7	13.70	75.7	69.3
CA3	1	479.5	19.36	74.9	68.5
	2	480.3	19.47	74.9	68.8
	3	481.2	19.31	74.7	69.5
	Average	480.3	19.38	74.8	68.9
CA4	1	455.5	14.65	74.9	68.0
	2	455.9	14.72	74.0	68.0
	3	458.3	14.80	74.9	67.5
	Average	456.6	14.72	74.6	67.8

Sample	Analysis No.	Tensile Strength (kg./cm.^{2})	Tear Strength (kg./cm.)	Hardness	HDT ($^\circ$C)
CA5	1	440.5	14.68	74.6	68.0
	2	441.4	14.58	74.3	68.0
	3	443.5	14.86	74.5	68.5
	Average	441.8	14.71	74.5	68.2
CA6	1	421.1	12.90	73.3	69.8
	2	423.4	12.70	73.4	70.0
	3	425.1	12.50	73.5	69.5
	Average	423.2	12.70	73.4	69.8
CA7	1	413.3	11.09	69.7	69.0
	2	414.3	11.13	69.8	69.0
	3	414.5	11.28	69.8	69.5
	Average	414.0	11.17	69.8	69.2
TA1	1	513.7	10.85	71.4	70.5
	2	514.3	10.73	70.0	70.5
	3	515.3	10.70	68.9	70.8
	Average	514.4	10.76	70.1	70.6
TA2	1	545.4	12.68	69.2	72.0
	2	538.9	12.81	72.3	71.5
	3	542.1	12.74	73.9	72.0
	Average	542.1	12.74	71.8	71.8
TA3	1	557.6	11.35	71.4	72.0
	2	560.3	11.38	70.9	72.0
	3	560.8	11.45	69.7	72.0
	Average	559.6	11.39	70.7	72.0
TA4	1	580.3	9.75	72.0	73.5
	2	585.9	9.70	72.6	73.2
	3	586.6	9.76	73.6	73.0
	Average	584.3	9.74	72.7	73.2
TA5	1	592.1	6.48	74.7	73.0
	2	595.3	6.50	75.0	73.5
	3	592.4	6.55	76.0	73.0
	Average	593.3	6.51	75.2	73.2
TA6	1	607.3	5.82	79.0	75.0
	2	605.3	5.80	78.2	75.0
	3	608.5	6.02	77.6	74.5
	Average	607.0	5.88	78.3	74.8
TA7	1	639.4	5.40	80.3	76.0
	2	636.2	5.45	79.6	76.0
	3	640.8	5.43	80.0	76.0
	Average	638.8	5.43	80.0	76.0

Table A13 Mechanical analysis data sheet of PVC compounds (repeated)

Sample	Analysis No.	Tensile Strength (kg./cm.^{2})	Tear Strength (kg./cm.)	Hardness	HDT ($^\circ$C)
A	1	467.2	11.40	61.8	72.5
	2	474.8	11.20	62.0	73.0
	3	463.7	11.15	62.5	73.5
	Average	468.6	11.25	62.1	73.0
B	1	475.2	8.45	69.5	72.8
	2	470.5	8.80	69.2	73.8
	3	472.5	8.10	68.2	73.5
	Average	472.7	8.45	69.0	73.4
MBS1	1	494.7	11.83	71.2	73.1
	2	497.8	12.38	71.2	73.0
	3	497.9	11.38	71.5	73.0
	Average	496.8	11.86	71.3	73.0
MBS2	1	453.5	10.59	67.9	72.5
	2	453.1	10.60	67.6	72.5
	3	453.0	10.45	67.4	73.0
	Average	453.2	10.55	67.6	72.7
MBS3	1	410.6	8.67	59.8	72.0
	2	413.2	8.64	59.7	72.5
	3	408.5	8.83	59.5	72.0
	Average	410.8	8.71	59.7	72.2
MBS4	1	400.2	8.22	52.0	71.0
	2	404.9	8.15	52.2	71.0
	3	395.5	8.45	52.1	70.5
	Average	400.2	8.27	52.1	70.8
MBS5	1	391.8	6.77	36.8	70.0
	2	378.8	6.74	36.7	70.5
	3	380.1	6.84	36.5	70.0
	Average	383.6	6.78	36.7	70.2
MBS6	1	379.5	7.83	27.2	69.8
	2	382.2	7.78	27.2	69.5
	3	378.0	7.98	27.1	69.5
	Average	379.9	7.86	27.2	69.6
ABS1	1	493.3	14.39	74.5	72.8
	2	490.5	14.48	74.3	72.5
	3	491.3	14.38	74.4	72.5
	Average	491.7	14.42	74.4	72.6

Table A13 Mechanical analysis data sheet of PVC compounds (repeated, continued)

