STRUCTURE-PROPERTIES RELATIONSHIP OF HYBRID TALC/CALCIUM CARBONATE FILLED IMPACT MODIFIED PVC COMPOSITES

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SEPTEMBER 2009

ABSTRACT

The main objective of this study was to investigate and compare the mechanical properties and processability of single-filler and hybrid poly(vinyl chloride) (PVC) composites. Calcium carbonate ($CaCO_3$) was used in this study to improve the impact strength of PVC while talc was used to improve stiffness. Filler was added into PVC at a constant loading level of 30phr. SM90 showed the most optimum properties in terms of impact strength and flexural modulus among all grades of $CaCO_3$ selected for hybrid study. Tests specimens were prepared by using dry blending, two roll milling and compression moulding processes. Flexural, impact and tensile tests were then performed to determine and compare the effect of fillers on mechanical properties of PVC composites. Talc filled PVC composite showed the highest flexural modulus but the lowest impact strength. The impact strength of hybrid PVC composites gradually increased with increasing SM90 content, but the flexural modulus showed an opposite behaviour. The flexural strength and impact strength were the highest among the hybrids when the talc/SM90 weight ratio was 20:10. The distribution and dispersion of the fillers in PVC matrix were observed by using SEM. The well dispersion and interfacial adhesion of SM90 and talc particles in PVC matrix had contributed and helped in improving the stiffness and the impact strength of PVC composite. The fusion time of hybrid talc/SM90 filled PVC composite gradually increased as the talc content was gradually replaced by SM90. However, the hybrid (10phr talc: 20phr SM90) filled PVC composite showed the longest fusion time among all PVC composites. TGA, DSC and HDT tests were also carried out to investigate the thermal properties of PVC composites. The incorporation of talc and $CaCO_3$ were found to improve the thermal stability and rigidity of PVC composites.

ABSTRAK

Tujuan utama kajian ini adalah untuk mengkaji dan membandingkan sifat-sifat mekanikal dan kebolehprosesan komposit PVC dengan pengisian pengisi tunggal (talkum atau $CaCO_3$) dan pengisi hibrid talkum/$CaCO_3$. Kalsium karbonat ($CaCO_3$) dan talkum dipilih sebagai pengisi dalam kajian ini adalah disebabkan sifat kedua-dua pengisi ini berkebolehan untuk meningkatkan kekakuan dan kekuatan hentaman komposit PVC. SM90 dipilih untuk kajian hibrid PVC komposit disebabkan ia merupakan gred $CaCO_3$ yang memberikan keputusan yang paling optima dalam kekuatan hentaman dan kekakuan untuk komposit PVC. Sampel-sampel untuk kajian ini disediakan melalui pencampuran kering, penyemperitan berskru kembar dan pengacuan mampatan. Ujian-ujian lenturan, hentaman dan regangan dijalankan untuk mengkaji dan membandingkan sifat-sifat mekanikal untuk komposit PVC. Komposit talkum/PVC memberikan modulus lenturan yang paling tinggi dengan kekuatan hentaman yang paling rendah. Komposit PVC dengan pengisi hibrid talkum/SM90 menunjukkan kekuatan hentaman meningkat secara perlahan-lahan dengan peningkatan kandungan SM90 dalam komposit. Walaubagaimanapun, modulus lenturan semakin menurun dengan penggantian kandungan talkum dengan SM90 secara perlahan-lahan. Komposit PVC hibrid yang diisi dengan 10phr talkum: 20phr SM90 pula didapati memberikan modulus lenturan dan kekuatan hentaman yang paling optima berbanding dengan semua hibrid komposit yang lain. Masa gabungan didapati semakin bertambah apabila talkum diganti secara berdikit-dikit dengan SM90. Walaubagaimanapun, PVC komposit diisi dengan (10phr talc: 20phr SM90) didapati mempunyai masa gabungan yang paling panjang di kalangan semua komposit hibrid. Ujian-ujian seperti TGA, DSC dan HDT juga dijalankan untuk mengkaji sifat-sifat terma komposit PVC. Daripada keputusan ujian-ujian ini, pengisian talkum dan $CaCO_3$ didapati boleh memperbaiki kestabilan terma dan kekerasan komposit PVC.

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L/D - Aspect ratio (length per diameter)

ρ - Density

$\rho_{additives}$ - Density of additives

ρ_c - Density of PVC composites

$\rho_{f,}$ - Density of fillers

ρ_{PVC} - Density of PVC resins

ρ_w - Density of water

T_{onset} - Thermal degradation onset temperature

T_g - Glass transition temperature

$T_{g\ onset}$ - Glass transition temperature onset

v% - Volume percentage

W - Weight Fraction

$W_{additives}$ - Weight fractions of additives

W_f - Weight fractions of fillers

W_{PVC} - Weight fractions of PVC resins

$W_{additives}$ - Weight fractions of additives

wt% - Weight percentage

LIST OF ABBREVIATIONS

ABS	-	Acrylonitrile Butadiene Styrene
CB	-	Carbon Black
CPE	-	Chlorinated Polyethylene
DDS	-	Dimethyldichlorosilane (DMSC) treated nano-SiO_2
DMSC	-	Dimethyldichlorosilane
DSC	-	Differential Scanning Calorimetry
EFB	-	oil palm empty fruit bunch
FPT	-	Fusion Percolation Threshold
GCC	-	Ground calcium carbonate
HCl	-	Hydrochloride Acid
HDT	-	Heat Deflection Temperature or Heat Distortion Temperature
iPP	-	Isotactic Polypropylene
KHS	-	γ-Methylacryloxypropyl Trimethoxy Silane treated nano-SiO_2
MFI	-	Melt Flow Index
MMA	-	Methyl Methacrylate
MMT	-	Montmorillonite
NPCC	-	Nano- Precipitated calcium carbonate
OPE	-	Oxidized Polyethylene
PC100	-	Precipitated $CaCO_3$ with 1μm in particles size
PCC	-	Precipitated calcium carbonate
phr	-	Parts per hundred
PMMA	-	Polymethyl Methacrylate
PP	-	Polypropylene

PS	-	Polystyrene
PVC	-	Polyvinyl Chloride
PVC-U	-	Unplasticized- Polyvinyl Chloride
RHA	-	Rice hush ash
rpm	-	Resolution per minute
SBS	-	Poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer
SEBS	-	Block copolymer poly(styrene- *b*-ethylene-*co*- butylene-*b*-styrene)
SEBS-g-MA	-	Block copolymer poly(styrene- *b*-ethylene-*co*- butylene-*b*-styrene) grafted with maleic anhydride
SEM	-	Scanning Electron Microscopy
SEP	-	Poly(styrene-*b*-ethylene-*co*-propylene) diblock copolymer
SM90	-	Ground untreated $CaCO_3$ with 0.98μm in particles size
SP-FG	-	Ground untreated $CaCO_3$ with 1.4μm in particles size
SP-FG-C	-	Ground treated $CaCO_3$ with 1.4μm in particles size
SRBC	-	Styrene rubber block copolymer blends
TEM	-	Transmission Electron Microscopy
TGA	-	Thermogravimetric Analysis
UK	-	United Kingdom
UPVC	-	Unplasticized- Polyvinyl Chloride
UTS	-	Untreated nano-SiO_2

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CHAPTER 1

INTRODUCTION

1.1 Background of Poly(vinyl chloride) (PVC)

Poly(vinyl chloride), (PVC) is one of the largest volume commodity plastics produced in the world and is expected to continue with a good high growth rate. The earliest commercial applications of PVC utilized the flexible plasticized form (Owen, 1984). The major objective of earliest PVC commercial applications was to find synthetic substitutes for rubber, and partly also because of the greater ease of processing plasticized compositions. It started to gain commercial importance when the problems caused by poor thermal stability were overcome by development of additives (Butters, 1988). PVC has played an important role in the development of the plastics industry for the past forty years. PVC found its first industrial applications just before the Second World War started. PVC is a rigid plastic in un-plasticized state, but, in the presence of plasticizers, PVC is a flexible plastic.

PVC is used in a wide range of applications because of its combined properties of high modulus, ease of fabrication, low flammability and low cost. PVC is easy to degrade when exposed to environmental attack and suitable researches and programs is ongoing to develop the cost-effective ultra-violet stabilizers. Despite on its commercial maturity, there are many research and development programs under way to increase the understanding of the properties of PVC and improve the PVC's properties in applications.

The pristine PVC can easily degrade with increasing of the processing temperature. For this reason, the entire PVC industry is heavily dependent on the formulation technology which transforms the otherwise intractable material into a myriad of useful substances (Meister, 2002). The applications of PVC compounds are numerous and the formulation highly dependent from very flexible wire coatings to rigid, glass fiber reinforced and high modulus composites. The rigid pipe and conduit is the single largest application in the UK and Western Europe as whole. According to Owen (1984), the earliest utilizations of PVC in pressure pipe for potable water was small in small diameters, but it is common now to extrude pipe for exacting duty in diameters up to 600mm.

Many studies of fillers such as talc (Leong *et al.*, 2005; Zhou *et al.*, 2005; Sancaktar and Walker, 2004), $CaCO_3$ (Wu *et al.*, 2004; Teixeira *et al.*, 2005), clay (Zhou *et al.*, 2005) , mica, natural fibres (Jiang *et al.*, 2003; Abu Bakar, 2006) have been carried out to improve mechanical properties of PVC and reduce resins cost. The main target in the development of PVC compound by using fillers is to achieve a good combination of properties and processability at a moderate cost.

Talc and calcium carbonate are used as filler in plastics. Talc is an important reinforcing extender for plastics, particularly in polypropylene. Thermoplastic polymers are produced and consumed in large quantities. In Malaysia, Industrial Resins Malaysia (IRM) and Malayan-Electron-Chemical industry (MECI) are the only two manufacturers of PVC resins in Malaysia. They supply about 70% to 80% of the total requirement of PVC resin in Malaysia. The rest 20% to 30% of the total requirement of PVC resin in Malaysia is imported from foreign suppliers. The grades of the PVC imported are different from the resins that manufactured locally.

Generally, the local fabricators of PVC products have four options in the procurement of PVC compounds, and these options are (Yee, 2001):

- Purchase the supply of the PVC resins from IRM or MECI.
- Import the PVC resins directly from foreign suppliers.
- Obtain from other local PVC compounders which are themselves end-products manufacturers.
- In-house manufacturing.

Grades of the PVC resins normally used in the country are the PVC resins with the K value of 60, 61, 65 and 66. In Malaysia, the K-66 resin is supplied by IRM under the trade code of MH-66 and the K-65 resin is supplied by MECI under the trade code of HP-65.

However, these materials are not used alone and usually compounded with mineral fillers. Although PVC is a major commercial thermoplastic, it processability and thermal stability are inferior to other commodity plastics such as polyethylene and polystyrene. Compounding PVC with inorganic fillers such as calcium carbonate can improve these properties. Besides, the mechanical properties of these composites are strongly related to the fillers ratio. Therefore, the nano-size fillers have attracted more attention (Xie *et al.*, 2004). A test result of study conducted by Yee (2001), shown that the finer particles size of calcium carbonate is more effective in impact strength retention for impact-modified unplasticized PVC. The impact strength can also be improved by using the surface treated calcium carbonate for better dispersion and adhesion purpose in the PVC matrix.

A study conducted by Leong *et al.* (2003), shown that the talc/calcium carbonate filled polypropylene hybrid composites have fared extremely well in weathering conditions due to excellent retention of mechanical properties. Chen *et al.* (2004) claimed that various nano-scale fillers have been reported to enhance mechanical and thermal properties of polymers, such as toughness, stiffness, and heat resistance. These fillers exhibit good reinforcing effects on many polymeric matrixes due to their large aspect ratio. However, this kind of filler with a high aspect ratio does not obviously improve the toughness and sometimes even decreases it. The low aspect ratio fillers with large surface area could result a strong interfacial interaction between fillers and polymeric matrixes.

1.2 Problem Statement

In development of commodity thermoplastics it is important to achieve a good balance of mechanical properties and processability. Previous studies have shown that the addition of calcium carbonate and talc improved the stiffness of unplasticized-PVC and the finer particles size of calcium carbonate is more effective in impact strength. Talc increases the flexural modulus or stiffness of a rigid PVC formulation, but this increase in stiffness is usually accompanied by a severe decrease in impact strength. $CaCO_3$ is effective in improving impact strength of PVC without decreases the flexural modulus of PVC. Previous studies also shown that surface treated calcium carbonate improves impact strength for better dispersion and adhesion purpose in un-plasticized PVC. However, no studies have yet been reported on the effect of hybrid talc/$CaCO_3$ on mechanical and processability of PVC. It is expected the use of hybrid $CaCO_3$/talc will result in PVC composites with balance in both impact strength and stiffness.

1.3 Objective of the Study

The overall objective of this study is to investigate the effect $CaCO_3$ content on mechanical properties, processability and thermal degradation of PVC hybrid Talc/$CaCO_3$ composites.

The overall objective is sub-divided into:

- To investigate the effect of different types and size of $CaCO_3$ on mechanical properties and processability of PVC.
- To investigate the effect of talc on mechanical properties and processability of PVC.
- To investigate the effect of different ratio of talc/$CaCO_3$ on mechanical properties and processability of hybrid talc/$CaCO_3$ PVC composites.

1.4 Scopes of the Study

1. The sample preparation involved three stages, the dry blending, the two roll milling and the compression moulding.

2. The PVC blend formulations used in this research are based on the commercial PVC window frames formulations with some modifications.

3. The different grade and particles size of calcium carbonate used in this research are SP-FG (uncoated ground calcium carbonate with 1µm in particles size), SP-FG-C (coated ground calcium carbonate with 1µm in particles size), SM90 (surface treated ground calcium carbonate with 0.9µm in particles size), Precarb 100 or PC100 (precipitated calcium carbonate with 1µm in particles size) and Nano-precipitated calcium carbonate.

4. The materials used in this research are suspension homopolymer Polyvinyl chloride (PVC) with solution viscosity K-value 66, tin stabilizer (T190), calcium stearate (Sak-CS-P), stearic acid (Kortocid PH10), acrylic polymer (Kane Ace PA-20), titanium oxide (TR92) and talc with mean particles diameter of 6.3µm.

1.5 Significant of study

Based on literature review, no study has been reported on the use of talc/$CaCO_3$ as hybrid fillers in PVC matrix. Many studies (Chen, *et al.*, 2006; Sun, *et al.*, 2006; Wiebking, 2006 and Xie, *et al.*, 2001) only involved in the investigation of the mechanical properties of single filler of $CaCO_3$ or talc filled PVC composites. Many researchers focused on the mechanical, thermal, fusion properties of $CaCO_3$ filled PVC composites compared to talc-filled PVC composite.

Generally, the incorporation of inorganic particles such as talc and $CaCO_3$ into PVC matrix not only can improve the stiffness and toughness of PVC composite, but also can reduce the cost of composite. According to Wiebking (2006) and Xie, *et al.* (2001), talc can be used to enhance the stiffness and strength of PVC, whereas $CaCO_3$ can be used to increase the impact strength of PVC without reduce the stiffness. However, the addition of talc in PVC composite could decrease the impact strength of PVC. Previously, the impact modifier was used by Weibking (2006) to increase the impact strength of talc filled PVC composite. However, the use of impact modifier significantly reduced the stiffness of PVC. $CaCO_3$ is suggested to use in this research to overcome this problem. This research is to develop a PVC compounding formulation which has good balance on mechanical properties, thermal characteristics and processability of PVC.

CHAPTER 2

LITERATURE REVIEW

2.1 Poly(vinyl chloride)

2.1.1 Suspension Polymerization of Vinyl Chloride

The PVC resin used in this research is the suspension homopolymer PVC with solution viscosity k-value 66, MH66. The PVC with the grade of K-value 66 is a medium molecular weight resins for general purpose, rigid and flexible application. The properties of PVC are as shown in Table 2.1. Suspension polymerization is referred to polymerization in an aqueous system or water with a monomer as a dispersed phase and resulting in a polymer as a dispersed solid phase. The suspension polymerization is carried out by suspending the polymer as droplets with the average sizes are in between 0.0001cm to 1cm in diameter in continuous phase (Mishra and Yagci, 2005). Yamamoto *et al.* (1994) reported that PVC with various molecular weights has been prepared by suspension polymerization at 35-70°C and the tensile properties such as tensile modulus, tensile strength and elongation at break of PVC samples are dependent on the molecular weight. The suspension polymerization of vinyl chloride is dominated in the market due to technological and economic advantages (Nass *et al.*, 1986).

Table 2.1: Properties of Poly(vinyl chloride) Resin MH-66 (Mishra and Yagci, 2005).

Appearance	White Powder
Degree of Polymerization	1000±50
K-Value	66
Specific Gravity at 23^{o}C	1.4
Volatile Matter, % Max	0.5
Foreign Matter, % Max	15
Bulk Density (g/cc)	0.5±0.05
Percentage of Particle Size	0.3

2.1.2 Morphology of Poly(vinyl chloride)

The morphology of PVC is responsible for the physical properties of the polymer. The morphology of PVC depends on many factors, including on the ways of manufacturing or producing PVC resins (Yee, 2001). The PVC resins or grains are normally prepared by commercial processes are known to consist of irregularly shaped and porous granuls with their average grain size is between 90 and 200μm in diameter.

The morphology of a polymer has a significant effect on the impact behavior of the material. The orientation and the organization of fillers particles can be observed to indicate the interaction between filler particles and the PVC matrix. The distribution of filler in the PVC matrix also can be observed. Since the use of filler increased the impact strength of PVC composites, the morphology observation is very important in investigating the effects of fillers such as $CaCO_3$ in the PVC matrix due to the toughening effect of PVC matrix. As an example, a study conducted by Chen *et al* (2003), the cavities were found on the fractured surface of the nano-$CaCO_3$ filled PVC/Blendex blend composites and were occupied by the $CaCO_3$ particles. The cavitation happens during the samples being impacted. This cavitation could absorb large amounts of energy and leading to the improvement of impact strength of the composites.

2.1.3 Fusion of Poly(vinyl chloride)

The fusion study was conducted in this research to measure the processability of the PVC composites. The fusion behavior and characteristics were studied by observing the changes of the torque and temperature with time. The fusion process is highly dependent on both shear and thermal history of the polymer. According to Chen *et al.* (1995b), to achieve good mechanical properties, grain boundaries must be eliminated and the microparticles must be altered and compacted together. The fusion behavior of grains is governed by the processing method and also by the additives added, which are normally present at the grains surfaces. The distribution of the additives on the PVC powder is been suggested to influence the grain fusion (Yee, 2001).

Many researches and development have been conducted to investigate and understand the fusion mechanisms of PVC compounds (Chen *et al.*, 1995d; Abu Bakar *et al.*, 2005; Cunha Lapa *et al.*, 2002). However, most of these studies are concentrated on investigating the effect of lubricants and impact modifiers on the fusion of neat PVC compounds. Lubrication is one of the most important factors that can influence the fusion of PVC compound during processing. The fusion characteristics of PVC compound are highly dependent to the composition of lubricants. Chen *et al.*, (1995d) reported that the use of lubricants such as calcium stearate and oxidized polyethylene (OPE) in PVC compound had significantly increased the fusion time. They also carried out an investigation on the effect of chlorinated polyethylene (CPE) which is commonly used as an impact modifier in PVC. However, they also reported that the fusion time of PVC/OPE/CPE compounds was the shortest compared to PVC/CPE and PVC/OPE compounds. This might be caused by the 0.3 phr OPE and 5 phr CPE interacted and formed a powerful and viscous material which acted as a glue that allowed the PVC resins particles to fuse together easily. They also reported that the fusion time of PVC/OPE compounds was the longest. This could be reasoned that more thermal energy was needed to be absorbed by PVC/OPE compounds in order to fuse the PVC resin particles together easily. Thus, the fusion temperatures of PVC/OPE compounds were the highest and resulted in decreasing the melt viscosity of samples in Haake torque rheometer. So, the fusion torques of PVC/OPE compounds were the lowest.

Chen *et al.* (2001) reported that the fusion percolation threshold (FPT) of rigid PVC compounds were strongly dependent on the processing conditions and also the formulations of these PVC compounds. They concluded that higher processing temperature results a lower FPT and also shorter fusion time. They also suggested that a higher concentration of CPE could promote the easy fusion of PVC resin particles. The FPT of PVC/CPE compounds decreased as the concentration of chlorinated polyethylene (CPE) increased. They also found that the interaction between calcium stearate and a higher concentration of OPE in PVC/OPE compounds could fuse the PVC resin particles easily in the beginning process of fusion.

Chen *et al*. (1995d) found that the fusion characteristics of PVC blends which were prepared at low starting temperature and low rotor speed did not give apparent fusion peaks. The fusion characteristics of PVC blends which prepared at high or medium starting temperature and high or medium rotor speeds is shown in Table 2.2.

Table 2.2: Fusion Characteristics of PVC Blends at Temperature of 190°C and rotor speed of 100rpm (Chen *et al.*, 1995d).

	PVC	**PVC/OPE**	**PVC/CPE**	**PVC/CPE/ OPE**
Fusion Temperature (°C)	189.0	198.0	193.5	189.0
Fusion Time (min)	0.80	1.30	1.05	0.70
Fusion Torque (g m)	2946	2468	2645	2724

- **Mechanisms of Fusion**

There are two types of fusion mechanisms, which are comminution mechanism and CDFE mechanism. In this research study, the mechanism involves is comminution mechanism. According to Wickson (1993), the breakdown or the comminution mechanism applies only high-shear equipment such as Banbury mixers (lab and plant scale) and laboratory Brabander mixers. In this research study, the fusion behavior was conducted by using Haake Torque Rheometer.

- **Assessment of Fusion Level**

In this research, the level of fusion is an important factor to assess or determine the mechanical strength and fracture behavior of the samples. The level of fusion can be studied or observed either by monitoring the level of progression of breakdown or by noting the state of the development of a continuous molecular network through SEM examination.

In this research, the stiffness can also be used to determine the level of fusion. Wickson (1993) explained that the mechanical properties associated with stiffness increase monotonically with increasing of stiffness. These mechanical properties associated with brittle or ductile transition behavior showed a maximum versus the level of fusion. 60% fusion gives the best balance of properties.

In this research, the thermal analysis such as DSC analysis can be related to fusion study in PVC composites. Gilbert and Vyvode (1981) have reported a thermal analysis technique that can be related to fusion in PVC. They found that an endothermic peak developed in compounds was a function of prior heat history. The endothermic peak showed up on the second heating which about the annealing temperature. The thermograms could thus be related to the previous processing temperatures and thereby can also be related to the fusion of the compounds (Wickson, 1993).

2.1.4 Consumption, Application and Issue of Poly(vinyl chloride)

PVC has been manufactured commercially for past 50 years. In 1985, it is the second largest volume thermoplastics manufactured in the world (Wickson, 1993). According to Nass *et al.* (1986), the total PVC resin production in 1983 was around 37.5 billion pounds worldwide and the international consumption was 25.5 billion pounds. PVC has a current global consumption of approximately 20 million tones per annum. Yao (2007) reported that the China's PVC sector continued to develop rapidly in 2006. PVC production capacity was 12.84 million tons per year, an increase of 31% over 2005. He also reported that output of PVC was 8.238 million tons in year 2006, an increase of 26.9% over 2005.

Now days, the industries and consumers are looked for products, which will give long service with minimum maintenance, low labour cost and giving the user time for other activities. PVC with suitable additive systems will give long and safe service in actual application for many years.

According to Owen (1984), the extrusion of rigid sections other than pipes, covers a multiple of the products, but the most important are all concerned with the building construction. The application in building construction include external cladding, window frames and sills, patio doors, architraves, skirting boards and ranch fencing. The application cladding of houses with hollow or foamed sections in UK, resembling painted weather boards, but maintaining their attractive appearance without the need for costly decoration and maintenance. The single application for PVC profiles in West Germany is the construction of window frames, which has consumed about 100000tones/annum in recent years.

The insulation and sheathing of cables constituted the first important use for plasticized PVC. The PVC is not suitable for very high voltage cables but successfully used for power transmission at intermediate voltage and conduit for electrical. It has excellent fire retardant properties, give a safer working environment and the properties of low electrical conductivity.

The application of rigid pipe and conduit is the single largest application in UK and Western Europe (Owen, 1984). The building and construction sector (piping, guttering, window profiles and wall plates) makes the broadest use of PVC (Mulder and Knot, 2001). They also reported that the other applications of PVC are flooring and wall coverings, electrical cables, consumption goods, packaging, cars (bumpers and interiors), tubes and medical applications such as blood bags.

The PVC paste or plastisols are the polymer produced in the form of very fine but dense particles, which have the property of interacting with a plasticizer at ambient temperature to form a stable dispersion of much higher viscosity compared to plasticizer alone (Owen, 1984).

2.2 Additives

PVC is known of its poor thermal stability and high sensitivity toward environmental attacks. Because of its poor heat stability, it cannot be processed without additives.

2.2.1 Processing Aids

In the past, PVC was considered as worthless plastics because the required processing temperature was too close to the temperature where the degradation took place rapidly. The processing aids are added with the specific intention of changing the fusion behaviour of rigid PVC compounds. The processing aids melt more readily than PVC and cause the PVC to become a viscous mix of processing aid and melt PVC particles is formed at low temperatures. Since this occurs at lower temperatures than would be the case for PVC alone, the melt viscosity is high due to long chains of processing aid. The long chain of the processing aid not only increases the viscosity of these melt, also causing a buildup heat from the processing shear. This flow is not just particle slippage but involves a melt flow component. Butters (1982) also reported that the essential fusion occurs earlier than would be the case in the absence of processing aids. The first function is to promote the PVC powder compound into melts that can be readily processed and the second function is to alter the melt rheology of the PVC compound.

As rigid PVC grew, clear applications were developed where good dispersion of the processing aid was an important property in minimizing gel-type defects. More sophisticated processing aids were developed which consisting of two-stage core-shell acrylic compositions. These core-shell structures and compositions improved the dispersion of the processing aids in clear compounds with little change in the other desirable properties of the processing aid (Wickson, 1993).

2.2.2 Lubricants

According to Butters (1980), lubricants are often loosely divided into so-called internal which affect the material to material friction and external which affect material friction with the wall of the processing equipment. Internal lubricants are incorporated into the mass and they disrupt the intermolecular forces among the polymer chains, thus reducing the melt viscosity. If the lubricant is noticeable at the surface, or appears to have modified surface properties, this lubricant is thought to be external. In other words, external lubricants prevent the polymers from sticking to the metallic surfaces of processing equipments and reduce the surface coefficient of friction. If the observations are contradictory, it may class both ways. Dick (1987) also reported that combinations of internal and external lubricants are used to obtain an optimum between shear and conductive heating of the compound.

The processing of rigid PVC would be impossible without lubricants. Lubricants are often added only to certain grades according to the processing method required or the desired surface effects. Mostly, the lubricants are used in rigid PVC to help reduce processing temperature and prevent thermal degradation during processing. Gachter *et al.* (1993) also quoted that without lubricants, heat will be produced by the polymers intermolecular friction and polymer molecular-surface friction during processing The lubricants presently used in PVC industry are fatty acids, fatty acid amides, metallic soaps, calcium stearate, zink stearate and stearic acids.

2.2.3 Stabilizers

Poly(vinyl chloride) (PVC) is very well known for its poor and low thermal stability. Stabilizers are added to PVC for protection against thermal degradation at high processing temperature. PVC is damaged by dehydrochlorination, autoxidation and mechanochemical chain scission at elevated temperatures during processing. These degradations must be minimized as far as possible by adding stabilizers. Dick (1987) mentioned that the dehydrochlorination of PVC not only decreases the physical properties of PVC, but also can cause a change in colour because of the conjugated unsaturation which absorbs lights at different wavelengths. There are many classes and grades of stabilizer used in commercial depend on the types of application.

The grade of tin stabilizer used in this research is Thermolite T190. The following are some commonly used classes of stabilizers used today (Gatchter *et al.,* 1993).

1. Organotin Stabilizers
2. Metal Carboxylate Stabilizers
3. Lead Stabilizers
4. Other Metal-Containing Stabilizers
5. Metal-Free Stabilizers
6. Costabilizer

2.2.4 Fillers

Fillers are added to the polymers to increase the polymer bulk, reduce costs and improve the properties of the polymers. Reasonable quantities of fillers can produce specific improvements in certain mechanical or physical properties. These fillers can slightly modify the tensile strength, hardness, rigidity, viscosity and colour of the plastics. The most common fillers used in PVC compounding are carbonates, clay, silicate and talc. Filler particles come in a variety of shapes and the shape of the particle is determined by the crystal structure of the mineral. One method of the shape measurement is the aspect ratio or L/D ratio, which is the value of the largest dimension of the filler particles divided by the smallest dimension of the filler particles.

PVC fillers can be classified into two categories, which are extenders fillers and reinforcing fillers. Practically, although all of the fillers exhibit some functional property, this classification is tied to the primary reason for using filler. The stiffness and modulus of elasticity are increased to some extent by all fillers even by the spherical calcium carbonate or glass spheres. Tensile strength can only be appreciably improved by reinforcing fillers. Gachter *et al.* (1993) also noted that the disadvantages of the reinforcing fillers are mainly attributed to the generally anisotropic or direction effect of the reinforcements.

Gatchter *et al.* (1993) also mentioned that the extenders fillers can result the following changes in the properties of thermoplastics:

- Increase in density,
- Increase in modulus of elasticity, as well as in compressive and flexural strength (stiffening),
- Low shrinkage,
- Increase in hardness and improve the surface quality,
- Increase in heat deflection temperature,
- Less temperature dependence of mechanical and physical properties,

- Cost reduction.

Elias (1997) and Martin-Martinez (2005) reported the most important factors that determine the effect of the filler on the properties of the filled polymer as followed:

- Particle shape,
- Particle size distribution curve and the top cut,
- Surface energy or surface tension,
- Surface coating.

In this research study, $CaCO_3$ and talc are used as fillers to achieve balance properties in stiffness and impact strength of PVC composites. Calcium carbonates used to reduce cost and provided little effect in strength improvement. Calcium carbonates have a broad particles size range. Some precipitated calcium carbonates have a particle size of less than 0.1 micron (Yee, 2001). Xie *et al.* (2004) investigated the effect of nano-size calcium carbonate in rheological and mechanical properties of PVC compounds. They found that the optimal properties of nano-$CaCO_3$ were achieved at 5%wt. PVC is a major resin that used calcium carbonate as filler.

2.2.4.1 Calcium Carbonate

Meister (2002) quoted that the carbonate fillers cover a broad range of materials from ground limestone to highly refined calcium carbonates. Calcium carbonate also well-known fillers for plastics because of their excellent combination of low cost, the ability to be used in high loading without stiffening the PVC and high brightness. Calcium carbonate used to reduce cost and provided little effect in strength improvement. The aspect ratio of calcium carbonate particles approach more of a spheroidal shape and is considered as an extender filler rather than reinforcing filler.

2.2.4.2 Talc

Talc is a natural hydrated magnesium silicate with the formula $3MgO.4SiO_2.H_2O$ and is also the softest mineral on the mohs scale about 1. Talc is more expensive than most grades of calcium carbonates and generally poorer in colour. It is also much higher in oil absorption or poorer packing than all the costly precipitated grades of calcium carbonate. Talc can be use at low concentrations to increase flexural and tensile modulus of rigid PVC, because of its very low packing fraction. The effect of talc and $CaCO_3$ on flexural and tensile properties of PVC is shown in Table 2.3 and these data were developed by Wickson (1993). These fillers are 4 micron average equivalent spherical diameter.

The use of talc typically results in a decrease in low-temperature impact strength. When this presents a problem, it is necessary to increase the content of the impact modifier. Wickson (1993) also quoted that talc also can adversely affect thermal stability which may require an increase of stabilizer. The influence of the filler is not only dependent on the degree of the filling but on the fineness of grind and the chemical nature of the talc grades concerned. Gachter *et al.,* (1993) also explained that the fine particle types of talc show pronounced nucleating effects in partially crystalline polymers such as polypropylene.

Table 2.3: Effect of Talc and $CaCO_3$ on Flexural and Tensile Properties of Rigid PVC (Wickson, 1993).

Parameter	**Filler**		
	None	**$CaCO_3$**	**Talc**
Flexural modulus, 10^5 psi	5.2	7.6	10.7
Tensile modulus, 10^5 psi	4.4	6.7	8.0
Tensile yield strength, 10^3 psi	8.2	6.3	7.9
Tensile elongation at yield, %	4.6	4.1	3.8

2.3 Reinforcement of PVC

2.3.1 Calcium Carbonate Filler as an Impact Modifier for unplasticized-PVC

Inorganic fillers have not been effective as impact modifiers for PVC. The notch or defect sensitivity of PVC and high is normally required in un-plasticized polyvinyl chloride have precluded the use of fillers as impact modifiers. The recent development has produced finer particles size calcium carbonate that used as an impact modifier has shown the effectiveness result in un-plasticized polyvinyl chloride.

Yee (2001) reported that the main point to performance is the complete dispersion of the filler in the polymer melt. The fine particles size and the coating assist in minimizing increase in melt viscosity and processing aid in dispersion, so that there is uniform stress distribution on impact that can minimize the localization of stresses that form cracks.

2.3.2 PVC composites reinforced by $CaCO_3$ with different particle sizes and surface treatments.

A research had been done by Sun *et al.* (2005) to investigate the effects of particles size and surface treatment of $CaCO_3$ particles on the microstructure and mechanical properties of PVC composites filled $CaCO_3$. The tensile and impact strength of $CaCO_3$/PVC greatly increased with the decreasing of $CaCO_3$ particles size. The decreasing of $CaCO_3$ particles size attributed to increase the interfacial contact area and enhance interfacial adhesion between $CaCO_3$ particles and PVC matrix. Sun *et al.* (2005), quoted that when the $CaCO_3$ particles are dispersed in the PVC matrix, the particles act as the concentration of stress which leads to the formation of cracks in the PVC matrix. The cracks would be stopped effectively when the cracks propagate to the surface of $CaCO_3$ particles. If a large amount of cracks are created in the composites, which absorb the impact energy, the toughness of the composites would be improved. However, if the interfacial adhesion between the particles and matrix is too weak, the micron-cracks would propagate along the interface between the matrix and the nano-$CaCO_3$ particles and the capability of inorganic particles to terminate the crack propagation would be weakened.

Besides, Sun *et al.* (2005) also quoted that if the nano-$CaCO_3$ particles disperse unevenly in the PVC matrix, severe aggregates will occur in the composites filled with nano-$CaCO_3$ particles. This agglomeration reduces the effective amount of nano-particles which would absorb the impact energy, hence reduces the toughness of the composites. The nano-particles had a more significant toughening effect on PVC matrix than the micron in size $CaCO_3$ particles. Sun *et al.* (2005) also found that the titanium-treated nano-$CaCO_3$/PVC composites had superior tensile and impact strength compared to the untreated or sodium-stearate-treated $CaCO_3$/PVC composites. The impact strength of the titanium-treated nano-$CaCO_3$/PVC composites was reported three times higher than the pure PVC materials.

Generally, the interfacial adhesion plays a very important role in improving the tensile strength of the composites. The tensile strength of composites is influenced by the filler fraction and the interfacial adhesion between particles and matrix. Sun *et al.* (2005) also reported that with the addition of the nano-$CaCO_3$ particles, the cross-section area of composites to bear load decreased, and only a small amount of could be transferred from the matrix to inorganic particles if a weak interfacial adhesion existed between the matrix and particles. Thus, the tensile strength of the nano-$CaCO_3$/PVC composites decreased with increasing content of nano-$CaCO_3$ particles. Sun *et al.* (2005) reported that the nano-$CaCO_3$ treated with titanate could significantly increase the tensile strength of PVC composites by improving the interfacial adhesion. They also found that the composite filled untreated nano-$CaCO_3$ particles had the poorest results and relatively poor interfacial adhesion.

A study had also been carried out by Chen *et al.* (2003), to investigate the effects of nano-scale $CaCO_3$ particles on the mechanical properties ductile polymer matrices. The impact strength, flexural modulus and Vicat softening temperature of PVC and PVC/Blendex blend were significantly enhanced after addition of 0-15phr nano-$CaCO_3$. In this research, Chen *et al.* (2003) proved that the nano-$CaCO_3$ had a better toughening effect on PVC/Blendex matrix than on the PVC matrix.

Xie *et al.* (2004) reported in their study that the mechanical properties of the PVC/$CaCO_3$ nano-composites indicate that $CaCO_3$ nano-particles stiffen and toughen the PVC. At the loading level of 5wt% nano-particles $CaCO_3$, the Young's modulus, tensile yield strength, elongation at break and Charpy notched impact energy were obtained the optimal properties. According to the result of detailed examinations of failure mechanisms of impact and tensile specimens, they found that $CaCO_3$ nano-particles acted as stress concentrators leading to interface debonding or voiding and matrix deformation. These mechanisms lead to the impact toughening of the nano-composites.

Chen *et al.* (2006) had conducted a study to investigate the effects of micron-scale and nano-scale $CaCO_3$ on the fusion, thermal, and mechanical characterization of PVC/$CaCO_3$ composites. They found that the fusion time, fusion temperature, and fusion percolation threshold (FPT) of rigid PVC/$CaCO_3$ composites increase with an increase in the addition of micro-scale or nano-scale $CaCO_3$. The fusion torque of rigid PVC/$CaCO_3$ composites decreases with an increase in the addition of micro-scale or nano-scale $CaCO_3$. They also found that first thermal degradation onset temperature (T_{onset}) of PVC/$CaCO_3$ is 7.5^{o}C lower than PVC. In mechanical testing results for PVC/micron $CaCO_3$ composites with 5-15phr micron $CaCO_3$ and PVC/nano-$CaCO_3$ composites with 5-20phr nano-$CaCO_3$ were better than PVC.

Wu *et al.* (2004) had carried out an investigation to specific the effects of chlorinated polyethylene in nano-$CaCO_3$ composites of PVC on mechanical properties, morphology and rheology. A moderate toughening effect was achieved for the nano-composites and the elongation at break and Young's modulus also been increased. The TEM study showed that the nano-$CaCO_3$ particles were uniformly dispersed in the PVC matrix and a few nano-particles of agglomeration were also found. The toughening effect of the $CaCO_3$ particles on PVC could be attributed to the cavitation of the PVC matrix, which consumed tremendous fracture energy. The incorporation of CPE into the nano-$CaCO_3$ composites can improve the notched Izod impact strength of the composites.

According to these studies, the nano-particles have a more significant toughening effect on PVC matrix than the micron in size $CaCO_3$ particles. From the SEM examination in previous studies, the $CaCO_3$ nano-particles or micron in size acted as stress concentrators leading to cavitation, interface debonding or voiding and matrix deformation. These mechanisms lead to the impact toughening of the nano-composites.

2.3.3 PVC Composites Reinforced by Talc Filler

Flexural modulus or also known as stiffness is an important physical property in many rigid PVC applications. A major area of rigid PVC applications is building products, such as window frames, siding and fencing.

Wiebking (1996) found that talc can stiffen and strengthen rigid PVC with trade-off in impact strength. He also found that the trade-off in impact strength became less as the particles size of talc decreased. If the shape of talc particles is unchanged, talc still can remain the ability to increase stiffness although the particles size of talc is reduced. The ability of talc to increase stiffness depends on the shape of particles, not the size. The incorporation of talc in PVC matrix can effectively resist on bending during applied flexural stress. From the study, it is possible to increase the impact strength without reducing stiffness by simultaneous addition of impact modifier and ultrafine talc. The use of impact modifier can impart the toughness of PVC compound, while the talc recovers the stiffness that would be lost if the impact modifier was used alone.

Xie *et al.* (2001) investigated the performance of talc in PVC by coating the talc surface with polymethyl methacrylate (PMMA) by the in-situ polymerization. The objective of the research was to improve the compatibility between the fillers and polymer matrix to reach an optimum result in the mechanical and other physical properties. The monomer layer of the polymer coated on the fillers particles reduces particles surface energy as well as promotes dispersion of the particles and interfacial adhesion. The in-situ polymerization of methyl methacrylate (MMA) on the surface of the micron-sized talc was performed by using the batch and semicontinuous elmusion process. The result discovered by Xie *et al.* (2001) was the PMMA covered on the surface of talc could improve the mechanical properties of the PVC matrix composites. From this research, they also found that the smaller the size of filler is the more effective it is in improving the toughness of the PVC composite.

Wiebking (2006) had been carried out a research to increase the flexural modulus of filled PVC with the acceptable value in impact strength. In another study of Wiebking (2006) showed that the addition of talc can significantly increase the flexural modulus of a rigid PVC compound. This increase will occur at elevated temperatures up to the temperature at which the resin begins to soften. He also discovered that the addition of PMMA increased the flexural modulus at the temperatures slightly above the softening point of unmodified compound. Wiebking (2006) also found that the increase in flexural modulus was lower in precipitated calcium carbonate or PCC (low aspect ratio) filled PVC composite compared to talc (high aspect ratio) filled PVC composite.

In the same study of Weibking (2006), he also reported that the use of talc and PMMA can lower the impact strength of a rigid PVC compound. The impact strength of PVC compound can be increased by the addition of relatively high levels of acrylic impact modifier. The addition of fine PCC can also improve the impact strength of the PVC compound. The acrylic impact modifier lowers the flexural modulus of PVC compound while the fine PCC does not lower the flexural modulus of PVC compounds. In rigid PVC compounds formulation, it is covering a wide range of impact-stiffness balance can be formulated by varying the levels of talc, PCC and impact modifier in a formulation. The addition of talc to increase stiffness of PVC compound is very cost effective, even the impact modifier level has to be increased to maintain impact strength. PMMA, a polymeric additive is effective in increasing the softening point of the PVC compound. Talc is added to a formulation with PMMA to achieve the required stiffness with lower levels of additive. Good understanding in combining the impact modifier, polymeric additives, talc and fine PCC can play an excellent role in increasing the elevated temperature performance of a rigid compound.

2.3.4 PVC Composites Reinforced by Other types of Fillers

Chen *et al.* (2006) had investigated the influence of the amount of carbon black on the yield strength, tensile strength and Young's modulus of PVC/carbon black composites, respectively. They found that the yield strength, tensile strength and the Young's modulus were improved as the amount of carbon black was increased. This was because the addition of carbon black can increase the rigidity of PVC/carbon black composite and thus increase the mechanical properties such as the yield strength, tensile strength and Young's modulus.

The notched impact strength, tensile yield stress and tensile strength of nano-SiO_2/PVC composites with different surface treatments and various weight ratios were investigated by Sun *et al.* (2006). It is noted that the impact strength of pure PVC material was 7.0kJ/m^2. They found that the incorporation of UTS (untreated nano-SiO_2) had no toughening the PVC composites. However, the addition of DDS (dimethyldichlorosilane or DMSC treated nano-SiO_2) and KHS (γ-methylacryloxypropyl trimethoxy silane treated nano-SiO_2) to PVC composite significantly increased the impact strength and reaches 9.9kJ/m^2 at weight ratio of 4/100. They also found that the treated nano-SiO_2 increased the tensile strength, while the untreated nano-SiO_2 particles reduced the tensile strength of the PVC composite. This could be explained by the introduction of inorganic particles into PVC matrix would reduce the tensile yield stress of composites with increasing the content of nano-SiO_2 particles.

Sun *et al.* (2006) also quoted that the tensile yield stress of particulate filled polymer is mainly affected by the content and effective interfacial interaction, which including the effect of interfacial adhesion, particles size, aggregation and dispersion of inorganic particles in polymer matrix. The loading stress could not be effectively transferred from the matrix to particles and the tensile yield stress of composites decreased with increasing particles content. They also found that the KHS and DDS had better dispersion in PVC matrix than UTS for their hydrophobic surface and the interface could transfer more stress from PVC matrix to inorganic, thus the PVC composites filled with KHS and DDS had higher tensile yield stress than the PVC composite filled with UTS.

