INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI®

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

Polyolefin Plastomers in Composites for Flooring Applications

Manar Bani-Hani

A Thesis
in
The School
for
Building
(Civil Engineering Program)
Presented in Partial Fulfillment of the Requirements
for the
Degree of Master of Applied Science
at
Concordia University
Montreal, Quebec, Canada
July, 1998

0-612-39471-9

ABSTRACT

Polyolefin Plastomers in Composites for Flooring Applications

Manar Bani-Hani

For flooring applications, calcium carbonate-filled poly(vinyl chloride), PVC, has long been the material of choice for both flexible sheeting and tile products. However, PVC-based formulations must be processed with plasticizers, which have recently raised some concerns from a sustainability point of view.

In the research work reported here, calcium carbonate-filled formulations based on polyolefin plastomers, POP, are prepared in a laboratory-scale mixer, and their mechanical properties are studied for flooring applications. Plastomers are olefin copolymers synthesized using new metallocene catalyst technologies. The POP plastomer used in this research is Affinity 1140 a copolymer of ethylene and octene, and does not require any plasticizers for processing. The key mechanical properties of the calcium carbonate-filled POP, which include tensile strength, elongation and impact strength, are found to compare very favourably to those of PVC formulations at filler loadings of 200 phr. In addition, the filled POP formulations are able to incorporate a significant amount of post-consumer polyethylene(PC-PE) while maintaining adequate physical properties. Two types of PC-PE are tested in this research work: the first one is a linear low density polyethylene (LLDPE), and the second is a high density polyethylene (HDPE). The DSC analysis technique is used to study the difference in behavior between the two recycled resins. Dimensional stability tests are also reported, indicating that POP composites contract slightly more than the PVC-based ones. Overall, this study shows that calcium carbonate-filled POP should be studied further as a more sustainable alternative to filled PVC for flooring applications.

TO MY PARENTS

ACKNOWLEDGMENTS

Thanks to GOD for every thing.

I wish to express my appreciation and gratitude to my supervisors, Dr. D. Feldman, and Dr. J. Campanelli, for their encouragement and guidance throughout the course of this work.

I am primarily indebted and grateful to Mrs. Dorina Banu, Research Associate, for having assisted in every step of this research work, and for her continuous encouragement and helpful suggestions regarding this work.

I wish to thank the technician who helped in this work, Mr. Joseph Hrib.

The financial support of the Natural Sciences and Engineering Research Council (NSERC) is gratefully acknowledged.

I am greatly thankful to my parents (Mr. Mohammed Aziz Bani-Hani and Mrs Intesar Al-Ghanma) who encouraged me to complete this degree. I am extremely grateful to them for their love, support and for being a constant source of inspiration.

This work would never have been possible without the help, encouragement, and patience of my husband, Dr. Mohammed Hayajneh. I am forever indebted to him for his understanding during the many days when I was wrapped up in the preparation of this work. I am indebted also to my son, Anas.

TABLE OF CONTENT

LIST OF FIGURES

CHAPTER 2

CHAPTER 3

CHAPTER 4

LIST OF TABLES

CHAPTER 2

CHAPTER 3

CHAPTER 4

ABBREVIATIONS

CD	Comonomer distribution
DBTL	Dibutyltin dilaurate
DOP	Dioctylphthalate
DSC	Differential scanning calorimetry
EHPP	Elastomeric homopolymers of propylene
EMA	Ethylene-methylacrylate
EPDM	Ethylene-propylene- diene monomer
EPR	Ethylene-propylene rubber
ESCR	Environmental stress crack resistance
EVAc	Ethylene-vinylacetate copolymer
HDPE	High density polyethylene
K	K-value
LLDPE	Linear low density polyethylene
MDPE	Medium density polyethylene
MW	Molecular weight
MWD	Molecular weight distribution
PC-HDPE	Post consumer high density polyethylene
PC-LLDPE	Post consumer linear low density polyethylene
PC-PE	Post consumer polyethylene
POE	Polyolefin elastomer
POP	Polyolefin plastomer