Sample	Analysis No.	Tensile Strength (kg./cm.^{2})	Tear Strength (kg./cm.)	Hardness	HDT (^{o}C)
ABS2	1	474.3	15.66	69.9	73.0
	2	474.1	15.37	70.0	73.2
	3	475.2	15.50	70.3	72.5
	Average	474.5	15.51	70.1	72.9
ABS3	1	459.5	13.68	64.8	74.5
	2	461.2	13.68	64.5	74.0
	3	459.0	13.45	64.5	74.0
	Average	459.9	13.60	64.6	74.2
ABS4	1	455.5	12.58	56.2	74.5
	2	453.3	13.04	56.5	74.5
	3	454.8	12.68	56.3	74.2
	Average	454.5	12.77	56.3	74.4
ABS5	1	424.4	12.31	51.7	75.0
	2	428.0	11.97	51.8	74.5
	3	428.3	11.95	51.8	75.0
	Average	426.9	12.08	51.8	74.8
ABS6	1	396.3	11.66	52.7	75.5
	2	395.5	11.72	52.5	75.2
	3	396.1	11.76	52.9	75.0
	Average	396.0	11.71	52.7	75.2
CPE1	1	475.3	14.25	76.2	72.0
	2	476.5	14.32	76.5	72.0
	3	477.7	14.40	76.4	72.5
	Average	476.5	14.32	76.4	72.2
CPE2	1	453.9	13.20	65.9	72.0
	2	453.9	13.18	65.4	72.0
	3	452.1	13.26	66.2	71.5
	Average	453.3	13.21	65.8	71.8
CPE3	1	423.2	11.80	58.6	72.4
	2	425.3	11.85	58.4	72.5
	3	424.4	11.90	59.2	72.8
	Average	424.3	11.85	58.7	72.6
CPE4	1	399.1	10.45	42.3	72.5
	2	401.2	10.40	42.4	72.5
	3	400.0	10.15	42.1	73.0
	Average	400.1	10.33	42.3	72.7

Table A13 Mechanical analysis data sheet of PVC compounds (repeated, continued)

Sample	Analysis No.	Tensile Strength (kg./cm.²)	Tear Strength (kg./cm.)	Hardness	HDT (°C)
CPE5	1	328.8	9.06	30.8	73.0
	2	328.5	9.10	30.7	72.5
	3	327.0	9.04	30.8	73.2
	Average	328.1	9.07	30.8	72.9
CPE6	1	292.5	8.90	14.9	74.5
	2	291.3	8.76	15.2	74.0
	3	293.4	8.80	15.3	74.0
	Average	292.4	8.82	15.1	74.2
PA1	1	516.3	10.30	70.9	71.0
	2	517.5	10.10	70.7	71.0
	3	517.2	10.40	71.6	71.2
	Average	517.0	10.27	71.1	71.1
PA2	1	504.8	10.95	71.4	71.0
	2	506.8	10.98	70.3	71.0
	3	504.6	10.82	72.2	71.0
	Average	505.4	10.92	71.3	71.0
PA3	1	510.5	13.68	72.4	71.5
	2	508.6	13.70	71.5	71.8
	3	510.2	13.54	71.6	71.5
	Average	509.8	13.64	71.8	71.6
PA4	1	535.3	13.08	71.1	72.5
	2	532.1	13.11	71.0	72.0
	3	532.6	13.04	71.3	72.0
	Average	533.3	13.08	71.1	72.2
PA5	1	530.8	12.01	71.9	72.5
	2	530.8	12.25	71.6	72.5
	3	529.5	12.10	71.8	72.6
	Average	530.4	12.12	71.8	72.5
PA6	1	508.2	9.86	71.8	74.0
	2	509.5	9.95	72.3	73.5
	3	508.6	9.90	72.1	73.2
	Average	508.8	9.90	72.1	73.6
LUB1	1	519.1	12.68	71.2	73.0
	2	519.3	12.70	70.4	72.5
	3	520.2	12.43	70.5	73.0
	Average	519.5	12.60	70.7	72.8

Table A13 Mechanical analysis data sheet of PVC compounds (repeated, continued)