The mechanical properties of PVC/Na$^+$-MMT and PVC/O-MMT nanocomposites with MMT loading varying from 0 to 5wt% were performed by Chen *et al.* (2005). They found that the mechanical properties of PVC/Na$^+$-MMT and PVC/O-MMT nanocomposites with 1-5phr of MMT were better than the unfilled PVC composite. They also found that the incorporation of Na$^+$-MMT and O-MMT into PVC matrix could enhance the mechanical properties of PVC. They also reported that with 3phr MMT content, the tensile strength, yield strength and elongation at break could be increased up to 16, 16 and 128% for PVC/Na$^+$-MMT nanocomposite and up to 29, 32 and 121% for the PVC/O-MMT nanocomposite, respectively. They explained that the intercalated structure in PVC/Na$^+$-MMT and the partially intercalated and partially exfoliated structures in PVC/O-MMT enhanced the mechanical properties of PVC/MMT nanocomposite.

Partially intercalated and disordered PVC/Na$^+$-MMT nanocomposites and partially intercalated and partially exfoliated PVC/organic MMT nanocomposites were obtained via a melt blending process by Wan *et al.* (2003).The stiffness and impact strength of these nanocomposites were found to improve simultaneously compared to pristine PVC, within treatment of MMT within 0.5-3wt%. They also noted that Na$^+$-MMT content was above 5wt%, the PVC/Na$^+$-MMT nanocomposites became optically opaque but still retain good mechanical properties. For the partially intercalated and partially exfoliated PVC/organic MMT nanocomposite, the processing stability deteriorated and PVC degraded above 5wt%. They also reported that the glass relaxation transition of these nanocomposites shifted a little higher temperature compared to pristine PVC.

2.3.5 The use of Talc and $CaCO_3$ as reinforcing fillers in other polymer.

Švehlová and Polouček (1994) had carried out an investigation on mechanical properties of talc/PP composite as concentration of talc up 40wt%. They reported that Young's modulus of talc filled PP showed a linear increase with talc concentration up to double the value of unfilled polymer. They also found that yield stress and Charpy notch toughness decreased with increasing talc content below matrix level at the highest filler content. However, the composite ultimate tensile elongation and tensile impact strength decreased sharply at the lowest filler concentration. The tensile impact strength also showed a slow linear dependence with increasing content and agglomerates of talc particles.

Mechanical behaviour of neat polypropylene, 40wt% talc-filled PP and 5wt% silicate-clay filled PP nanocomposite were investigated and evaluated by Zhou *et al.* (2005). They found that the filling of 40wt% of talc particles in PP could increase the modulus and decomposition temperature, but decrease the yield strength and fatigue strength and has no effect on glass transition temperature and melt temperature. The addition of 5wt% of nano-clay could improve both modulus and yield strength by 90% and 5%, respectively. They also found that silicate clay also can increase the decomposition temperature, but has no effect on glass transition temperature and melt temperature.

Denac *et al.* (2004) had investigated and examined the structure-property relationships of isotactic polypropylene (iPP/styrenic block copolymer blends filled with talc by optical and scanning electron microscopy, wide-angle X-ray diffraction and tensile and impact strength measurement. The composites were analyzed as a function of poly(styrene-*b*-ethylene-*co*-propylene) diblock copolymer (SEP) and the poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer (SBS) content in the range from 0 to 20vol% as elastomeric components and with 12vol% of aminosilane surface-treated talc as a filler. They found that talc crystal incorporated in the iPP matrix accommodated mostly parallel to the surface of the samples and strongly affected the crystallization process of the iPP matrix. However, they also found that SBS block copolymer disoriented plane-parallel talc crystals more significantly than the SEP block copolymer. They also reported that the changes in supermolecular structure of the studied blends and composites reflected the mechanical properties. The much significantly lower modulus values for iPP/SBS/talc composites than for the iPP/SEP/talc composites could be explained by the higher disorientation degree of encapsulated talc crystals.

Denac *et al.* (2005) studied the mechanical properties of isotactic polypropylene/styrene rubber block copolymer blends (iPP/SRBC) as well as the iPP/talc/SRBC composites with 12vol% of aminosilane surface treated talc. They reported that elongation at yield of the iPP/talc/SEBS-g-MA composites and impact strength of the iPP/talc/SEBS composites showed a synergistic effect at high elastomer content of 20vol%. Higher molecular weight of thicker SEBS layers around highly oriented talc crystals and higher miscibility of SEBS than SEBS-g-MA with iPP chains seem to contribute to enormous impact strength of the iPP/talc/SEBS composites.

2.4 Reviews on Processability Studies of Filled PVC Composites.

2.4.1 Fusion Characteristics of $CaCO_3$ filled PVC Composites.

Chen *et al.* (2006) studied the fusion properties (fusion time, fusion torque and fusion temperature) of PVC/ micron-$CaCO_3$ and PVC/nano-$CaCO_3$ by using a Haake torque rheometer at 170°C and 60rpm for a blending time of 5 minutes. They reported that the fusion time of PVC/micron-$CaCO_3$ and PVC/nano-$CaCO_3$ were longer than the fusion time of PVC (without any addition of $CaCO_3$). The increase in fusion time of PVC/nano-$CaCO_3$ and PVC/micron-$CaCO_3$ was caused by the existence of fatty acid on the surface of $CaCO_3$ filler. The fatty acid on the surface of $CaCO_3$ acted like an external lubricant that can lengthen the fusion time of PVC. Chen *et al.* (2006) reported that at $CaCO_3$ content less than or equal to 10phr, the fusion time of PVC/$CaCO_3$ composites were found similar to the fusion time of PVC/nano-$CaCO_3$ composites. As the $CaCO_3$ increased to above 10phr, the fusion time of PVC/nano-$CaCO_3$ composites became significantly longer than the fusion time of PVC/ micron-$CaCO_3$ composites. The fatty acid on the surface of $CaCO_3$ acted like an external lubricant during the PVC compounding. The high amount of the fatty acid in the PVC compound caused the PVC molecule not to fuse together at the temperature of 170^{o}C and 60rpm in a blending time of 5 min. This was due to the nano-$CaCO_3$ had more surface area than micron-$CaCO_3$. Higher surface area of nano-$CaCO_3$ generated more fatty acid.

Chen *et al.* (2006) also reported that the increasing in $CaCO_3$ also increased the fusion percolation threshold (FPT) of PVC/micron-$CaCO_3$ and PVC/nano-$CaCO_3$ composites as shown in Table 2.4. The PVC/micron-$CaCO_3$ and PVC/nano-$CaCO_3$ composites showed higher fusion percolation threshold (FPT) value than the PVC compound without any addition of $CaCO_3$. The FPT of the PVC/nano-$CaCO_3$ composite was higher than the PVC/micron-$CaCO_3$ composite for the same controlled weight. The increasing in the fusion time implied that more thermal energy was required to be absorbed to fuse PVC particles together. The FPT was increased as the fusion time was increased. They also found that with an increase in the addition of micron-$CaCO_3$ or nano-$CaCO_3$ content also increased the fusion temperature of PVC/$CaCO_3$ composites. This resulted from the fact that longer fusion time needed more thermal energy to fuse the PVC particles together. The thermal energy was proportional to the fusion temperature. The fusion torque was reduced by an increase in the addition of micron-$CaCO_3$ and nano-$CaCO_3$. This was because of the increasing in fusion temperature had reduced the melt viscosity of the PVC compound.

Table 2.4: Fusion Properties (e.g. Fusion Time, Fusion Torque, Fusion Temperature and Fusion Percolation Threshold) of PVC/micron-$CaCO_3$ and PVC/nano-$CaCO_3$ composites (Chen *et al.*, 2006).

Sample	**$CaCO_3$ Content (phr)**	**Fusion time (min)**	**Fusion Torque (Nm)**	**Fusion Temperature (°C)**	**FPT (Nm)**
PVC	0	0.490	41.10	155.5	15.40
PVC/ micron-$CaCO_3$	5	0.545	37.90	157.0	15.65
	10	0.560	35.90	157.0	16.75
	15	0.725	32.65	158.5	18.55
	20	0.855	32.30	161.5	19.90
	25	1.205	30.40	165.5	23.25
PVC/nano-$CaCO_3$	5	0.510	40.95	156.5	16.30
	10	0.580	40.30	156.5	21.10
	15	1.775	34.50	165.0	29.25
	20	3.690	32.10	168.5	29.10
	25	No fusion occurred			

2.4.2 Fusion Characteristics of Rigid PVC Composites Filled with Natural Fibres

Currently, the wood-plastic composites have emerged as an important family of material engineering. Matuana and Kim (2007) had investigated the effects of wood flour contents, woods species (softwood and hardwood) and particles size on the fusion characteristics (such as fusion time, temperature, torque and energy) of rigid PVC/wood-flour composites in a rheometer. Matuana and Kim (2007) found that the surface quality of PVC/wood-flour composites was strongly dependent on the wood species used (softwood or hardwood). They also found that the presence of poor surface quality was caused by the lack of monitoring and poor control of the fusion of PVC compounds. They results showed that with an increase in charge weight can cause a drastic decrease in fusion time, fusion temperature and energy. However, it also can cause an increase in maximum fusion torque.

Matuana and Kim (2007) also found that the addition of wood flour into PVC matrix increased the fusion time, irrespective of wood species and the fusion time also increased as the amount of wood flour in the composites increased. The incorporation of wood flour into PVC resin also caused a significant increase in fusion temperature and fusion energy. Thus, it was also leading to increase fusion torque. They explained that the increase in fusion time was because of the higher heat capacity of wood which needed higher amount of energy to increase the temperature compound and fuse the compound together. The heat capacity of dried wood at processing temperature of 180^{o}C (~1.86J/gK) is greater than the heat capacity of neat PVC (0.9J/gK). They concluded that the addition of wood flour into PVC matrix delayed the resin particles to breakdown due to the higher heat capacity of wood.

The effects of EFB filler on processability of unmodified and acrylic impact modified PVC-U was investigated by Abu Bakar *et al.* (2005a). They reported that the incorporation of EFB filler decreased the fusion time of unmodified PVC-U composites. However, they also found that the fusion time remained comparatively constant with further increase in EFB to 40phr. They explained that the decrease of fusion time was due to EFB filler containing the oil palm residues and this oil caused the filler to migrate out onto the EFB filler surface and accelerated by shearing actions of mixer blades and frictional heat during the mixing process. They also reported that the fusion times increased with the filler content (more than 20phr) for the acrylic impact modified samples. However, these fusion times were still lower than the unmodified samples. They explained that the increase of EFB filler content might hinder the acrylic from functioning as a processing aid effectively. They also found that the PMMA polymer which is a processing aid also became less effective with increasing EFB filler content. The end torque value is an indication of EFB filler reduced the melt viscosity of PVC-U compound.

A processability study was conducted by Hassan and Sivaneswaran (2005) to investigate the behaviour of RHA (rice hush ash) filled ABS (Acrylonitrile Butadiene Styrene) modified PVC-U by using Brabender Torque Rheometer. Their results showed that the fusion time decreased upon the incorporation of 10phr RHA. However, with further RHA loading, the fusion time started to increase. They explained that the increase in RHA loading could hinder the processing aid from functioning effective to promote fusion. They also noted that the other reason for the increase in fusion time is the tendency of filler agglomeration increases with filler loading. This might increase the separation between PVC resin particles and result a decrease in the heat transfer throughout the PVC compound. They also found that the incorporation of RHA filler reduced the end torque of PVC-U compound. Their results also showed that the PVC compound treated with coupling agent also increased the fusion time.

2.4.3 Fusion Characteristics of PVC Composites filled with other types of Fillers

Influence of the carbon black on the fusion torque of PVC/Carbon Black (CB) composites melted in a Haake Torque Rheometer at a temperature of 170^{o}C with a rotor speed of 60rpm and a blending time of 5 minutes was investigated by Chen *et al.* (2006). They discovered that the fusion torque of PVC/CB composite was increased as the amount of CB was increased. This was because the CB particles increased the friction in blending system and resulted increase of the fusion torque when the unfused PVC/CB compound reached a void-free state in the mixer and started to melt at the interface between the compacted material and the hot metal surface. They also found that the FPT of PVC/CB composite deceased when the amount of CB increased. They explained that the CB particles can promote the friction in the system, increase the transfer of heat and shear throughout the PVC grains and then decrease the FPT of PVC/CB composite. They also found that the fusion time of PVC/CB composite was decreased as the amount of CB increased. The decrease in fusion time was caused by the promotion of friction in the system and increased the heat and shear transfer throughout the PVC grains, thus the fusion process of PVC/CB can occur more quickly.

Sun *et al.* (2006) studied the processability of nano-SiO_2 particles with different surface treatments filled PVC by melted in the Haake Torque Rheometer at the processing temperature of 170°C with a rotor speed of 60rpm. They found that the equilibrium torques of all nano-SiO_2/PVC binary composite were much higher than the pure PVC material. They also discovered that the equilibrium torque of PVC composites filled with UTS (untreated nano-SiO_2) was higher than the composites filled with DDS (dimethyldichlorosilane (DMCS) treated nano-SiO_2). The composites filled with KHS (γ-methylacryloxypropyl trimethoxy silane treated nano-SiO_2) showed the lowest equilibrium torque. They explained that increase in equilibrium torque of inorganic particles filled polymer usually caused by the adhesion of the polymer to filler and the aggregation of filler. They also found that with the decreasing of particles size, the probability of collision and friction among the inorganic particles increases, which leads to the improvement of equilibrium torque and viscosity. As the inorganic nanoparticles were introduced, the aggregation of nanoparticles occurred severely and improved the probability of the collision and fraction rapidly.

2.5 Reviews on Thermal Properties of PVC Composites

As mentioned in the processability studies, the increasing of fusion time, fusion percolation threshold (FPT) and fusion temperature of PVC/$CaCO_3$ composites were resulted by the existence of fatty acid on the surface of $CaCO_3$ filler. The existence of fatty acid on the fillers surface such as $CaCO_3$ surface would lengthen the fusion time of the PVC composite. The fatty acid acted like an external lubricant that could increase the fusion time, and the increase in fusion time would require more thermal energy to fuse the PVC particles together. Thus, it would increase the fusion temperature. To investigate the total fatty acid content on the surface of the micron- $CaCO_3$, nano-$CaCO_3$

and talc fillers, TGA was used in this research to analysis the contents of the $CaCO_3$ or talc filler and also the content all filled PVC composites. Chen *et al.* (2006) found that the thermal degradation temperature of micron-$CaCO_3$ and nano-$CaCO_3$ were about 260^0C and the contents of fatty acid on the surface of micron-$CaCO_3$ and nano-$CaCO_3$ were 1.2 and 4 wt%. They also reported that the micron-$CaCO_3$ and nano-$CaCO_3$ were degraded into calcium oxide and carbon dioxide at the temperature about 710^oC.

The TGA results of Chen *et al.* (2006) showed the effect of the addition of $CaCO_3$ on T_{onset} of the rigid PVC/micron-$CaCO_3$ and PVC/$CaCO_3$ composites. The T_{onset} of the PVC/micron-$CaCO_3$ composite was about 7.5^oC lower than the PVC compound without any addition of $CaCO_3$. This was due to the fusion level and the entanglement degree of PVC molecules were inhibited by the existence of micron-particles. The T_{onset} of the PVC/micron-$CaCO_3$ did not significantly vary with the addition of $CaCO_3$. The $CaCO_3$ particles size was more important than the addition of $CaCO_3$ content on T_{onset} of PVC/$CaCO_3$ composites. For a controlled or fixed weight of $CaCO_3$ content, the total surface area contact between the nano-$CaCO_3$ particles and PVC matrix could be more than the total surface area contact between the micron-$CaCO_3$ particles and PVC matrix. Thus, the PVC matrix was protected from the heat and the T_{onset} of PVC/nano-$CaCO_3$ was increased nearly 30% by the addition of 10phr nano-$CaCO_3$. From the conclusion of the study carried out by Chen *et al.* (2006), there were two main factors that can affect the T_{onset} of the PVC/$CaCO_3$, which were the particles size of $CaCO_3$ and the addition content of $CaCO_3$. The particles size was significantly dominated the T_{onset} of the PVC/$CaCO_3$ composite and the T_{onset} of the PVC/nano-$CaCO_3$ composite was at least 10^0C higher than the T_{onset} of the PVC/micron-$CaCO_3$ composite.

It was noted that talc has been labeled as a strong nucleating agent by Leong *et al.* (2004b) and this can be measured by using DSC. They also reported that the talc, $CaCO_3$ and kaolin have nucleating effect on PP matrix. They also found that the talc is the strongest nucleating agent while kaolin is the weakest. The composite is expected to obtain a higher modulus, dimensional stability and strength with an increase in the crystallinity of polymer matrix.

2.6 Reviews on Hybrid Fillers in Polymers Composites

2.6.1 Hybrid $CaCO_3$/Talc in Polypropylene

A research was carried out by Leong *et al.* (2004a) to investigate the mechanical and thermal properties of talc/$CaCO_3$ filled polypropylene hybrid composites. They found that most of the hybrid composites maintained certain properties, depended on the type of filler that more dominant and the individual filler itself on the properties of PP. They also found that the talc dominant hybrid composites have higher flexural and tensile modulus and modulus, whereas the $CaCO_3$ dominant hybrid composites are more deformable and tougher.

A synergistic hybridization effect was successfully achieved when the talc/$CaCO_3$ weight ratio in the PP hybrid was 15:15. In this weight ratio, the flexural strength and impact strength were the highest compared to other weight ratio of talc/$CaCO_3$ (Leong *et al.*, 2004a). The influence of talc as the main nucleating agent, the hybrid fillers showed the significant improvements in terms of the nucleating ability, and this contributed to the increase in or retention of the mechanical properties of the hybrid composites.

A research was carried out by Leong *et al.* (2005) to investigate the effects of filler treatments on the mechanical, flow, thermal and morphological properties of hybrid talc/$CaCO_3$ polypropylene composites. The treatment of stearic acid improved the filler dispersion of the composites and thus increased the MFI. This form of treatment reduces filler-matrix interactions and results decreases in composite strength and ductility. The silane treatment increases both the filler matrix and filler-filler interactions and these interactions can hinder the polymer melt flow. However, the strength of composites treated with silane was either the same or lower than the untreated composites, despite the improvement in filler-matrix interaction. Leong *et al.* (2005) reported that the titanate treatments also increased the elongation at break and MFI of all the composites and can be attributed to chain scission of the polymer matrix. The titanate-treated hybrid talc/$CaCO_3$ polypropylene composite with the filler ratio of 15:15 had superb impact strength, overshadowing the superiority of $CaCO_3$-filled PP which in its untreated form was thought to have the best impact characteristics of all.

Kim *et al.* (2004) was carried out a study research to investigate the effects of stearic acids coated talc, $CaCO_3$ and mixed talc/$CaCO_3$ particles on the rheological properties of polypropylene compounds. The stearic acids lower the interfacial force between the filler surface and the resin matrix and followed by a favorable processing. At very low shear stresses, the viscosity of the uncoated talc compounds was higher than the uncoated $CaCO_3$ compounds. At very high shear stresses, the uncoated talc compounds became lower than the uncoated $CaCO_3$ compounds. Stearic acid treated calcium carbonate particles significantly reduced the shear or dynamic viscosity. However, the talc compound did not exhibit the considerable reduction. This is implying that stearic acid is more effective on calcium carbonate filled compound than talc compounds. The viscosity of talc compound is the highest, followed by the viscosity of talc/$CaCO_3$ compound and the viscosity of $CaCO_3$ compound is the lowest.

2.6.2 Hybrid Talc/$CaCO_3$ in Polystyrene

An experimental study carried out by Kim and White (1999) to investigate the rheological properties of talc, calcium carbonate and mixed talc and calcium carbonate of polystyrene (PS). In this experimental study, the shear viscosity over a very wide range of shear rates in capillary, cone-plate and sandwich rheometers were investigated. The unaxial extensional flow characteristics were measured by a uniaxial elongational rheometer based on floating samples on a silicone oil bath. In this study, the compounds were found to absorb silicone oil. The mixed particles compounds exhibit a steady shear viscosity. The shear viscosity of the mixed talc and calcium carbonate is generally higher than the calcium carbonate compounds, but lower than the talc compounds. The 20 v% calcium carbonate and 20v% talc compound were found to have yield value in elongational flow.

2.6.3 Hybrid Wood Flour/Glass Fiber Filled PVC Composites

Jiang *et al.* (2003) added glass short fibers into poly(vinyl chloride)/wood-flour composites as reinforcement agents and investigated the effects of adding glass short fibers on the mechanical properties of PVC/wood flour composites. They found that the impact strength of PVC/wood flour/glass short fibers hybrid composites could significantly increased without losing the flexural properties by adding type L glass fibers. They also found that there was no improvement in impact strength by using type S glass fiber. Jiang *et al.* (2003) also reported that the impact strength of hybrid composites increased along with the increase of the type L glass fiber proportion in fillers at 50% PVC content level. The main failure mode of impact fracture surface of hybrid composites are wood particles and glass fiber pullout. However, they also found that the interfacial debonding was the dominant fracture mode at higher loading filler concentrations. The significant improvement in impact strength of hybrid composites was attributed to the formation of the three dimensional network glass fiber architecture between type L glass fibers and wood flour.

2.6.4 Hybrid Talc/Kaolin in Polypropylene Composite

Abu Bakar *et al.* (2007) carried out an investigation on the mechanical, flow and morphological properties of hybrid talc/kaolin filled polypropylene composites. They found that most of the hybrid composites showed a significant decrease in flow, tensile, flexural and impact properties compared to the single filler filled PP composites. However, they also found that a hybridization effect was achieved for PPT20K10 hybrid composites through the synergistic coalescence of positive characteristics from 20wt% of talc and 10wt% of kaolin of PPT20K10 hybrid composites. The T20K10 filled PP hybrid composite showed a more balance and comparable results in stiffness and strength compared to the other hybrid composites. They also reported that an aggregation of fillers was clearly seen in the PP matrix when the 10wt% of talc was replaced with kaolin, which contributed to the reduction in the mechanical properties of hybrid composites.

2.7 Impact Modified Unplasticized-PVC

Hassan and Haworth (2006) in his research on the influence of temperature to the impact properties of acrylate rubber-modified PVC has shown that all the acrylate rubber-toughened PVC blends have successfully shifted the ductile-brittle transition points to lower temperature. However, the impact modifiers were also found to differ in their efficiency to shift the ductile to brittle transition.

Yee (2001) used different sizes and types of calcium carbonate fillers were used to determine the most optimum formulation in terms of mechanical properties of modified UPVC and cost. He found that the impact-modified PVC with 20phr of 0.8µm precipitated calcium carbonate was the most optimum formulation based on the criteria.

The effects of EFB on the mechanical and thermal properties of unplasticized PVC have been investigated by Abu Bakar *et al.* (2005b). The flexural modulus increased with increasing of EFB fibre content in the PVC composites. The increasing in EFB fibre content also caused a slight increase in T_g. Abu Bakar *et al.* (2005b) reported that the restriction of segmental mobility of the polymer chains in the fibres vicinity contributed to the increase in the flexural modulus and T_g. This restriction of chains failed to improve the HDT. The agglomeration of fibres and their poor distribution in PVC matrix are the main reasons that the impact and flexural strength decreased with increasing of fibre contents.

In another study of Abu Bakar (2006) on the effect of oil palm fruit bunch-filled impact modified UPVC found that the use of EFB fibre contributed to the enhancement of stiffness, but decreased the ductility and flexural strength of the PVC-U composites. His results also have shown that the addition of acrylic and CPE impact modifier improved the toughness but reduced the flexural properties of EFB-filled composites.

The processability study of ABS impact modified PVC-U composites was conducted by Hassan and Sivaneswaran (2005) to investigate the effect of rice husk ash (RHA) fillers and coupling agents by using Brabender torque. In this study, the RHA loading increased the fusion time and the torque decreased with RHA loading in the ABS impact modified PVC. The PVC compound treated with coupling agent, LICA 12 also increased with the fusion time.

2.8 Summary for Literature Reviews

From all these previous studies, the effects of talc, $CaCO_3$ and talc/$CaCO_3$ have been studied to define the problem statement of this research study. According to Wiebking (2006), talc can improve the stiffness but decrease the impact strength of PVC. Previously, the impact modifiers were used together with talc to improve the impact strength. However, the use of impact modifiers can reduce the stiffness of PVC and not really cost effective. According to the previous studies on $CaCO_3$ filled PVC composites, $CaCO_3$ can increase the impact strength of the impact strength of PVC without any reduction of stiffness. The $CaCO_3$ is the most suitable filler to be used together with talc in the hybrid study to achieve the optimum result in the flexural properties and impact strength.

According to the previous studies in hybrid polymer, the hybrid talc/$CaCO_3$ polypropylene composite was successfully achieved a synergistic hybridization effect with the ratio of talc/$CaCO_3$ at 15:15. The finer particles size of fillers and surface treated fillers can give the better results in improving the stiffness and impact strength. From the previous studies above, the heat deflection temperature of composite is mainly influenced by the rigidity of composite. Increase in the rigidity of PVC composites could lead to increase the heat deflection temperature of composites.

From the reviews on processability studies, the incorporation of fillers, especially $CaCO_3$ could significantly increase the fusion time of PVC compound. The presence of fatty acid on the surface of $CaCO_3$ particles acted like external lubricant that can prolong the fusion time of PVC. Besides, the increase in fusion time of filled polymer is usually caused and influenced by the structure and shape of filler particles, specific surface area of filler, the interfacial adhesion of the polymer to the filler and the aggregation of filler particles (Sun *et al.,* 2006). The longer fusion time needed more thermal energy to fuse PVC particles together.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

PVC used in this study is suspension PVC with K-value 66 supplied by Industrial Resin Malaysia Sdn. Bhd. (IRM Sdn. Bhd.). The properties for suspension homopolymer (MH-66) are presented in Figure 2.1.

Five different grades of $CaCO_3$ with specifications as shown in Table 3.1 were used as fillers in this research. They are SP-FG (Ground untreated $CaCO_3$ with 1.4µm in particles size), SP-FG-C (Ground treated $CaCO_3$ with 1.4µm in particles size), SM90 (Ground untreated $CaCO_3$ with 0.98µm in particles size), PC100 (Precipitated $CaCO_3$ with 1µm in particles size) and NPCC (Nano-precipitated $CaCO_3$). The SP-FG, SP-FG-C and SM90 were supplied by Sun Mineral (M) Sdn. Bhd. while PC100 was supplied by Shaeferhonaik (M) Sdn. Bhd. The NPCC was provided by NanoMaterials Technology (NMT) Pte Ltd.

Talc with the specification as shown in Table 3.2 also used as filler in this study. Talc was supplied by Chung Chemical Sdn. Bhd.

Several additives used in this study were tin stabilizer (T190), calcium stearate (Sak-CS-P), stearic acids (Kortocid PH10), acrylic polymer (Kane Ace PA-20) and titanium dioxide (Tioxide TR92). These additives were supplied by Industrial Resins Malaysia Sdn. Bhd. A summary of all the materials used in this research is shown in Table 3.3.

Table 3.1: Specification of calcium carbonate used.

Specification	**SP-FG**	**SP-FG-C**	**SM90**	**Precarb 100**
Description	Uncoated ground $CaCO_3$ or GCC	Coated GCC	Uncoated GCC	Uncoated precipitated $CaCO_3$
Diameter at 50%, µm	1.7	1.7	0.98	1
Diameter at 98%, µm	2.98	8.0	6.7	-
Density, g/cm^3	2.7	2.7	2.7	-
Specific surface, cm^2/g	24640.56	≈8600	≈8600	-

Table 3.2: Specification of talc filler used.

Density, g/cm^3	**2.79**
Hardness, Moh's scale	**1**
Mean particles diameter , µm	**6.3**

Table 3.3: Summary of materials used.

Materials	**Types/Trade name**	**Supplier**	**Description**
1. Polymer			
Poly(vinyl chloride)	MH-66	Industrial Resins (M) Sdn. Bhd.	- K-value of 66 - powder form - white colour
2. Additives			
a. Calcium Carbonate	i. SP-FG	Sun Minerals Sdn. Bhd.	Untreated GCC
	ii. SP-FG-C		Treated GCC
	iii. SM90		Untreated GCC
	iv. Precarb 100	Schaeferhonaik (M) Sdn.Bhd.	Untreated Precipitated $CaCO_3$
	v. NPCC-201	NanoMaterials Technology (NMT) Ptd Ltd, Singapore.	Treated Precipitated $CaCO_3$
b. Talc	-	Chung Sdn Bhd-	Untreated Talc
c. Tin Stabilizer	Thermolite 190	IRM Sdn. Bhd.	-Octyltin thioester -Liquid form
d. Internal Lubricant	Sak-CS-P	IRM Sdn. Bhd.	-Calcium Stearate
e. External Lubricant	Kortacid PH10	IRM Sdn. Bhd.	-Stearic Acids
d. Processing Aid	Kane Ace PA-20	IRM Sdn. Bhd.	-acrylic polymer
g. Pigment	Tioxide TR92	IRM Sdn. Bhd.	-Titanium Dioxide

3.2 PVC Blend Formulations

The PVC blend formulations used in this research were based on the commercial PVC window frames formulations with some modifications. The PVC blend formulations were shown in Tables 3.4 to 3.6. The contents of the fillers were varied according to the commercial loading level. Table 3.4 was used to find out the type of $CaCO_3$ that gives the highest impact strength and flexural modulus. Table 3.5 was used to find out the talc/$CaCO_3$ ratio that gives the most optimal properties in impact strength and flexural modulus.

Table 3.4: PVC Blend Formulation 1.

Ingredient	**Compound Formulations, parts**				
Types of fillers	**SP-FG** 30	**SP-FG-C** 30	**SM90** 30	**PC100** 30	**Talc** 30
Polyvinyl chloride, PVC (Resin)	100	100	100	100	100
Tin Stabilizer (Stabilizer)	2	2	2	2	2
Calcium Stearate (Internal Lubricant)	0.5	0.5	0.5	0.5	0.5
Stearic Acid (External Lubricant)	0.6	0.6	0.6	0.6	0.6
Titanium Dioxide, TiO_2 (Pigment)	4	4	4	4	4
Acrylic Polymer (Processing Aids)	1.5	1.5	1.5	1.5	1.5

Table 3.5: PVC Blend Formulation 2

Ingredient		Compound Formulations, parts						
Polyvinyl chloride, PVC (Resin)		100	100	100	100	100	100	100
Filler	Talc	0	5	10	15	20	25	30
	Calcium Carbonate (SM90)	30	25	20	15	10	5	0
Tin Stabilizer (Stabilizer)		2	2	2	2	2	2	2
Calcium Stearate (Internal Lubricant)		0.5	0.5	0.5	0.5	0.5	0.5	0.5
Stearic Acid (External Lubricant)		0.6	0.6	0.6	0.6	0.6	0.6	0.6
Titanium Dioxide, TiO_2 (Pigment)		4	4	4	4	4	4	4
Acrylic Polymer (Processing Aids)		1.5	1.5	1.5	1.5	1.5	1.5	1.5

3.3 Methodology

3.3.1 Preparation of Hybrid Talc/Calcium Carbonate Filled PVC

Preparation process of talc/calcium carbonate filled PVC sample involved the dry blending, followed by two roll milling and lastly compression molding.

3.3.1.1 Dry Blending

The PVC resin and additives were blended by using a high speed laboratory mixer to homogenize the formulation. Dry blend of the PVC compound consisted of dispersing as uniformly as possible the powdered ingredients. The mixing time of the dry blending process was 5 minutes with the rotor speed of mixing was 50rpm.

3.3.1.2 Two Roll Milling

After dry blending of the PVC compound formulations, the dry blends of the PVC powder and additives were melted and sheeted on a two roll mill machine (as shown in Figure 3.1) under the operating conditions as shown in Table 3.7. The milling was continued for 5 minutes after the fusion of PVC.

Table 3.6: The Operating Conditions of Two Roll Milling

Material Quantity, g	217.2±50
Roll Time, minutes	5 to 7
The temperature of the front roll, ^{o}C	180±5
The temperature of the back roll, ^{o}C	180±5

Figure 3.1: The two milling machine used in melting the PVC dry blends.

3.3.1.3 Compression Molding

The sheets of compounded samples were cut to two rectangular sizes with the parameter of 12.40cm x 1.2cm and 6.2cm x 1.2cm. The samples with the parameters of 12.40cm x 1.2cm were used to prepare the samples of flexural testing and the samples with the size parameter of 6.2cm x 1.2cm were used to prepare the samples for Izod impact testing. Two moulds are specially designed and fabricated for compression molding of samples. The first plate mould was used to prepare the flexural testing samples, as shown in Figure 3.2. The second plate mould was used to prepare the samples that used in notched impact test, as shown in Figure 3.3. The hot press process was firstly preheating the samples at 190^{o}C for 8 minutes, followed by compressing at the same temperature for another 8 minutes and lastly cooling down to the room temperature under pressure. The moulded samples were removed from the mould and then cut the test shape specimen.

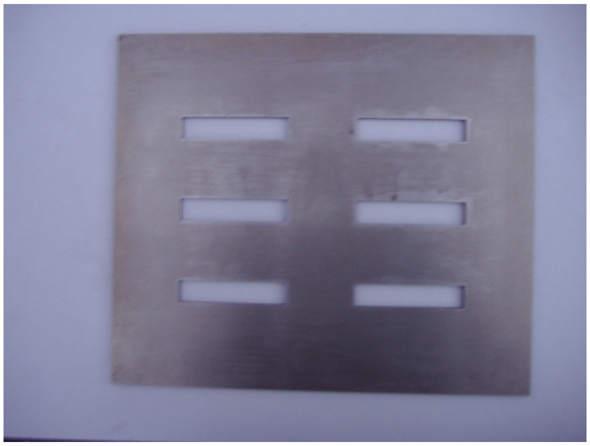


Figure 3.2: The plate mould used to prepare the Izod impact testing samples.

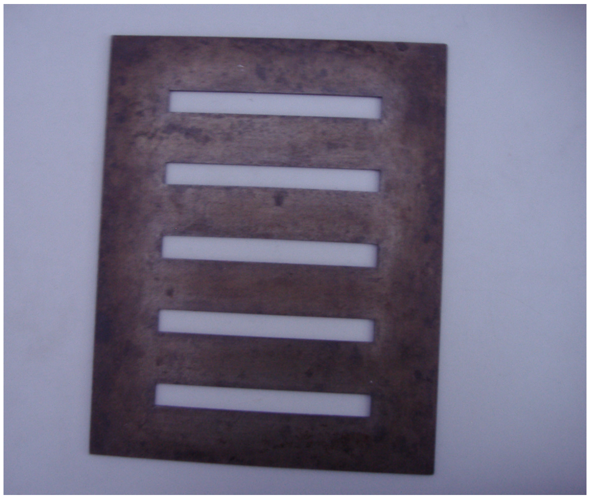


Figure 3.3: The plate mould used to prepare the samples of flexural testing.

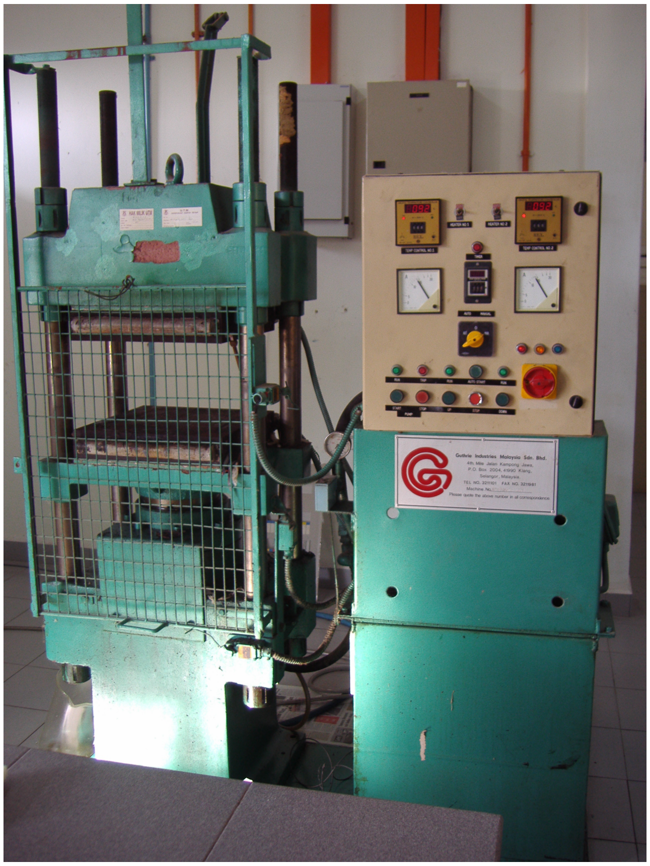


Figure 3.4: The hot press machine for compression moulding samples for flexural, Izod impact and tensile tests.

3.3.2 Izod Impact Test

The notch Izod impact strength was measured under the ASTM D256-93 standard test method. The specimens of Izod impact were notched with a 45^{o}C angle and 2.5mm depth with an Automatic Notcher Machine as shown in Figure 3.5. The Izod tests were carried out at room temperature. The purpose of this testing was to determine the pendulum impact resistance of notched specimen of plastic. The thickness, of each sample was determined and the impact strength reported was the average of ten specimens.

Figure 3.5: The Automatic Notched Machine used to notch the specimens for Izod impact test.

3.3.3 Flexural Test

The flexural test was conducted according to the ASTM D790-86 standard test method by using the Instron machine model 5567. The samples were tested at crosshead speed of 3mm/min and the support span for the flexural testing is 50mm. The results of flexural strength and flexural modulus were the average of ten specimens.

3.3.4 Tensile Test

The tensile test was carried out by using the Instron machine model 5567 under the ASTM D 638. The samples were tested under a crosshead speed of 5mm/min. The results of tensile strength and Young's modulus were the average of eight specimens.

3.3.5 Scanning Electron Microscopy Analysis

The morphologies of the fracture surface of all samples were observed in a JEOL model JSM-6301F SEM. The samples were immersed into liquid nitrogen for 45 minutes. The samples were brittle after immersion of liquid nitrogen, and could be easily fractured by using a spanner. The fractured surface samples were cut to a smaller portion to mount on the copper stub. The samples were then coated with a thin layer of gold before scanning electron microscopy (SEM) examination.

3.3.6 Thermogravimetric Analysis

A Perkin Elmer-TGA 7 was the thermogravimetric analyzer was used to analysis the thermal characteristics of the samples. The samples were firstly placed in an open platinum sample pan. After that, the samples were scanned from temperature 50^{o}C to 700^{o}C at a heating rate of 10^{o}C/min under a nitrogen environment. The thermal degradation onset temperature and the thermal degradation weight loss of samples were recorded and analyzed.

3.3.7 Processability Study

The processability of the dry blended sample was studied by determining the fusion characteristics. The dry blended sample was placed in the mixing chamber of a Haake Torque Rheometer through a loading chute. After the dry blended sample had been loaded, a 5kg weight-piston was immediately inserted in place. Then, this piston was pressed gently to force all dry blended samples completely into the mixing chamber to achieve the best reproducibility and comparability of the test result. The dry blended samples were melted and mixed at a constant rotor speed of 45rpm and at mixer temperature of 180^{o}C.

3.3.8 Heat Deflection Temperature Test

The heat deflection temperature test was carried out by using Toyo-Seiki HDT S-3 tester under the ASTM D 648. The standard dimension of the samples used in this testing was 125 x 13 x $3mm^{3}$. The samples were immersed into a heated bath of silicone oil under the flexural load of 1.2kg. The heating rate was set at 2 ± 0.2^{o}C/min. The temperature of the silicone oil was measured when the deflection of samples reached 0.250mm. The measured temperature was recorded as the deflection temperature under flexural load of the test sample. The heat deflection temperature values reported in this test were the average of three specimens.

3.3.8 Determination of Density

The densities of the samples were determined according to the ASTM D 792 water displacement method (method A) with the following equation:

$$\rho = [W_1/(W_1-W_2)]\,\rho_w$$

Where W_1 and W_2 are the sample weights in air and water, respectively, and ρ_w is the density of water.

The sample weights in air and in water were determined by using Mettler Toledo Analytical Balance Model Ax201glass pyknometer. The theoretical density of PVC composites, ρ_c was calculated using the following equation:

$$\rho_c = 1/\{(W_f/\rho_f)+(W_{PVC}/\rho_{PVC})+(W_{additives}/\rho_{additives})\}$$

Where, W_f, W_{PVC} and $W_{additives}$ are weight fractions of filler, PVC resin and additives in composites, respectively. ρ_f, ρ_{PVC} and $\rho_{additives}$ refer to the density of filler, PVC resin and additives, respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Mechanical Properties

4.1.1 Effect of Different Types of Fillers and Particles Size

4.1.1.1 Flexural Strength

Figure 4.1 illustrates the effect of fillers on the flexural strength of PVC composites. It can be seen that the incorporation of all types of fillers into PVC composites decreased the flexural strength of PVC composites. It is interesting to note that the flexural strength of talc filled PVC composite was significantly higher than all $CaCO_3$ filled PVC composites. The reduction for the talc filled composites was only 4 %, whereas the reduction for the $CaCO_3$ filled composites ranges between 10 to 20 %. The high aspect ratio of talc particles in PVC composite was the factor that contributed to the relatively high flexural strength of the talc filled composite compared to the $CaCO_3$ filled composites. It is widely reported that the aspect ratio of talc was much higher than the aspect ratio of $CaCO_3$ (Leong *et al.*, 2004a and Wiebking, 2006). The average aspect ratio of talc particles was measured and found to have an average value of 8 as shown in Section 4.2. This revealed that the aspect ratio of talc was much higher than $CaCO_3$. Talc is a reinforcing filler because of its platy nature with high aspect ratio and able to orient to the polymer flow during processing. Although talc particles have higher aspect ratio than $CaCO_3$, the talc particles are small and short enough and would not be easily breakdown into shorter particles like short fiber during processing. The high aspect ratio of talc increases the wettability of the filler by the PVC matrix, thus increasing the interaction between the filler and matrix. The increased filler-matrix interaction also enables higher stress to be transferred from the matrix to the filler during external loading. The reason for the relatively lower flexural strength of $CaCO_3$ filled PVC composite is the lower aspect ratio of $CaCO_3$ hence poor interaction between the filler and PVC matrix. In addition to that, formation of cavities could be another possible reason for poor flexural strength.

Leong *et al.* (2004a) also reported that the flexural strength of $CaCO_3$ filled PP composites was lower than the unfilled PP which is consistent with the present study. However the talc filled PP was slightly higher than the unfilled PP. The PC100 filled PVC composite showed the highest flexural strength among all $CaCO_3$ filled PVC composite. PC100 is a precipitated $CaCO_3$ with fine particles and a very narrow particles size distribution in comparison to ground $CaCO_3$. This shows that uniformity in filler size is important to produce strong PVC composites. It is also noted that SP-FG-C filled PVC composite has a higher flexural strength values than SP-FG filled composites. This maybe due to the surface coating of SP-FG-C reduces particle-particle interaction and this leads to better particle dispersion in PVC matrix.