PE	Polyethylene
phr	Per hundred parts resin
PP	Polypropylene
PVC	Poly(vinyl chloride)
T_g	Glass transition temperature
T_m	Melting temperature
UHMWPE	Ultra high molecular weight polyethylene
UV	Ultraviolet
VAc	Vinyl acetate
VC	Vinyl chloride
VLDPE	Very low density polyethylene
VOC	Volatile organic compounds
VLDPE	Very low density polyethylene

1

INTRODUCTION

Poly(vinyl chloride), PVC, has a wide variety of applications. It is second in volume only to polyethylene, with sales in North America of 6.2 billion kg in 1995 [1]. Roughly 53% of PVC resin production is used in the building industry [2]. Indoor applications include wall coverings, coatings, flexible flooring, baseboards, blinds, and profiles for windows and doors.

PVC homopolymer is quite stiff and rigid. The same is true of the PVC copolymers used in flooring applications. These physical characteristics can be altered through the addition of plasticizers, low molecular weight additives that act to reduce molecular binding forces and increase flexibility. Typical families of compounds used as plasticizers include the phthalates and benzoates. The plasticizers are miscible with both homopolymer and copolymers, and can thus be present in a wide range of concentrations depending on the finished product. Extruded profiles require relatively low levels, while the plastisols used for flexible flooring, and the organosols used for coatings, require much higher plasticizer concentrations. Plasticizers have been traditionally considered to be inert and non-volatile. However, there is growing evidence that plasticized PVC products can be a source of volatile organic compounds (VOC) in buildings [3].

Plasticizers are known to exude to the surface of a PVC product over time. At the surface, they may become volatilized, or subjected to microbial degradation. This kind of degradation is especially prevalent in humid environments. As a result, plasticized PVC flooring products often suffer from discoloration due to unsightly bacterial and fungal growths. In addition to the esthetic drawbacks, microbial growth on plasticizers also presents a number of risks to human health and well-being. The microorganism break down the plasticizer molecule into more volatile components, which are subsequently released into the enclosed building environment. Inhabitants may thus be subjected to long-term exposure of low-level VOC. The microorganisms may also increase the susceptibility of the polymer chain itself to biodegradation, leading to the possibility of volatilizing halogenated organics. Finally, the plasticized surfaces may provide a breeding ground for microorganisms, which can then spread throughout the building. Moreover the exudation of the plasticizer to the surface will lead to loss in mechanical properties of the material such as toughness and elongation. These considerations point to the need for research into more sustainable alternatives to PVC-based indoor building materials.

In many ways, plasticized PVC is ideally suited to flooring applications. The PVC imparts excellent impact resistance, stiffness and toughness to the final product, even at filler loadings in the range of 200 to 300 phr (parts per hundred resin). Conventional polyolefins, produced by Ziegler-Natta catalyst technologies, have been unable to match the balance of properties required for flooring applications. However, new families of polymers have recently been commercialized based on metallocene catalysis.

Metallocene catalysts allow for site-specific polymerization of olefins and other monomers. The resulting polymers tend to have narrower polydispersity, a controlled degree of branching, a controlled length of the branches, and the ability to incorporate a variety of comonomers into the backbone. These polyolefin copolymers may be termed either a polyolefin plastomer (POP), or a polyolefin elastomer (POE), depending on whether the comonomer amount is low or high, respectively. Because of this flexibility in polymer synthesis, metallocene-based resins have a wider range of physical properties than traditional polyolefins [4]. The properties can also be carefully controlled to suit specific applications [5]. For this reason, the new resins are making quick inroads into packaging, wire and cable, and some specialty markets [6]. In the preliminary study presented here, formulations of filled POP have been produced at the laboratory scale, and tested for flooring applications.