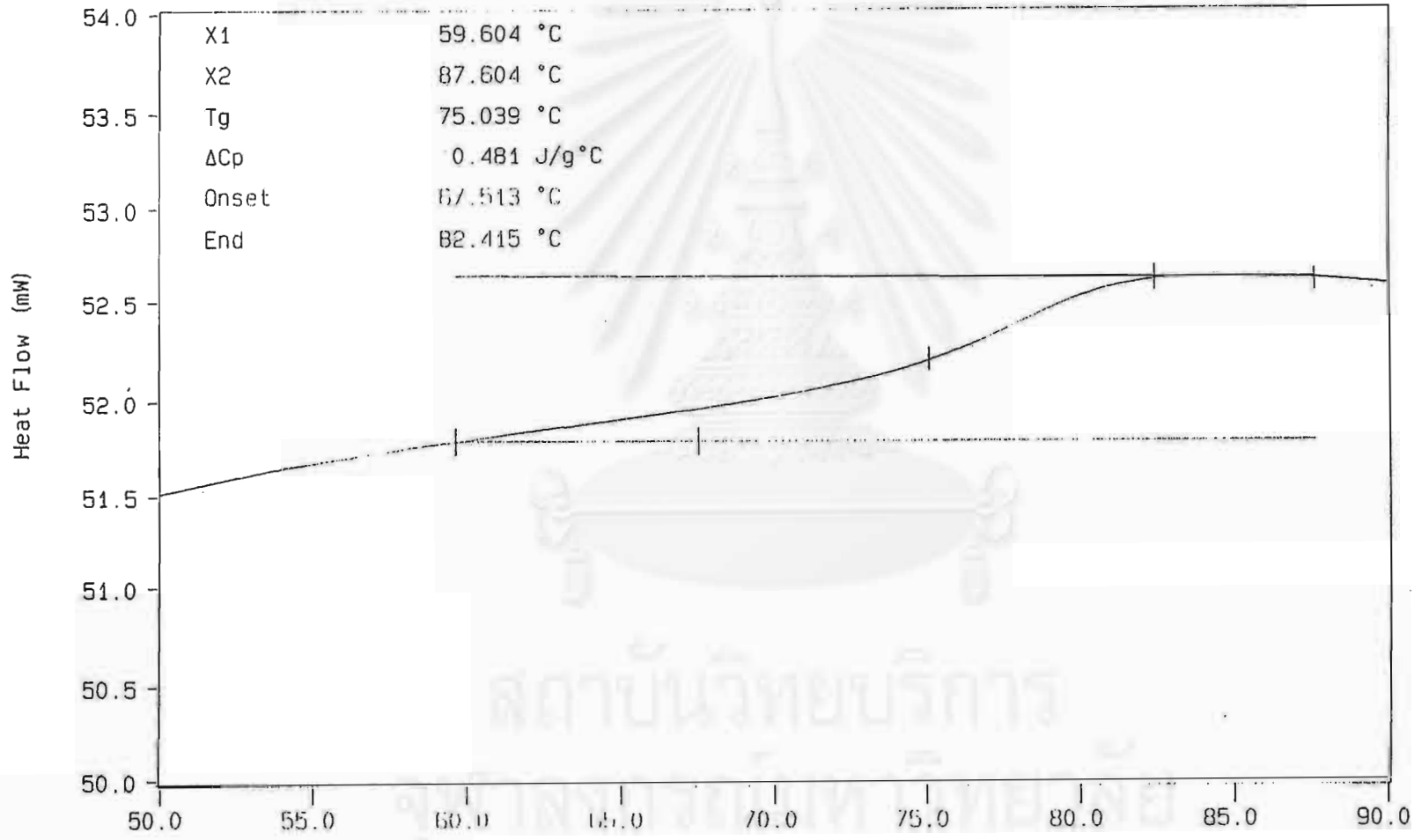| Sample	Analysis No.	Tensile Strength (kg./cm.^{2})	Tear Strength (kg./cm.)	Hardness	HDT ($^\circ$C)
LUB2	1	505.8	11.24	71.1	72.0
	2	506.8	11.30	70.8	72.5
	3	506.9	11.05	70.3	72.0
	Average	506.5	11.20	70.7	72.2
LUB3	1	529.3	11.16	72.3	72.0
	2	530.9	11.14	71.8	71.5
	3	530.8	11.30	72.1	71.5
	Average	530.3	11.20	72.1	71.7
LUB4	1	514.3	9.50	70.4	71.0
	2	514.2	9.48	70.8	71.0
	3	516.4	9.50	70.7	71.5
	Average	515.0	9.49	70.6	71.2
LUB5	1	525.1	9.55	70.6	69.5
	2	523.2	9.43	70.5	69.5
	3	523.7	9.59	71.0	69.0
	Average	524.0	9.52	70.7	69.3
LUB6	1	518.3	9.02	70.6	69.0
	2	516.5	9.01	70.7	69.8
	3	517.5	8.95	70.9	69.5
	Average	517.4	8.99	70.7	69.4
CA1	1	522.3	13.61	75.6	68.0
	2	523.9	13.65	75.6	68.0
	3	520.1	13.40	76.0	68.5
	Average	522.1	13.55	75.7	68.2
CA2	1	500.8	13.68	75.7	69.5
	2	501.8	13.85	75.8	69.0
	3	499.8	13.58	75.6	69.5
	Average	500.8	13.70	75.7	69.3
CA3	1	482.1	19.53	74.7	68.5
	2	480.8	19.40	74.5	68.5
	3	479.2	19.62	74.9	69.0
	Average	480.7	19.52	74.7	68.7
CA4	1	454.3	14.67	74.4	67.5
	2	456.8	14.45	74.6	68.0
	3	455.7	14.92	75.0	67.5
	Average	455.6	14.68	74.7	67.7

Table A13 Mechanical analysis data sheet of PVC compounds (repeated, continued)