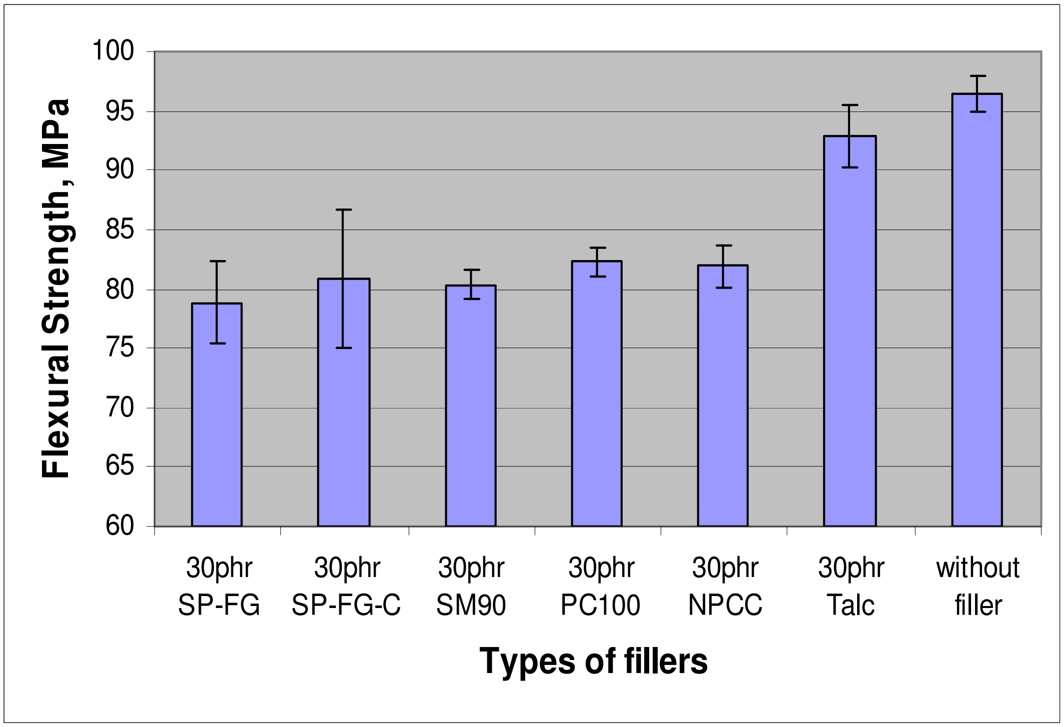


Figure 4.1: Effect of different types of fillers on flexural strength of PVC composites.

4.1.1.2 Flexural Modulus

Figure 4.2 shows that the incorporation of talc and all types of $CaCO_3$ improved the flexural modulus of the PVC composite. The flexural modulus of talc filled PVC composite was significantly higher than all types of $CaCO_3$ filled PVC composites. The SM90 filled PVC composite showed the highest flexural modulus among all types of $CaCO_3$. The flexural modulus results were similar to the study reported by Wiebking (2006). He reported that talc can both stiffen and strengthen rigid PVC. However, he also found that $CaCO_3$ is not as effective as talc in increasing the flexural modulus of PVC composite. This could be explained by the aspect ratio of talc particles was much higher than the aspect ratio of $CaCO_3$ particles. According to Abu Bakar *et al.* (2007) and Leong *et al.* (2004b), the higher enhancement in stiffness observed in platy talc could be attributed to the high aspect ratio and particles orientation of talc particles in PVC matrix. The talc particles were oriented parallel to each other in PVC matrix (as mentioned in Section 4.2 on SEM study) and the orientation of talc particles was the result of the high aspect ratio of talc particles and the motion of talc in a viscous melt during two roll milling. The platy talc particles in PVC matrix improved the flexural modulus of PVC composite by resist the bending during the application of stress in flexural tests.

It is also interesting to note that the difference between flexural modulus of SP-FG and SP-FG-C filled PVC composites were very small. However, the flexural modulus of SP-FG-C filled PVC composite also showed a very high standard deviation compared to all $CaCO_3$ filled PVC composites. This might be caused by the flexural samples of SP-FG-C filled PVC were not properly melted and molded during compression moulding. Some of these samples still remained the compounded sheets structure, thus created a big variation during performing the flexural test. The SP-FG-C filled PVC composite could be considered to have high flexural modulus. This also indicates that the surface coating of SP-FG-C particles could effectively improve the flexural modulus of PVC composite. According to Wu *et al.* (2004), the PVC composites gave higher performance in stiffness with the addition of $CaCO_3$, which could be attributable to the improvement of rigidity of PVC composites. From Figure 4.2, the addition of all $CaCO_3$ into PVC matrix evidently increased the flexural modulus except NPCC filled PVC composite. The poor flexural modulus result of NPCC filled PVC composite might be attributed to agglomeration of NPCC in PVC matrix, which could reduce the resistance on bending (as shown in Figure 4.17).

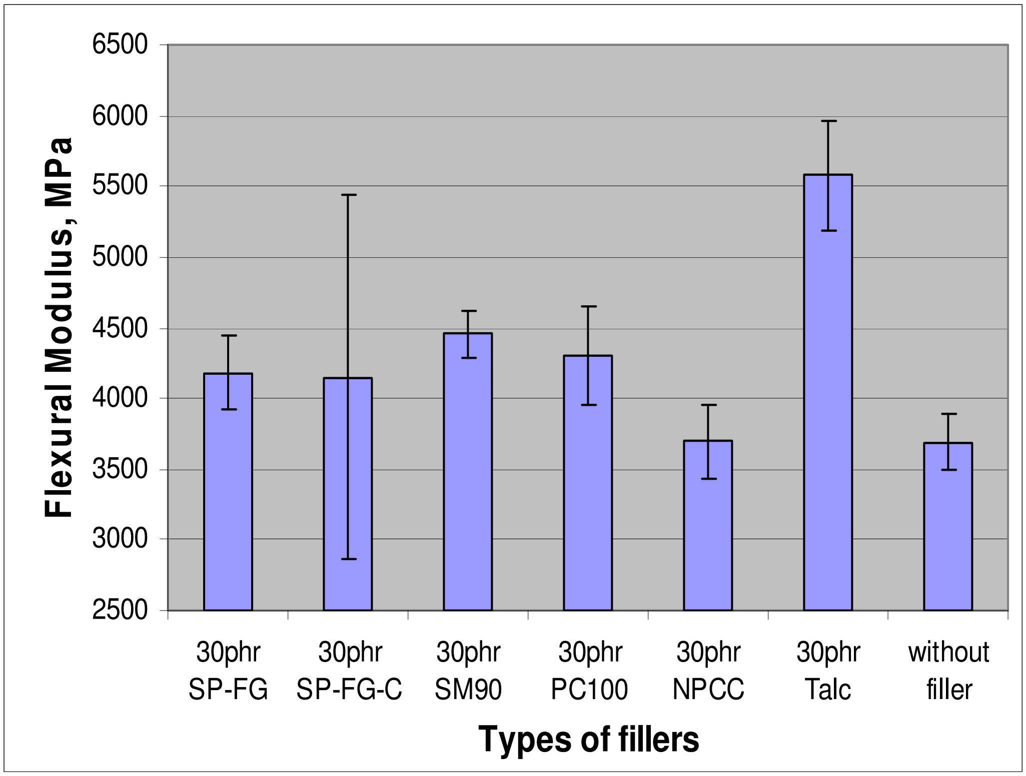


Figure 4.2: Effect of different types of fillers on flexural modulus of PVC composites.

4.1.1.3 Impact Strength

Figure 4.3 shows the impact strength of the unfilled PVC composite and PVC composites filled with different types of fillers. The incorporation of $CaCO_3$ (especially SM90 and PC100) significantly improved the impact strength of PVC composite. The SM90 filled PVC composite showed the highest impact strength among all filled PVC composites. This was due to SM90 having the finest particles size (0.98µm) compared to other types of $CaCO_3$. The particles size of filler was the main factor in increasing impact strength. Sun *et al.* (2005) reported that the finer particles size of $CaCO_3$ could result a great increase in the specific area of filler particles, which lead to increase the interfacial contact area between the filler and PVC matrix. Wu *et al.* (2004) reported that the micron $CaCO_3$ can resist the propagation of the crack, so the primary crack had to bend between the neighboring particles. The finer particles of SM90 led to more particles in PVC matrix which can resist the propagation of the crack. Besides, the good interfacial adhesion between $CaCO_3$ particles and PVC matrix also can prevent cracks from propagating along the interface between the matrix and the $CaCO_3$ particles. The capability of SM90 to terminate the crack propagation would be improved. The SM90 filled PVC composite was found to have higher standard deviation compared to the others filled PVC composites. This was attributed to the skin formed during the molding of the specimens, which could withstand the impact stress applied to the specimens.

The PC100 filled PVC composite showed the second highest impact strength. This was because of the PC100 had narrower particles size distribution which led to better adhesion with the PVC matrix and resulting in a more effective crack propagation resistance (Sun *et al.,* 2005). The impact strength of SP-FG-C filled PVC composite was slightly higher than impact strength of SP-FG filled PVC composite. This shows that the surface coating of SP-FG-C improved the interfacial adhesion between the particles and PVC matrix. The particles size of SP-FG and SP-FG-C are bigger than PC100 and SM90, they had fewer effective particles that can prevent the cracks propagating.

The NPCC filled PVC composite showed the lowest impact strength among the $CaCO_3$ filled PVC composites. Sun *et al.* (2005) reported that the nano-$CaCO_3$ was better than micron-$CaCO_3$ in improving impact strength of PVC. However, present study shows that the impact strength result of NPCC filled PVC composites is poorer than micron-size $CaCO_3$ filled PVC. Wu *et al.* (2004) explained that the nano-sized $CaCO_3$ might not be as effective as micron-sized $CaCO_3$ as in resisting the crack propagation. According to Sun *et al.* (2005), the nano-$CaCO_3$ filler particles dispersed into the PVC matrix acted as the concentration of stress which led to cracks formation in the PVC matrix. When the cracks propagated to the surface of particles, the cracks could be effectively stopped by the particles. If large amount of cracks are created in the PVC matrix, these cracks could absorb the impact energy and thus improved the toughness of the PVC composites. However, Wu *et al.* (2004) reported that the toughening effect of nano-$CaCO_3$ particles on PVC could be contributed to another mechanism. According to this mechanism, the nano-$CaCO_3$ could act as stress concentration sites, which could promote cavitation at the particles-PVC matrix boundaries during loading. The cavitation could release the plastic constraints and trigger mass plastic deformation of the matrix, leading to the enhancement of impact strength of nano-$CaCO_3$ filled PVC composites.

The weakening effect on the impact strength of PVC composites by formation of NPCC agglomerates in this study might be caused by the unevenly dispersion of NPCC in the PVC matrix (refer to Figure 4.17 in Section 4.2). The particles of NPCC dispersed unevenly in the PVC matrix and led to the occurrence of severe NPCC aggregates in the PVC matrix. The agglomeration of NPCC reduced the effective number of nano-particles which would absorb the impact strength (Sun *et al.,* 2005). Because of the weak interfacial adhesion between NPCC particles or aggregates and PVC matrix, the cracks would propagate along the interface between the matrix and the NPCC particles. Thus, the ability of NPCC to terminate the crack propagation would be weakened.

The talc filled PVC composite showed the lowest impact strength of PVC composite. This is consistent with previous study by Wiebking (2006) reported that talc can produce poor impact performance to a rigid PVC formulation. For talc filled PVC composite, the high aspect ratio of talc particles caused the talc particles to be orientated parallel with each others throughout the PVC composite. The high aspect ratio and the orientation of talc particles increase the resistance of the local plastic deformation of PVC matrix, thus making the polymer matrix become more brittle as discussed by Abu Bakar, *et al.* (2007) in their study. They also mentioned that the crack propagation in talc filled composite is very fast because of the talc filled composite is lacking the ability to absorb the impact energy through plastic deformation.

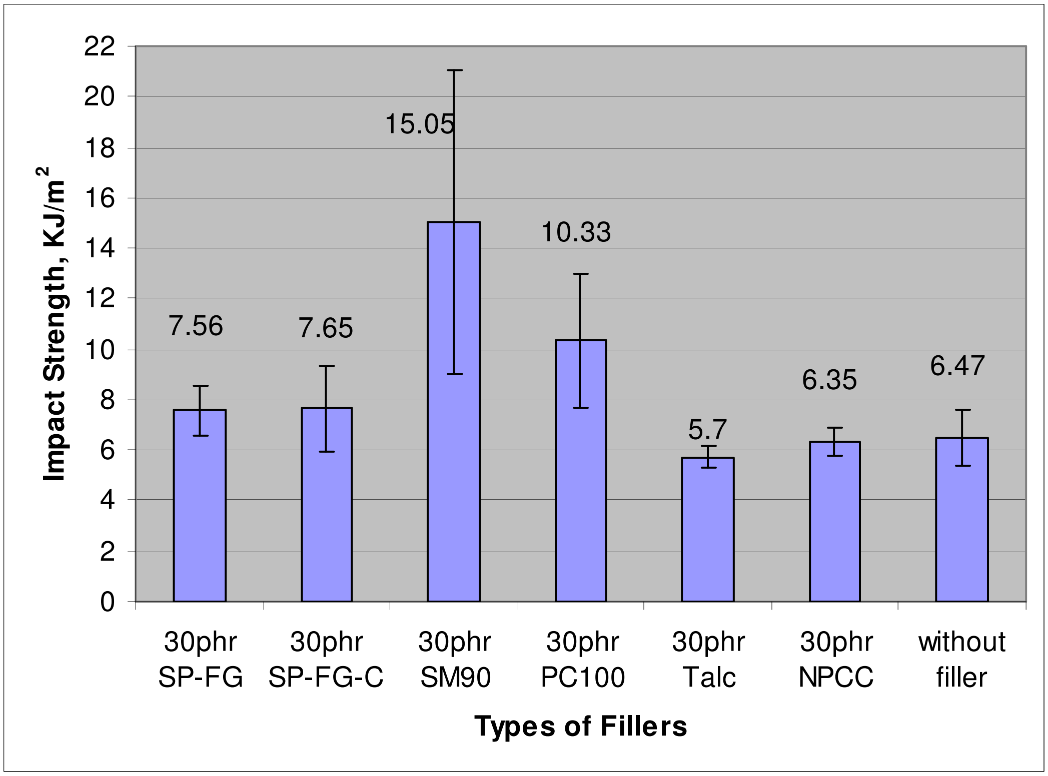


Figure 4.3: Effect of different types of fillers on impact strength of PVC composites.

4.1.2 Overall Discussion on flexural modulus and impact strength

The selection of the types of $CaCO_3$ for the hybrid fillers study was based upon the type of $CaCO_3$ which can give the optimum properties in terms of impact strength and flexural modulus. From Figure 4.4, talc filled PVC composite showed higher flexural modulus but lower impact strength compared to all $CaCO_3$ filled PVC composites. Talc filler was selected to the hybrid study due to its ability that can highly increase the flexural modulus of PVC composite. However, the addition of talc filler also can lower the impact strength of PVC composite. To overcome this problem, the types of $CaCO_3$ which can provide the PVC composite with the optimum properties in both impact strength and flexural modulus was selected to the hybrid study. SM90 was selected for the hybrid study due to its highest impact strength and flexural modulus compared to all types of $CaCO_3$ as shown in Figure 4.4.

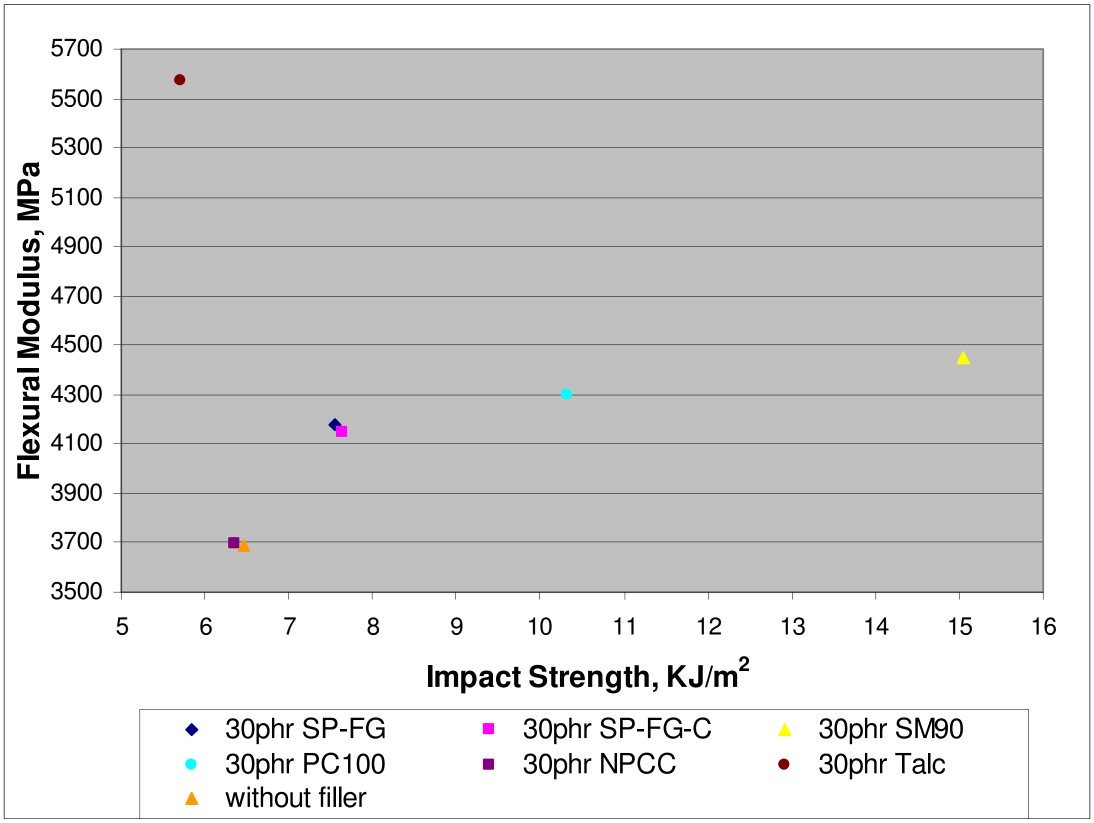


Figure 4.4: Comparison between the flexural modulus and impact strength of PVC composites filled with different types of fillers.

4.1.3 Effect of Hybrid Talc/SM90 Fillers

4.1.3.1 Flexural Strength

As discussed in Section 4.1.2, SM90 was selected for the hybrid fillers study because it gave the most optimum property in terms of impact strength and flexural modulus. For the hybrid fillers study, the total filler content was kept constant at 30phr with SM90 gradually replacing the talc. From Figure 4.5, the 30phr talc filled PVC composite showed the highest flexural strength and gradually decreased with increasing SM90 content. The reason for talc filled PVC composite having the highest flexural strength was the high aspect ratio of talc particles as previously mentioned. Besides the low aspect ratio, the other reason for the decrease of flexural strength with increasing SM90 content is the formation of cavities in SM90 filled PVC (refer to Sections 4.2 and 4.5). The formation of cavities around SM90 particles reduced the wettability of SM90 by the matrix, thus decreased the SM90-matrix interaction. The decreased SM90-matrix interaction also reduced the stress to be transferred from matrix to the SM90 particles during external loading.

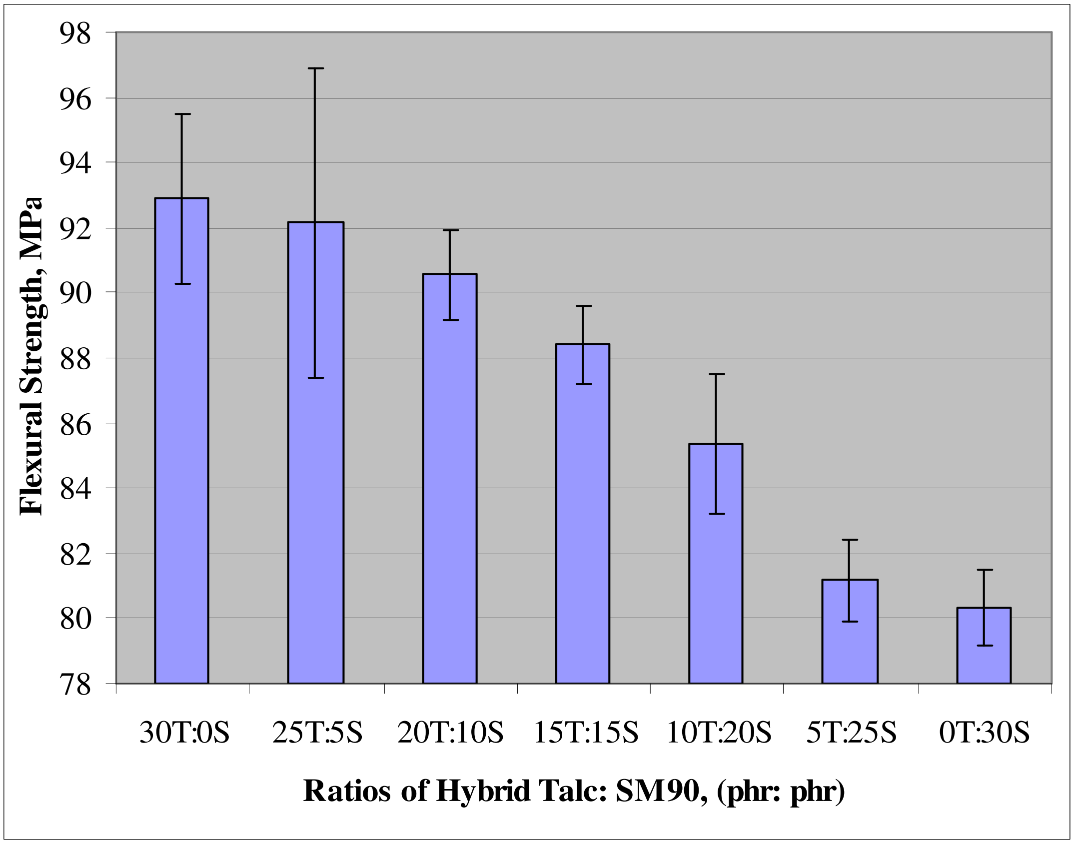


Figure 4.5: Effect of different Talc/SM90 ratio on flexural strength of the hybrid Talc/SM90 filled PVC composites.

4.1.3.2 Flexural Modulus

From Figure 4.6, the flexural modulus of talc filled PVC composite exhibited maximum value when the content of talc was 30phr. According to Wiebking (2006), the flexural modulus of PVC composite increased as the level of talc increased. From these results, they concluded that the addition of talc is a cost effective method of increasing stiffness of PVC.

According to Figure 4.6, the flexural modulus of hybrid composites decreased gradually with the increase of SM90 content. This could be attributed by the higher aspect ratio of talc particles than the SM90 particles. The effectiveness of talc filler in improving the flexural modulus of PVC composite was contributed by the high aspect ratio of talc particles as mentioned earlier. The SM90 filled PVC composite had a slight or little improvement effect on the flexural modulus when compared to the talc filled PVC composite. This was because the SM90 filler had a relatively low particles aspect ratio when compared to the aspect ratio of talc filler. As the 20phr talc was replaced by 20phr SM90 (hybrid 10phr talc: 20phr SM90 filled PVC composite), a synergistic hybridization was reached which gave a higher flexural modulus than the hybrid (20phr talc: 10phr SM90) and (15phr talc: 15phr SM90) filled PVC composites. This might be caused by the good distribution and orientation of talc and SM90 particles in PVC matrix and reduced the formation of cavities in PVC matrix as discussed in Section 4.5 (determination of densities). The formation of cavities can reduce the wettability of the fillers by PVC matrix, thus reduced the interaction between filler and PVC matrix. The poor filler-PVC matrix interaction also reduced the stress to be transferred from the matrix to the filler during external stress applied. The % cavities of hybrid (10phr Talc: 20phr SM90) filled PVC was 2.1%, which was lower than hybrid 20phr Talc: 10phr SM90 (3.2%) and hybrid 15phr Talc: 15phr SM90 filled PVC composites (2.5%). The reduction of cavities led to improve the flexural modulus of PVC and this was one of the reasons the hybrid 10phr Talc: 20phr SM90 filled PVC showed higher flexural modulus than hybrid (20phr Talc: 10phr SM90) and hybrid (15phr: 15phr SM90) filled PVC composites. The 30phr SM90 filled PVC composite gave the lowest flexural modulus compared to 30phr talc filled composite and the hybrids composites.

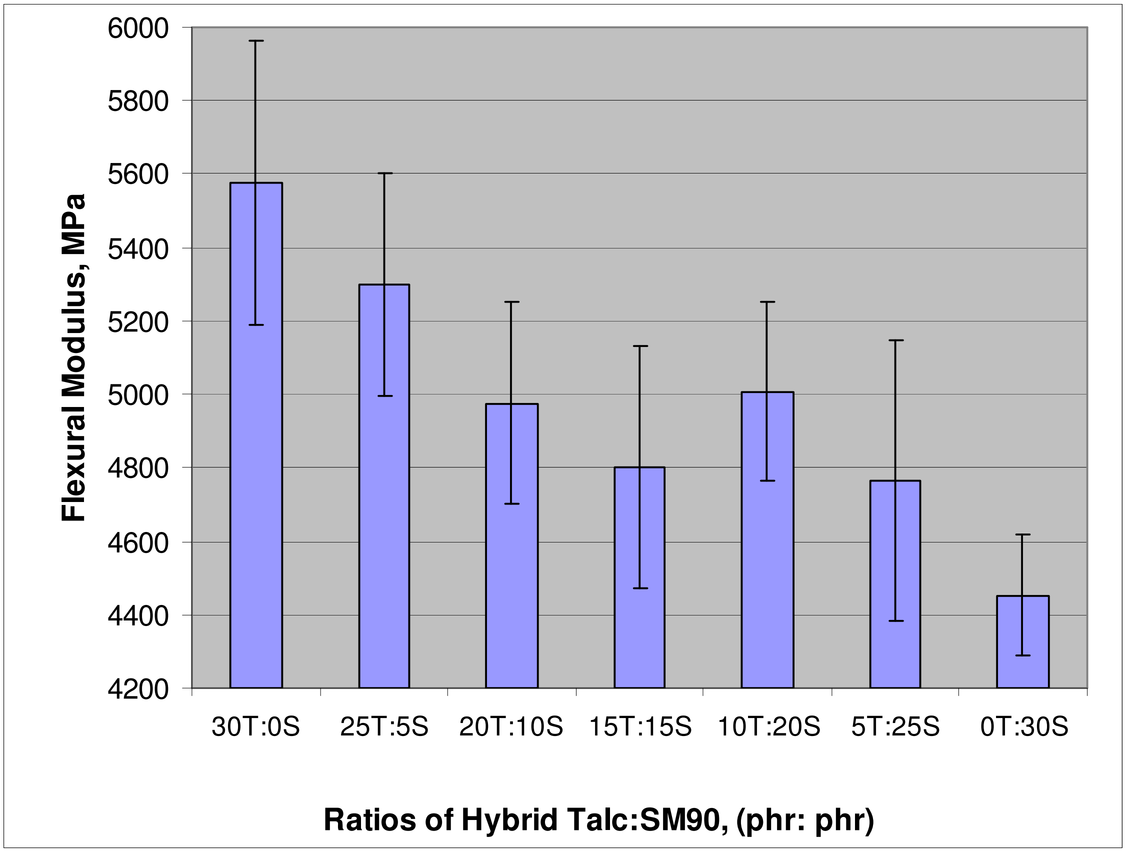


Figure 4.6: Effect of different Talc/SM90 ratio on flexural modulus of the hybrid Talc/SM90 filled PVC composites.

4.1.3.3 Impact Strength

From Figure 4.7, as the talc content was slowly replaced by increasing content of SM90, the impact strength had increased gradually as expected. According to Wu, *et al.* (2004) and Leong *et al.* (2003), the $CaCO_3$ filler played a dominant role in improving the impact properties of hybrid composites. In this study, the impact strength was dramatically influenced by the replacement of talc content with SM90. The SM90 filler had played an important role in improving impact strength of PVC composite as discussed in earlier study, thus all hybrids composites showed better result in impact strength than the 30phr talc filled PVC composites.

As discussed earlier, both the aspect ratio and the anisotropic particles orientation of talc particles were the main factor that contributed to decrease the impact strength of PVC composite. The replacement of talc content with increasing SM90 content led to increase the cavities formation and the effective SM90 particles that can resist the crack propagation as mentioned in earlier study. The presence of SM90 particles in PVC matrix could stop the propagation of crack.

From Figure 4.7, the impact strength of hybrid (5phrTalc: 25phr SM90) filled PVC composite and 30phr SM90 filled PVC composite showed a very high standard deviation compared to all hybrid PVC composites. This might be caused by the samples of hybrid (5T: 25S) and 30phr SM90 filled PVC composites were not totally melted and molded during compression moulding and these samples still maintained the compounded sheets structure. The improperly melted samples could not resist the impact energy well as the properly melted and prepared samples. This situation could create a big variation between the impact strength values of same types of samples. As discussed before, the high standard deviation of these samples also can be attributed to the formed of skin on the surface of specimens during the molding of samples.

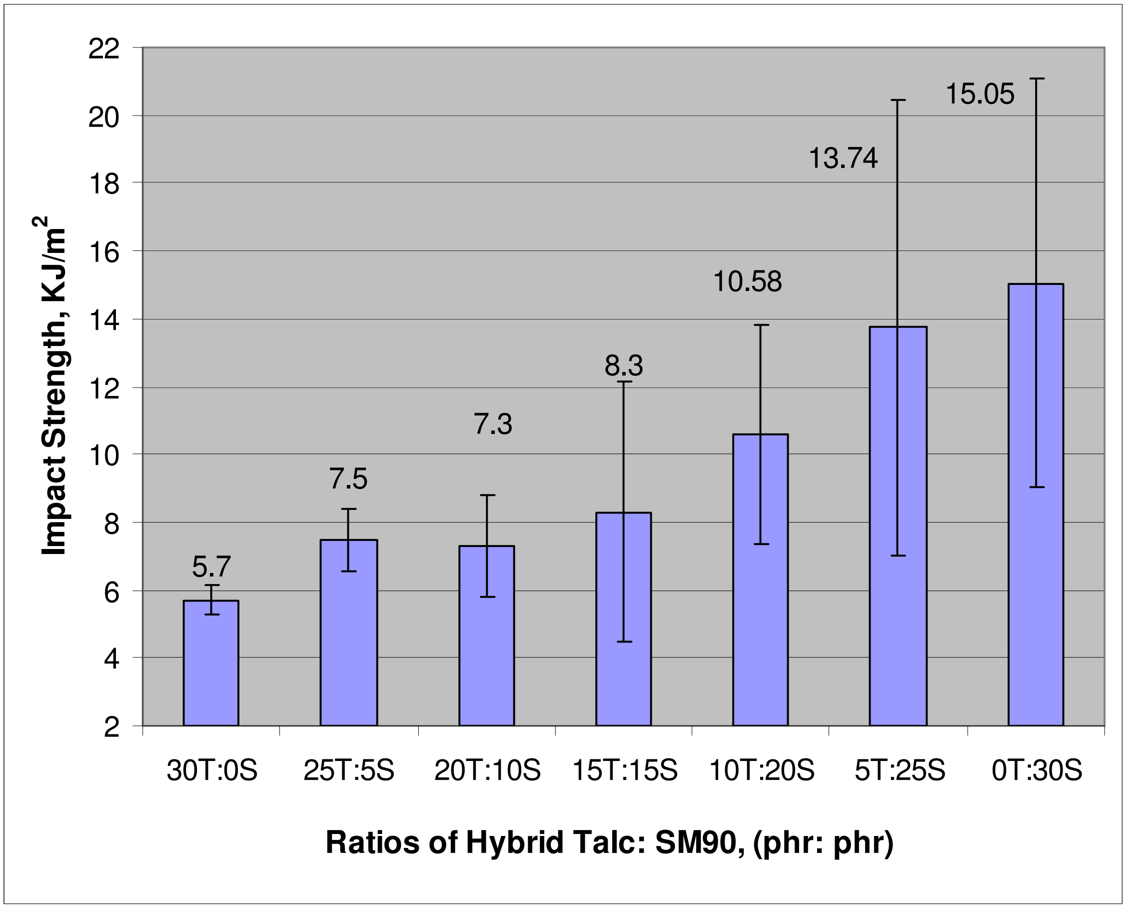


Figure 4.7: Effect of different Talc/SM90 ratio on impact strength of the hybrid Talc/SM90 filled PVC composites.

4.1.3.4 Tensile Strength

Figure 4.8 illustrates the tensile strength of PVC composites filled with single filler of talc or SM90 and hybrid fillers with different ratio of talc/SM90. It can be seen that the tensile strength of PVC composites were found to decrease gradually with increasing SM90 content to replace talc. The tensile strength of unfilled PVC composite was the highest among all filled PVC composites. Sun *et al.* (2005) reported that the tensile strength of composites is influenced by filler fraction and the interfacial adhesion between particles and matrix. So, the replacement of talc by SM90 increased the amount of voids and weakened the interfacial adhesion between PVC matrix and filler. The weak and poor interfacial adhesion between the PVC matrix and filler had reduced a large amount of stress that could be transferred from the PVC matrix to fillers particles as reported by Sun *et al.* (2005). Sun *et al.* (2005) found that the interfacial adhesion plays a crucial role in improving the tensile strength of the composites. They also explained that the better interfacial adhesion between the filler particles and matrix, the larger the stress that can be transferred to inorganic particles from the matrix, which leads to higher tensile strength.

The results of tensile strength in this study were found similar to tensile strength results of Leong *et al.* (2006), where they also reported that replacement of talc with $CaCO_3$ decreased the tensile strength of polypropylene composites. This could be attributed to the formation of cavities around $CaCO_3$ particles, which these cavities could have detrimental effects on the tensile strength of PP composites. However, the increment in tensile strength of talc filled PVC composite was minimal. This might be due to the platy nature of talc and possesses the ability to orient to the PVC flow during processing. The platy talc filler had high aspect ratio and this increased the wettability of the filler by the matrix, thus creating fewer voids and increasing the interaction between the filler matrix.

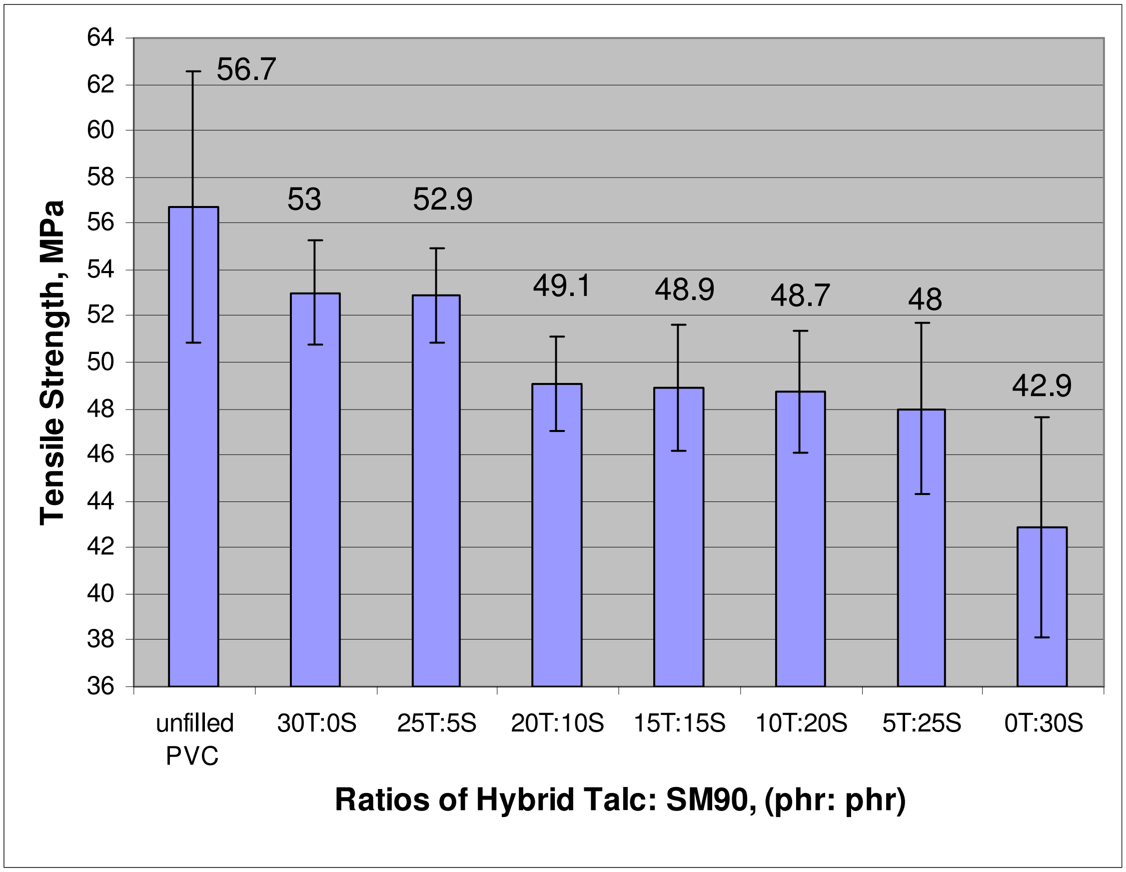


Figure 4.8: Effect of different Talc/SM90 ratio on tensile strength of the hybrid Talc/SM90 filled PVC composites.

4.1.3.5 Young's Modulus

Figure 4.9 shows the effects of different talc/SM90 loading on the Young's modulus of hybrid talc/SM90 filled PVC composites. Obviously from Figure 4.9, the Young's modulus of hybrid PVC composites gradually decreased with an increasing replacement of talc by SM90. However, all filled PVC composites were found to have higher Young's modulus than the unfilled PVC composite. The filled PVC composites had higher Young's modulus than the unfilled PVC composite might be caused by the rigidity of the fillers and also the filler particles orientation, as mentioned by Leong *et al.*

(2004a). Wu *et al.* (2004) and Leong *et al* (2004a) reported that the use of fillers such as $CaCO_3$ and talc could effectively increase the rigidity of PVC composites.

The trend of Young's modulus results in this study was found similar to the results of a study carried out by Leong *et al.* (2004a). The results of Leong *et al.* (2004a) showed that with an increase in the $CaCO_3$ content to replace talc, the tensile modulus of PP composites gradually decreased.

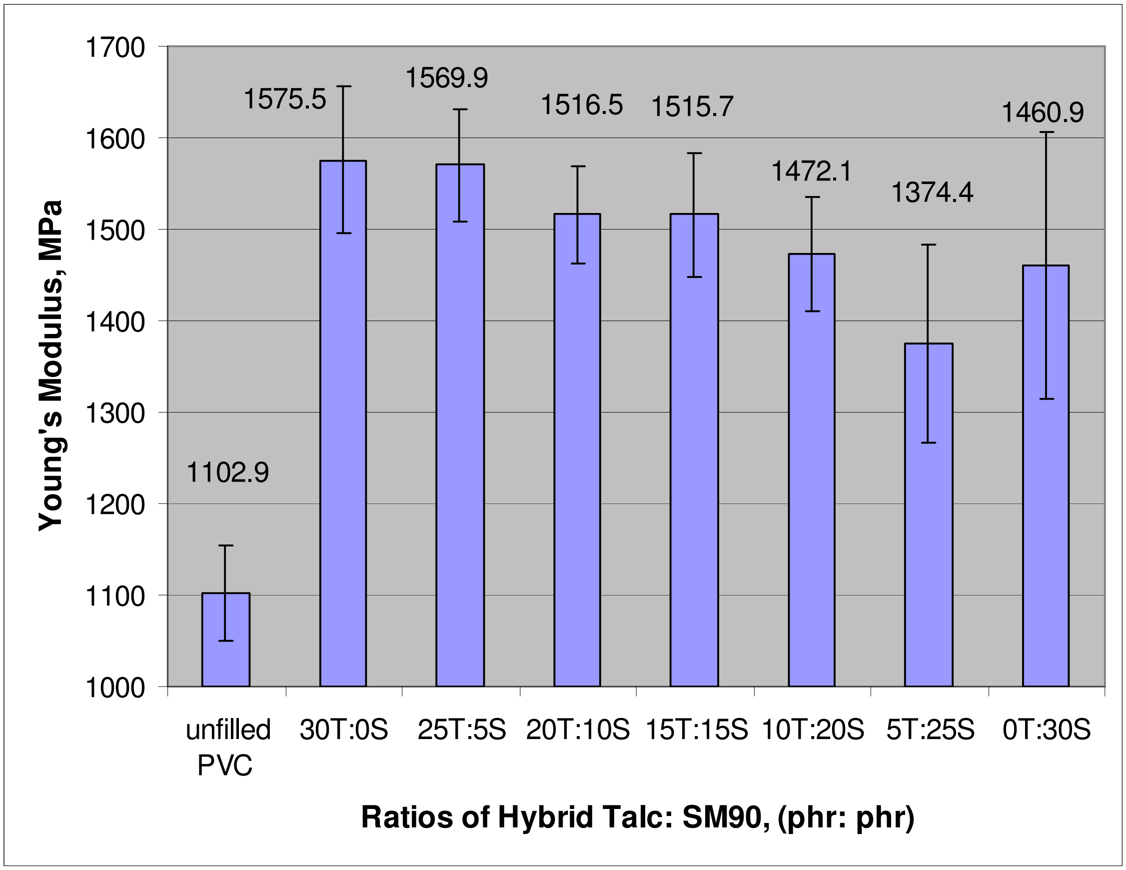


Figure 4.9: Effect of different Talc/SM90 ratio on Young's Modulus of the hybrid talc/SM90 filled PVC composites.

4.1.4 Overall Discussion on flexural and impact properties of Hybrid Talc/SM90 filled PVC composites

In building construction application, the flexural properties and impact strength are more important than tensile properties. From Figures 4.10 and 4.11, most of the hybrids composites maintained certain properties based on the types of filler that was more dominant and the influence of the filler itself on the properties of PVC. The SM90 dominant composites showed higher impact strength than talc dominant hybrids composites. The talc dominant hybrids composites gave higher flexural properties (flexural strength and modulus) than SM90 dominant hybrids composites. From the results in flexural modulus and impact strength, the hybrid (10phr talc: 20phr SM90) filled PVC composite posed the optimum properties in impact strength, flexural properties when compared with the other ratio of hybrid talc/SM90 filled PVC composites.

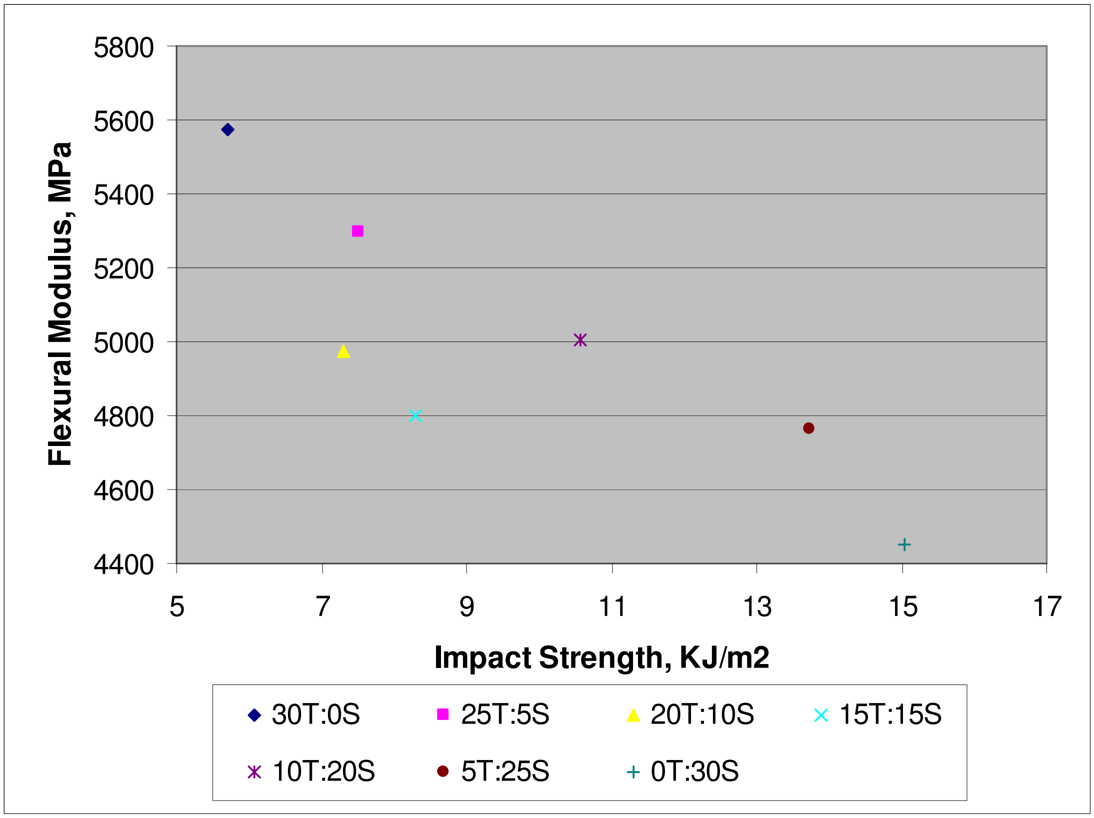


Figure 4.10: Comparison between the flexural modulus and impact strength of hybrid Talc/SM90 filled PVC composites filled with different ratio of Talc/SM90.