POP-based formulations can have important advantages over PVC-based ones. The first advantage is that filled POP can be processed without the use of plasticizers, thus avoiding problems associated with VOC emissions and microbial degradation. The second advantage in using POP is the potential for incorporating post-consumer recycle. Over 75% of recycled plastics is estimated to consist of polyolefins. Incorporation of these materials into PVC flooring tiles would lead to large reductions in physical properties because of the poor miscibility between PVC and polyolefins. POP, on the other hand, is compatible with recycled polyolefin resins, which could thus be used as extenders to lower costs. The effect of recycle content on POP formulations is therefore studied as well in this work.

2

LITERATURE REVIEW

The literature related to the polyolefins, metallocenes as olefin polymerization catalysts, and PVC flooring tiles is reviewed in this chapter.

2.1 POLYOLEFINS

Polyolefins have established themselves as some of the most widely used commodity polymers during the last four decades. The global thermoplastics market, representing approximately 10% of the global chemical industry, was about 90 million tons in 1995, 60% of which is accounted for by polyolefins. This percentage is made up of 16 % low- density polyethylene (LDPE), 16% high- density polyethylene (HDPE), 9% linear low-density polyethylene (LLDPE), and 19% polypropylene (PP) homo- and copolymers [7].

Polyolefins are both economically and ecologically attractive materials. Modern gas phase and liquid pool polymerization technologies do not require solvents for polymer purification. Polyolefins are known for their low energy demand during polymerization and melt processing. They also offer advantages over other plastics in recycling. They may be degraded by catalytic hydrogenation, cracked, or used as a source for incineration. New polyolefinic resins are aimed at expanding the range of physical properties to encompass areas traditionally occupied by more sophisticated, expensive, and sometimes hazardous materials. This trend is possible through recent advances in olefin catalysis.

2.1.1 Polyolefin Structure-Property Relationships

A classification of polyolefins and their corresponding densities appears in Table 2.1. In general, the following polymer characteristics and performance properties increase with increasing density: chain linearity; stiffness; tensile strength; tear strength; softening temperature, and brittleness. On the other hand, some polyolefin properties such as impact strength, flexural strength, and environmental stress crack resistance (ESCR) decrease as the polyolefin density increases.

Polyolefins macromolecules cannot crystallize completely due to structural irregularities such as chain ends, short -chain branches (SCB), and long-chain branches (LCB). As the amount of SCB or LCB increases, the crystallinity is decreased, resulting in a lower density and a lower modulus of elasticity [8]. This in turn, affects the performance properties listed above. A synopsis of polyolefin catalyst/technology-structure-property interdependence is presented in Figure 2.1.

Polyolefins are used in several different applications primarily because of their wide range of resin characteristics and end product properties. These properties, particularly processability and the physical and mechanical properties, are highly dependent on the average molecular weights(MW) and molecular weight distribution (MWD) . For example, injection molding requires resins with low melt viscosity and elasticity, whereas blow molding requires resins characterized by high MW and MWD which possess high melt viscosity and elasticity. These MW characteristics also influence properties such as molded part warpage, and ESCR.

The operating temperatures of the different polyolefins are limited by the glass transition temperature (T_g) at the low end and the crystalline melting point (T_m) at the upper end. However, the degree of mechanical property retention is better related to either the heat deflection temperature (ASTM D 648 [9]) or the Vicat softening point (ASTM D 1525 [10]). The specific heat of polyolefins are in the order polyethylene > polypropylene > polybutene-l. Polypropylene has about the lowest thermal conductivity and thermal expansion coefficient. All of the polyolefins generally have good ESCR, with PP being better than PE; but all polyolefins require some degree of stabilization against all forms of degradation.