Sample	Analysis No.	Tensile Strength (kg./cm.²)	Tear Strength (kg./cm.)	Hardness	HDT (°C)
CA5	1	443.1	14.69	74.6	68.5
	2	442.3	14.75	74.6	68.0
	3	442.1	14.65	74.4	68.0
	Average	442.5	14.70	74.5	68.2
CA6	1	424.3	12.90	74.5	70.0
	2	425.3	12.90	74.3	70.0
	3	424.5	12.80	74.5	70.5
	Average	424.7	12.87	74.4	70.2
CA7	1	415.1	11.32	69.9	69.0
	2	417.5	11.16	69.8	68.5
	3	416.1	11.20	69.8	69.0
	Average	416.2	11.23	69.8	68.8
TA1	1	514.4	10.73	69.1	70.8
	2	513.8	10.65	69.9	70.5
	3	516.8	10.53	69.7	70.0
	Average	515.0	10.64	69.6	70.4
TA2	1	543.3	12.55	73.5	72.0
	2	542.4	12.70	70.5	72.0
	3	538.1	12.73	70.2	72.5
	Average	541.3	12.66	71.4	72.2
TA3	1	559.5	11.32	71.5	72.0
	2	557.8	11.45	72.4	72.0
	3	554.9	11.42	71.8	72.0
	Average	557.4	11.40	71.9	72.0
TA4	1	582.1	9.72	72.0	73.0
	2	580.9	9.68	71.6	72.5
	3	582.2	9.64	72.8	73.0
	Average	581.7	9.68	72.1	72.8
TA5	1	594.1	6.60	76.2	72.5
	2	595.4	6.61	75.1	73.0
	3	593.3	6.43	75.6	73.0
	Average	594.3	6.55	75.6	72.8
TA6	1	609.5	6.05	78.9	75.0
	2	610.5	5.82	76.1	75.5
	3	610.8	5.94	78.6	75.0
	Average	610.3	5.94	77.9	75.2
TA7	1	641.1	5.42	79.2	75.8
	2	640.3	5.55	79.8	76.3
	3	638.1	5.60	81.1	76.0
	Average	639.8	5.52	80.0	76.0

Curve 1: DSC
File info: y13   Mon Jan 5 10:38:58 1970
Sample Weight: 10.570   mg
ABS 1

X1	59.604 °C	
X2	87.604 °C	
Tg	75.039 °C	
ΔCp	0.481 J/g°C	
Onset	67.513 °C	
End	82.415 °C	

Heat Flow (mW)

Temperature (°C)   Y

TEMP1: 10.0 C   TIME1: 0.1 min RATE1: 10.0 C/min
TEMP2: 90.0 C

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7 Series Thermal Analysis System
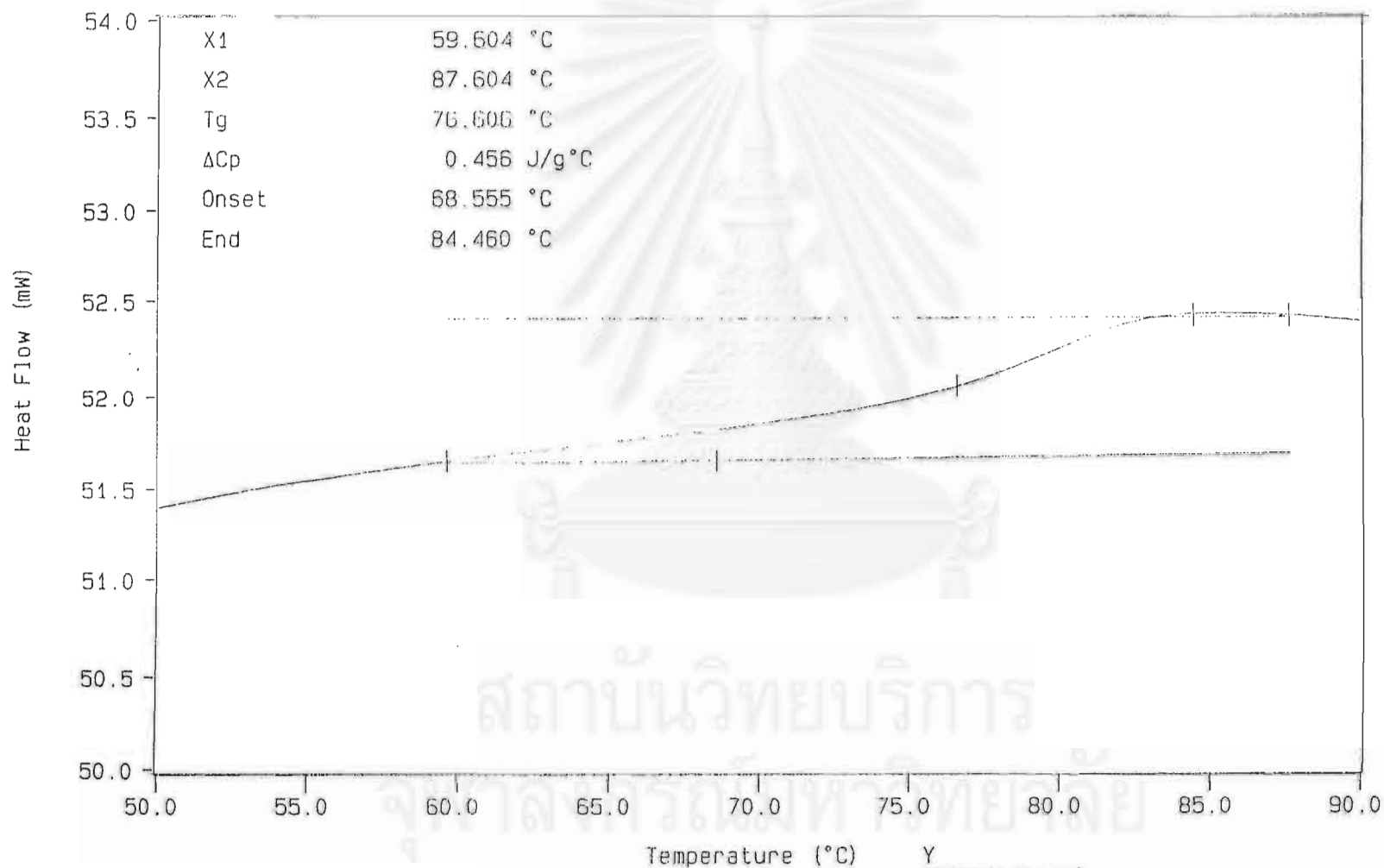Mon Jan 5 13:37:17 1970