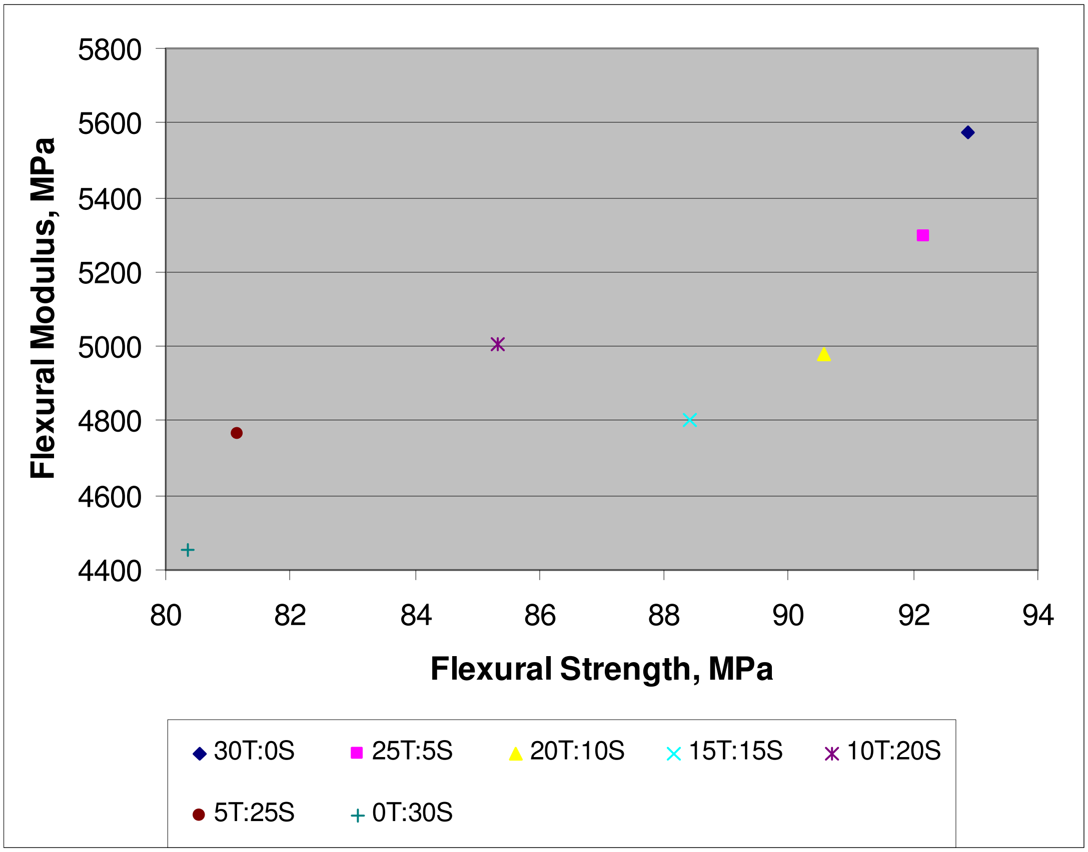


Figure 4.11: Comparison between the flexural modulus and flexural strength of hybrid Talc/SM90 filled PVC composites with different ratio of Talc/SM90.

4.2 Morphologies Observation of Different Types of Fillers

Figures 4.12 to 4.18 illustrate the SEM micrographs of an unfilled PVC composite and PVC composites filled with different types of fillers. From Figure 4.12, unfilled PVC composite was found to contain some small particles which were evenly dispersed in the PVC matrix. The particle sizes of these small particles were smaller than 0.5micron and believed to be the unfused particles of the PVC resin as reported by Chen *et al.* (1995a) in their study. The PVC resin powder did not melt and fuse fully during milling and compounding. The presence of voids was also observed at the interface between the unfused PVC particles and PVC matrix.

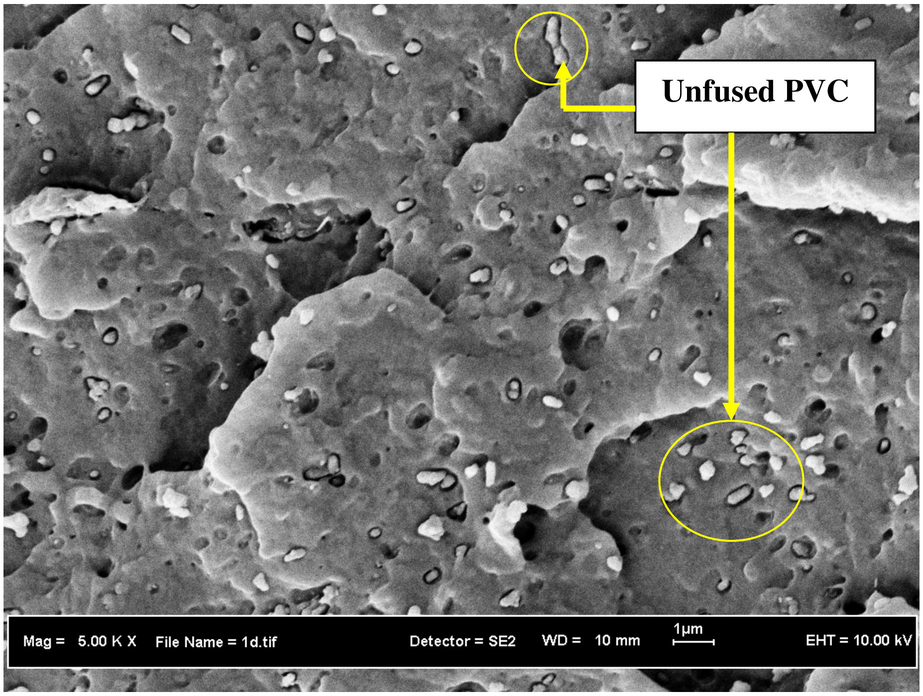


Figure 4.12: SEM photograph of the unfilled PVC composite at 5000X.

Figure 4.13 demonstrates the SP-FG particles were well dispersed in the PVC matrix. The particles size distribution of SP-FG was found to be broader than SM90, PC100 and NPCC. Obviously, the presence of voids also found at the interface between the SP-FG and PVC matrix. From Figures 4.1, 4.2 and 4.3, the SP-FG filled PVC composite was found to have poor results in both flexural properties (flexural modulus and strength) and impact strength. However, the use of SP-FG filler still improved the flexural modulus and impact strength of PVC composite. Sun *et al.* (2003) reported that the effect of filler on the flexural properties and impact strength were strongly dependent on the presence of voids, particles size distribution, microstructure and aggregate size. The poor interfacial adhesion between SP-FG particles and PVC matrix was believed to be the main reason that contributed to the presence of voids at the filler-matrix interface as observed in Figure 4.13. The broader particles size distribution of SP-FG filler also led to reduce the interfacial contact area between the SP-FG particles and PVC matrix, thus reducing the mechanical properties.

From Figure 4.14, the presence of voids or cavities and SP-FG-C particles in PVC matrix could be obviously seen. The SP-FG-C particles were found in the PVC matrix with bigger particles compared to unfused PVC and the presence of cavities also could be observed in Figure 4.14. These cavities were believed to be occupied by the particles of SP-FG-C before the sample was being fractured. The particles of SP-FG-C also found to have broader particles size distribution than SM90, PC100 and NPCC. The broader particles size distribution of SP-FG-C and larger particles size of SP-FG-C particles meant that the effective amount of SP-FG-C particles to stop cracks propagation in PVC matrix was smaller than SM90 and PC100 filled PVC composites. This was one of the reasons that SP-FG-C filled PVC composite showed lower impact strength than SM90 and PC100 filled PVC composite. The presence of voids at the interface between SP-FG-C particles and PVC matrix was found to be smaller than the voids in the PVC matrix of SP-FG filled composite as mentioned in Section 4.5 (determination of densities). This shows that the surface coating of SP-FG-C filler can improve the interface adhesion between SP-FG-C particles and PVC matrix compared to SP-FG filler. The flexural modulus and impact strength of the SP-FG-C filled PVC composite was nearly similar to the SP-FG filled PVC composite. However, in considering the higher standard deviation of the flexural properties (flexural strength and modulus) and impact strength, SP-FG-C filled PVC composite could be considered to have better mechanical properties than SP-FG filled PVC composite. This also shows that better interface adhesion between the particles of filler and PVC matrix also can significantly improve the mechanical properties of PVC composite.

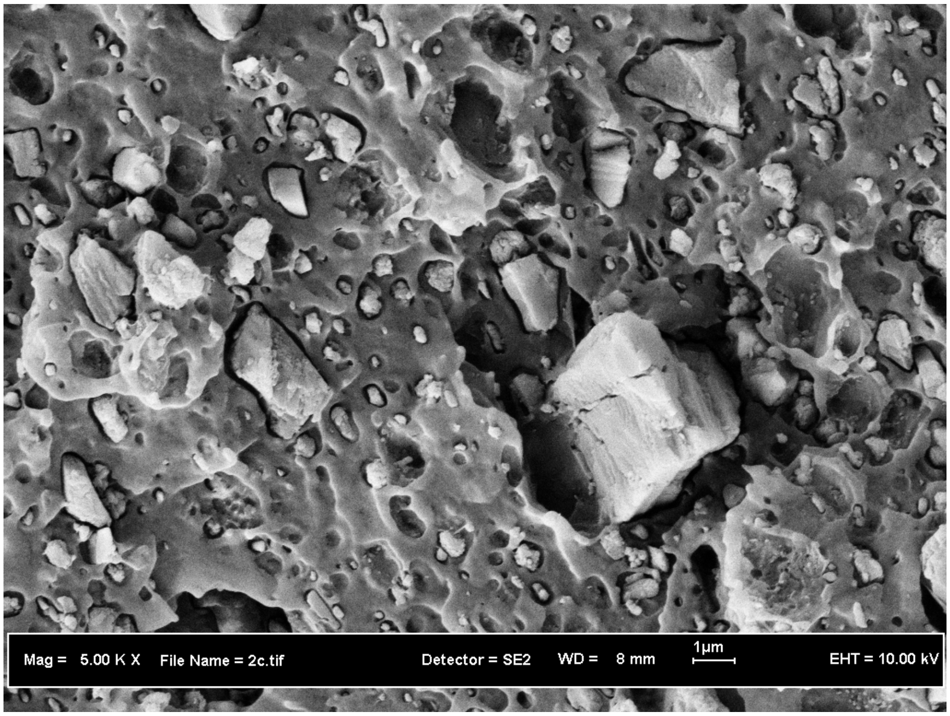


Figure 4.13: SEM photograph of 30phr SP-FG filled PVC composite at 5000X.

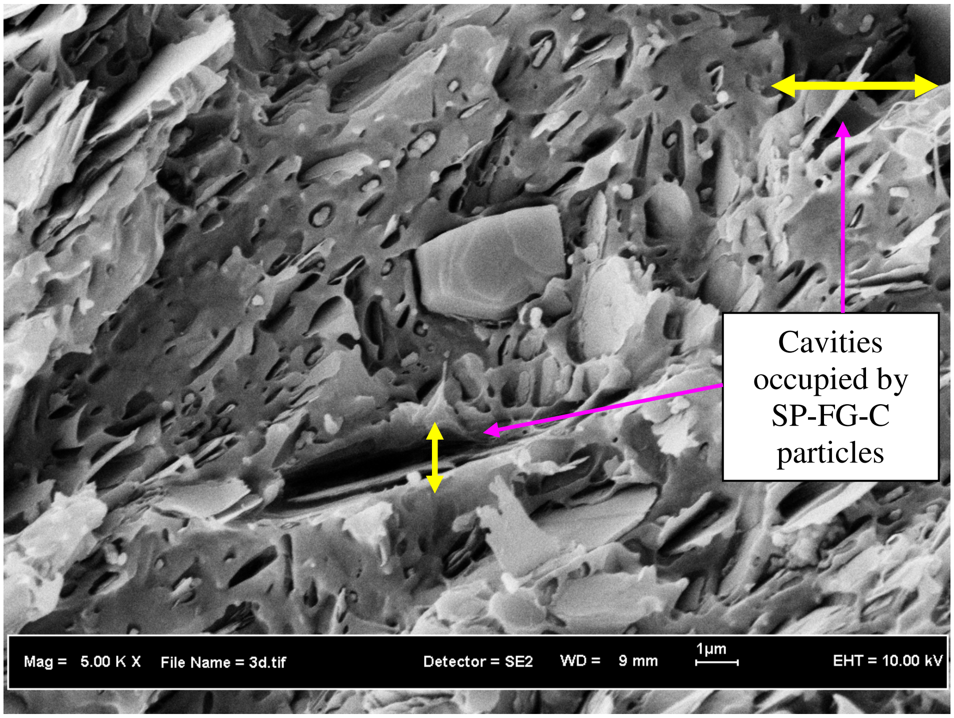


Figure 4.14: SEM photograph of 30phr SP-FG-C filled PVC composite at 5000X.

Figure 4.15 illustrates the presence of voids and SM90 particles in PVC matrix. The cavities or voids in PVC matrix were found less than the other $CaCO_3$ filled PVC composites as measured and discussed in Section 4.5 (Determination of densities). From Figure 4.15, the SM90 particles were evenly and well dispersed in the PVC matrix. The SM90 filler had a smaller particles size and narrower distribution size than SP-FG and SP-FG-C. The smaller particles size of SM90 filler had led to better surface interfacial adhesion between the particles and the PVC matrix by reducing the cavities. The smaller particles size and narrower particles size distribution of SM90 had increased the effective amount of SM90 particles in PVC matrix, which can effectively stop the propagation of cracks in PVC matrix. The strong interfacial adhesion between SM90 particles and PVC matrix can also help to prevent the crack to propagate along the interface between the PVC matrix and SM90 particles as mentioned by Sun *et al.* (2005) in their study. The finer particles size of SM90 filler and good interfacial adhesion between SM90 and PVC matrix were the main reasons that contributed to the highest impact strength and flexural modulus among all types of $CaCO_3$ filled PVC composites.

From Figure 4.16, the PC100 was found to have smaller particles size and narrower particles size distribution than SM90. However, the voids in the PVC matrix were estimated through Section 4.5 (Determination of densities) and found higher than SM90 filled PVC composite. Figure 4.16 illustrates that the particles of PC100 filler were unevenly dispersed and distributed in the PVC matrix and had a poor dispersion and interfacial adhesion compared to SM90. The poor dispersion of PC100 particles had caused the agglomeration of PC100 particles in the PVC matrix with some of the aggregate sizes were reached up to 1.5 micron. The agglomeration of PC100 particles was also clearly observed in Figure 4.16. The agglomeration of PC100 particles in PVC matrix promoted the existence of voids cavities within the particles and PVC matrix. The higher amount of voids or cavities had led to a reduction in the interfacial contact area between the PC100 particles and PVC matrix and the resistance of cracks to propagate along the interface between PC100 particles or aggregates and PVC matrix would be weakened. Thus, it was slightly reduced the effectiveness of PC100 in improving the impact strength.

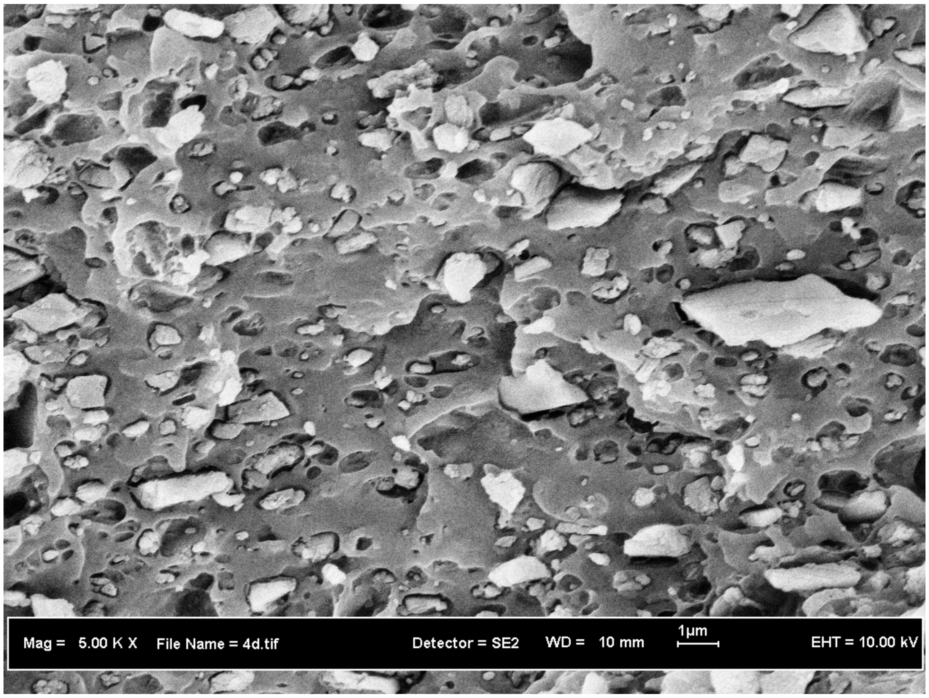


Figure 4.15: SEM photograph of 30phr SM90 filled PVC composite at 5000X.

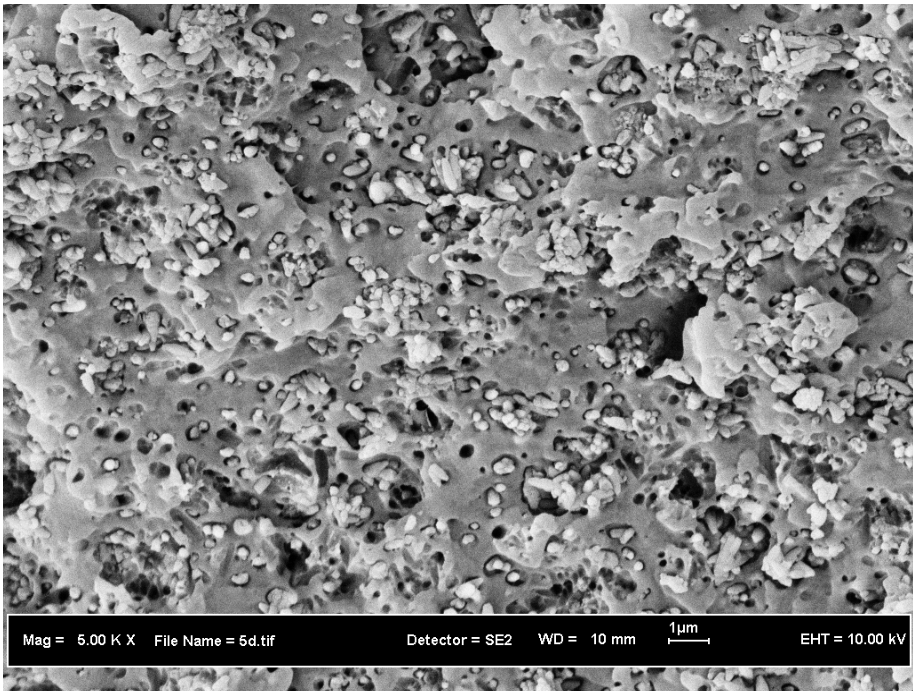


Figure 4.16: SEM photograph of 30phr PC100 filled PVC composite at 5000X.

From Figure 4.17, the NPCC particles were poorly dispersed in PVC matrix and revealed the poorest interfacial adhesion between NPCC and PVC matrix compared to others $CaCO_3$ filled PVC composites (Figures 4.13 to 4.16). The poor dispersion of NPCC particles in the PVC matrix was the main cause to the agglomeration of NPCC particles. Obviously from Figure 4.17, the NPCC particles were found to be severely aggregated and agglomerated in the PVC matrix. Some of the NPCC agglomerated were found to reach up to 1 micron. The agglomeration of NPCC had contributed to the presence of cavities in PVC matrix. These cavities or voids were found to be occupied by the NPCC particles or aggregates and PVC matrix. As discussed earlier, poor dispersion of NPCC particles in PVC matrix can promote the agglomeration of NPCC. The NPCC particles that can act as stress concentration sites also became fewer, which theses particles can play an important role in resisting impact stress. The total amount of effective particles that could act as stress concentration sites also had been reduced and thus decreased the impact strength as previously mentioned in Section 4.1.1.3 (impact strength). Thus, the poor interfacial adhesion between NPCC particles and PVC matrix was the main caused the NPCC filled PVC composite to have the lowest impact strength compared to all $CaCO_3$ filled PVC composite.

From Figure 4.18, the talc particles could be observed in the platelike structure with high aspect ratio. The talc particles were found to disperse and distribute evenly in the PVC matrix. The talc particles were orientated in parallel to each other in PVC matrix. The average aspect ratio (L/D) of talc particles was measured and estimated to be nearly 8. This shows that the talc particles have higher particle aspect ratio than all $CaCO_3$. The talc filled PVC composite showed the lowest impact strength among all filled PVC composites. The high aspect ratio and the orientation of talc in PVC matrix increased the resistance of local plastic deformation of the PVC matrix, which can reduce the ability to absorb impact energy through plastics deformation.

However, the talc filled PVC composite showed the highest flexural strength and flexural modulus compared to all filled PVC composites. This may be attributed to the ability of the talc particles in PVC matrix to resist bending during the application of flexural stress. Both the aspect ratio and particles orientation played an important role in improving the flexural modulus of PVC composite. The appearance of voids also could be seen in the PVC matrix in Figure 4.18. The lower experimental density of talc filled PVC composite (as determined in Section 4.5) shows that the presence of voids in talc filled PVC composite was more than others filled PVC composites.

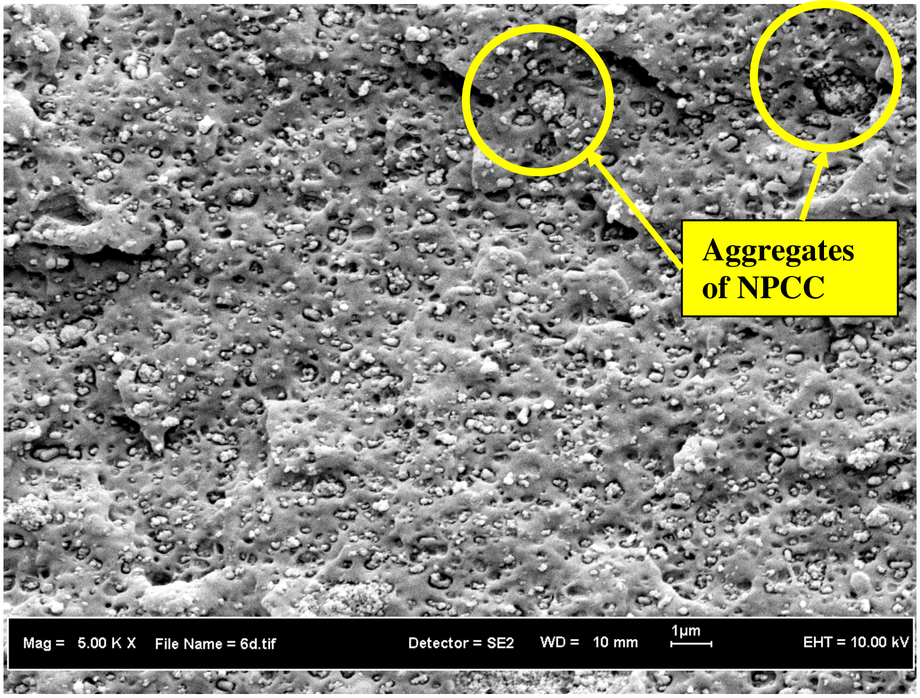


Figure 4.17: SEM photograph of 30phr NPCC filled PVC composite at 5000X.

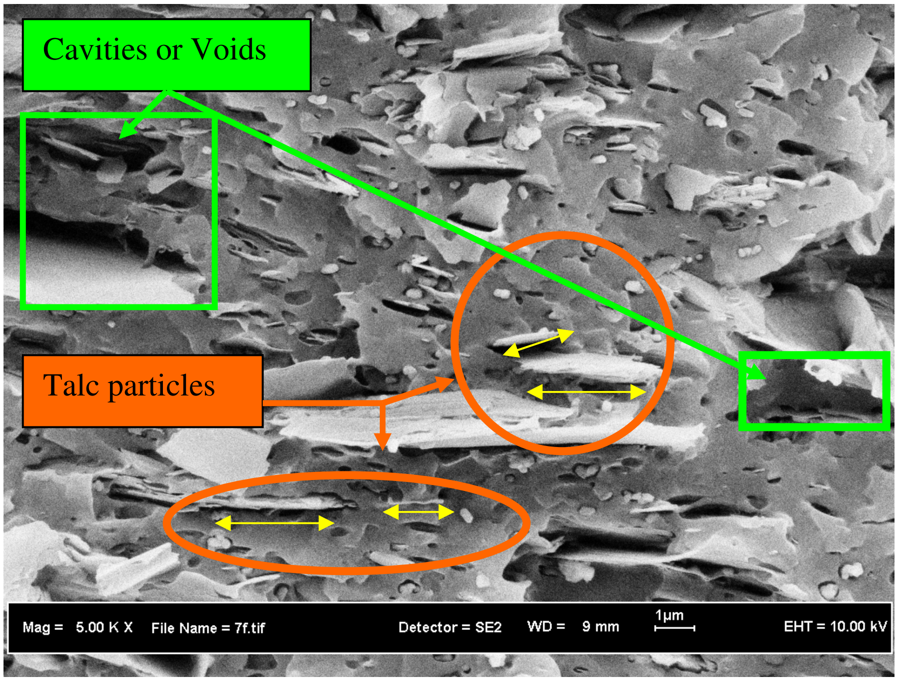


Figure 4.18: SEM photograph of 30phr talc filled PVC composite at 5000X.

4.3 Thermal Properties

Thermal properties of PVC composite were investigated by conducting heat deflection temperature (HDT) and thermogravimetry analysis (TGA).

4.3.1 Heat Deflection Temperature (HDT)

4.3.1.1 Effect of Different Types of Fillers and Particles Size

Figure 4.19 reveals the heat deflection temperature (HDT) of PVC composites filled with different types of fillers. It can be seen that the heat deflection of unfilled PVC composite was 68.3^{o}C which is consistent to the heat deflection temperature value of unfilled PVC composite reported by Abu Bakar (2006). The talc filled PVC composite had the highest heat deflection temperature value of 71.5^{o}C. Apparently, the addition of talc into PVC matrix had significantly increased the heat deflection temperature. The heat deflection temperature of SP-FG-C and SP-FG filled PVC composites were the second and the third highest compared to all filled PVC composites. The SM90 and PC100 filled PVC composites gave the fourth and fifth highest HDT values. However, the heat deflection temperatures of SM90 and PC100 filled PVC composites were very close until the difference between the heat deflection temperature value could be negligible. The NPCC filled PVC composite had the lowest heat deflection temperature value among all filled PVC composites.

From Figure 4.20, the addition of talc and different types of $CaCO_3$ had improved the heat deflection temperature of PVC composite. According Yuan *et al.* (2003), the heat deflection temperature of polymers could be improved by the incorporation of fillers. From the results in mechanical properties, the addition of talc and different types of $CaCO_3$ had improved the flexural modulus or stiffness of PVC composite. The improvement in stiffness or flexural modulus had increased the rigidity of PVC composite. Abu Bakar (2006) also reported that the flexural modulus and strength of PVC composites could be increased as the rigidity of PVC composite increased. The increase in rigidity of PVC composite contributed to the improvement in heat deflection temperature of PVC composite.

The improvement in heat deflection temperature of all filled PVC composites had supported that the incorporation of fillers (talc and all types of $CaCO_3$) can increase the flexural modulus of PVC composites. The talc filled PVC composite showed the highest heat deflection temperature value consistent with its highest flexural modulus. Although the SM90 and PC100 filled PVC composites gave higher flexural modulus than the other types of $CaCO_3$ filled PVC composites, the heat deflection temperature values were still lower than 30phr SP-FG and 30phr SP-FG-C filled PVC composites. The high impact strength of SM90 and PC100 were also contributed to the improvement in ductility of PVC composites. This was the main reason that the heat deflection temperature values of SM90 and PC100 filled PVC composites were lower the SP-FG and SP-FG-C filled PVC composites even they imparted higher flexural modulus.

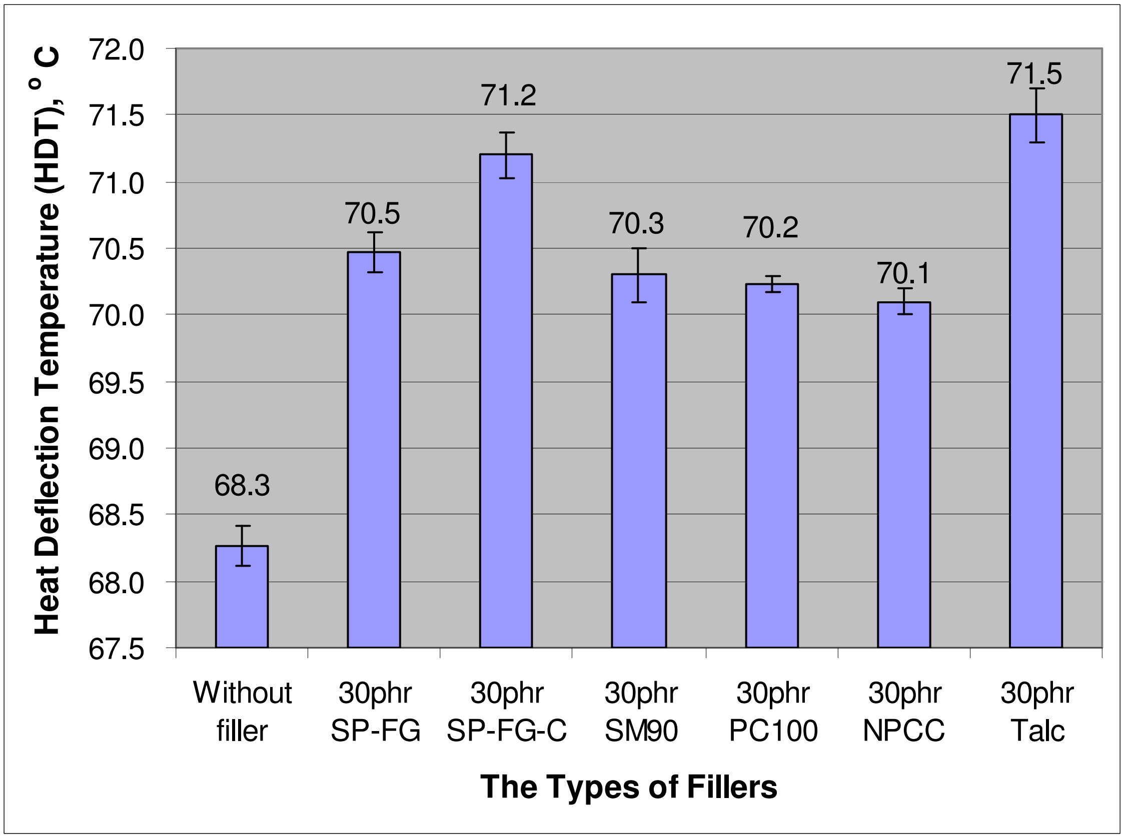


Figure 4.19: The heat deflection temperature of PVC composites filled with different types of fillers.

4.3.1.2 Effect of Hybrid Talc/SM90 Fillers

Figure 4.20 reveals the heat deflection temperature of hybrid talc/SM90 filled PVC composites with different ratio of talc/SM90. The heat deflection temperature of hybrid talc/SM90 filled PVC composites gradually decreased with increasing of SM90 content to replace talc. From the results of flexural modulus and impact strength, the 30phr talc filled PVC composite had the highest flexural modulus and the 30phr SM90 filled PVC composite showed the highest impact strength. As mentioned earlier, the rigidity of PVC composite had contributed to the increase in heat deflection temperature. The highest flexural modulus of 30phr talc filled PVC composite had increased the rigidity of PVC composite, thus the heat deflection temperature of 30phr talc filled PVC had also been increased. The replacement of 5phr talc with 5phr SM90 content had slightly decreased the heat deflection temperature of PVC composite. With further replacement of talc content with SM90, the heat deflection temperature of the hybrid PVC composites decreased insignificantly and these decreases were too small and could be negligible.

Obviously from the results of mechanical properties, the replacement of talc content with SM90 significantly reduced the flexural modulus of hybrid PVC composite. The decrease in flexural modulus would lead to a reduction in the rigidity of PVC composite. Thus, the heat deflection temperature value also decreased as the rigidity of hybrid PVC composites decreased. Abu Bakar (2006) also quoted that the rigidity played an important role in improving the heat deflection temperature value.

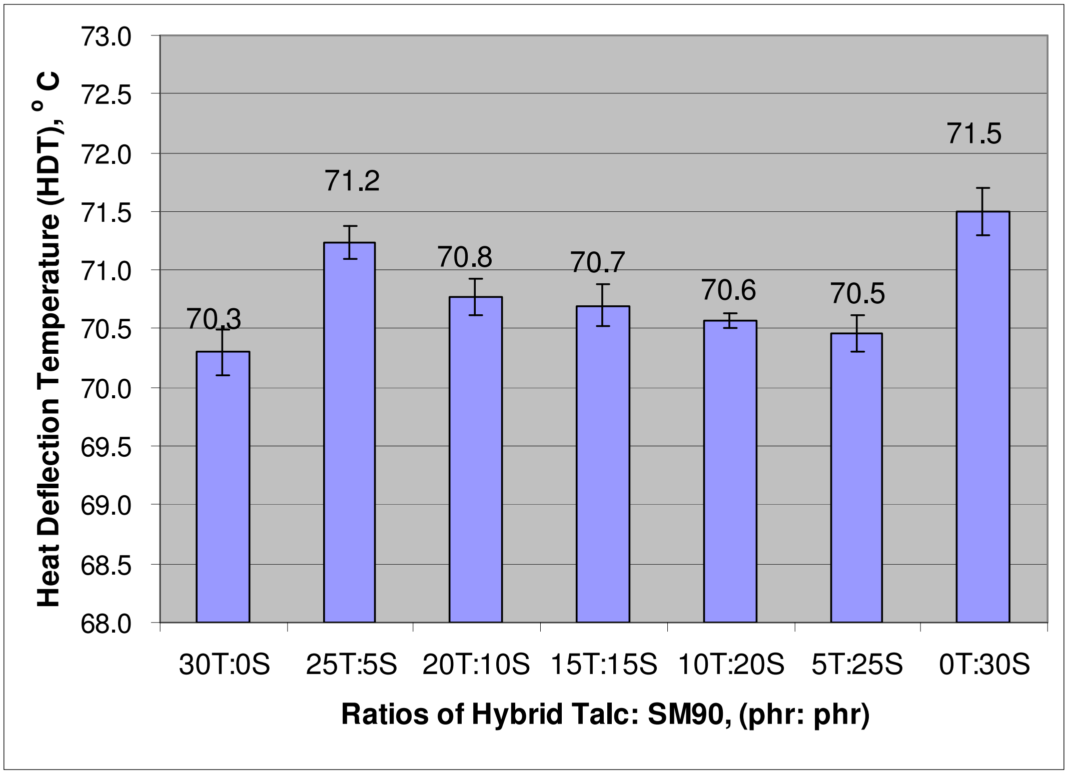


Figure 4.20: The heat deflection temperature of hybrid Talc/SM90 filled PVC composites with different ratio of talc/SM90.

4.3.2 Thermogravimetry Analysis (TGA)

Thermogravimetry analysis (TGA) were carried out to estimate and investigate the thermal stability of PVC composite and the influence of fillers (all types of $CaCO_3$ and talc) on thermal stability of PVC composite.

4.3.2.1 Effect of Different Types of Fillers and Particles Size

The TGA curves for unfilled PVC and PVC composites, which carried out in an atmosphere of nitrogen at the rate of 10^{o}C/min. Figure 4.21, TGA curve for unfilled PVC reveals that the degradation of PVC composite followed a two step process. The first step of degradation falls in the range of 230^{o}C to 380^{o}C while the second step occurs in the range of 400^{o}C to 550^{o}C. According to Figures 4.22 to 4.27, the TGA curves of all PVC composites filled with single filler (all types of $CaCO_3$ and talc) show that the degradation and decomposition of PVC composites also occurred in two significant steps of degradation. The first step of degradation was within the range of 280^{o}C to 300^{o}C and mainly due to the HCl-elimination reaction of PVC and formation of a polyenes structure. The second step of degradation was in the range of 450^{o}C to 470^{o}C and attributed to the thermal degradation of carbon chain of PVC that produced flammables volatiles. This result whereby the degradation and decomposition of PVC composites occurred in two significant steps is consistent with previous studies such as Chen *et al.* (2006), Abu Bakar (2006) and Sivalingam and Madras (2004).

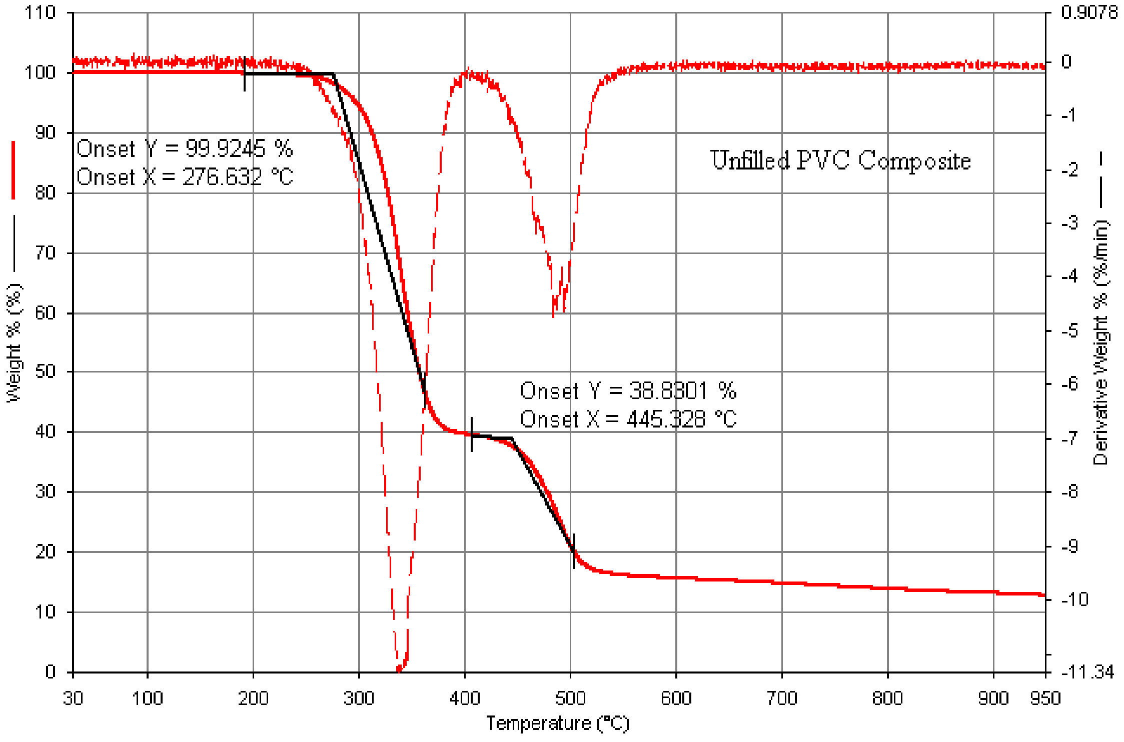


Figure 4.21: TGA curve for unfilled PVC composite.

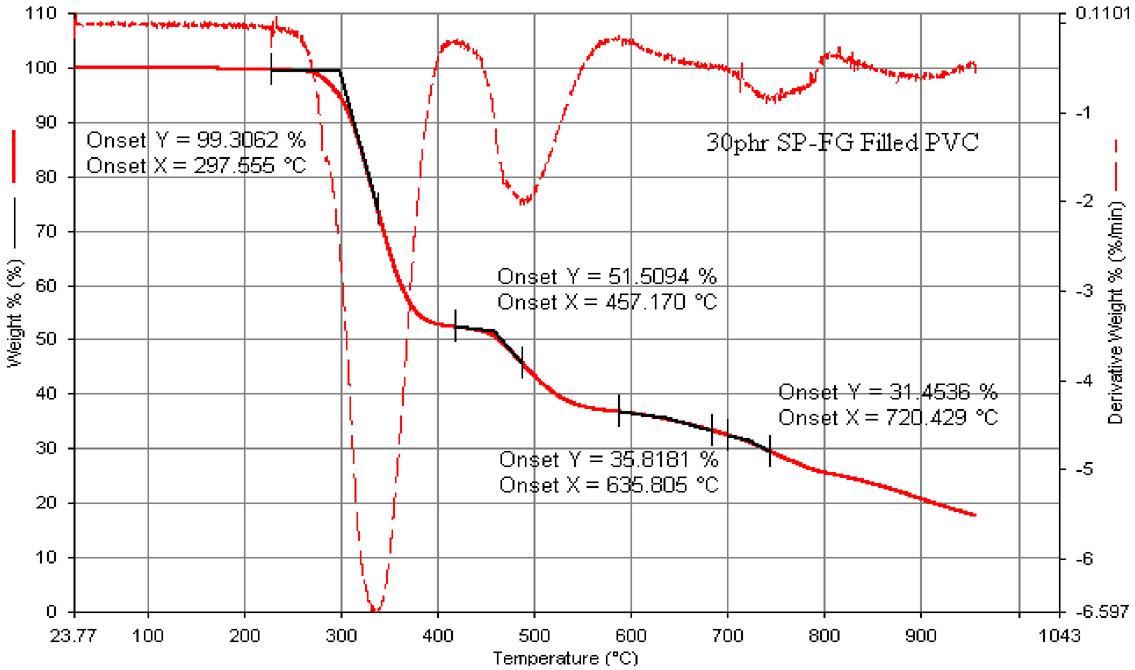


Figure 4.22: TGA curve of 30phr SP-FG filled PVC composite.