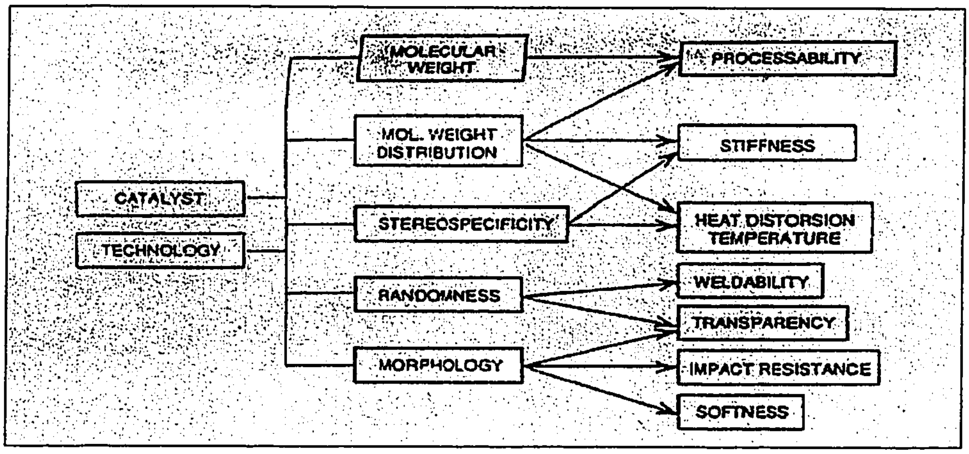

Figure 2.1: Catalyst/technology-structure-property relationship of polyolefins[7].

Table 2.1: Classification and Density of Polyolefins [7].

Polyethylene type	Macromolecular classification	Density range (g/cm^3)
Low-density polyethylene (LDPE)	Homopolymer	0.910-0.925
Medium-density polyethylene (MDPE)	Homopolymer	0.926-0.940
Linear low-density polyethylene (LLDPE)	Copolymer	0.910-0.940
Very-low-density polyethylene (VLDPE)	Copolymer	0.890-0.915
High-density polyethylene (HDPE)	Homopolymer	0.960 and higher
HMW polyethylene (HMWPE)	Homopolymer	0.947-0.955
UHMW polyethylene (UHMWPE)	Homopolymer	0.940
Polypropylene	Homopolymer	0.904-0.906
Ethylene-propylene copolymer	Copolymer	0.904-0.907
Polybutene- 1	Homopolymer	0.910
Poly(4-methyl pentene-l)	Homopolymer	0.830

2.2 METALLOCENES AS OLEFIN POLYMERIZATION CATALYSTS

Metallocene technology for the homogenous polymerization of olefins is revolutionizing the polyolefin business world- wide. Interest in metallocene catalysis has exploded since Walter Kaminsky's discovery that methyl aluminoxane functions as a highly efficient cocatalyst for the primary catalyst in olefin polymerization. This work was performed using biscyclopentadienyl metal catalysts. Early work on the metallocene catalysts did not yield sufficient activity in polymerizing ethylene to warrant significant investment and commercialization. Since 1989, the pace in polyolefin development with metallocene catalysts has been accelerating, following the discovery of the extraordinary activating efficiency of methylauminoxane (MAO) with simple biscyclopentadienyl metal compounds [6]. Many adaptations to this general catalyst structure, shown in Figure 2.2, have since been developed.

These catalysts have a constrained transition-metal site, usually a group 4b metal(Zr, Ti, or Hf). The metal site is sandwiched between ring structures to form a sterically hindered site. Variations include ring bridging with either a Si or C atom, ring functionalization with various alkyl or aromatic groups, R, and metal coordination to either a halogen or alkyl group, X [11].

The main reason for the high degree of interest in the metallocenes is because a metallocene catalyst has a single active site. The individual steps by which the catalyst links up the monomer units into a polymer chain are known in principle. Comonomers can also be incorporated in a strictly statistical manner into the polymer chain. Using metallocene catalysts, polymer producers can create new grades, and even completely new families of