Figure B1. DSC curve of ABS1

Curve 1: DSC
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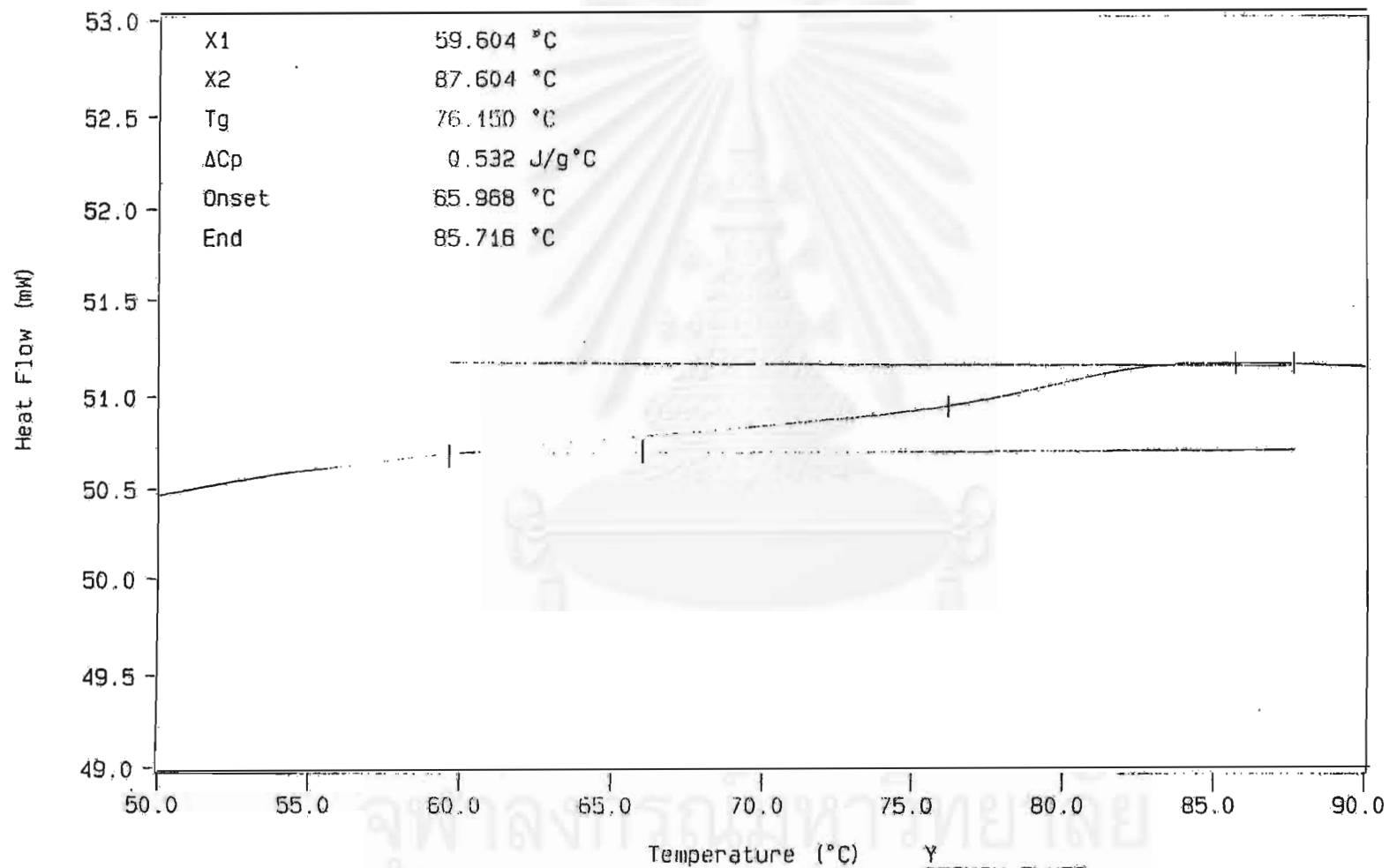Sample Weight: 9.910   mg
ABS 2