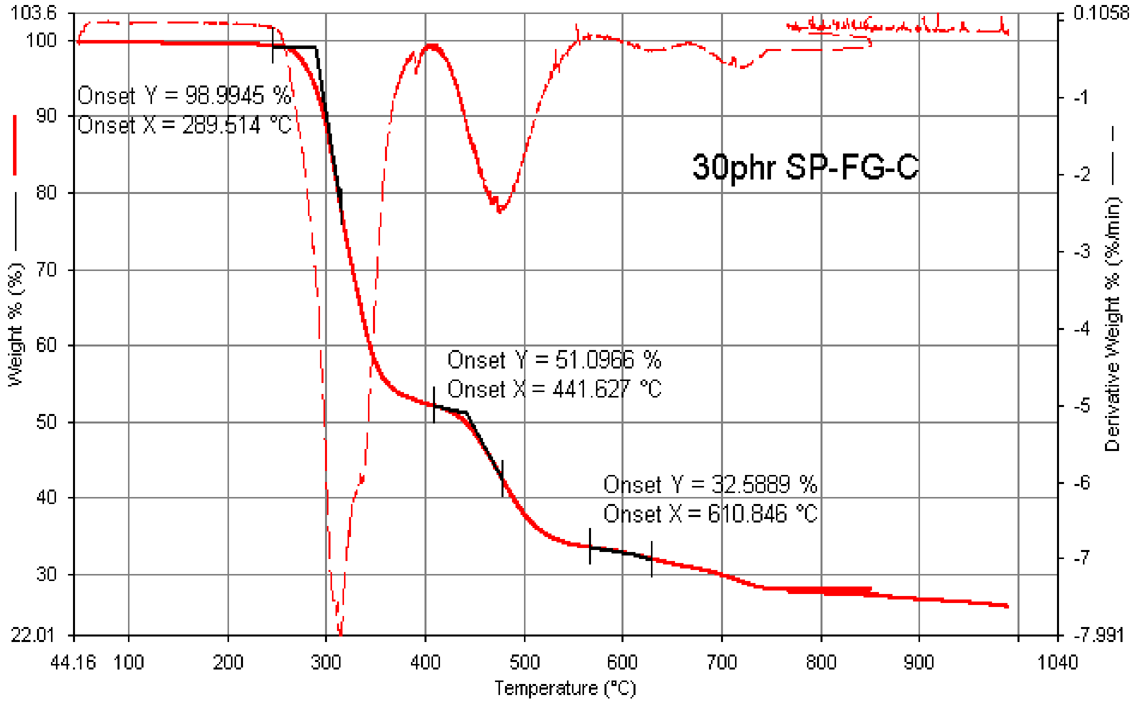


Figure 4.23: TGA curve of 30phr SP-FG-C filled PVC composite.

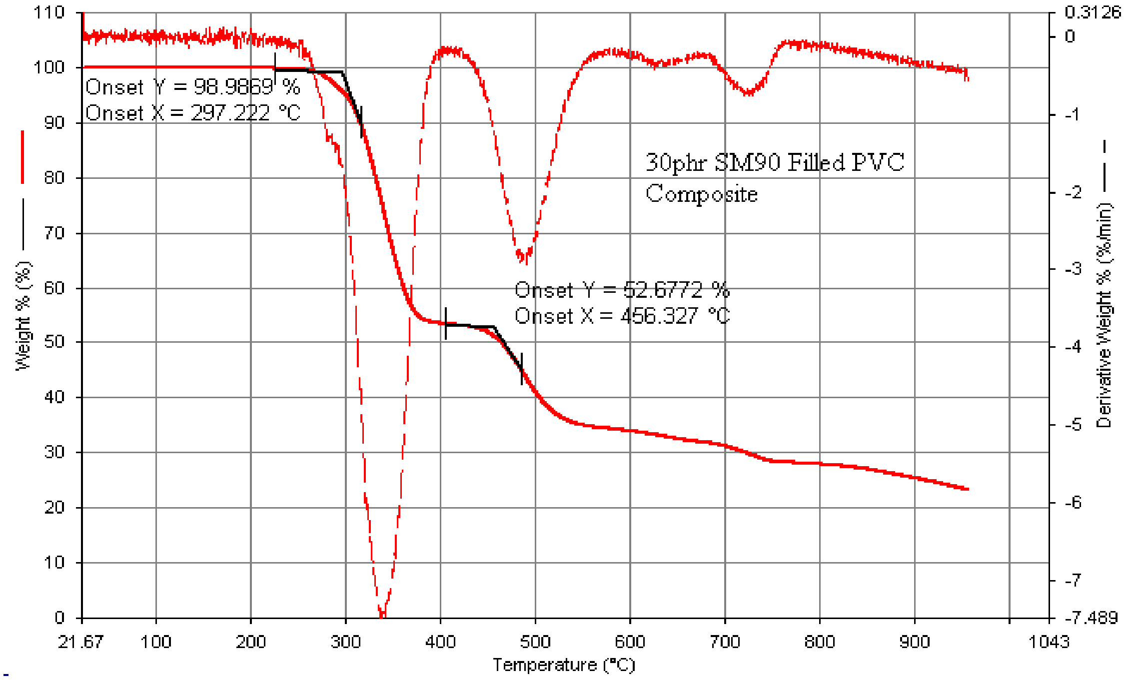


Figure 4.24: TGA curve of 30phr SM90 filled PVC composite.

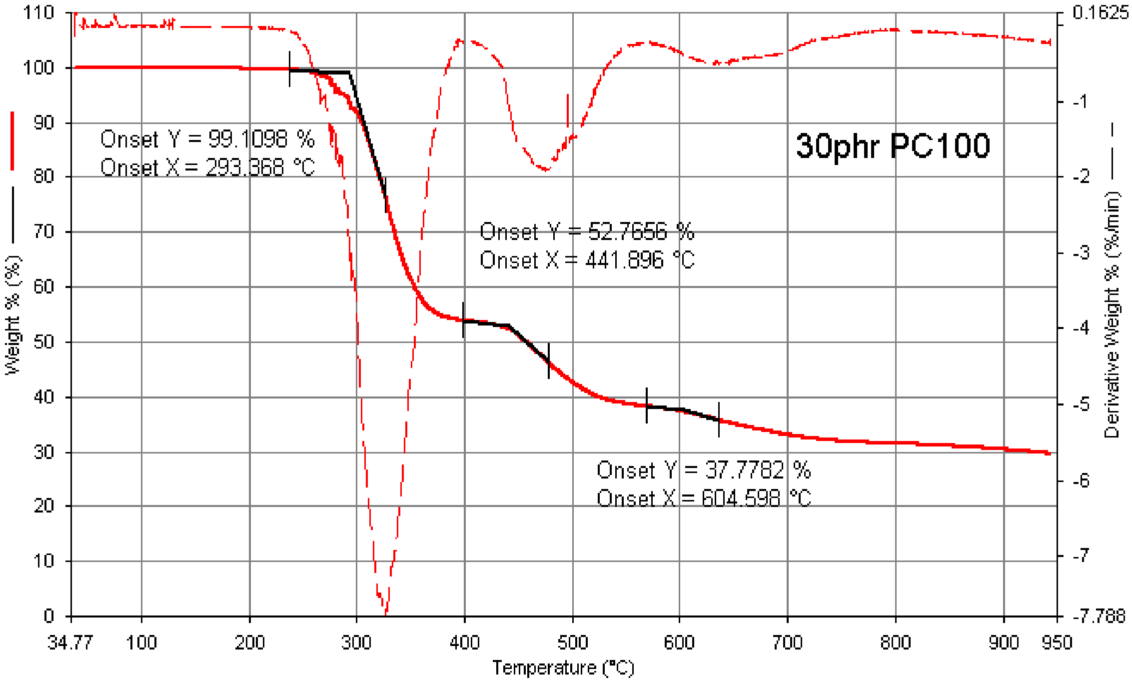


Figure 4.25: TGA curve of 30phr PC100 filled PVC composite.

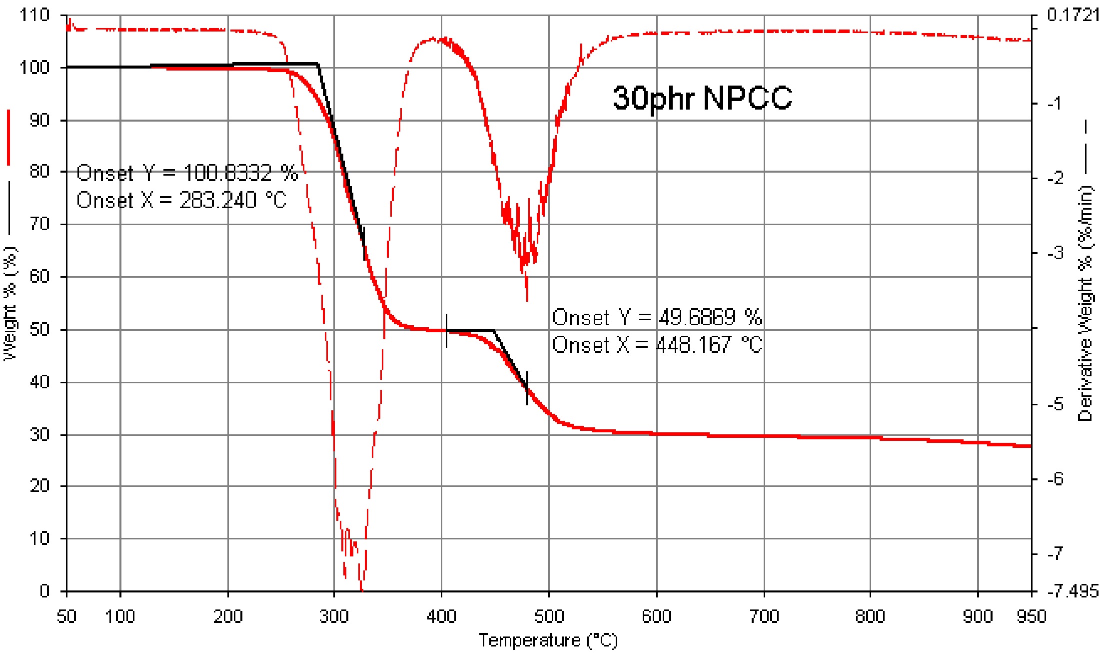


Figure 4.26: TGA curve of 30phr NPCC filled PVC composite.

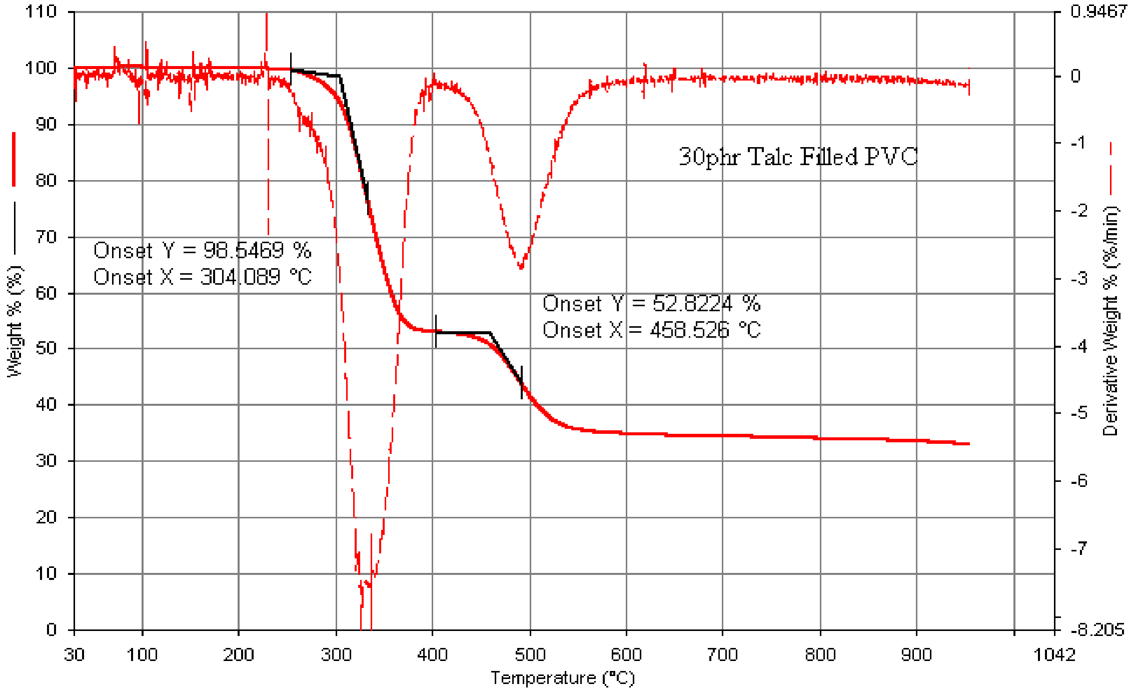


Figure 4.27: TGA curve of 30phr Talc filled PVC composite.

- **Range of degradation temperature and Thermal degradation onset temperature**

Tables 4.1 and 4.2 show the range of degradation temperature and thermal degradation onset temperature at the first stage and second stage of unfilled PVC and PVC composites filled with different types of fillers. Obviously from Table 4.1, the incorporation of fillers (all types of $CaCO_3$ and talc) significantly improved the thermal stability of PVC composite by increasing the range of degradation temperature and thermal degradation onset temperature of PVC composite. The increase in the ranges of decomposition temperature and thermal degradation onset temperatures of PVC composites showed that the addition of $CaCO_3$ and talc can improve the thermal stability of PVC composite. Chen (2003) mentioned that an improvement in thermal stability would mean an increase of thermal degradation onset temperature and the range of decomposition temperature for the composites.

The presence of $CaCO_3$ and talc improved the thermal stability of PVC composites considerably. Talc was the best in improving the thermal stability of PVC composites as shown by the largest increase in the range of decomposition temperature and T_{onset} of talc filled PVC composite. The SP-FG, SP-FG-C, SM90 and PC100 filled PVC composites also showed a significant increase in first thermal degradation onset temperatures ($T_{onset\ 1}$) and ranges of decomposition temperature, (ΔT_1). The increase in first thermal degradation onset temperature ($T_{onset\ 1}$) and range of decomposition temperature, (ΔT_1) implied that the addition of $CaCO_3$ (except NPCC) and talc could delay the HCl-elimination reaction of PVC composites.

However, the NPCC filled PVC composite had a lower thermal degradation temperature than all filled PVC composite. The increase in range of decomposition temperature was also small compared to all filled PVC composites. The NPCC filled PVC composite showed the poorest thermal stability among all filled PVC composites. The present of large voids content in NPCC filled PVC composite was believed to be the main reason for lower thermal stability. The SP-FG, SM90 and talc filled PVC composites showed a great increase in $T_{onset\ 2}$ while the SP-FG, PC100 and NPCC filled PVC composites showed an insignificant results in $T_{onset\ 2}$.

Table 4.1: The ranges of decomposition temperatures of PVC composites filled with different types of fillers.

Types of filler	**First Step of Degradation**	**Second Step of Degradation**
	Range of decomposition temperature (ΔT_1), ^{o}C	**Range of decomposition temperature, (ΔT_2), ^{o}C**
SP-FG	250-400	420-580
SP-FG-C	250-400	410-560
SM90	250-410	410-580
PC100	240-400	400-570
NPCC	230-400	410-550
Talc	260-420	430-590
Unfilled PVC	230-390	400-500

Table 4.2: The T_{onset} of the unfilled PVC and PVC Composites filled with different types of fillers.

Types of Fillers	**Grades of Fillers**	**Thermal Degradation Onset Temperature ($T_{onset\ 1}$), °C**	**Thermal Degradation Onset Temperature ($T_{onset\ 2}$), °C**
SP-FG	1.4µm, treated Ground $CaCO_3$	298	457
SP-FG-C	1.4µm, untreated Ground $CaCO_3$	290	442
SM90	0.98µm, untreated Ground $CaCO_3$	297	456
PC100	1µm, Precipitated $CaCO_3$	294	442
NPCC	40nm, treated NPCC	283	448
Talc	6.3µm in mean particles diameter	304	463
Without Filler	-	276	445

- **Percentages of Weight Loss at 300^{0}C**

As mentioned earlier, the talc filled PVC composite showed the best thermal stability compared to all filled PVC composites. From Figure 4.28, the addition of fillers also can reduce the percentage of weight loss of PVC composites at the temperature of 300^{o}C. Among all filled PVC composites, the talc and SM90 filled PVC showed the lowest %weight loss at 300^{o}C. The lower %weight loss at 300^{o}C was attributed to the addition of filler in PVC matrix, which decreased the amount of PVC for each blending at a constant controlled sample weight as discussed by Chen *et al.* (2006). The addition of filler into PVC significantly reduced the weight fraction of PVC resin for each blending.

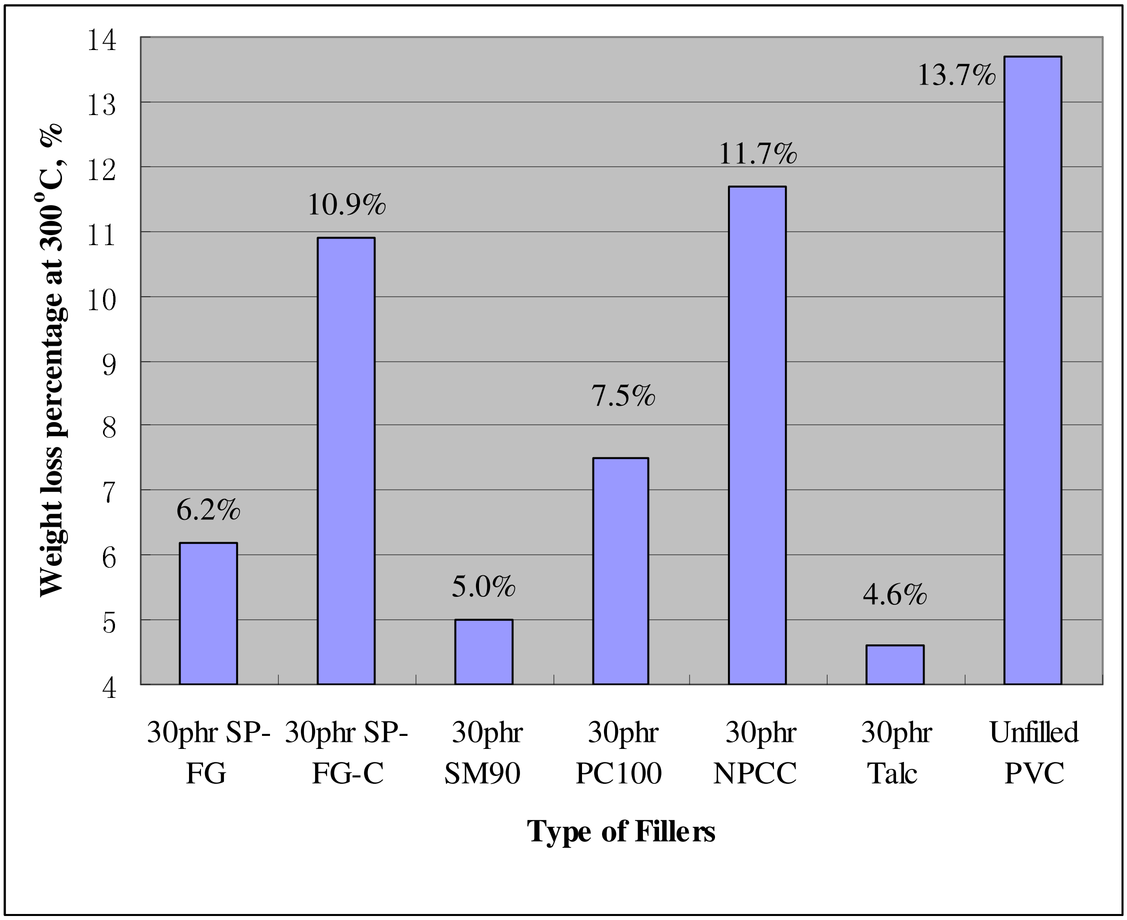


Figure 4.28: The weight loss percentage of PVC composites filled with different types of fillers.

- **Temperature at 5% weight loss (*$T_{5\%}$*)**

Figure 4.29 illustrates the temperatures at 5% weight loss ($T_{5\%}$) of an unfilled PVC and PVC composites filled with different types of fillers. According to Figure 4.29, the temperature at 5% weight loss ($T_{5\%}$) of PVC composites were shifted to higher temperature with the incorporation of talc and all types of $CaCO_3$. The thermal stability of PVC composite was improved considerably with the incorporation of talc and all types of $CaCO_3$. According to Abu Bakar (2006) and Yuan *et al.* (2003), the improvement on thermal stability of polymer composites also could be indicated by the increase in temperature at 5% weight loss ($T_{5\%}$).

From Figure 4.29, the incorporation of NPCC into PVC composite only increased the $T_{5\%}$ of PVC composite by 3.3^{o}C and gave the smallest increase on $T_{5\%}$ among all types of fillers. The SP-FG-C incorporated PVC composite also showed a small increase of 5.5^{o}C on $T_{5\%}$. However, the incorporation of SP-FG, SM90 and PC100 into PVC composites had greatly increased the $T_{5\%}$ of PVC composite by 11.6^{o}C, 13.2^{o}C and 12.3^{o}C, respectively. The SP-FG, SM90 and PC100 could significantly result in better improvement effect on thermal stability of PVC composites than SP-FG-C and NPCC. The SM90 incorporated PVC composite showed the highest increase in $T_{5\%}$ compared to other $CaCO_3$ filled PVC composites. The addition of SM90 can improve the thermal stability by delaying the HCl-elimination reaction of PVC.

The talc incorporated PVC composite showed the highest increase in $T_{5\%}$, compared to all types of fillers. The incorporation of talc highly increased the $T_{5\%}$ from 282.4^{o}C to 302.9^{o}C with an increase of 20.5^{o}C. As mentioned by Yuan *et al.* (2003), the highest value of $T_{5\%}$ indicated that the addition of talc into PVC matrix could result the highest improvement on thermal stability of PVC composite. The addition of talc in PVC matrix can effectively delay the HCl-elimination reaction of PVC and increase the $T_{5\%}$ of PVC composite, thus improve the thermal stability of PVC.

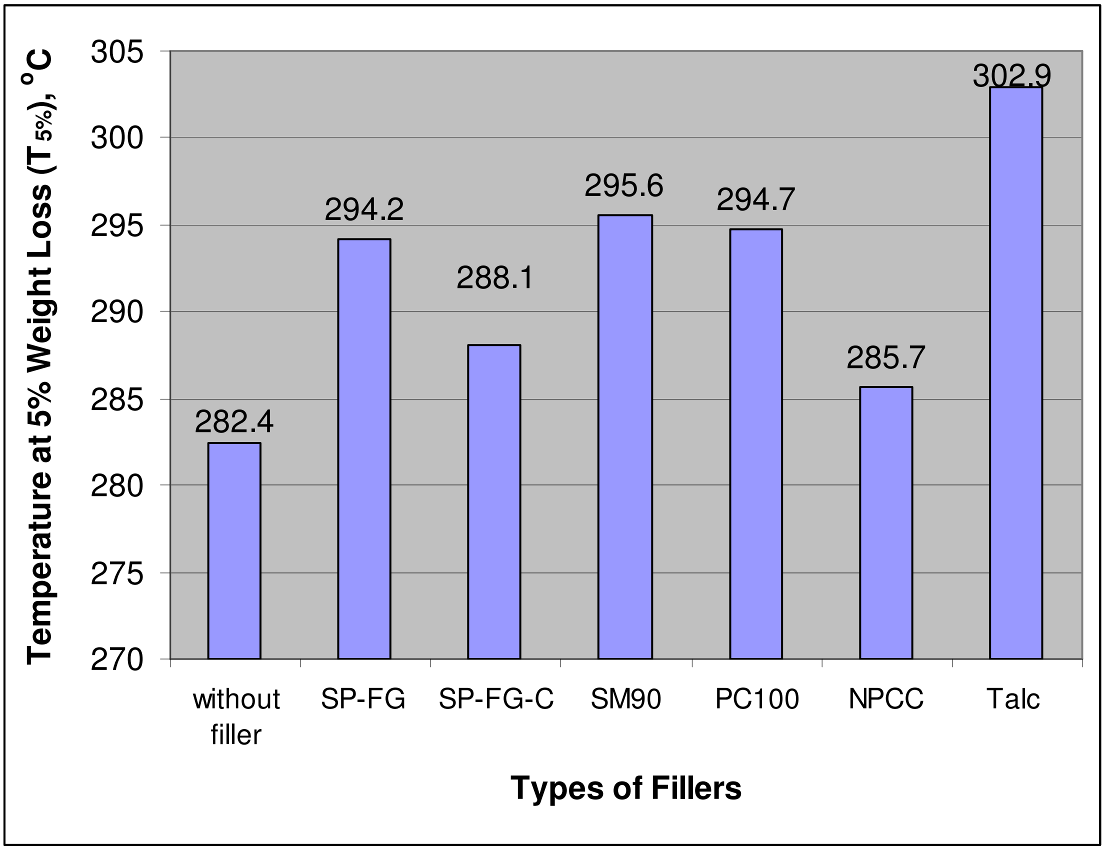


Figure 4.29: Effect of different types of fillers on the temperatures at 5% weight loss ($T_{5\%}$) of PVC composites.

4.3.2.2 Effect of Hybrid Talc/SM90 Fillers

Figure 4.30 illustrates the TGA curves for SM90 and talc fillers, in an atmosphere of nitrogen at the rate of 10°C/min. It can be seen that the degradation of SM90 and talc filler only occurred only after 600°C. The addition of SM90 and talc in PVC matrix would not promote the degradation of PVC composites at the temperature lower than 600°C.

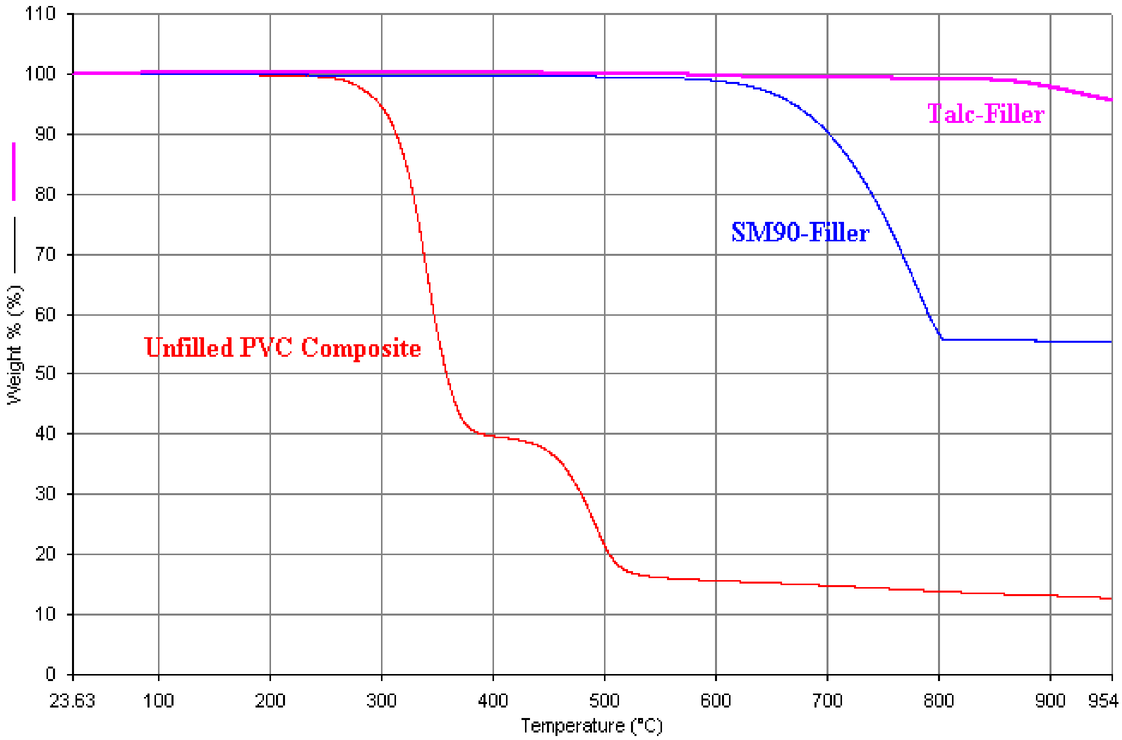


Figure 4.30: TGA curves for unfilled PVC, SM90 and talc fillers in an atmosphere of nitrogen at the rate of 10°C/min.

- **Ranges of degradation temperature and thermal degradation onset temperature**

Table 4.3 reveals that the ΔT_{H1} and ΔT_{H2} (ranges of decomposition temperature of first and second stages degradation) of hybrid talc/SM90 filled PVC composites were slightly increased with increasing talc content. From Table 4.3, the talc filler gave better result in improving the thermal stability of PVC composite compared to SM90 and all hybrids talc/SM90 filled PVC composites. This might be due to the talc filler had higher decomposition temperature than SM90 ($CaCO_3$) filler. However, the increases in the ranges of decomposition temperature of hybrid talc/SM90 filled PVC composites were very small.

Table 4.4 illustrates the first thermal degradation onset temperature ($T_{onset\ H1}$) and the second degradation onset temperature ($T_{onset\ H2}$) increased with the increasing of talc content. However, these increases in $T_{onset\ H1}$ and $T_{onset\ H2}$ were very small. The replacement of SM90 by talc showed an insignificant increase in thermal degradation onset temperatures of hybrid talc/SM90 filled PVC composites. This was because both fillers of talc and SM90 have higher degradation onset temperature compared to PVC composites and also can significantly increase the T_{onset} of PVC composites, respectively. The replacement of SM90 by talc showed an insignificant effect on thermal stability of hybrid PVC composites.

Table 4.3: The ranges of decomposition temperature of Hybrid Talc/SM90 filled PVC composites with different ratio of talc/SM90.

The ratio of Talc/SM90, phr	**First Step of Degradation**	**Second Step of Degradation**
	Range of decomposition temperature (ΔT_{H1}), °C	**Range of decomposition temperature (ΔT_{H2}), °C**
30T: 0S	260-420	430-600
25T: 5S	260-430	430-600
20T: 10S	260-420	430-590
15T: 15S	250-410	430-560
10T: 20S	250-410	420-560
5T: 25S	250-410	420-580
0T: 30S	250-410	410-580
Unfilled PVC	230-390	400-550

Table 4.4: The T_{onset} of Hybrid Talc/SM90 filled PVC Composites with different ratios of Talc/SM90.

The ratio of Talc/SM90	Thermal degradation onset temperature ($T_{onset\ H1}$), ^oC	Thermal degradation onset temperature ($T_{onset\ H2}$), ^oC
30T: 0S	304	463
25T: 5S	304	461
20T: 10S	304	459
15T: 15S	303	457
10T: 20S	302	456
5T: 25S	301	455
0T: 30S	297	456
Unfilled PVC	276	445

- **Weight Loss percentage at 300^{o}C**

As explained in Section 4.3.2.1, talc filled PVC composite showed the best thermal stability compared to all $CaCO_3$ filled PVC composites. From Figure 4.31, the weight loss percentage at 300^{o}C of talc filled PVC composite was found to be the lowest with the value of 4.6%. According to Figure 4.32, talc filler started to degrade at the temperature higher than SM90 as mentioned earlier. The weight loss percentage at 300^{o}C of PVC composites slightly increased with increasing SM90 content. However, these increases were very small and insignificant. The replacement of talc filler with SM90 could slightly decrease the thermal stability of PVC composite. From this result, talc was proved to have better thermal stability than SM90.

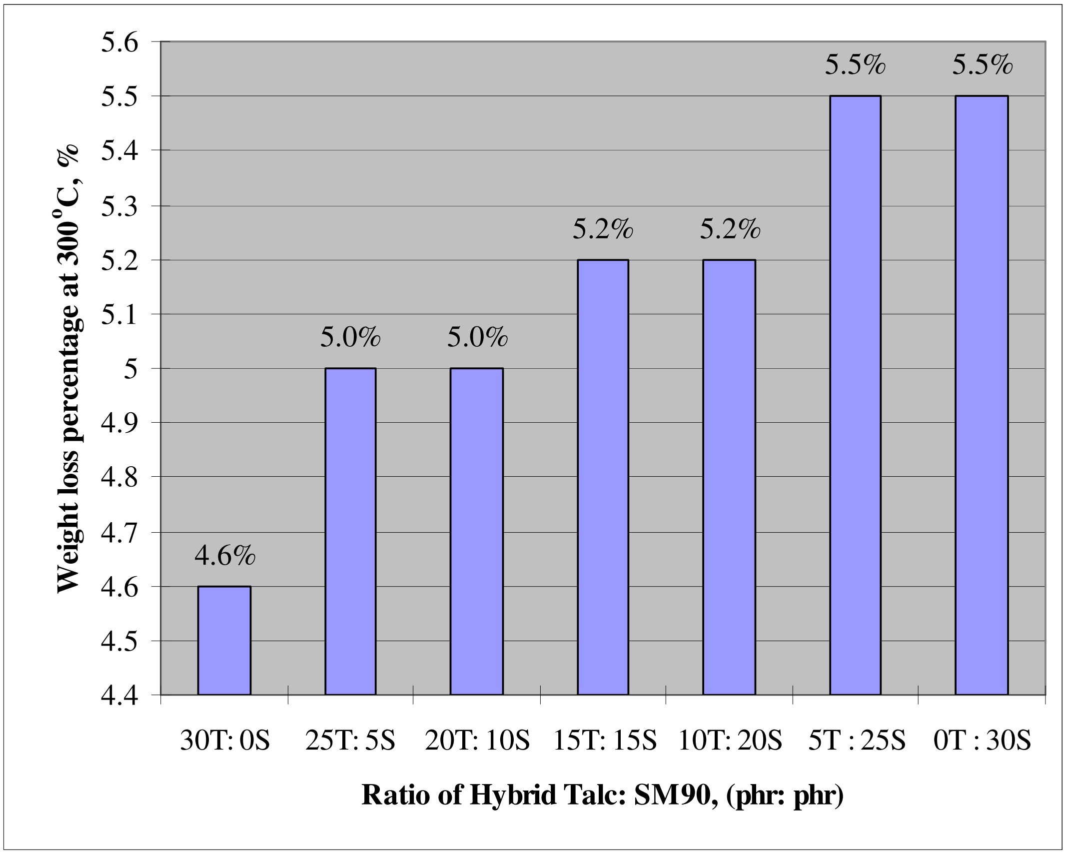


Figure 4.31: The weight loss percentage at 300°C of hybrid Talc/SM90 filled PVC composites filled with different ratio of talc/SM90 fillers.

- **Temperature at 5% weight loss ($T_{5\%}$)**

Figure 4.32 demonstrates the effect of increasing SM90 content to replace talc in PVC composite on temperatures at 5% weight loss ($T_{5\%}$) of PVC composites. From Figure 4.32, the temperatures at 5% weight loss ($T_{5\%}$) of PVC composites were slightly decreased from 302.9°C to 295.6°C with the talc content was gradually replaced by SM90. However, these decrease in $T_{5\%}$ of hybrid PVC composites were small especially at ratios of (15phr Talc: 15phr SM90), (10phr Talc: 20phr SM90) and (5phr Talc: 25phr SM90) and could be considered as insignificant. As discussed earlier, the incorporation of talc into PVC composite showed better result in improving the thermal stability than SM90 filled PVC composite. From Table 4.6, talc filler showed the $T_{5\%}$ of 961°C while the SM90-$CaCO_3$ filler gave the $T_{5\%}$ of 667°C. This indicated that the talc and SM90 fillers have high thermal stability compared to unfilled PVC composite. Obviously, the $T_{5\%}$ of talc was much higher than the $T_{5\%}$ of SM90. This showed that the incorporation of talc into PVC composite could impart a higher thermal stability than SM90.

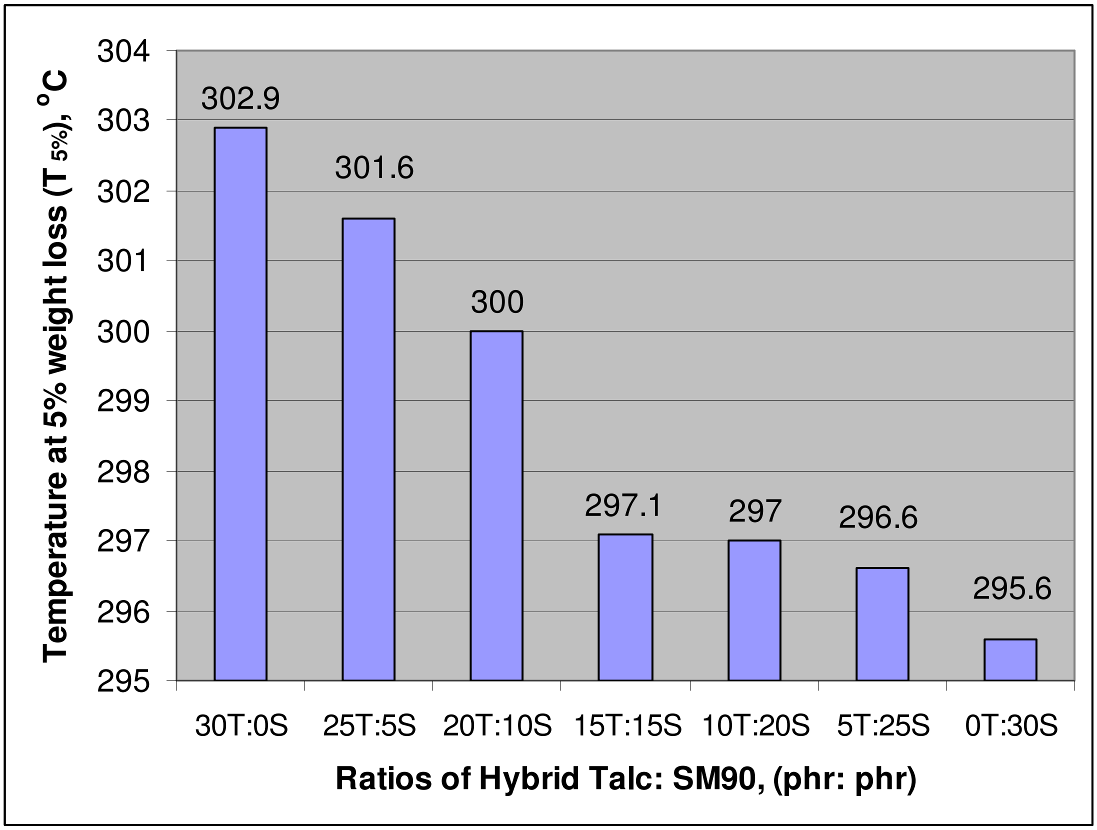


Figure 4.32: Variation of temperature at 5% weight loss ($T_{5\%}$) with the increasing SM90 content to replace talc.

Table 4.5: Temperatures at 5% weight loss ($T_{5\%}$) of unfilled PVC composite, talc and SM90 fillers.

The types of filler	Temperatures at 5% weight loss ($T_{5\%}$), °C
SM90	667
Talc	961

4.4 Processability Studies of Hybrid Talc/SM90 Filled PVC Composites

4.4.1 Fusion Characteristics of PVC Composite in General

Figure 4.33 illustrates a typical fusion curve of an unfilled PVC compound melted in a Haake torque rheometer at a starting temperature of 180^{o}C with a rotor speed of 45rpm and a blending time of 5 minutes. From the fusion curve in Figure 4.33, the first point, L stands for the sample loading. The second point, B is generated because of the balance between sample loading and the driving force of free material flow. Then, the torque starts to increase and reaches the third point, F. The third point, F is generated due to compaction and onset of fusion.

At point F, the material reaches a void free state and starts to melt at the interface between the compacted material and the hot surface of metal. If the sample is melted and fused in the mixer for a long time, the temperature of sample slightly increases due to some thermal energy is absorbed by the sample. The increase in temperature results in decreasing the melt viscosity of sample. Therefore, the torque slowly decreases and increases the blending time of sample. The blending time of sample is defined as the period of time between the point, L and the stopping point (Chen *et al.,* 2006a). The fusion time is defined as the period of time between the point L and the fusion point F. The fusion percolation threshold (FPT) is defined as the torque variation between the point B and the fusion point F.

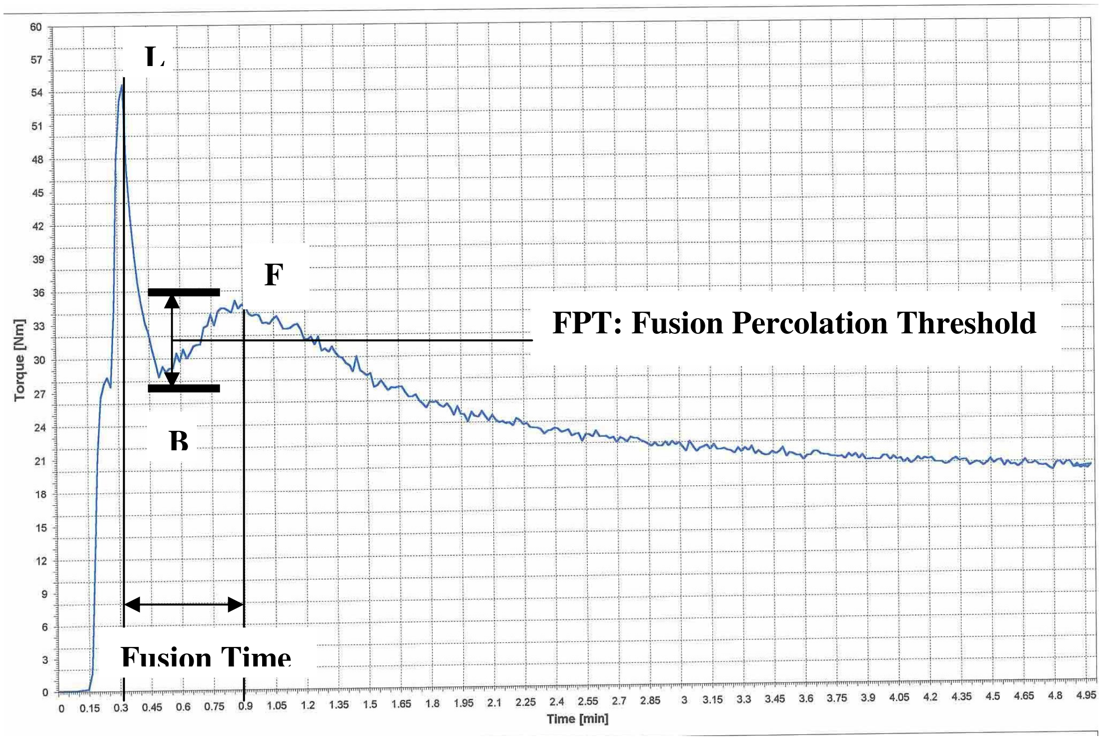


Figure 4.33: Typical fusion curve of an unfilled PVC compound which melted in a Haake Torque Rheometer at a temperature of 180^{0}C with a rotor speed of 45rpm and a blending time of 5minutes.

4.4.2 Fusion Time

4.4.2.1 Effect of Talc and SM90 fillers

Figure 4.34 illustrates the fusion time of unfilled PVC and PVC composites filled with single filler of talc and SM90 ($CaCO_3$), which were melted and fused at processing temperature of 180^{o}C with a rotor speed of 45rpm in a Haake Torque Rheometer for a blending time of 5 minutes.

From Figure 4.34, the unfilled PVC composite showed the shortest fusion time among all filled PVC composites. The addition of fillers such as talc and SM90 significantly increased the fusion time of PVC composite. The addition of 30phr SM90 into PVC compound had greatly lengthen the fusion time nearly 6 times longer than the fusion time of the unfilled PVC composite and also 3 times longer than the fusion time of 30phr talc filled PVC composite. The increase in fusion time of talc filled PVC composite might be caused by the platlike structure, low specific surface area and poor adhesion property of talc particles in PVC matrix which PVC resin particles could not be fused together easily. However, the great increase in fusion time of SM90 filled PVC composite might be caused by the presence of fatty acid on the surface of SM90 which acted like an external lubricant during PVC compounding (Chen *et al.*, 2006a). According to Chen *et al.* (2006), the thermal degradation temperature for the fatty acid on the surface of micron-$CaCO_3$ and nano-$CaCO_3$ are about 260^oC. Similarly from Figure 4.36, a small decrease in weight % of SM90 was observed to be occurred at the temperature range of 230^oC to 290^oC. The content that degraded at this temperature range was believed to be the fatty acid on the surface of SM90. The content of fatty acid on the surface of SM90 is about 0.2wt%.