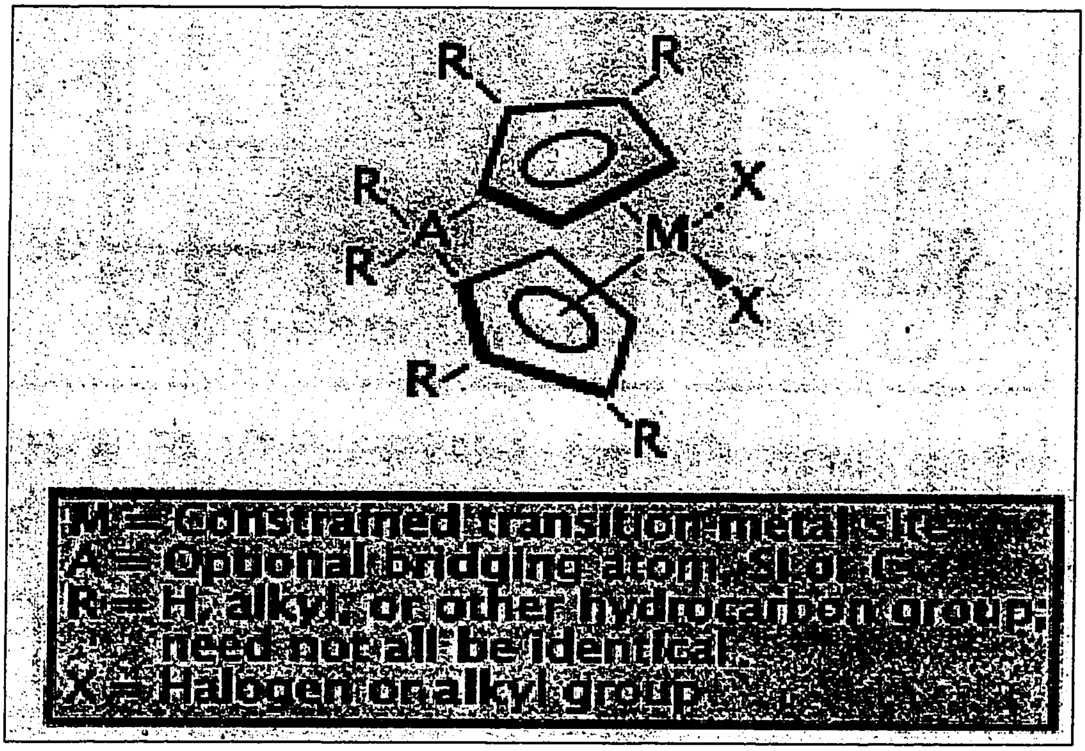

Figure 2.2:General structure of metallocene catalysts [5].

polymers that have the following characteristics :

1. narrower MWD, thereby creating resins with improved ESCR and better optical properties[12],
2. copolymerization of dissimilar monomers, such as styrene and ethylene, which can be incorporated as branches or included in the polymer backbone,
3. even spacing of the monomers of the chains,
4. even length and degree of branching of the chains.

The resulting products have a wider range of physical, chemical and electrical properties, with much more uniformity than is possible using traditional Ziegler-Natta catalysts[13].

Metallocenes are extremely efficient catalyst systems, allowing yields in excess of one ton of polymer per gram of catalyst per hour. Efficiencies as high as 25 tons of PE per gram have been reported [14].

Ziegler-Natta polymers are bound by trade-offs among the key resin properties of hardness, stiffness, impact resistance and transparency. A gain in one property is compensated by a decline in the others. With metallocenes, the trade- off still exists, but, at the same time, a much wider range of properties is achievable, as shown in Figures 2.3 and 2.4.