X1	59.604 °C
X2	87.604 °C
Tg	76.606 °C
ΔCp	0.456 J/g°C
Onset	68.555 °C
End	84.460 °C

TEMP1: 10.0 C   TIME1:   0.1 min RATE1:   10.0 C/min
TEMP2: 90.0 C

Y
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Mon Jan 5 13:34:37 1970

⊃ curve of ABS2

Curve 1: DSC
File info: y15   Mon Jan 5 11:21:40 1970
Sample Weight: 5.320   mg
ABS 3

Figure B3. DSC curve of ABS3

Curve 1: DSC
File info: y16   Mon Jan 5 11:45:51 1970
Sample Weight: 6.050   mg
ABS 4

X1	59.604	°C
X2	87.604	°C
Tg	76.701	°C
ΔCp	0.520	J/g°C
Onset	67.134	°C
End	85.792	°C

Heat Flow (mW)

Temperature (°C)

TEMP1: 10.0 C   TIME1:   0.1 min RATE1:   10.0 C/min

Y
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Mon Jan 5 11:24:36 1970

TEMP2: 90.0 C

Figure B4. DSC curve of ABS4

Curve 1: DSC
File info: y17   Mon Jan 5 12:16:31 1970
Sample Weight: 10.190   mg
ABS 5

X1	59.604	°C
X2	87.604	°C
Tg	76.708	°C
ΔCp	0.475	J/g°C
Onset	68.121	°C
End	85.092	°C