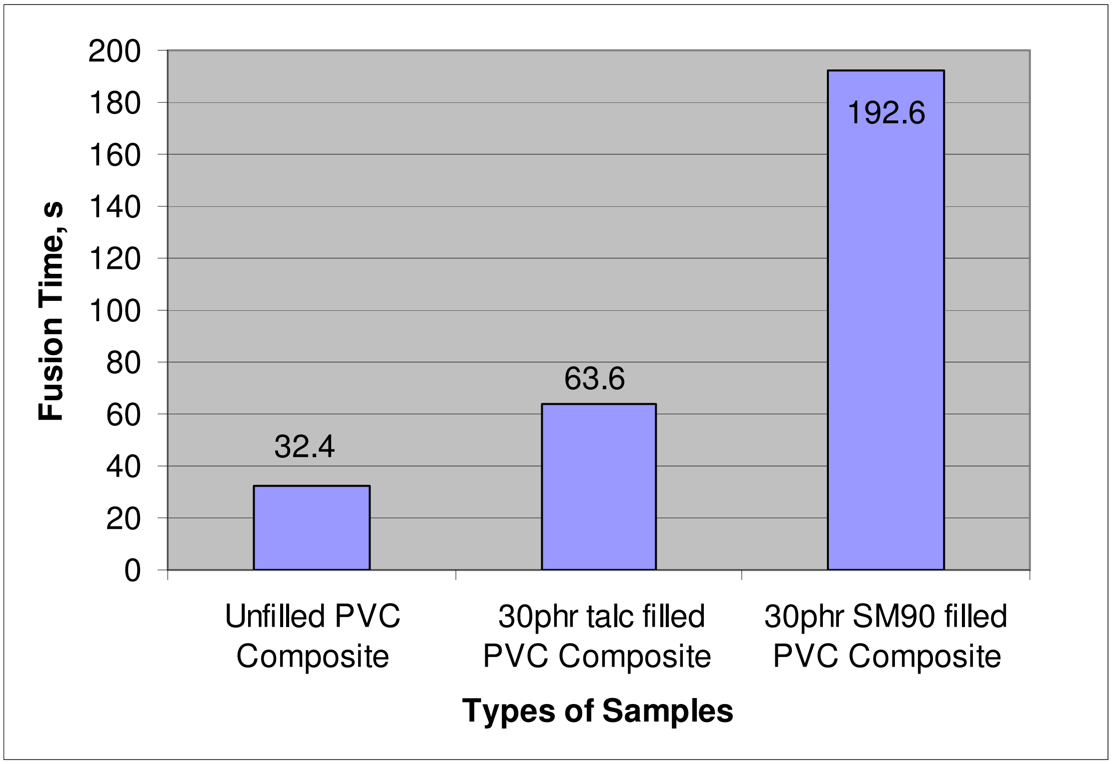


Figure 4.34: Effect of the talc and SM90 on fusion time of rigid PVC composites, respectively.

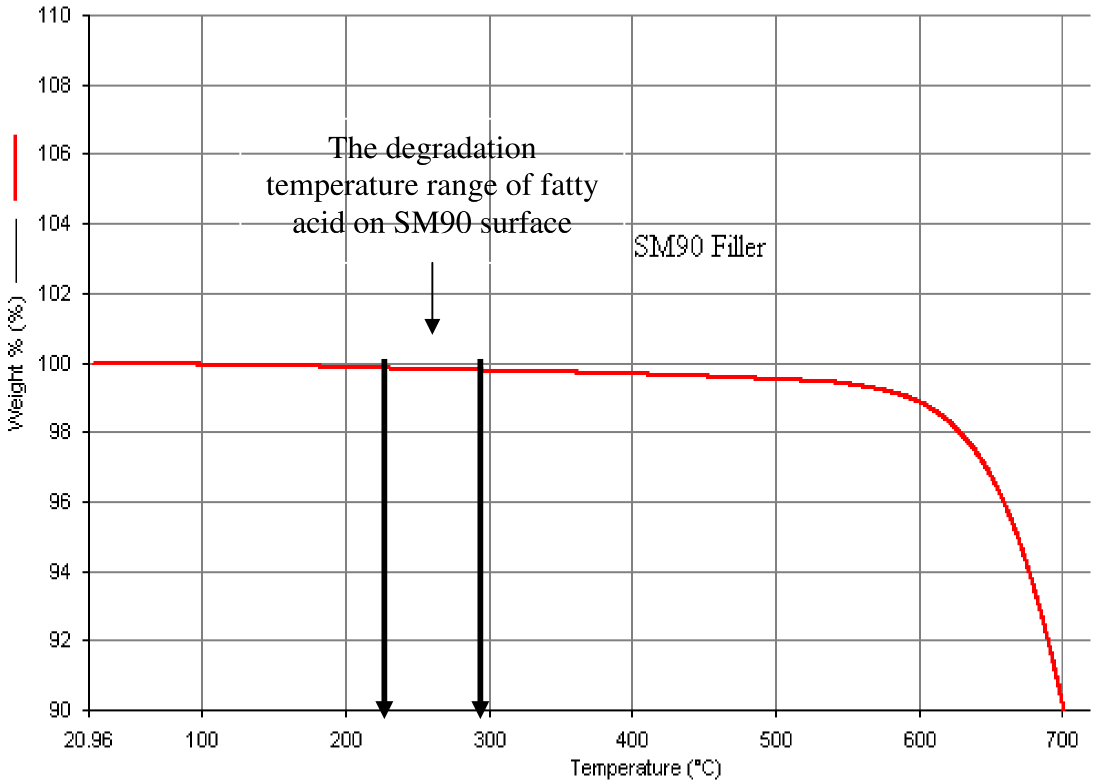


Figure 4.35: The degradation temperature range of fatty acid on SM90-CaCO$_3$ filler.

4.4.2.2 Effect of Hybrid Talc/SM90 Fillers

Figure 4.36 shows the effect of increasing SM90 content to replace talc content in PVC matrix on fusion time of the hybrid talc/SM90 filled PVC composites. The replacement of talc content with SM90 showed greater increase in fusion time than 30phr talc filled PVC composite. As talc slowly replaced by SM90, the presence of fatty acid generated on the surface of SM90 also increased. Increase in SM90 content resulted in more fatty acid generated in PVC composite. The presence of fatty acid on the surface of SM90 which can act like an external lubricant during PVC compounding and increase the fusion time as discussed earlier. The increase in the fatty acid amount caused the PVC molecules could not be fused together easily as the unfilled PVC composite. Chen *et al.* (2006a) explained that the existence of fatty acid on the surface of $CaCO_3$ functioned like an external lubricant that can lengthen the fusion time of PVC.

The hybrid (10phr talc + 20phr SM90) filled PVC composite showed the longest fusion time among all hybrid talc/SM90 filled PVC composites. This might be caused by the combination of the high amount of fatty acid present on the surface of SM90 particles and the different particles shape of talc and SM90 particles in PVC matrix. The uneven in shape of talc and SM90 particles caused the PVC molecules very hard and difficult to be fused together, thus increased the fusion time of PVC compound.

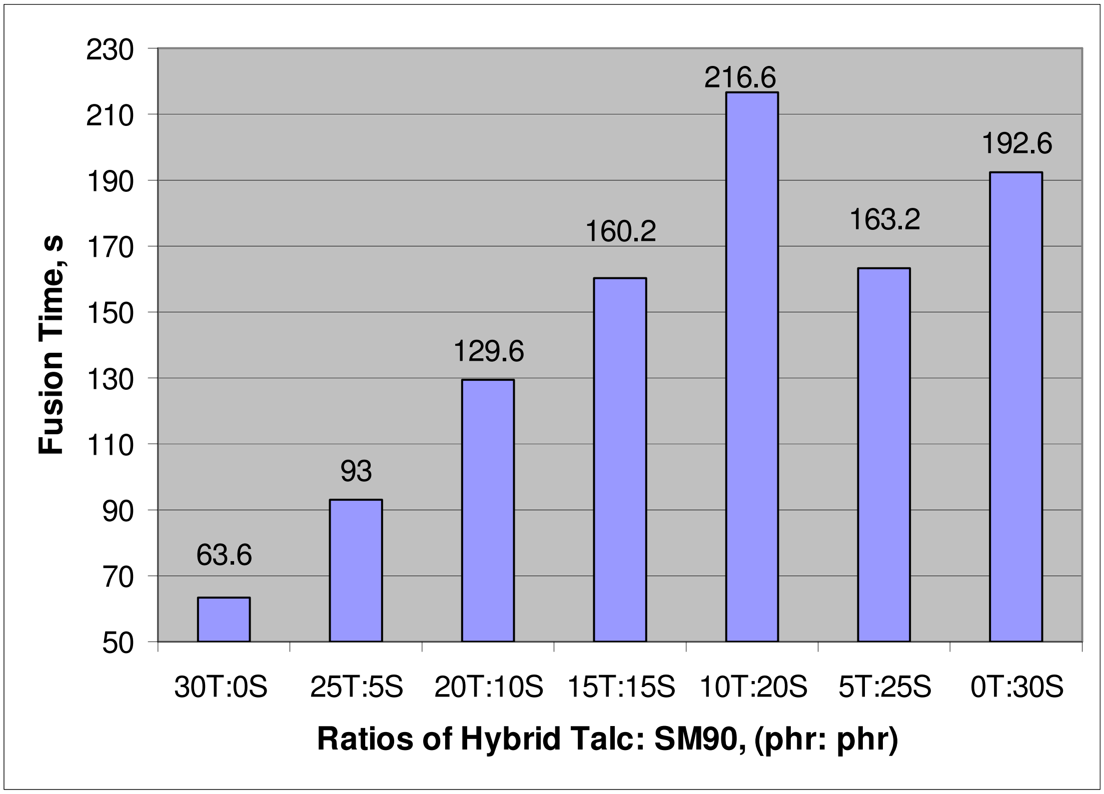


Figure 4.36: Effect of different ratio of Talc/SM90 on fusion time of the hybrid talc/SM90 filled PVC composites.

4.4.3 Fusion Torque

4.4.3.1 Effect of Talc and SM90 fillers

Figure 4.37 demonstrates the effect of talc and SM90 ($CaCO_3$) on fusion torque of rigid PVC composites. It can be seen that the unfilled PVC composite posed the highest fusion torque among all filled PVC composites. Obviously, the fusion torque of PVC composite was reduced by the incorporation of fillers, either talc or SM90. According to Chen *et al.* (2006a) in his study, the fusion torque was reduced by the incorporation of micron-$CaCO_3$ or nano-$CaCO_3$. The fusion torque of PVC composite was gradually reduced as the addition amount of micron-$CaCO_3$ or nano-$CaCO_3$ slowly increased. Chen *et al.* (2006) explained that this was because the fusion temperature increased when the addition of micron-$CaCO_3$ or nano-$CaCO_3$ was increased. Increasing in fusion temperature led to a reduction in melt viscosity of PVC compound. Thus, the fusion torque needed to maintain at 60rpm in his research was decreased as the fusion temperature increased.

Similar to the explanation of Chen *et al.* (2006), the addition of talc and SM90 into PVC matrix also can increase the fusion temperature of PVC compound, irrespective of talc and SM90. The increase in fusion temperature can reduce the melt viscosity of PVC compound and the fusion torque needed to maintain at rotor speed of 45rpm also significantly decreased. From Figure 4.37, the fusion torque of 30phr SM90 filled PVC composite obtained lower value than 30phr talc filled PVC composite. The incorporation of 30phr talc into PVC matrix showed a small reduction in fusion torque compared to 30phr SM90 filled PVC composites. According to Chen *et al.* (2001), the transfer of heat and shear throughout the PVC grains was increased with the addition of talc and SM90 fillers. The heat and shear transfer could increase the fusion temperature and reduce the melt viscosity of PVC compound. Thus, the fusion torque needed to maintain at 45rpm also decreased.

The presence of fatty acid on the surface of SM90 acted like an external lubricant which can promote the slippage between PVC and SM90 molecules. More occurrence of slippage between the PVC and SM90 particles significantly led to generate more friction energy and increased the heat and shear transfer throughout the PVC grains. For talc filled PVC composite, the platelike structure and poor surface adhesion of talc particles and the orientation of talc particles in PVC matrix were the main factors that promoted to generate friction energy between PVC molecules and talc particles.

However, the limited slip between the particles of PVC and talc and the PVC particles and hot metal surface did not generate more friction energy than SM90 filled PVC composite. The heat and shear transfer throughout PVC grains in talc filled PVC was much lower than SM90 filled PVC. As mentioned before, the lower heat and shear transfer led to a small increase in fusion temperature of talc filled PVC. The melt viscosity of talc filled PVC compound was higher than SM90 filled PVC compound. Thus, the fusion torque of talc filled PVC that needed to maintain the rotor speed at 45rpm was also higher than SM90 filled PVC.

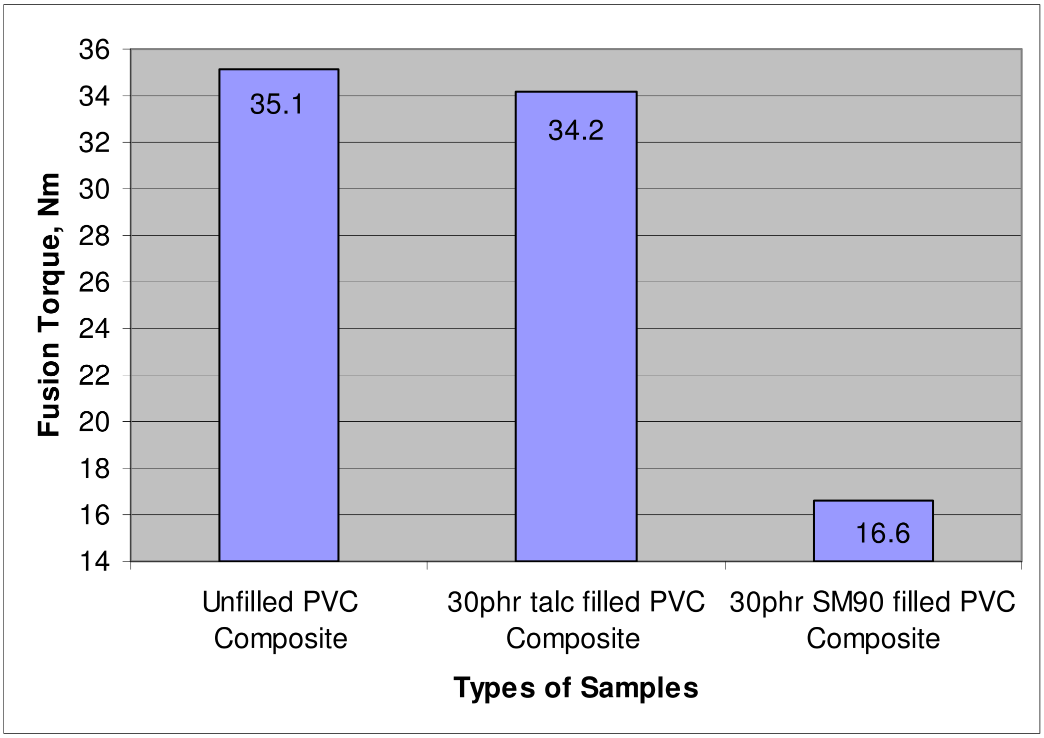


Figure 4.37: Effect of the talc and SM90 fillers on the fusion torques of rigid PVC composites, respectively.

4.4.3.2 Effect of Hybrid Talc/SM90 Fillers

Figure 4.39 shows the change in fusion torque of PVC composite varying with the different ratio of talc/SM90. The fusion torque of 30phr SM90 filled PVC composite obtained the lowest value among all hybrid talc/SM90 and 30phr talc filled PVC composites. The incorporation of 30phr talc into PVC matrix showed the smallest reduction in fusion torque among all hybrid talc/SM90 and 30phr SM90 filled PVC composites. From Figure 4.39, the fusion torque of PVC composite was slightly decreased as the talc content gradually replaced with SM90. But, the fusion torque of all hybrid talc/SM90 filled PVC composite was still higher than the 30phr SM90 filled PVC composite. 30phr SM90 filled PVC contained the highest SM90 amount compared to all hybrid PVC compound. The increase in SM90 content can result more fatty acid generated on surface of SM90 particles. The existence of fatty acid on SM90 surface can act like an external lubricant and reduce the friction between PVC and SM90 particles as discussed earlier. Thus, the fusion torque needed to maintain at a rotor speed of 45rpm also decreased. However, with further increasing of SM90 content used to replace talc content, the change in fusion torque of PVC composite became very small and insignificant until could be negligible.

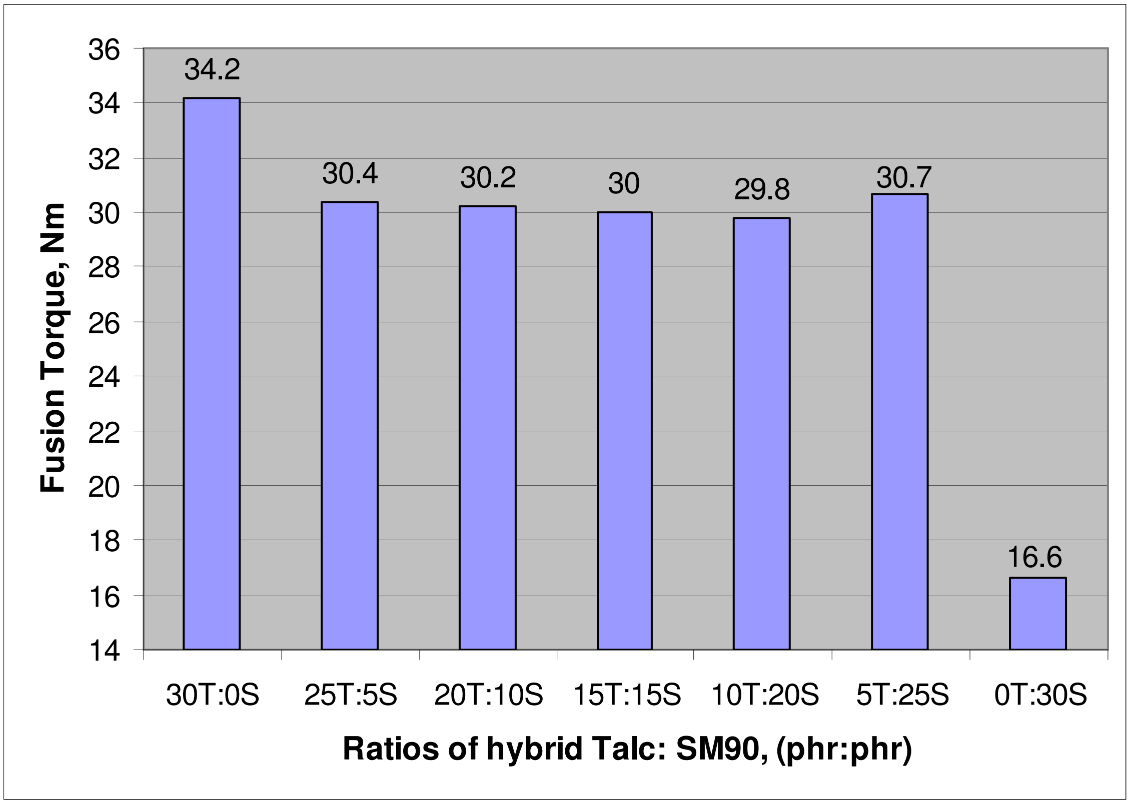


Figure 4.38: Effect of different ratio of Talc/SM90 on fusion torques of the hybrid talc/SM90 filled PVC composites.

4.4.4 Fusion Percolation Threshold (FPT)

4.4.4.1 Effect of Talc and SM90 fillers

Figure 4.39 shows the effect of talc and SM90 ($CaCO_3$) fillers on fusion percolation threshold (FPT) of PVC composites. The processing temperature and torque were fixed at 180^{o}C and 45rpm for a blending time of 5 minutes. From Figure 4.40, talc filled PVC and SM90 filled PVC composites showed a longer fusion time and FPT than the unfilled PVC composite. The FPT of PVC composite was sharply increased almost 3.5 times compared to the unfilled PVC composite by the addition of 30phr talc. The increase in FPT of 30phr SM90 filled PVC composite was nearly 2 times lower than the 30phr talc filled PVC composite. Obviously, the addition of talc or SM90 apparently increased the FPT of PVC composite.

As mentioned before, the addition of fillers, either talc or SM90 can significantly increase the fusion time of PVC composites. Chen *et al.* (2006a) explained that the lengthening of fusion time resulted in increasing the FPT of PVC composite. Increasing in the fusion time implied that more thermal energy is required to be absorbed to fuse PVC molecules and filler particles together. If the thermal energy was not enough to pass the FPT, the PVC compounds could not be fused. The incorporation of 30phr SM90 into PVC composite highly increased the FPT up to 1.6 times of the FPT of the unfilled PVC composite. The indicated that the 30phr SM90 filled PVC compound needed to absorb more thermal energy for passing the FPT, so the SM90 filled PVC compound could be fused together. However, the FPT of 30phr talc filled PVC composite was almost 2 times higher than the FPT of 30phr SM90 filled PVC composite. This implied that the 30phr talc filled PVC compound needed to absorb nearly 2 times of thermal energy that required by 30phr SM90 filled PVC compound to pass the high FPT. The dry blend of 30phr Talc filled PVC was harder to reach the starting point of melt and fuse together compared to 30phr SM90 filled PVC at the same temperature. The 30phr talc filled PVC needed more time than 30phr SM90 filled PVC to reach the melt and fuse starting point. The high FPT of PVC dry blend might cause some of the dry blend had degraded during milling before it starting to melt and fuse together.

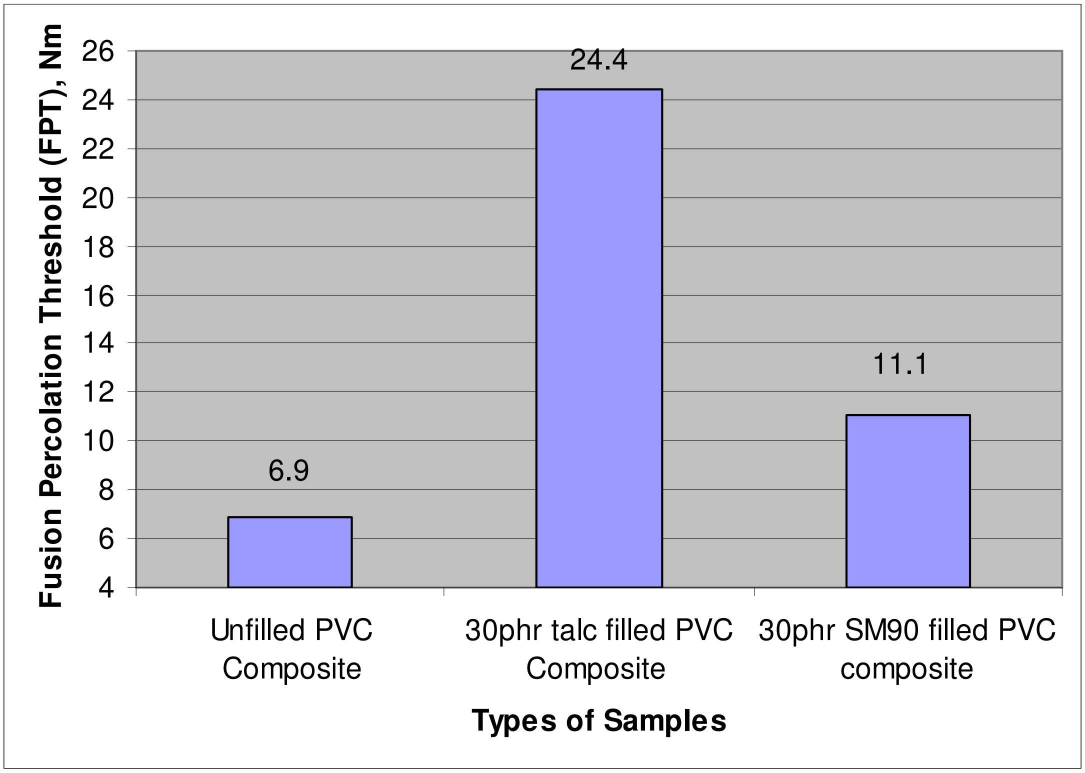


Figure 4.39: Effect of the talc and SM90 fillers on fusion percolation threshold (FPT) of PVC composites.

4.4.4.2 Effect of Hybrid Talc/SM90 Fillers

Figure 4.40 illustrates the effect of different ratio of talc/SM90 on the fusion percolation threshold of PVC composites. It can be seen that all hybrid talc/SM90 filled PVC composites showed a higher FPT than the 30phr talc filled PVC and 30phr SM90 filled PVC composites. As discussed earlier, the increase in the fusion time showed that more thermal energy is required to be absorbed to fuse PVC molecules and filler particles together. From Figure 4.40, the FPT of PVC composite was slightly increased as the talc content slowly replaced with SM90. With further increase in SM90 content used to replace the talc content, the increase in FPT of PVC composite was too small and insignificant and could be negligible. The incorporation of hybrid talc and SM90 fillers in PVC matrix led to higher FPT of PVC composite. All hybrid talc/SM90 filled PVC composites needed to absorb more thermal energy than the single filler of talc or SM90 filled PVC composite to pass the FPT and fuse the PVC, talc and SM90 particles together.

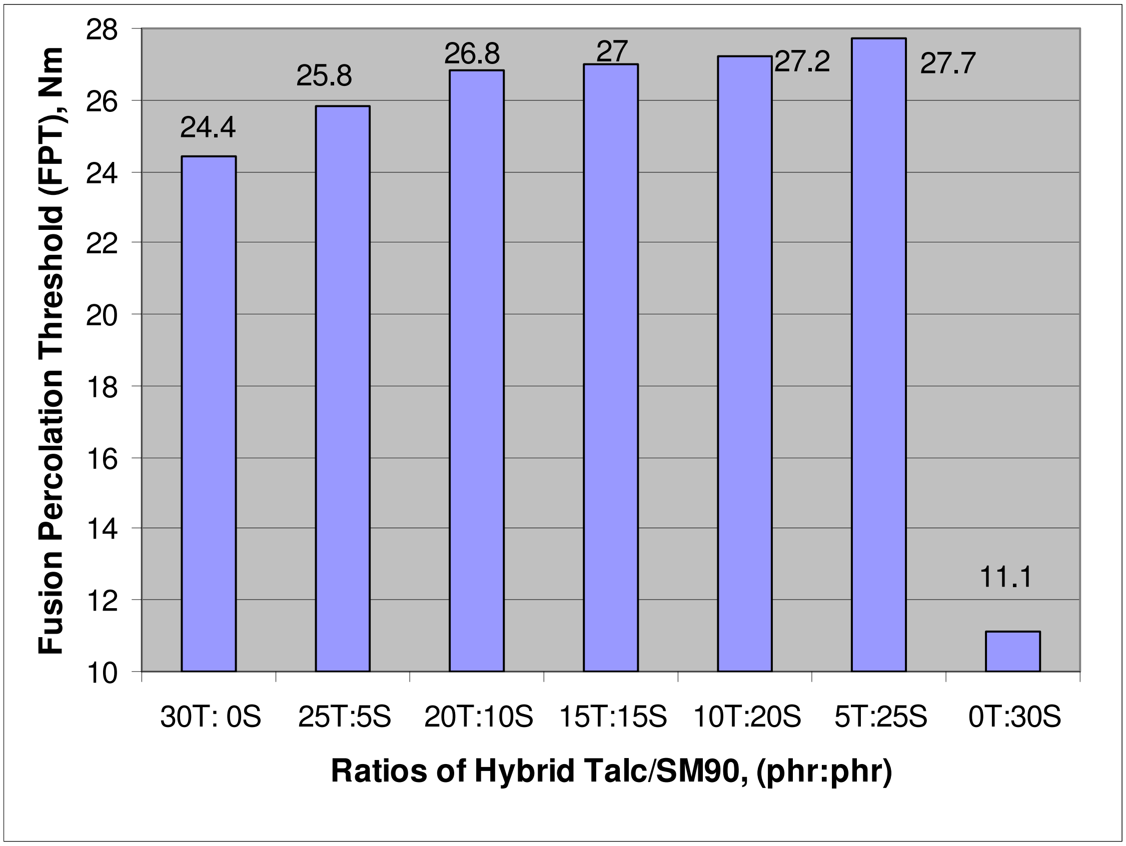


Figure 4.40: Effect of different Talc/SM90 ratio on fusion percolation threshold (FPT) of the hybrid talc/SM90 filled PVC composites.

4.5 Determination of Densities

4.5.1 Effect of Different Types of Fillers

Figure 4.41 shows the comparison between the theoretical and experimental densities of unfilled PVC composite and PVC composites filled with different types of fillers. It can be seen that all filled PVC composites were found to have higher density than the unfilled PVC composite. The experimental density of the unfilled PVC composite was 1.406g/cm^3 and this density value was nearly similar to the density value reported by Abu Bakar (2006) in his study. The incorporation of fillers such as SP-FG, SP-FG-C, SM90, PC100, NPCC and talc significantly increased the densities of PVC composites. However, all the experimental densities obtained were lower than the theoretical densities.

The lowering in experimental densities of PVC composites was attributed by the presences of voids in PVC matrix. Abu Bakar (2006) also reported that the voids probably existed in the PVC matrix at the filler-matrix interface or within the filler bundles. The SEM micrographs in Figures 4.12 to 4.18 show the presence of voids at $CaCO_3$-matrix interface in the composites. The presence of voids in SM90 filled PVC composite as shown by SEM micrograph shown in Figure 4.15 was smaller and fewer than the others filled PVC composites. This was the main reason that the lowering in experimental density of SM90 filled PVC composite was minimal. The experimental density of NPCC filled PVC composite experienced the biggest drop when compared to the theoretical density of NPCC filled PVC composite. This was attributed by the severe agglomeration of NPCC particles in PVC matrix and led to increase voids content at the aggregate-matrix. Thus, the increase of voids content in PVC matrix greatly decreased the experiment density of NPCC filled PVC composite.

The lowering of experimental density of talc filled PVC composite was also very high in comparing to other filled PVC composites except for the NPCC filled PVC composite. From the SEM micrograph in Figure 4.18, the voids existed not only in the PVC matrix at the talc-matrix interface and also within the talc bundles. The platy particles of talc and poor surface adhesion between talc particles and PVC matrix were believed to be the main reason led to increase the presence of voids in talc filled PVC composite. The lowering in experimental density of unfilled PVC composite was attributed to the presence of voids in between the unfused and unmelted PVC particles and matrix interface as shown by SEM micrograph in Figure 4.12.

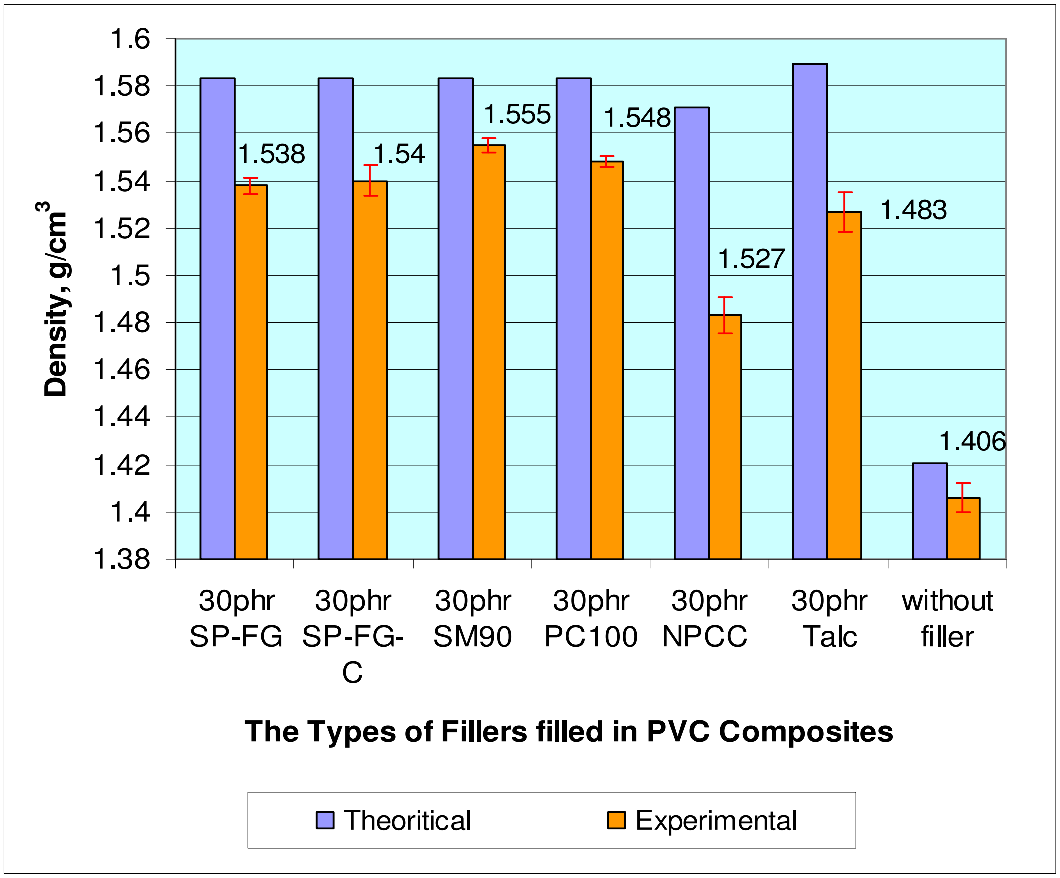


Figure 4.41: Comparison between the theoretical densities and experimental densities of unfilled PVC and PVC composites filled with different types of fillers.

4.5.2 Effect of Hybrid Talc/SM90 Fillers

Figure 4.42 demonstrates the comparison between the theoretical densities and experimental densities of hybrid talc/SM90 filled PVC composites with different ratios of talc/SM90. From Figure 4.42, the theoretical density of 30phr talc filled PVC composite was obviously the highest among all hybrid composites. However, the experimental density of 30phr talc filled PVC composite was significantly the lowest and the 30phr SM90 filled PVC composite gave the highest experimental density. From Figure 4.42, the theoretical densities of hybrid composites slightly decreased as the talc content was gradually replaced with SM90. However, the experimental densities of hybrid composites slowly increased as the talc was gradually replaced by SM90.

Obviously, the experimental densities of hybrid talc/SM90 filled composites were totally opposite to the theoretical densities of hybrid talc/SM90 filled PVC composites. This might because that the addition of talc in PVC matrix can lead to increase more voids content in PVC matrix than SM90 due to the particles size and shapes of talc particles. As mentioned before, the platy structure of talc particles not only contributed to the presence of voids at filler-matrix, but also led to create voids at within the talc particles bundles as shown by SEM micrograph in Figure 4.18. The poor surface adhesion between talc particles and PVC matrix also contributed to the presence of voids at the interface between talc filler and PVC matrix as mentioned earlier.

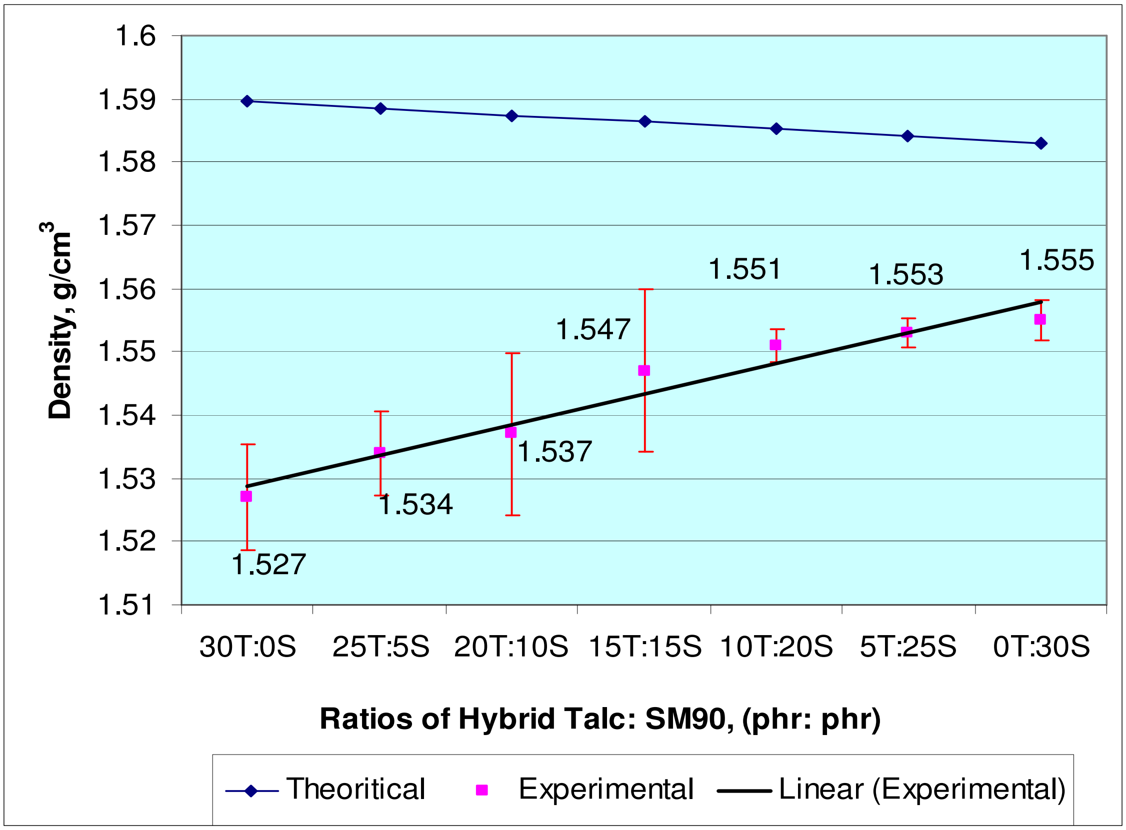


Figure 4.42: Comparison between the theoretical densities and experimental densities of hybrid Talc/SM90 filled PVC composites with different ratio of Talc/SM90.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORKS

5.1 Conclusions

The characteristics of mechanical, thermal and fusion of hybrid talc/$CaCO_3$ filled PVC composite have been studied by using different talc/SM90 ratio. The addition of fillers such as talc and $CaCO_3$ into PVC composite could increase the flexural modulus of PVC composite. However, the addition of talc and $CaCO_3$ significantly decreased the flexural strength of PVC composite and the decrease in flexural strength of talc filled PVC composite was the most minimal. The impact and flexural result showed that the talc filled PVC composite to have higher flexural modulus but lower impact strength compared to all $CaCO_3$ filled PVC composites. For $CaCO_3$ filled PVC composites, SM90 showed the most optimum properties in terms of impact strength and flexural modulus. The SM90 filled PVC composites gave the highest impact strength and flexural modulus among all $CaCO_3$ filled PVC composites was selected for the hybrid study.

The impact strength of hybrid talc/SM90 $CaCO_3$ PVC composites increased gradually with increasing SM90 content. However, the flexural modulus of hybrid talc/SM90 $CaCO_3$ PVC composites decreased gradually with increasing SM90 content. The results of flexural modulus and impact strength have shown that a synergistic hybridization was reached when 20phr talc replaced by 20phr SM90 (hybrid 10phr talc +

20phr SM90 filled PVC composite). For the hybrid talc/SM90 PVC composites, Talc/SM90 (10phr:20phr) filled PVC composite showed the most optimum properties in balancing impact strength and flexural modulus.

The tensile strength of hybrid talc/SM90 filled PVC composites decreased gradually with increasing content of SM90. The addition of talc and SM90 decreased the tensile strength of PVC composite. However, the incorporation of talc and SM90 increased the Young's modulus of PVC composite. The Young's modulus of hybrid talc/SM90 filled PVC composites gradually decreased with an increasing replacement of talc content by SM90.

The SEM micrographs showed that the addition of all types of fillers could significantly increase the cavities in PVC matrix. The agglomeration of NPCC particles increased the cavities in PVC matrix. The SEM micrograph of SM90 has shown that the SM90 particles were evenly dispersed in PVC matrix compared to the other types of $CaCO_3$. The SEM micrograph of talc filled PVC composite has shown that the talc particles were found in platlike structure with high aspect ratio and orientated in parallel to each other in PVC matrix. It is also shown that the particles of talc were clearly invisible and the talc particles were also tending to be embedded inside the polymer matrix.

From the results of DSC thermograms, the addition of all types of fillers had improved the glass transition temperature onset of PVC composite. For hybrid Talc/SM90 filled PVC composites, the glass transition temperature onset slowly decreased as the talc gradually replaced by SM90. However, the hybrid (10phr talc: 20phr SM90) filled PVC composite showed the highest glass transition temperature onset compared to all hybrid talc/SM90 filled PVC composites.

The heat deflection temperature (HDT) revealed that the addition of fillers (different types of $CaCO_3$ and talc) had improved the HDT of PVC composite. The talc filled PVC composite showed the highest HDT compared to all filled PVC composites. The improvement in flexural modulus had increased the rigidity of PVC composite and the increase in rigidity had contributed to the improvement in HDT value. The HDT of the hybrid PVC composites decreased as the talc content was slowly replaced by SM90. However, the increases in HDT value were very small and could be negligible

TGA curves have shown that the incorporation of fillers significantly increased the thermal degradation onset temperatures and ranges of decomposition temperature of hybrid talc/SM90 filled PVC composites. The first step thermal degradation onset temperatures $T_{onset\ 1}$ and second step thermal degradation onset temperatures, $T_{onset\ 2}$ of hybrid talc/SM90 filled PVC composites were increased as the SM90 content was slowly replaced by talc. The %weight losses of hybrid talc/SM90 composites were significantly decreased with the addition of fillers.

The fusion results have shown that the addition of talc and SM90 significantly increased the fusion time of PVC composite. At 30 filler content, the fusion time of SM90 filled PVC composite was three times longer than talc filled PVC composites. The fusion time of hybrid talc/SM90 filled PVC composite increased with increasing SM90 content. The hybrid (10phr Talc: 20phr SM90) filled PVC composite showed the longest fusion time among all PVC composites. Talc and SM90 decreased the fusion torque of PVC composite. At 30 filler content, the fusion torque of SM90 filled PVC composites was more than two times lower than talc filled PVC composites. The fusion torque of hybrid talc/SM90 filled PVC composite decreased with increasing SM90 content. All the hybrid composites showed higher FPT value compared to single talc or SM90 filled PVC.

The densities results have shown that the incorporation of fillers significantly could increase the densities of PVC composites. The experimental densities of unfilled

PVC composite and PVC composites filled with different types of fillers were lower than the theoretical densities. The lowering in experimental densities of PVC composites was attributed by the presences of voids in PVC matrix.

5.2 Recommendations for Future Works

a. The effect of surface treatments can be studied
  - **i.** The talc and SM90 used in hybrid talc/SM90 filled PVC composites can be treated with different surface treatment such silane, titanate, sodium stearate in order to improve the bonding of filler particles PVC matrix.
  - **ii.** The PC100 and NPCC used in this study also can be treated with different surface treatments to improve the surface adhesion between the fillers particles and PVC matrix and prevent the particles PC100 and NPCC from severe agglomerated.

b. The distribution of hybrid talc and SM90 fillers in PVC matrix can be observed by using SEM. The morphological properties of hybrid composites can be studied and correlated the mechanical properties of hybrid composites in this study.

c. The rheological properties of hybrid PVC composites can be studied to investigate the effect of hybrid fillers on the shear and complex viscosity of PVC compound.

d. The effect of other inorganic filler such as clay, kaolin and mica on the mechanical properties of hybrid PVC composite can be investigated and compared to the results in this study.

REFERENCES

Abu Bakar, A., Hassan, A. and Mohd Yusof, A.F. (2005a). Effect of Oil Palm Fruit Bunch and Acrylic Impact Modifier on Mechanical Properties and Processability of Unplasticized Poly(Vinyl Chloride) Composites. *Polymer-Plastics Technology and Engineering*. 44, 1125-1137.

Abu Bakar, A., Hassan, A. and Mohd Yusof, A.F. (2005b). Mechanical and Thermal Properties of Oil Palm Empty Fruit Bunch-Filled Unplasticized Poly(Vinyl Chloride) Composites. *Polymer and Polymer Composites*. 13, 607-617.