Exxon Chemical Co. expanded the range of useful biscyclopentadienyl compounds for ethylene and propylene polymerization [15]. Exxon was the first company to make metallocene catalysts commercially practical. This led to the development of the company's high-pressure Exxpol process utilizing biscyclopentadienyl zirconium, which was commercialized for ethylene polymerization in 1991 for the production of the company's

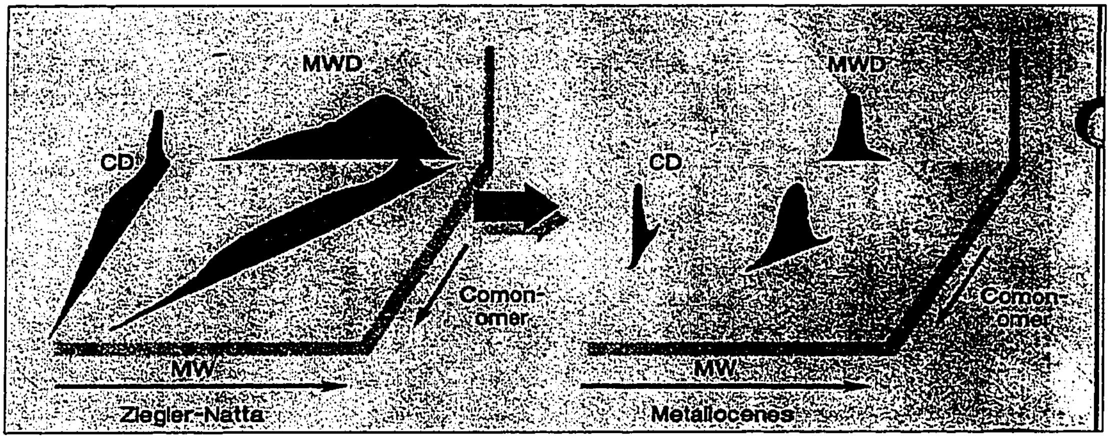

Figure 2.3 : Using metallocenes polymer properties can be more accurately controlled than with Zieglar- Natta catalysts [22].

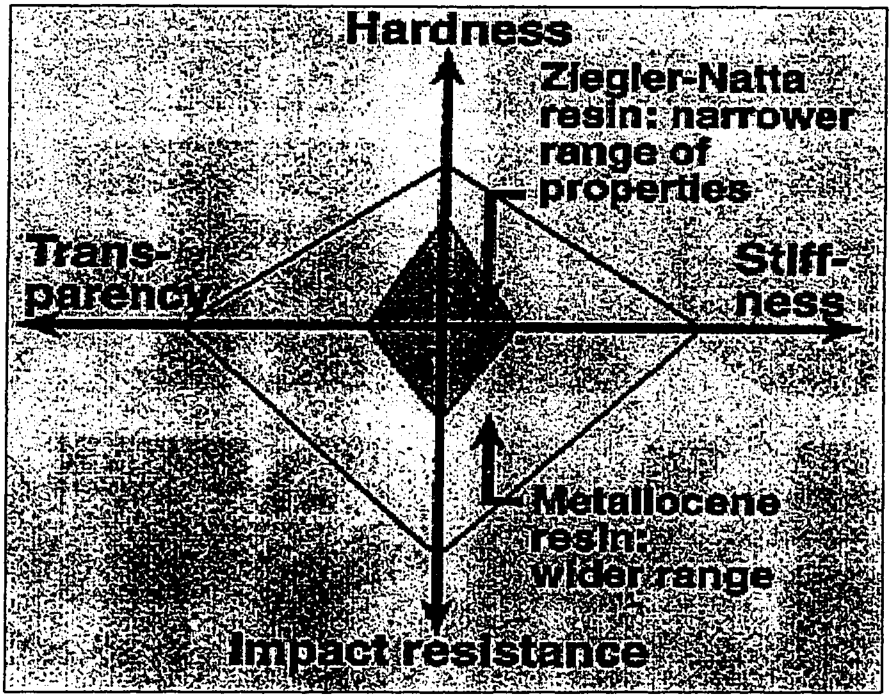

Figure 2.4: Metallocene catalysts offer better polymer properties [13].

metallocene- based Exact resins. These resins are termed plastomers, or elastomeric, linear low-density PE's of 0.88 to 0.910 g/cm^3 density. They use butene or hexene as the comonomers, or both of them together to make a terpolymer. Exxon's current metallocene-based capacity is 20 million kg/year. Applications include packaging, wire and cable, health care, modified polymers and specialty uses. Exxon has produced 40 commercial and developmental resins since the first plant began operating in 1991 in Baton Rouge [16,17].