TEMP1: 10.0 C   TIME1:   0.1 min RATE1:   10.0 C/min
TEMP2: 90.0 C

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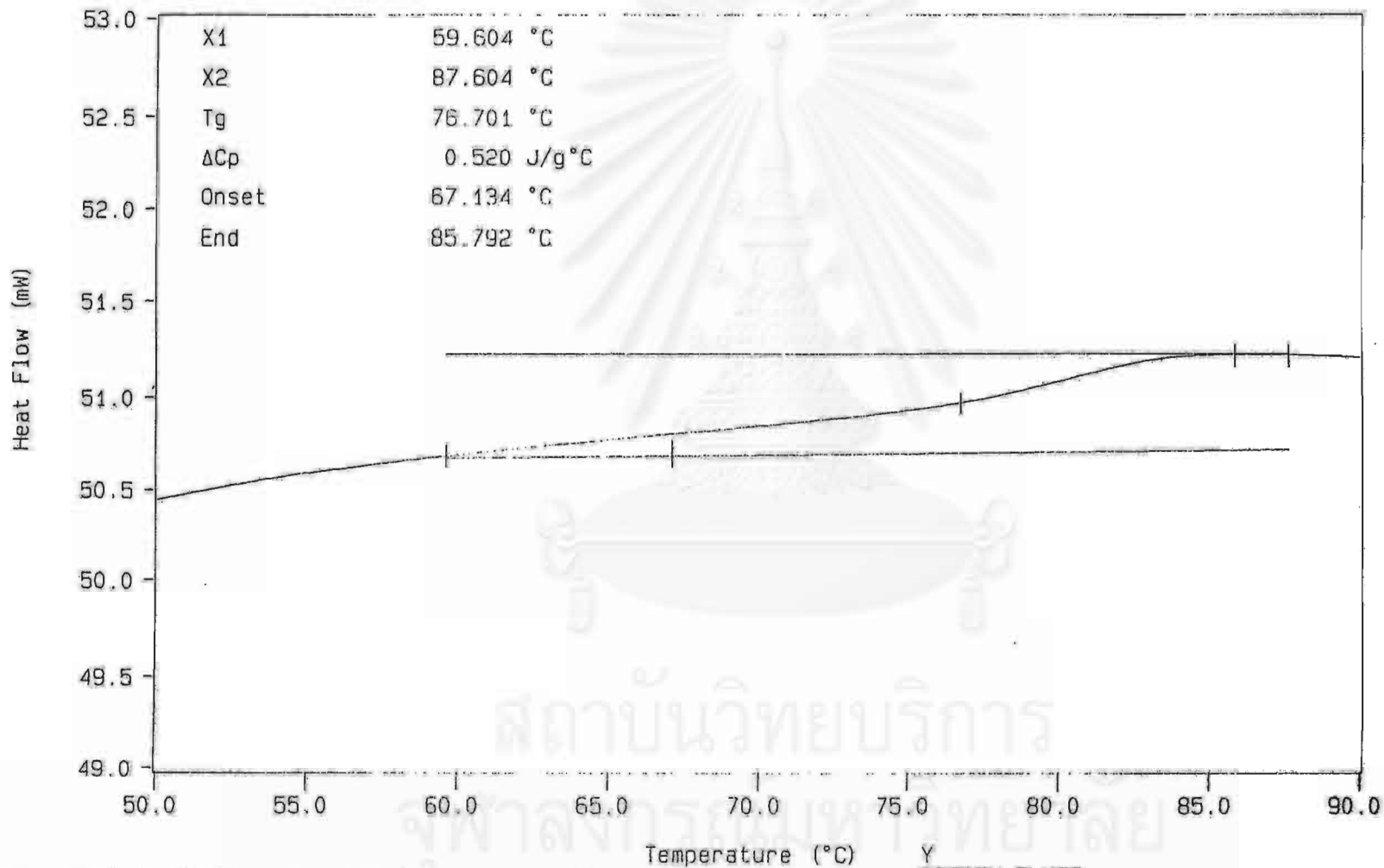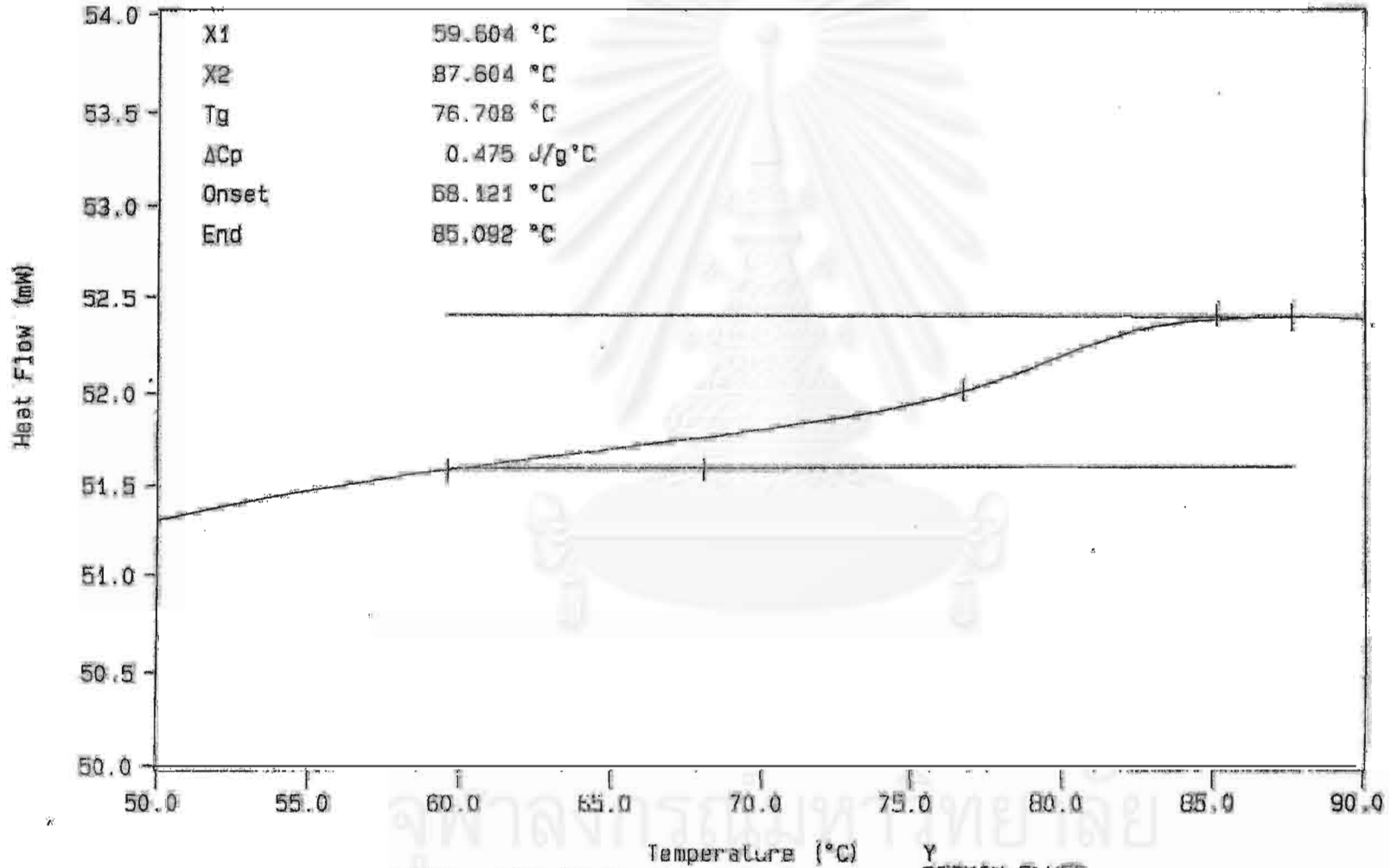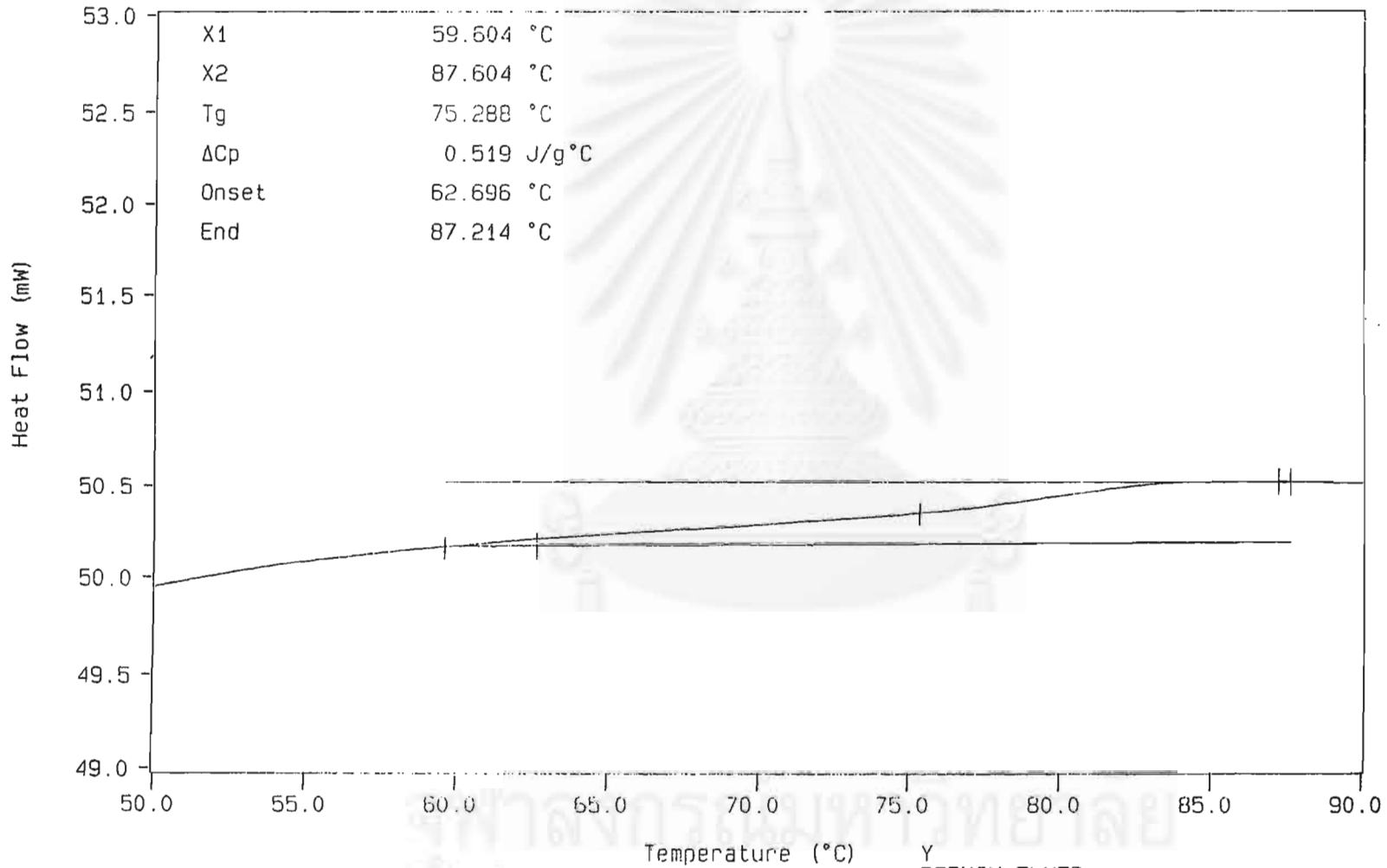Mon Jan 5 12:19:49 1970

Figure B5. DSC curve of ABS5

Curve 1: DSC
File info: qsav1   Mon Jan 5 13:06:17 1970
Sample Weight: 4.010   mg
ABS 6

Figure B6. DSC curve of ABS6

X1	59.604 °C
X2	87.604 °C
Tg	75.288 °C
ΔCp	0.519 J/g°C
Onset	62.696 °C
End	87.214 °C

TEMP1: 10.0 C   TIME1:   0.1 min RATE1:   10.0 C/min
TEMP2: 90.0 C

Y
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7 Series Thermal Analysis System
Mon Jan 5 13:12:15 1970

VITAE

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