Abu Bakar, A. (2006). *Mechanical, Thermal and Processing Properties of Oil Palm Empty Fruit Bunch-Filled Impact Modified Unplasticized Poly(Vinyl Chloride) Composites*. Doctor Philosophy, Universiti Teknologi Malaysia, Skudai. 63-64.

Abu Bakar, A., Hassan, A and Mohd Yusuf, A.F. (2006). The Effect of Oil Extraction of Oil Palm Empty Fruit Bunch on Processability Impact and Flexural Properties of PVC-U Composites. *International Journal of Polymeric Materials.* 55, 1-15.

Abu Bakar, M.B., Leong, Y.W., Ariffin, A. and Mohd Ishak, Z.A. (2007). Mechanical, Flow, and Morphological Properties of Talc- and Kaolin-Filled Polypropylene Hybrid Composites. *Journal of Applied Polymer Science.* 104, 434-441.

Azimipour, B. and Marchand, F. (2006). Effect of Calcium Carbonate Particle Size on PVC Foam. *Journal of Vinyl and Additives Technology.* 12, 55-57.

Butters, G. (1982). *Particulate Nature of PVC-Formulation, Structure and Processing*. (1-9, 145-160, 174-176). London:Applied Science Publishers LTD.

Chen, C.H., Wesson, R.D., Collier, J.R. and Lo, Y.W. (1995a). Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. I. Morphological Characteristics of Poly(vinyl chloride)/Chlorinated Polyethylene (PVC/CPE) Blends. *Journal of Applied Polymer Science.* 58, 1087-1091.

Chen, C.H., Wesson, R.D., Collier, J.R. and Lo, Y.W. (1995b). Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. II. Determination of the Fusion Level. *Journal of Applied Polymer Science.* 58, 1093-1099.

Chen, C.H., Wesson, R.D., Collier, J.R. and Lo, Y.W. (1995c). Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. III. Correlation of Compounding Energy with Fusion Level. *Journal of Applied Polymer Science.* 58, 1101-1105.

Chen, C.H., Wesson, R.D., Collier, J.R. and Lo, Y.W. (1995d). Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. IV. Fusion Characteristics and Morphology Analyses. *Journal of Applied Polymer Science.* 58, 1101-1105

Chen, C.H., Mao, C.F. and Lo, Y.W. (2001).Study of Fusion Percolation Thresholds of Rigid PVC Compounds. *Journal of Applied Polymer Science.* 81, 3022-3029.

Chen, C.H., Teng, C.C. and Yang, C.H. (2005a). Preparation and Characterization of Rigid Poly(vinyl chloride)/MMT Nanocomposites. *Journal Applied Polymer Science.* 43, 1465-1475.

Chen, C.H., Teng, C.C., Su, S.F., Wu, W.c. and Yang, C.H. (2006a). Effect of Microscale Calcium Carbonate on the Fusion, Thermal, and Mechanical Characterization of Rigid Poly(vinyl chloride)/Calcium Carbonate Composites. *Journal of Polymer Science: Part B: Polymer Physics.* 44, 451-460.

Chen, C.H., Li, H.C., Teng, C.C. and Yang, C.H. (2006b) Fusion, Electrical Conductivity, Thermal, and Mechanical Properties of Rigid Poly(vinyl chloride)/Carbon Black (CB) Composites. *Journal Applied Polymer Science.* 99, 2167-2173.

Chen, N., Wan, C.Y., Zhang, Y. and Zhang, Y.X. (2003). Effect of Nano-$CaCO_3$ on Mechanical properties of PVC and PVC/Blendex Blend. *Polymer Testing.* 23, 169-174.

Chen, N., Wan, C.Y., Zhang, Y., Zhang, Y.X., and Zhang, C.M. (2005). Fracture Behavior of PVC/Blendex/Nano-$CaCO_3$ Composites. *Journal of Applied Polymer Science.* 95, 953-961.

Clough, R.L., Billingham, N.C. and Gillen, K.T. (1995). *Polymer Durability-Degradation, Stabilization and Lifetime Prediction.* The American Chemical Society.

Cunha Lapa, V.L.D., Visconte, L.L.Y., Sena Affonso, J.E.D. and Nunes, R.C.R. (2002). Aluminum hydroxide and carbon black filled NBR/PVC composites-vulcanization and processability studies. *Polymer Testing.* 21, 443-447.

Denac, M., Musil, V. and Šmit, I. (2004). Structure and Mechanical Properties of Talc-Filled Blends of Polypropylene and Styrenic Block Copolymers. *Journal of Applied Polymer Science.* 42, 1255-1264.

Denac, M., Musil, V. and Šmit, I. (2005). Polyepropylene/talc/SEBS (SEBS-g-MA) composites. Part 2. Mechanical properties. *Composites. Part A: Applied Science and Manufacturing*. 36, 1283-1290.

Dick, J.S. (1987). *Compounding materials for the polymer industries: a concise guide to polymers, rubbers, adhesives, and coatings*. Park Ridge, N.J.: Noyes Data.

Feldman, D., Banu, D., Manley, R.S.J. and Zhu, H. (2003). Highly Filled Blends of a Vinylic Copolymer with Plasticized Lignin: Thermal and Mechanical Properties. *Journal of Applied Polymer Science.* 89, 2000-2010.

Gachter, R., Muller, H. and Klemchuk, P.P. (1993). *Plastics Additives Handbook-Stabilizers, Processing Aids, Plasticizers, Fillers, Reinforcements, Colorants for Thermoplastics.* (4th ed). New York: Hanser Publishers, Munich Vienna New York Barcelona.

Gilbert, M. and Vyvode, J.C. (1981). Thermal Analysis technique for investigating gelation of rigid PVC compound. *Polymer.* 22(8), 1134-1136.

Hassan, A and Haworth, B. (2005). Impact Properties of Acrylate Rubber-Modified PVC: Influence of Temperature. *Journal of Materials Processing Technology.* 172, 341-345.

Hassan, A. and Kannan, S.K. (2001). Effect of Titanate,Zirconate and Silane Coupling Agents in Rice Husk Ash-Filled PVC-U Composites. *Journal of The institute of Materials Malaysia.* 2(2), 31-42.

Hassan, A and Sivaneswaran, K. (2005). Processability of ABS Impact Modified PVC-U- Effect of Rice Hush Ash (RHA) Fillers and Coupling Agents. *Jurnal Teknologi.* 42(F), 67-74.

Jiang, H.H., Pascal Kamdem, D., Bezubic, B. and Ruede, P. (2003). Mechanical Properties of Poly(vinyl chloride)/Wood Flour/Glass Fiber Hybrid Composites. *Journal of Vinyl and Additive Technology.* 9, 138-145.

Kim, K.J., and White, J.L. (1999). Rheological Investigations of Suspensions of Talc, calcium Carbonate, and Their Mixtures in Polystyrene Melt. *Polymer Engineering And Science.* 39(11), 2189-2198.

Kim, K.J., White, J.L., Shim, S.E., and Choe, S.J. (2004). Effects of Stearic Acids Coated Talc, $CaCO_3$ and Mixed Talc/$CaCO_3$ Particles on the Rheological Properties of Polypropylene Compounds. *Journal of Applied Polymer Science.* 93, 2105-2113.

Klemchuk, P.P. (1985). *Polymer Stabilization and Degradation.* Washington: American Chemical Society.

Kumar, S., Jog, J.P. and Natarajan, U. (2003). Preparation and Characterization of Poly(mrthyl methacrylate-Clay Nanocomposites via Melt Intercalation: The Effect of Organoclay on the Structure and Thermal Properties. *Journal of Applied Polymer Science.* 89, 1186-1194.

Leong, Y.W., Abu Bakar, M.B., Mohd Ishak, Z.A. and Ariffin, A. (2003). Characterization of Talc/Calcium Carbonate Filled Polypropylene Hybrid Composites Weathered in a Natural Environment. *Polymer Degradation and Stability.* 83, 411-422.

Leong, Y.W., Mohd Ishak, Z.A. and Ariffin, A. (2004a). Mechanical and Thermal Properties of Talc and calcium Carbonate Filled Polypropylene Hybrid Composites. *Journal Applied Polymer Science.* 91, 3327-3336.

Leong, Y.W., Abu Bakar, M.B., Mohd Ishak, Z.A., Ariffin, A. and Pukanszky, B. (2004b). Comparison of the Mechanical Properties and Interfacial Interactions Between Talc, Kaolin, and Calcium carbonate Filled Polypropylene Composites. *Journal Applied Polymer Science.* 91, 3315-3326.

Leong, Y.W., Abu Bakar, M.B., Mohd Ishak, Z.A. and Ariffin, A. (2005). Effects of Filler Treatments on the Mechanical, Flow, Thermal, and Morphology Properties of talc and Calcium Carbonate Filled Polypropylene Hybrid Composites. *Journal Applied Polymer Science.* 98, 413-426.

Martin-Martinez, J. M. (2005). *Macromolecular Symposia-Fillers for Formulations*. Germany, Weinheim: Wiley-VCH Verlag GmbH and KGaA.

Matuana. L.M and Kim, J.W. (2007). Fusion Characteristics of Rigid PVC/Wood-Flour Composites by Torque Rheometry. *Journal of Vinyl and Additive Technology.* 13, 7-13.

Meister, J.J. (2000). Polymer Modification-Principles, Techniques and Applications. New York, Basel: Marcel Dekker, Inc.

Mishra, M.K. and Yagci, Y. (2005). *Handbook of Radical Vinyl Polymerization*. Marcel Dekker, Inc.

Mulder, K. and Knot, M. (2001). PVC Plastic: a history of systems development and entrenchment. *Technology in Society.* 23, 265-286.

Nass, L.I. and Heiberger, C.A. (1986). *Encyclopedia of PVC.* (2nd ed). Marcel Dekker, Inc.

Ngoo, K.H. (2007). *Effect of Nano and Micron-Sized Calcium Carbonate on Mechanical, Thermal and Flammability Properties of ABS/PVC Blends*. Degree of Master, Uinversiti Teknologi Malaysia, Skudai.

Owen, E.D. (1984). *Degradation and Stabilisation of PVC.* London: Elsevier Applied Science.

Qiu, W.L., Mai, K.C. and Zeng, H.M. (2000). Effect of Silane-Grafted Polypropylene on the Mechanical Properties and Crystallization Behavior of Talc/Polypropylene Composites. *Journal Applied Polymer Science.* 77: 2974-2977.

Sancaktar, E. and Walker, E. (2004). Effect of Calcium Carbonate, Talc, Mica, and Glass-Fiber Fillers on the Ultrasonic Weld Strength of Polypropylene. *Journal Applied Polymer Science.* 94, 1986-1998.

Sharida, M.M. (2006). *Polypropylene Hybrid Composites Filled With Talc and Kaolin: Characterization of Mechanical, Morphological and Thermal Properties*. Degree of Master, Universiti Sains Malaysia, Perak.

Sivalingam, G. and Madras, G. (2004). Thermal Degradation of Ternary Blends of Poly(ε-caprolactone/Polyvinyl acetate)/Poly(vinyl chloride). *Journal Applied Polymer Science.* 93, 1378-1383.

Sun, S.S., Li, C.Z., Zhang, L., Du, H.L., and Burnell-Gray, J.S. (2005). Interfacial structures and mechanical properties of PVC composites reinforced by $CaCO_3$ with different particle sizes and surface treatments. *Polymer International.* 55, 158-164.

Sun, S.S., Li, C.Z., Zhang, L., Du, H.L., and Burnell-Gray, J.S. (2006). Effects of surface modification of fumed silica on interfacial structures and mechanical properties pf poly(vinyl chloride) composites. *European Polymer Journal.* 42, 1643-1652.

Švehlová, V. and Polouček, E. (1994). Mechanical Properties of talc-filled polypropylene. *Die Angewandle Makromolekulare Chemie.* 214, 91-99.

Teixeira, S.C.S., Moreira, M.M., Lima, A.P., Santos, L.S., Rocha, B.M.D., Lima, E.S.D., Costa, R.A.A.F.D., Silva, A.L.N.D., Rocha, M.C.G. and Coutinho, F.M.B. (2005). Study of blends of HDPE and different grades of $CaCO_3$. Part I. Factorial experimental design. *Polymer Testing.* 24, 983-987.

Wan, C.Y., Qiao, X.Y., Zhang, Y. and Zhang, Y.X. (2003). Effect of different clay treatment on morphology and mechanical properties of PVC-clay nanocomposites. *Polymer Testing.* 22, 453-461.

Wickson, E.J. (1993). *Handbook of PVC Formulating*. John Wiley and sons, Inc.

Wiebking, H.E. (1996). The Performance of Ultrafine Talc in Rigid PVC. *Journal of Vinyl and Additives Technology.* 2, 187-189.

Wiebking, H.E. (2006). Increasing the Flexural Modulus of Rigid PVC at Elevated Temperatures. *Journal of Vinyl and Additives Technology.* 12, 37-40.

Wu, D.Z., Wang, X.D., Song, Y.Z., and Jin, R.G. (2004). Nanocomposites of Poly(vinyl chloride) and Nanometric Calcium Carbonate Particles: Effects of Chlorinated Polyethylene on Mechanical Properties, Morphology, and Rheology. *Journal of Applied Polymer Science.* 92, 2714-2723.

Xie, X.L., Li, B.G., Pan, Z.R., Li, K.Y. and Tiong, S.C. (2001). Effect of Talc/MMA In Situ Polymerization on Mechanical properties of PVC-Matrix Composites. *Journal of Applied Polymer Science.* 80, 2105-2112.

Xie, X.L., Liu, Q.X., Li, K.Y., Zhou, X.P., Zhang, Q.X., Yu, Z.Z. and Mai, Y.W. (2004). Rheological and Mechanical Properties of PVC/$CaCO_3$ Nanocomposites Prepared by In Situ Polymerization. *Polymer.* 45, 6665-6673.

Yamamoto, K., Maehara, T., Mitani, K. and Mizutani, Y. (1994). Preparation and Application of Low-Molecular-Weight Poly(vinyl chloride). V. Preparation and characteristics of Blended Poly(vinyl chloride) by Two-Step Suspension Polymerization. *Journal of Applied Polymer Science.* 54, 1161-1169.

Yao, G. (2007). 2006 Review of China's PVC Market. *China Chemical Reporter.* 14, 18-19

Yee, J W. (2001) *Effect of Calcium Carbonate fillers on Mechanical Properties of Impact-Modified Unplastised Polyvinyl Chloride*. Degree of Master, Universiti Teknologi Malaysia, Skudai.

Yuan, Q., Jiang, W., An, L.J., Li, R.K.Y. and Jiang, Z.H. (2003). Mechanical and Thermal Properties of High-density Polyethylene Toughened with Glass Beads. *Journal Applied Polymer Science.* 89, 2102-2107.

Zhou, Y.X., Rangari, V., Mahfuz, H., Jeelani, S. and Mallick, P.K. (2005). Experimental study on thermal and mechanical behaviour of polypropylene, talc/polypropylene and polypropylene/clay nanocomposites. *Materials Science and Engineering A*. 402, 109-117.

Appendix A

The collected data, mean and standard deviation of impact strengths for PVC composites.

The collected data, mean value and standard deviation of impact strength for unfilled PVC and PVC composites filled with SP-FG and SP-FG-C.

Number of Sample	**Izod Impact Strength, KJ/m^2**		
	Unfilled PVC	**30phr SP-FG-C Filled PVC**	**30phr SP-FG Filled PVC**
1	5.858	8.705	7.241
2	4.147	5.561	7.657
3	7.229	5.940	7.851
4	7.412	6.788	6.475
5	5.499	5.563	5.864
6	6.842	6.747	8.857
7	5.757	10.333	7.929
8	7.323	9.240	8.040
9	7.216	8.981	6.683
10	7.389	8.599	8.984
Mean value	6.467	7.646	7.558
Standard Deviation	1.103	1.723	1.005

The collected data, mean and standard deviation of impact strength for unfilled PVC and PVC composites filled with SM90, PC100, NPCC and Talc.

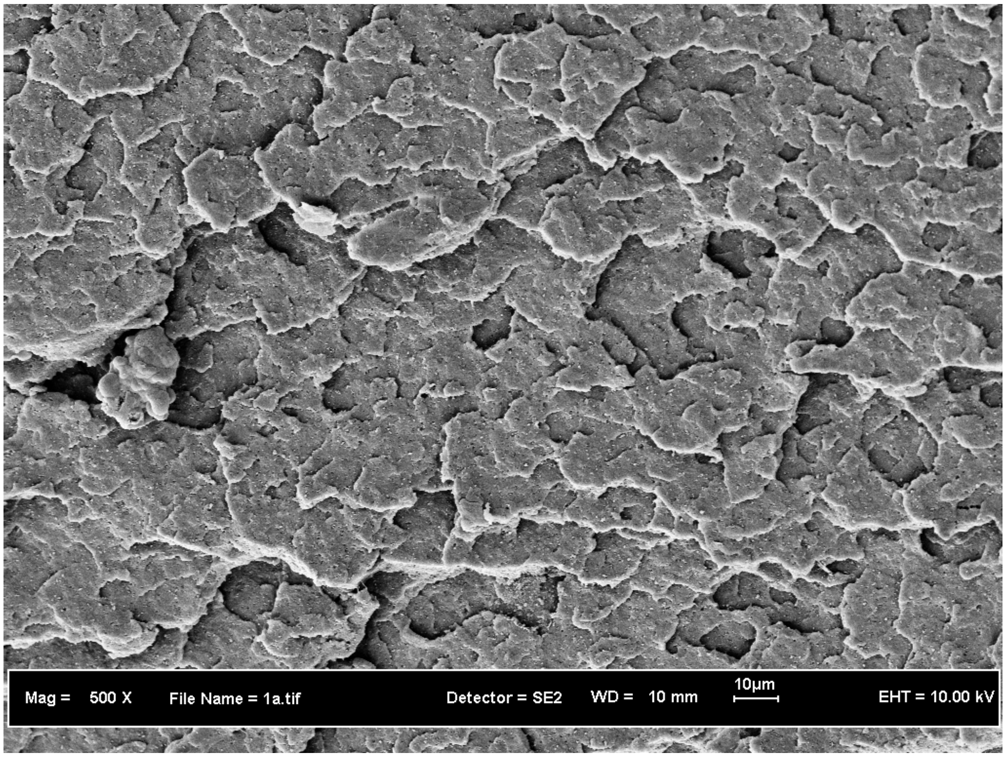
Number of Sample	**Izod Impact Strength, KJ/m^2**			
	30phr SM90 Filled PVC	**30phr PC100 Filled PVC**	**30phr NPCC Filled PVC**	**30phr Talc Filled PVC**
1	19.685	9.472	6.819	7.689
2	18.083	9.566	6.650	5.790
3	10.173	8.933	6.543	5.439
4	8.258	17.683	5.369	5.167
5	11.678	19.120	6.394	5.140
6	12.782	8.531	6.458	5.957
7	25.108	10.5128	6.198	5.973
8	11.121	10.777	5.850	5.632
9	10.226	9.7153	6.309	6.490
10	23.435	9.348	7.494	8.708
Mean value	15.0549	10.333	6.345	5.698
Standard Deviation	6.030	2.678	0.549	0.434

The collected data, mean and standard deviation of impact strengths for Hybrid Talc/SM90 filled PVC composites with different ratios of talc/SM90.

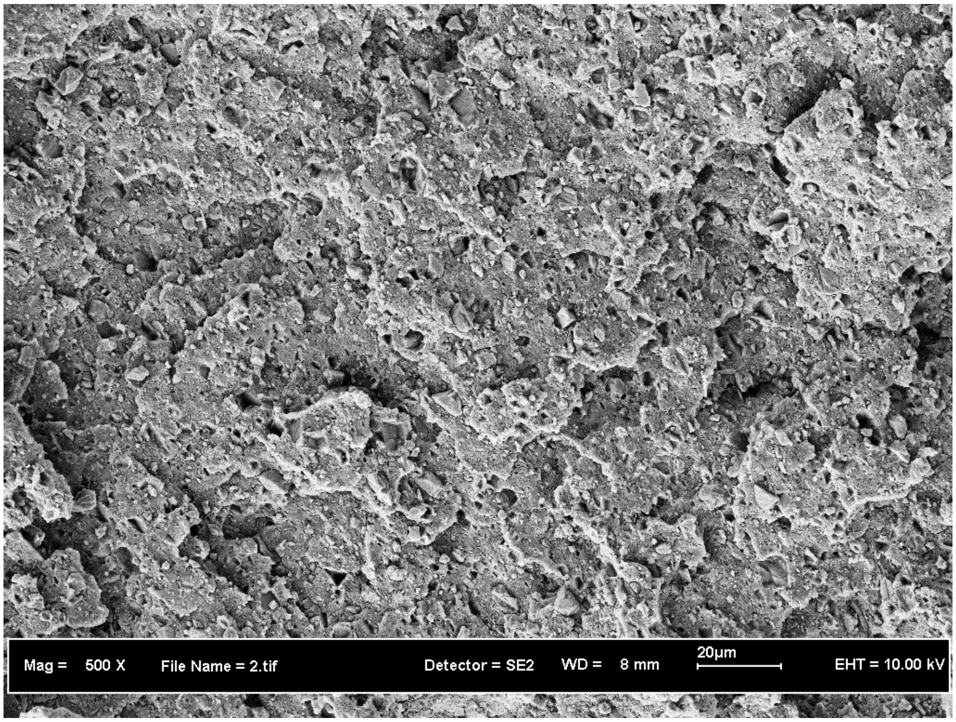
Number of Sample	**Izod Impact Strength, KJ/m^2**						
	30T:0S	**25T:5S**	**20T:10S**	**15T:15S**	**10T:20S**	**5T:25S**	**0T:30S**
1	7.689	7.750	6.005	6.562	8.743	26.774	19.685
2	5.790	7.650	7.310	7.419	15.220	10.499	18.083
3	5.439	7.121	8.971	6.391	8.060	15.142	10.173
4	5.167	8.072	10.226	6.425	8.223	9.285	8.258
5	5.140	6.293	8.436	8.948	13.601	25.237	11.678
6	8.708	5.900	6.356	7.650	11.595	10.333	12.782
7	5.957	8.948	5.865	7.158	9.113	11.386	25.108
8	5.973	8.480	7.630	7.272	7.669	8.994	11.121
9	5.632	7.330	6.326	18.928	15.809	10.443	10.226
10	6.490	7.469	5.895	6.309	7.730	9.285	23.435
Mean	5.698	7.501	7.302	8.306	10.576	13.738	15.0549
Standard Deviation	0.434	0.923	1.502	3.186	3.216	6.706	6.030

Appendix B

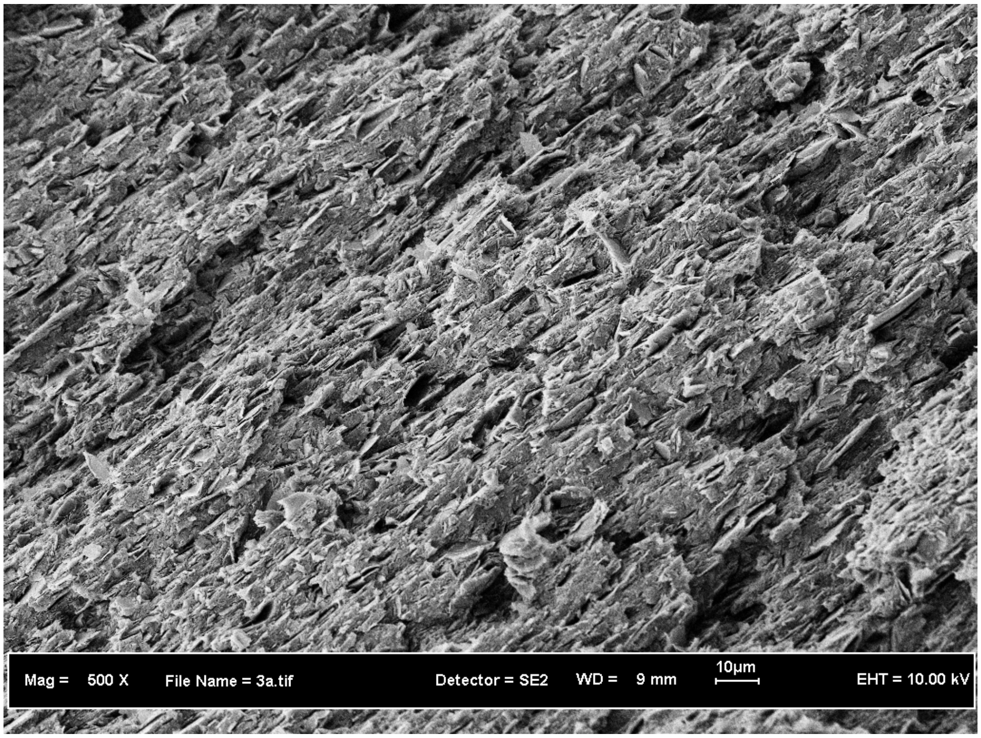
SEM micrographs of different types of fillers filled PVC composites.



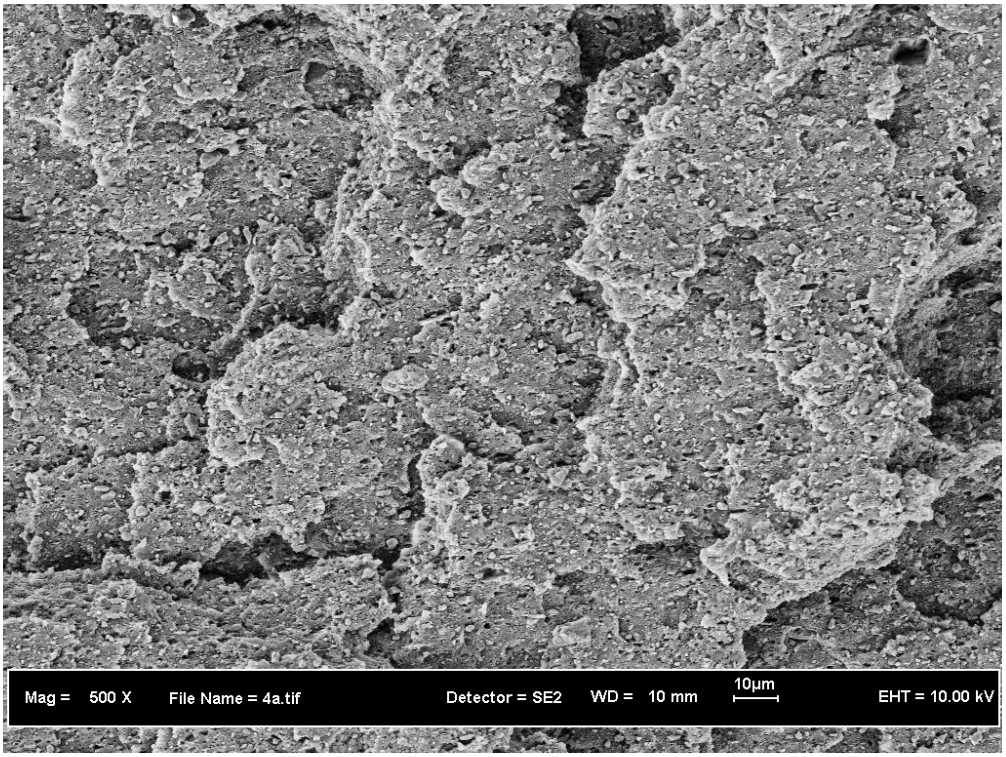
SEM photograph of Unfilled PVC composite at 500X.



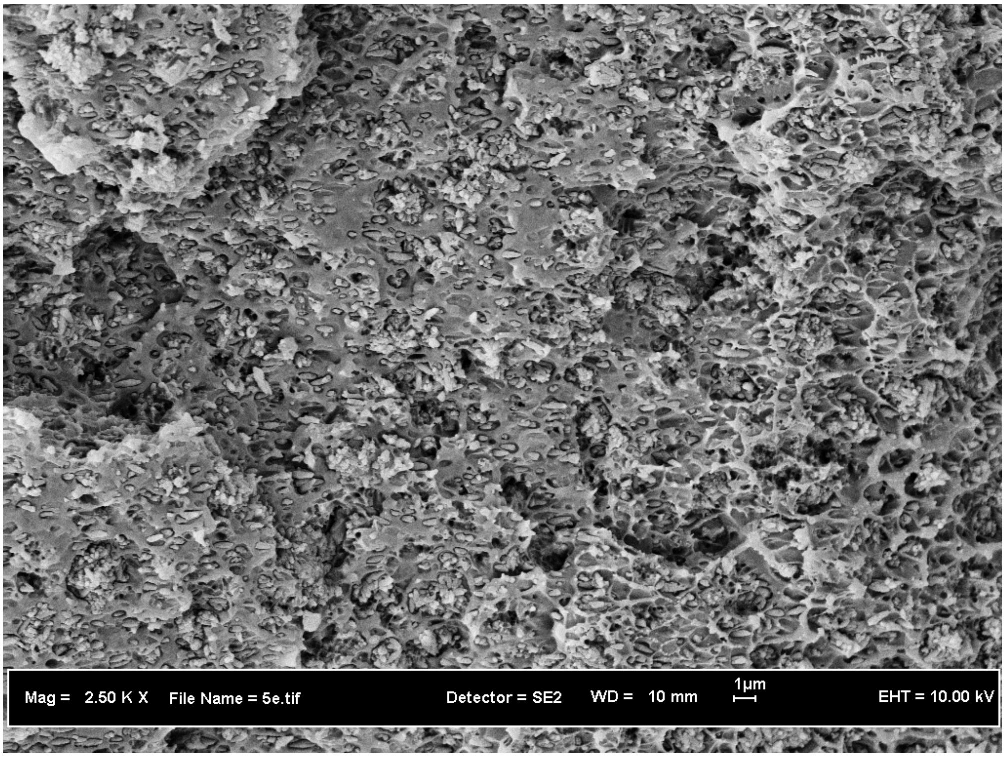
SEM photograph of 30phr SP-FG Filled PVC Composite 500X.



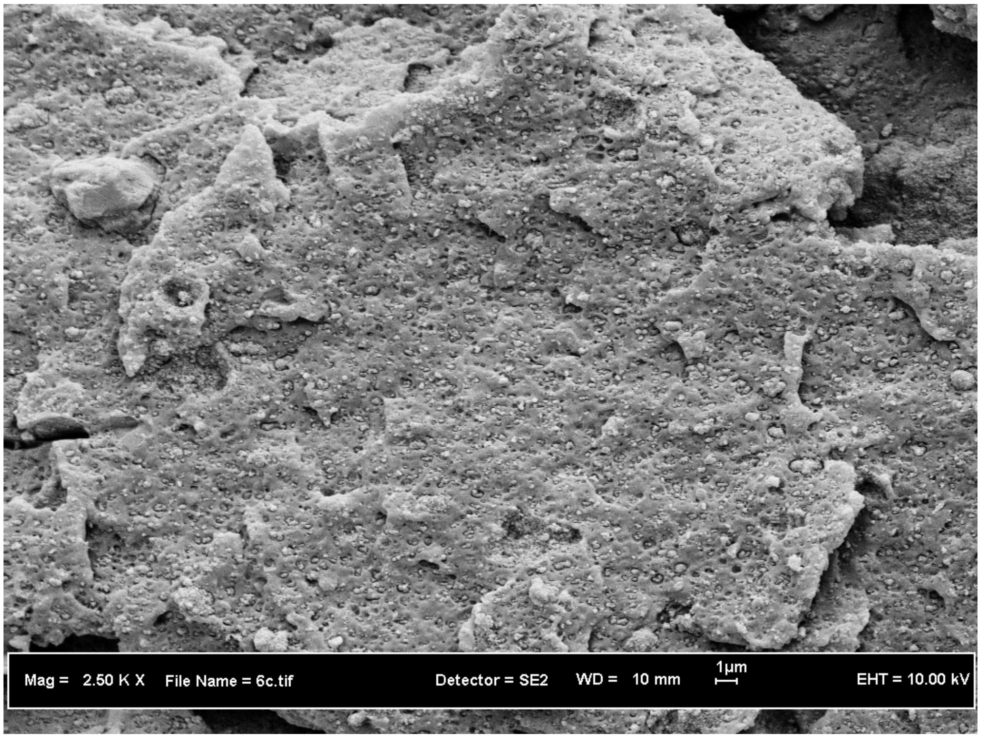
SEM photograph of 30phr SP-FG-C Filled PVC Composite at 500X.



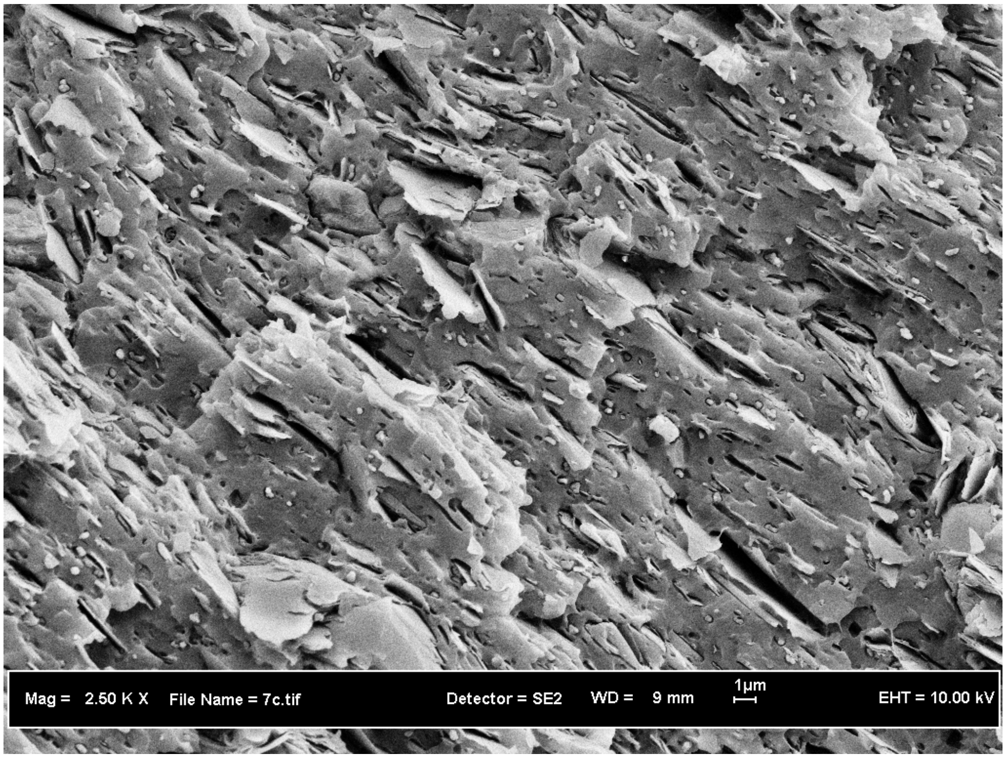
SEM photograph 30phr SM90 Filled PVC Composite at 500X.



SEM photograph of 30phr PC100 Filled PVC Composite at 2.50KX.



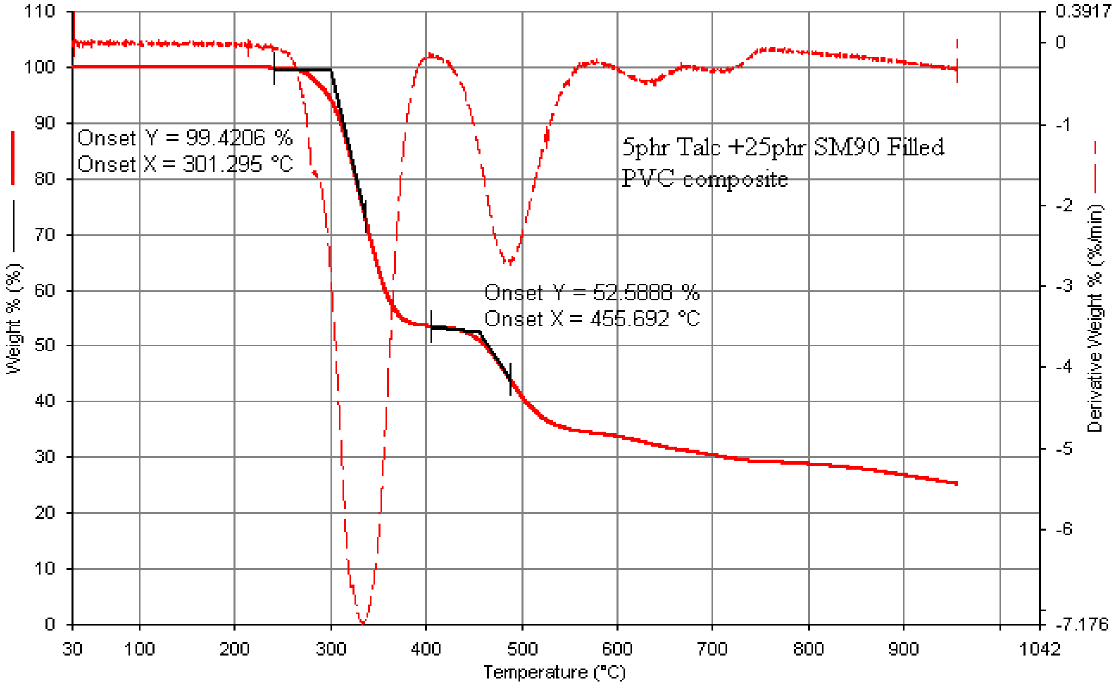
SEM photograph of 30phr NPCC Filled PVC Composite at 2.50KX.



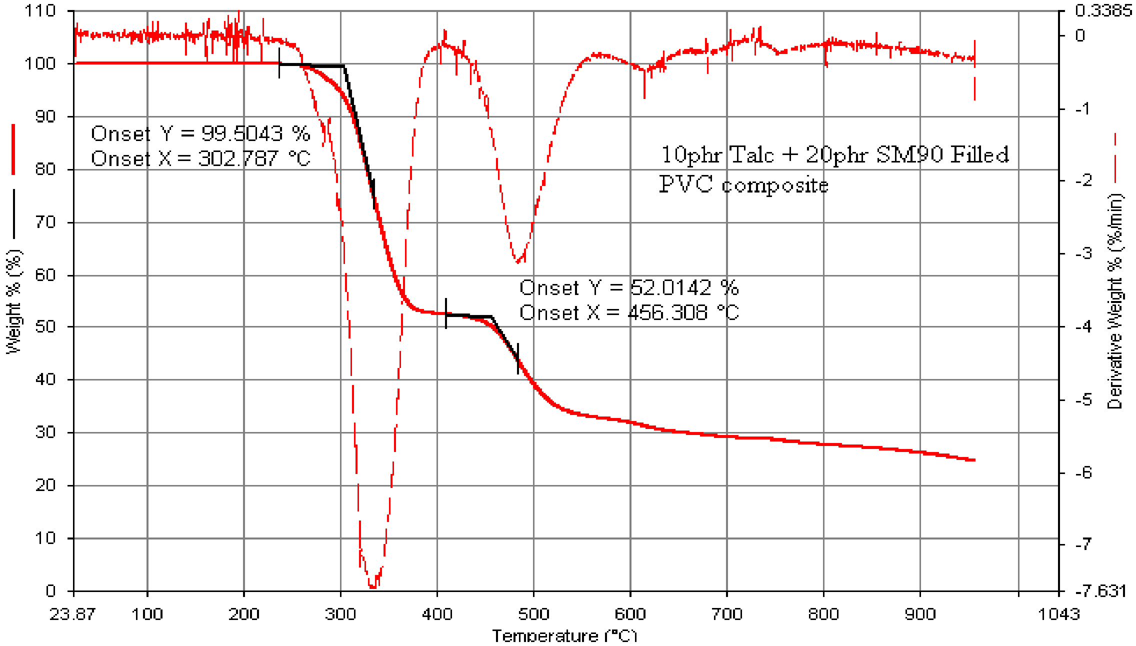
SEM photograph of 30phr Talc Filled PVC Composite at 2.50KX.

Appendix C

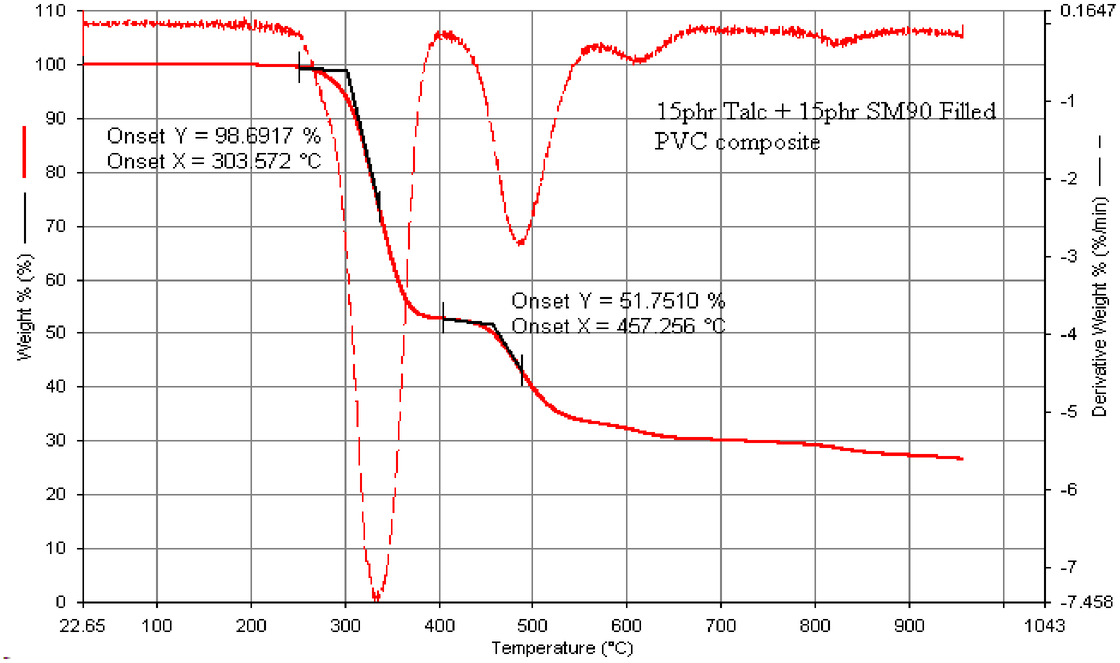
TGA curves for all hybrid Talc/SM90 filled PVC composites



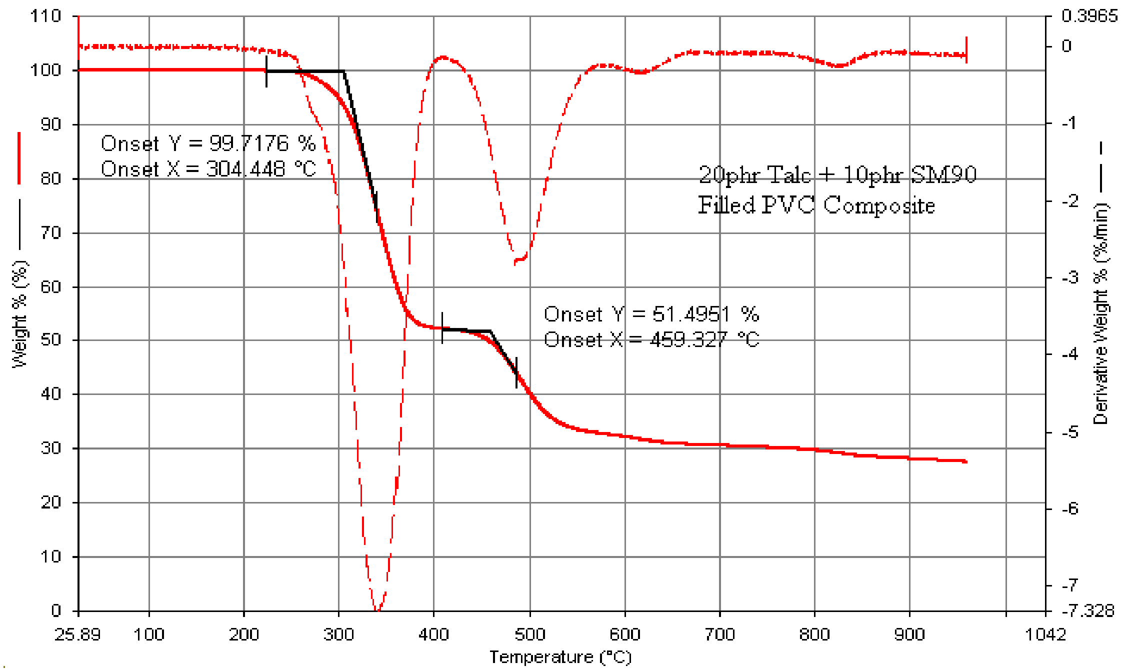
TGA curve for hybrid (5phr Talc: 25phr SM90) filled PVC composite.