Dow Chemical presented several higher value-added applications based on its single-site, constrained geometry catalyst technology (CGCT). This technology produces ethylene-octene copolymers with narrow MW and comonomer distributions, which normally results in poor processability. However, by inserting less than one long-chain branch per polymer molecule, Dow has created low-density polyolefin elastomers (>20% octene) and plastomers (<20% octene) that are easily processed.

Dow compared peroxide-cured, low viscosity polyolefin elastomer (POE) compounds with high viscosity EPDM (ethylene-propylene diene monomer) compounds in automotive hose, cable, and molded-seal applications. The POE's readily accepted standard compounding ingredients, and could be cured with either peroxides or silanes. In all cases, POE compounds of similar hardness exhibited higher tensile strengths than EPDM despite the lower viscosity. The heat-aging performance of the POE compounds in automotive hose and cable was outstanding.Virtually 100% elongation was retained after seven days at elevated temperatures, while the EPDM compounds showed considerable deterioration under the same conditions. Dow reported similar results for POE compounds designed for low-voltage flexible-cable, and thermoplastic polyolefin modification applications. The pelletized POEs were readily compounded in Banbury mixers or twin-screw extruders, requiring only minor procedural modifications.

Two new polyolefin plastomers (POPs) for packaging resins were designed to have unusually high moduli and Vicat softening temperatures for their low heat-seal temperatures to produce films with low blocking tendencies and high package integrity. Dow also reported that blown films from one product, designed to be an alternative to LLDPE and ULDPE, exhibited intermediate heat-seal characteristics and Elmendorf tear strength, but higher modulus and dart impact strength, and much lower blocking tendencies. Blown films from a second resin, designed to be a specialty-film replacement, were compared with products from a Dow POP, an EVA, and an ionomer. New and older POPs had better heat-seal characteristics than the EVA and the ionomer. Modulus was equivalent to that of the ionomer films, but much higher than those of the older POPs and the EVA films [17].

Metallocene polyolefins are thus expected to penetrate a broad array of polymer markets. The higher priced speciality markets have been targeted initially, followed by the high volume and commodity markets. New markets are also expected to be created with the development of new classes of polymers that were not possible with conventional Ziegler-Natta technologies. It is estimated that by the end of the century, over 20 million tons per year of metallocene- based polymers will be produced, accounting for 10% of the global thermoplastics and elastomers markets.

2.2.1 Metallocene Based Olefinic Elastomers

Major global suppliers of metallocene EPR/EPDM (ethylene-propylene rubber/ethylene-propylene diene monomer) include Dow, Exxon, and DSM [18].

Dow markets its constrained geometry catalyst-produced ethylene polymers under the trade names "Affinity" polyolefin plastomers and "Engage" polyolefin elastomers. Improved processability is claimed because of long-chain branching in the macromolecular structure. Targeted applications include packaging, automotive, medical devices, and wire and cable. To date, Dow has commercialized 23 Affinity and Engage polymers. Affinity grades containing up to 20 wt% octene are called polyolefin plastomers. They are flexible and thermoplastic, thereby matching the properties of conventional LLDPEs and very-low-density polyethylenes (VLDPEs). Engage resins containing more than 20 wt % of octene are called polyolefin elastomers. Their flexibility, clarity, and tensile strength enable them to replace flexible thermoplastics like PVC, EVAc, EMA, and styrene block copolymers as well as EPR and EPDM [19,20].

Amoco, with Fiber Web North America, Simpsonville, developed elastomeric homopolymers of polypropylene (EHPP). Amoco uses a metallocene catalyst to graft blocks of crystalline and atactic side-chains alternately on the molecule. This produces less costly elastomeric olefin. The EHPP is made in a single reactor using propylene monomer and patented metallocene catalyst technology. The resultant homopolymer exhibits elastomeric properties found in high impact copolymer. Properties are similar to flexible PVC, styrene-butadiene rubber, and amorphous PP.