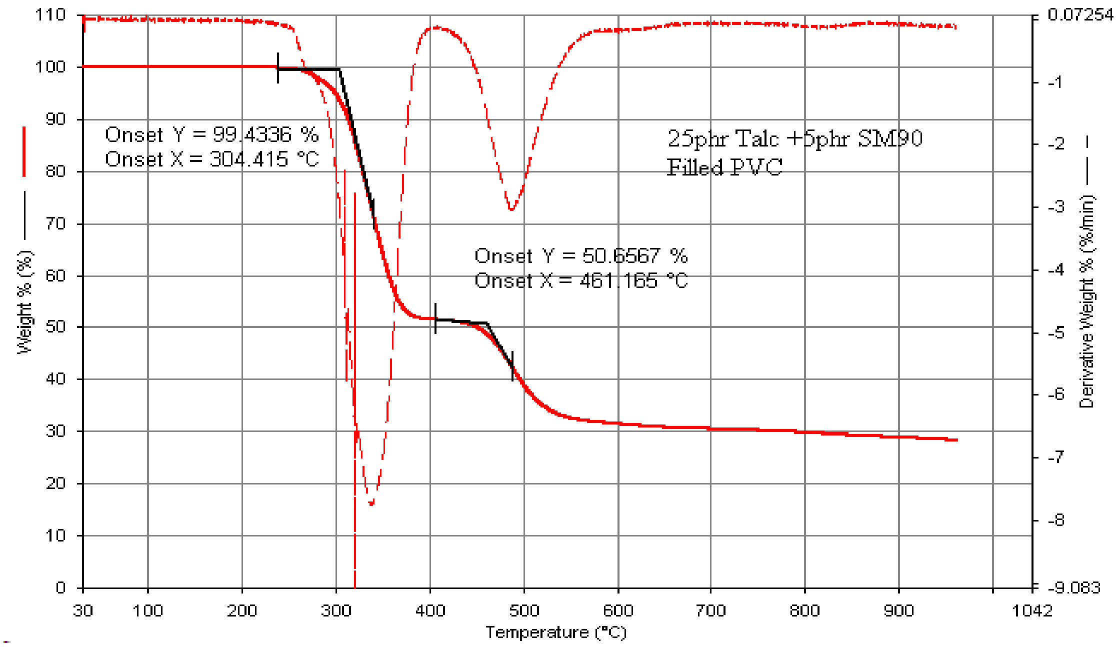
TGA curve for Hybrid (10phr Talc: 20phr SM90) filled PVC composite.



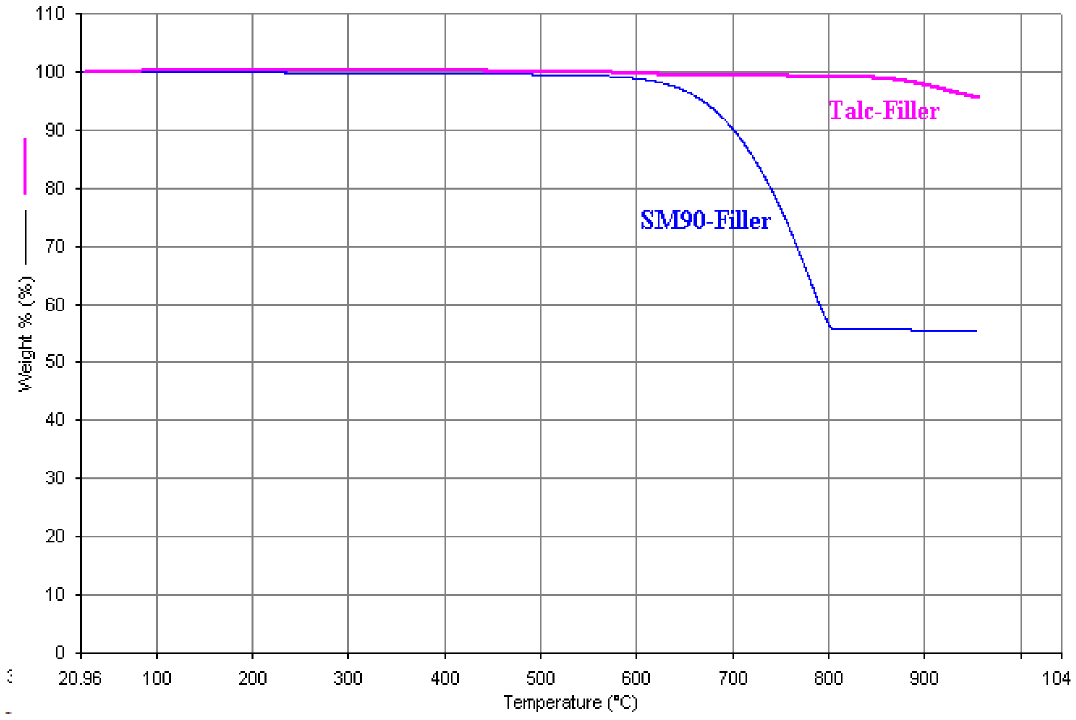
TGA curve for hybrid (115phr Talc: 15phr SM90) filled PVC composite.



TGA curve for hybrid (20phr Talc: 10phr SM90) filled PVC composite.



TGA curve for hybrid (25phr Talc: 5phr SM90) filled PVC composite.



TGA curve for talc and SM90 fillers.

Appendix D

Calculation of theoretical densities of unfilled PVC and all filled PVC Composites

Density for Unfilled PVC Composite

Ingredient	**Formula Weight, g**	**Density (*ρ*), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.9208	0.6577
Tin Stabilizer	2	1.08	0.0184	0.0170
Sak-CS-P	0.5	1.03	0.0046	0.0045
Stearic Acid	0.6	0.84	0.0055	0.0065
Processing Aid	1.5	1.53	0.0138	0.0090
TiO_2	4	4.05	0.0369	0.0091
Total	**108.6**		**1.0000**	**0.7038**

Density of unfilled PVC = 1/0.7038

= 1.4209g/cm^3

Density for 30phr SP-FG filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (ρ), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
SP-FG	30	2.70	0.2165	0.0802
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6317**

Density of 30phr SP-FG filled PVC composite = 1/0.6317
= 1.5830g/cm^3

Density for 30phr SP-FG-C filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (ρ), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
SP-FG-C	30	2.70	0.2165	0.0802
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6317**

Density of 30phr SP-FG-C filled PVC Composite = 1/0.6317
= 1.5830g/cm^3

Density for 30phr SM90 filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (*ρ*), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
SM90	30	2.70	0.2165	0.0802
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6317**

Density of 30phr SM90 filled PVC Composite = 1/0.6317

= 1.5830g/cm^3

Density for 30phr PC100 filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (*ρ*), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
PC100	30	2.70	0.2165	0.0802
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6317**

Density of 30phr PC100 filled PVC Composite = 1/0.6317

= 1.5830g/cm^3

Density for 30phr NPCC filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (ρ), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
NPCC	30	2.55	0.2165	0.0849
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6364**

Density of 30phr SP-FG filled PVC composite = 1/0.6364

= 1.5713g/cm^3

Density for 30phr Talc filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (ρ), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
SP-FG	30	2.79	0.2165	0.0776
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6291**

Density of 30phr SP-FG filled PVC composite = 1/0.6291

= 1.5896g/cm^3

Density for Hybrid (25phr Talc: 5phr SM90) filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (*ρ*), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
Talc	25	2.97	0.1804	0.0646
SM90	5	2.70	0.0361	0.0134
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6295**

Density of 30phr SM90 filled PVC Composite = 1/0.6295

= 1.5885g/cm^3

Density for Hybrid (20phr Talc: 10phr SM90) filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (*ρ*), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
Talc	20	2.97	0.1443	0.0517
SM90	10	2.70	0.0722	0.0267
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6299**

Density of 30phr SM90 filled PVC Composite = 1/0.6299

= 1.5874g/cm^3

Density for Hybrid (15phr Talc: 15phr SM90) filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (ρ), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
Talc	15	2.97	0.1082	0.0388
SM90	15	2.70	0.1082	0.0401
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6304**

Density of 30phr SM90 filled PVC Composite = 1/0.6304

= 1.5864g/cm^3

Density for Hybrid (10phr Talc: 20phr SM90) filled PVC Composite

Ingredient	**Formula Weight, g**	**Density (ρ), g/cm^3**	**Weight Fraction (*W*)**	***W/ρ***
PVC resins (K-66)	100	1.40	0.7215	0.5154
Talc	10	2.97	0.0722	0.0259
SM90	20	2.70	0.1443	0.0534
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6308**

Density of 30phr SM90 filled PVC Composite = 1/0.6308

= 1.5852g/cm^3

Density for Hybrid (5phr Talc: 25phr SM90) filled PVC Composite

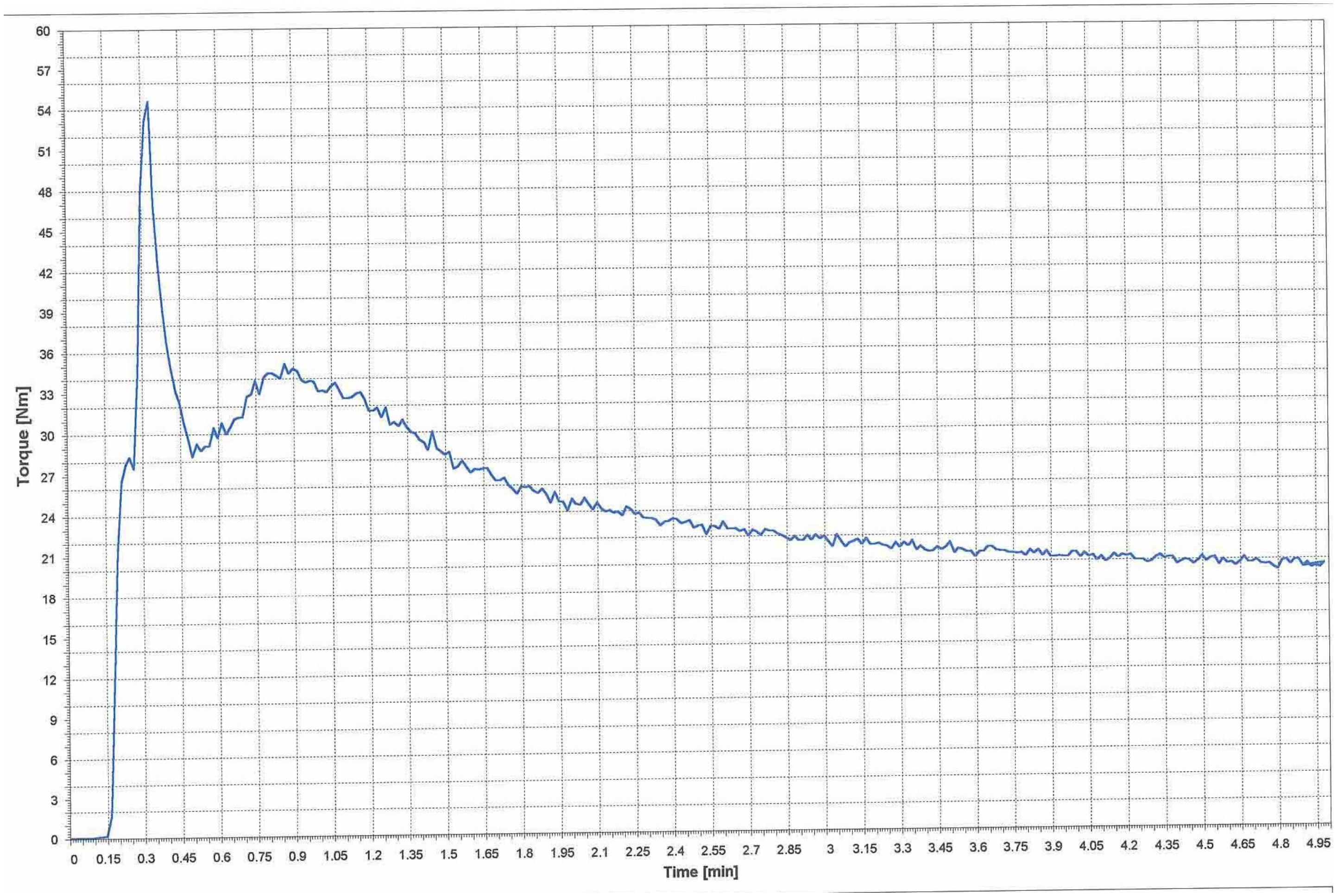
Ingredient	**Formula Weight, g**	**Density (ρ), g/cm^3**	**Weight Fraction (*W*)**	***W*/ρ**
PVC resins (K-66)	100	1.40	0.7215	0.5154
Talc	5	2.97	0.0361	0.0129
SM90	25	2.70	0.1804	0.0668
Tin Stabilizer	2	1.08	0.0144	0.0133
Sak-CS-P	0.5	1.03	0.0036	0.0035
Stearic Acid	0.6	0.84	0.0043	0.0051
Processing Aid	1.5	1.53	0.0108	0.0071
TiO_2	4	4.05	0.0289	0.0071
Total	**138.6**		**1.0000**	**0.6312**

Density of 30phr SM90 filled PVC Composite = 1/0.6312

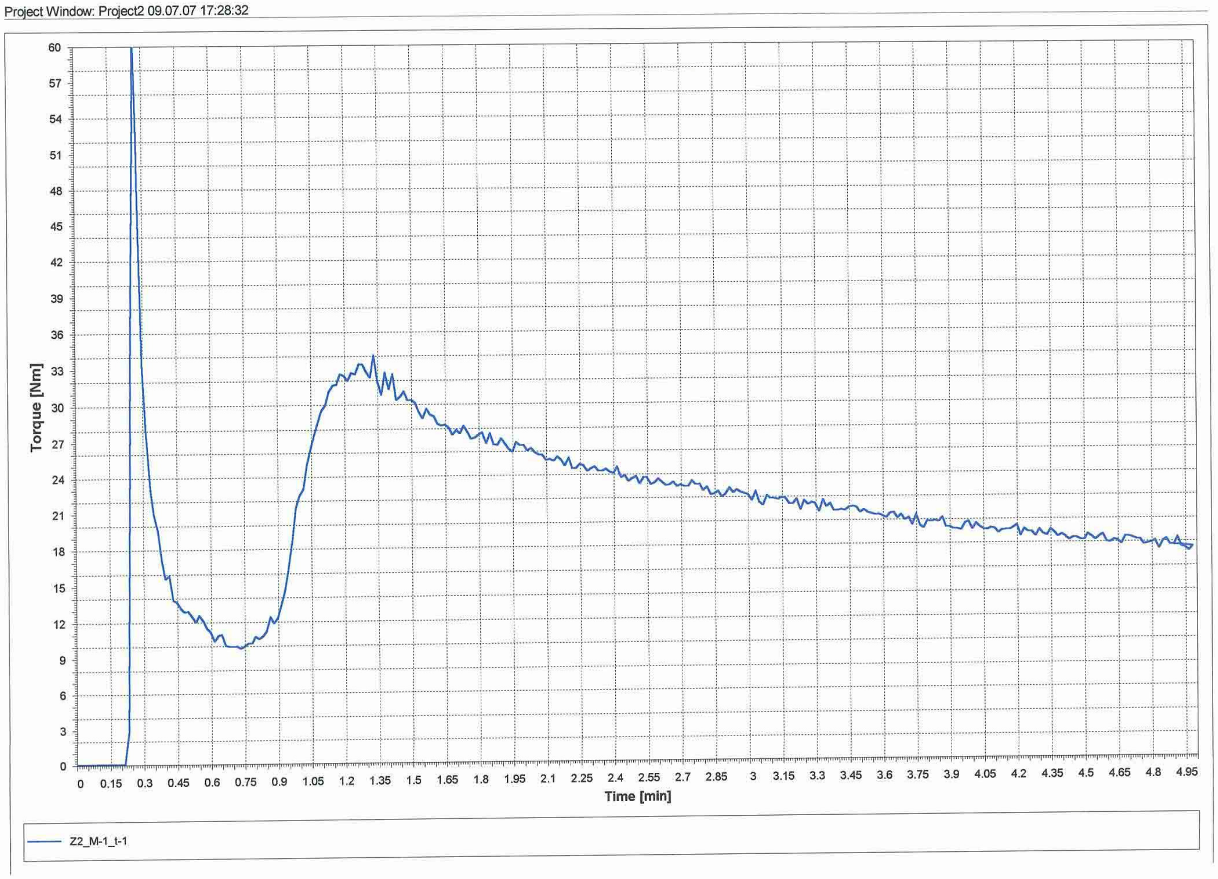
= 1.5843g/cm^3

Appendix E

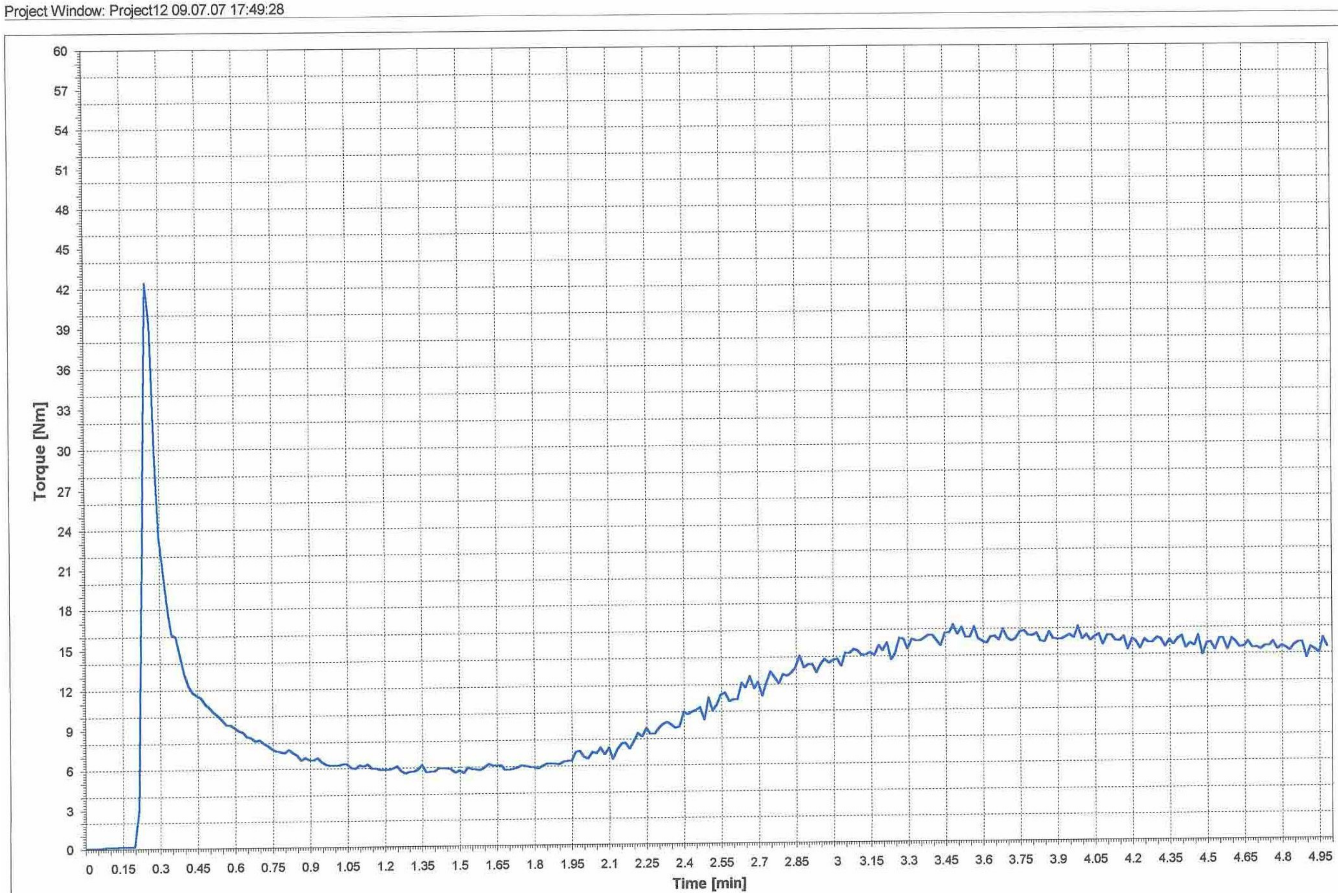
Fusion curves of unfilled PVC and Hybrid Talc/SM90 filled PVC composites



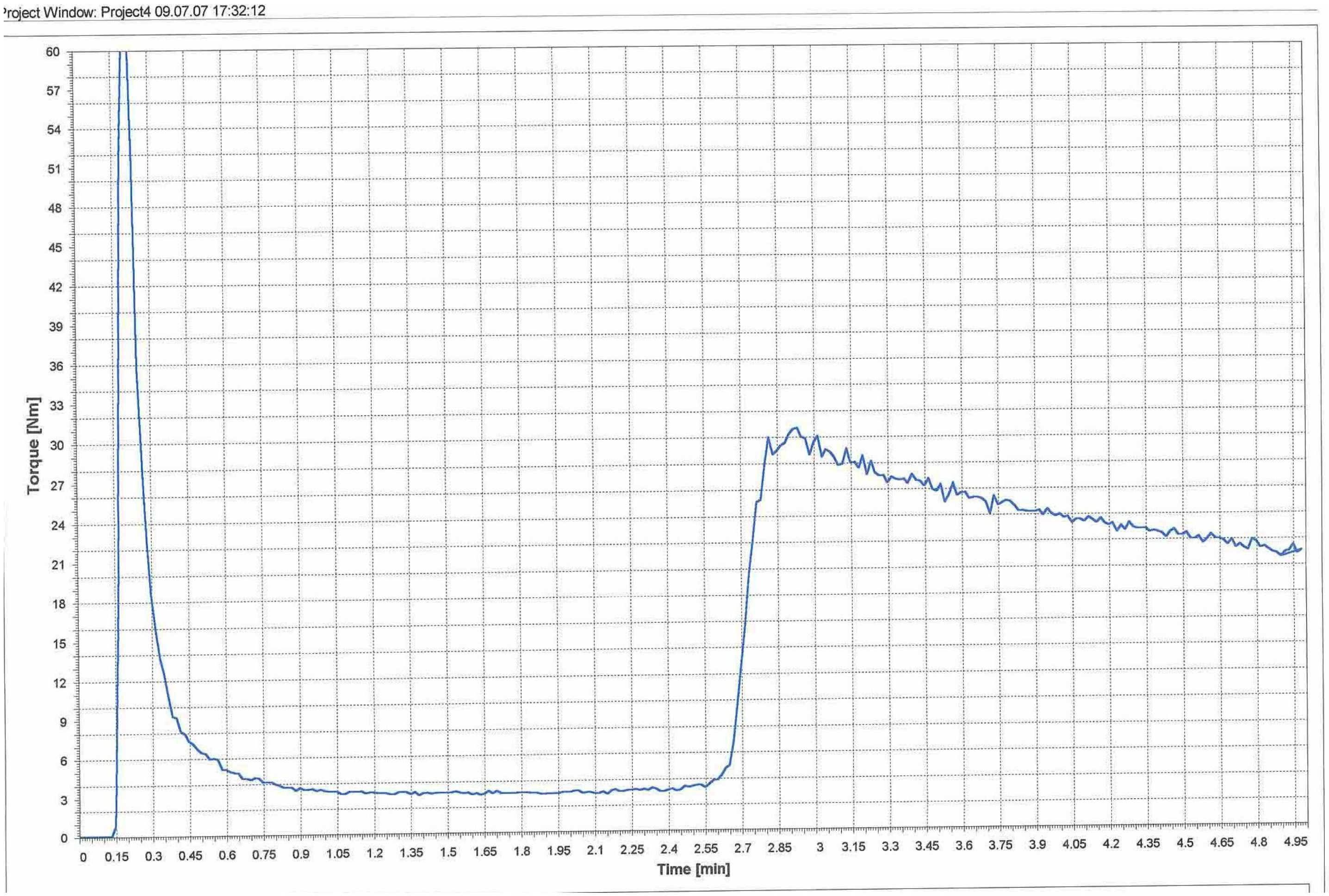
Fusion curve of unfilled PVC composite which melted in a Haake Torque Rheometer at a temperature of 180^0C with a rotor speed of 45rpm.



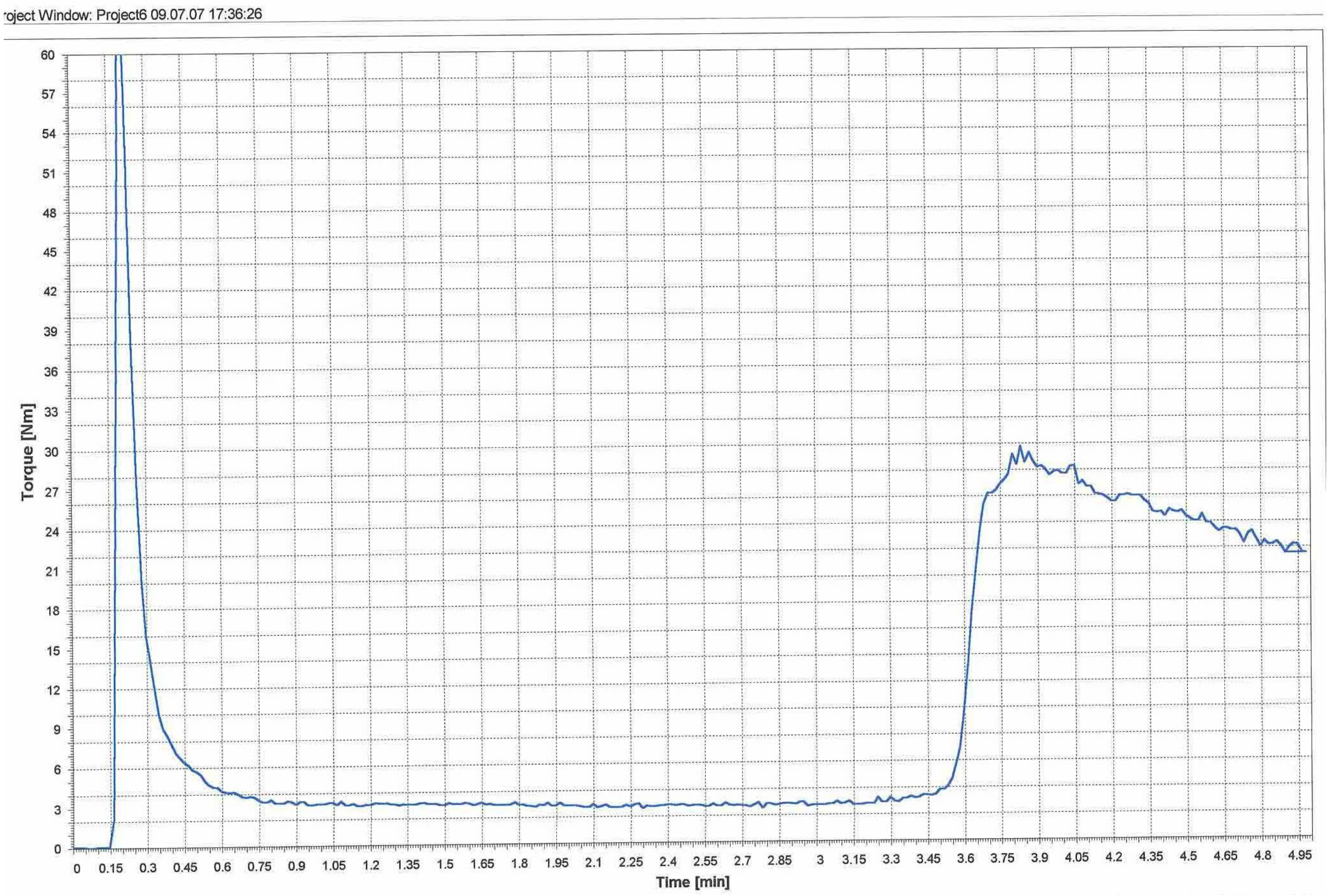
Fusion curve of 30phr Talc filled PVC composite which melted in a Haake Torque Rheometer at a temperature of 180^0C with a rotor speed of 45rpm.



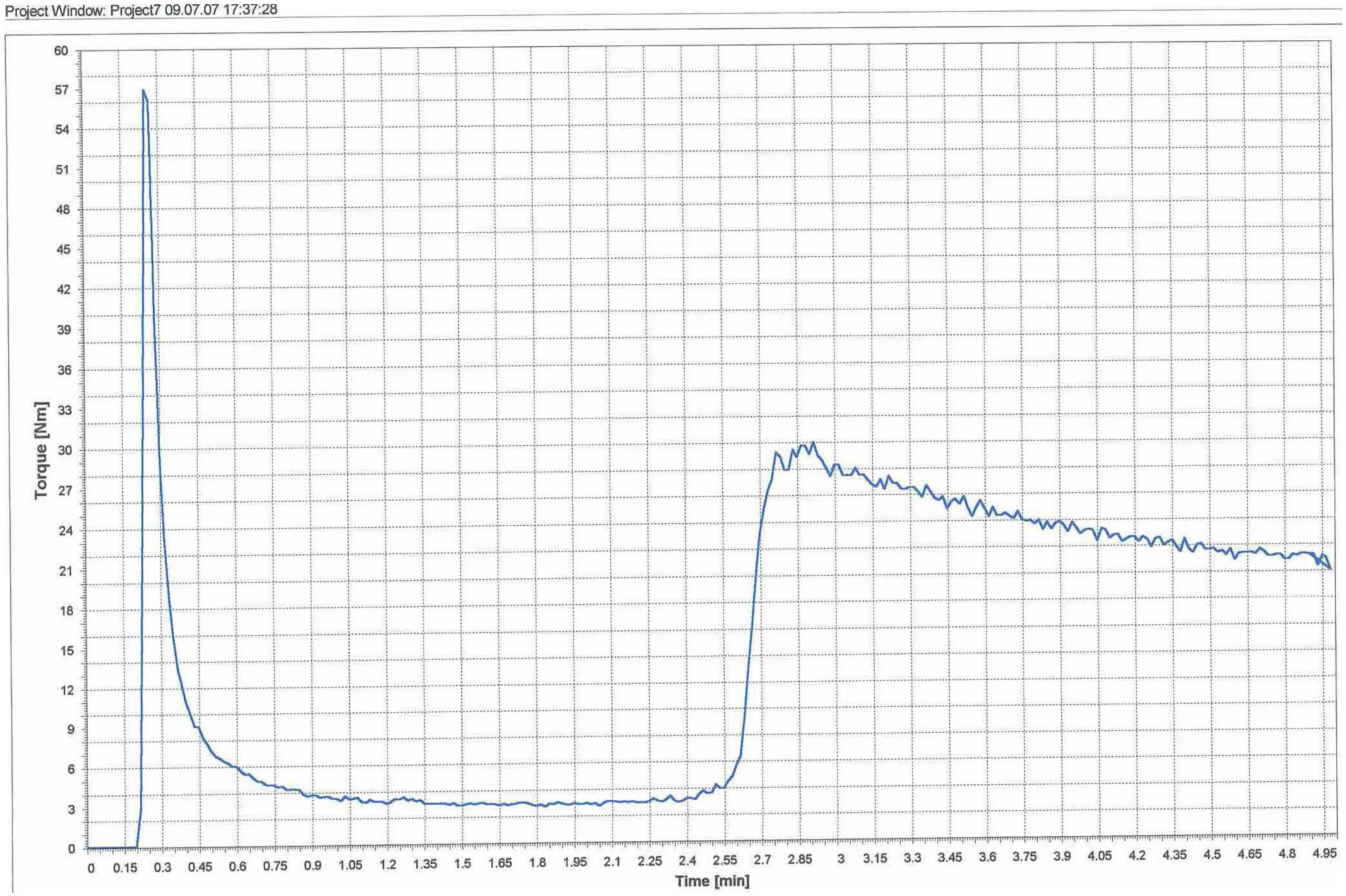
Fusion curve of hybrid (25phr Talc: 5phr SM90) filled PVC composite which melted in a Haake Torque Rheometer at a temperature of 180^{0}C with a rotor speed of 45rpm.



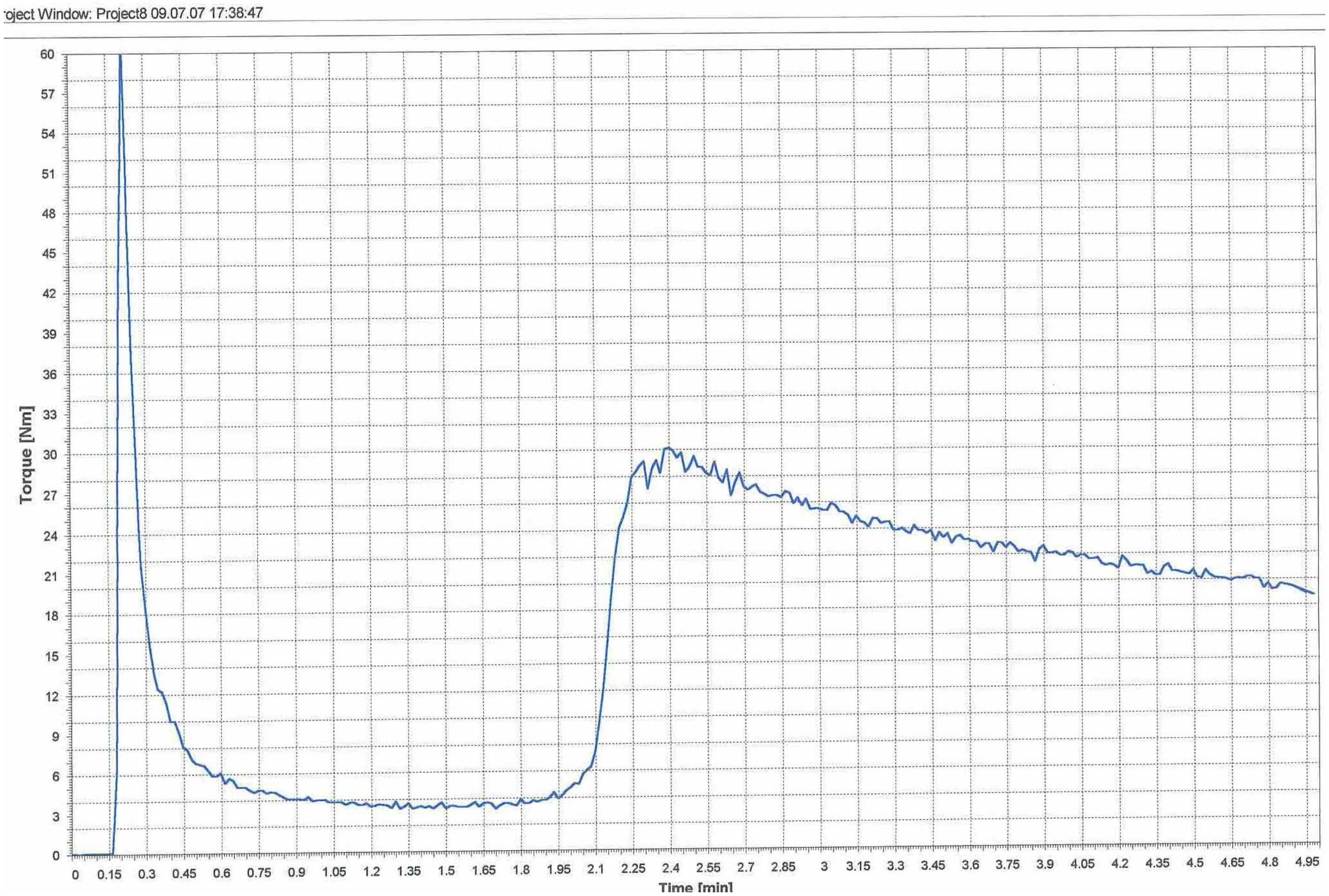
Fusion curve of hybrid (20phr Talc: 10phr SM90) filled PVC composite which melted in a Haake Torque Rheometer at a temperature of 180^{0}C with a rotor speed of 45rpm.



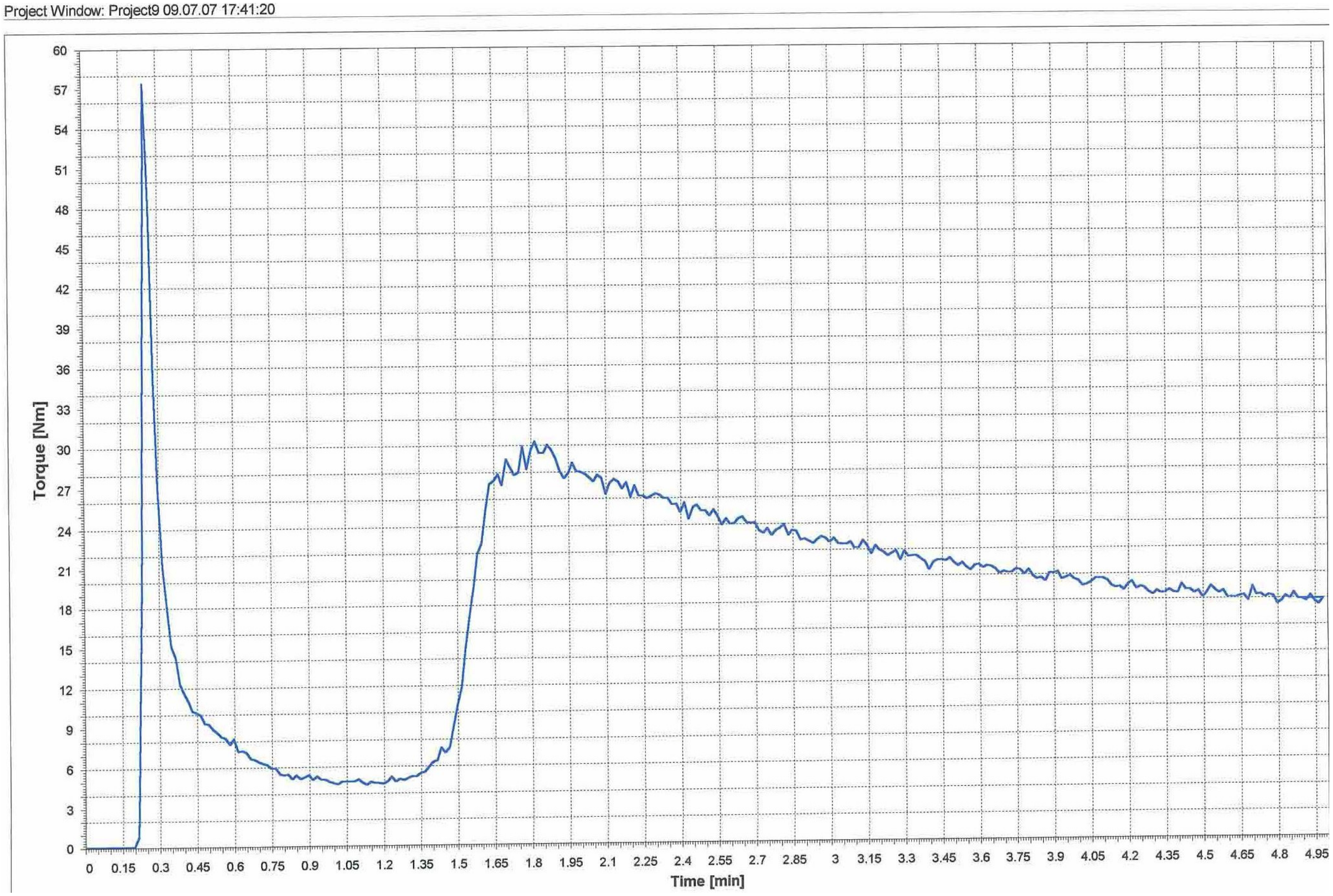
Fusion curve of hybrid (15phr Talc: 15phr SM90) filled PVC composite which melted in a Haake Torque Rheometer at a temperature of 180^{0}C with a rotor speed of 45rpm.



Fusion curve of hybrid (10phr Talc: 20phr SM90) filled PVC composite which melted in a Haake Torque Rheometer at a temperature of 180^{0}C with a rotor speed of 45rpm.



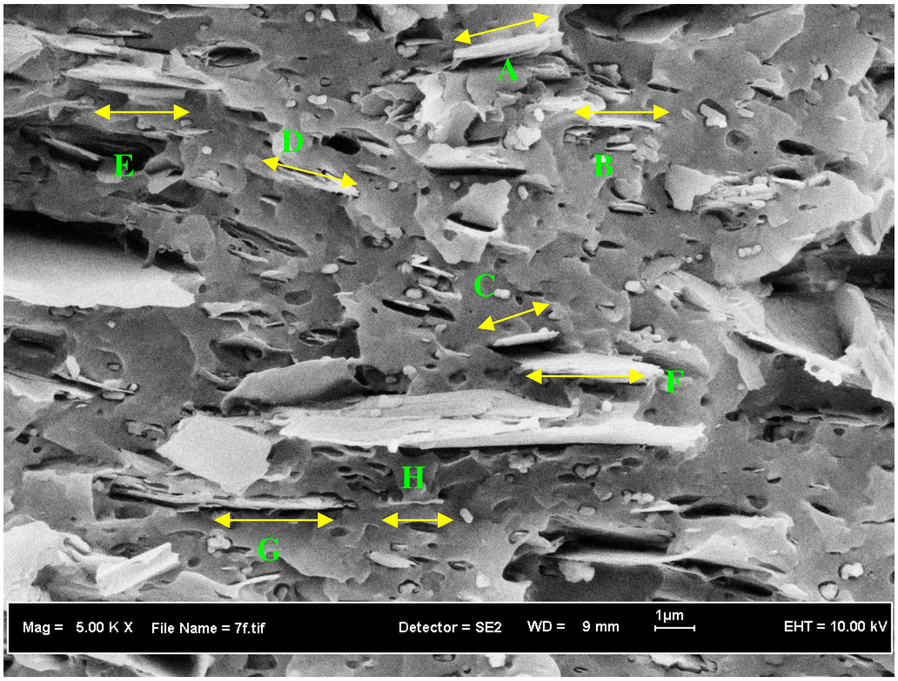
Fusion curve of hybrid (5phr Talc: 25phr SM90) filled PVC composite which melted in a Haake Torque Rheometer at a temperature of 180^{0}C with a rotor speed of 45rpm.



Fusion curve of 30phr SM90 filled PVC composite which melted in a Haake Torque Rheometer at a temperature of 180^{0}C with a rotor speed of 45rpm.

Appendix F

Calculation of the average aspect ratio for the talc particles.



SEM photograph for 30phr Talc filled PVC composite.

Average aspect ratio of talc particles

= (Length / Diameter) for 8 particles of talc

= (1.6/0.2 + 1.1/0.15 + 1.1/0.15 + 1.4/0.15 + 1.3/0.15+ 2.1/0.3 + 2.1/0.25 + 1.2/0.15)

= 8