Table 2.2: Major suppliers of metallocene-based polymers [21]

Supplier	Material	Process	Location of dedicated capacity
BP Chemicals London, UK	mPE	gas-phase	UK
BASF, Germany	mPE, mPP	gas-phase, loop slurry, high pressure LDPE	Germany
Dow Chemical, MI	mPE,SPS	solution	USA
DSM, Netherlands	mPE	solution	Holland
Exxon Chemical, TX	mPE, mPP	gas-phase, loop slurry, solution, high pressure LDPE,	USA
Fina,Dallas, TX	SPP	loop slurry	h
Hoechst AG, Germany	mPP,CO	gas-phase	Germany
Mobil chemical,Norwalk,CT	mPE	gas-phase	h
Mitsui,Tokyo, Japan	mPE,CO	gas-phase	Japan
Phillips, Bartlesville , OK	mPE	loop slurry	h
Ube,Yamaguchi, Japan	mPE	gas-phase	h
Union Carbide, Danbury,CT	mPE	gas-phase	h

m= metallocene- based , PE=polyethylene, PP=polypropylene, SPS=syndiotactic polystyrene, SPP=syndiotactic PP, CO=cyclic olefins, h: no dedicated facility is running.

2.3 FLOORING TILES

Flooring tiles are manufactured from sheets, often around 2.5 mm thick, and about 2.5 m wide[23]. The function of these tiles is decorative as well as functional. Solid vinyl polymer and vinyl polymer-asbestos tiles are used as flooring along with other plastics, such as PP in carpeting, chip-filled liquid urethane, and quartz-filled liquid urethane [24]. Calcium carbonate -filled PVC- composites have long been the materials of choice for both flexible sheeting and tile products.

The most widely used PVC flooring material is produced by calendering compounds based on vinyl chloride-vinyl acetate copolymer filled with calcium carbonate . In general, the copolymers for flooring applications contain about 13-15% vinyl acetate [25]. The PVC matrix imparts excellent impact resistance, stiffness and toughness to the final product, a filler loading in the range from 100 to 300 phr is commonly used. A typical formulation of PVC tiles is provided in Table 2.3. The role of each component of formulation is discussed in a later section.

Table 2.3: Basic vinyl polymer tile formulations [26].

Resin: PVC	100 parts
Plasticizer: e.g: Dioctylphthalate (DOP)	35-50 parts
Stabilizer :e.g:Dibutyltin dilaurate (DBTL)	2-3 parts
Co-stabilizer: Epoxydised soya bean oil	3-5 parts
External lubricant: Calcium stearate	1 part
Filler: Calcium Carbonate	100-300 parts

2.3.1 Tests Performed on a PVC Tile

Floor tiles are usually installed in kitchens. Therefore, they must be resistant to common household substances, such as ketchup, mustard, shoe polish, vegetable oil, and a variety of cleaners (Mr.Clean, Spic and Span). Various tests are usually made to study the effect of these substances on the tile by coating samples of each test substance onto a tile. After 24 hours, they are removed by washing. By visual inspection for discoloration, the effect of these substances can then be detected.

Resistance to abrasion is an important consideration. Abrasion is roughening or scratching of the surface layer due to removal or displacement of material when hard particles slide or roll across the surface under pressure. PVC tiles are typically coated with a polyurethane wear layer to improve the abrasion resistance. The ASTM D1044 [27] standard test is used to study abrasion resistance.

Impact resistance is important for handling, installation, and end-use of the composite. It is the ability of a material to resist breaking under a shock loading, or the ability to resist the fracture under stress applied at high speed. The impact strength of polymeric materials is a measure of toughness: the higher the impact strength, the higher the toughness. The notched Izod impact procedure given in ASTM D256[28] is commonly used to study this property for both resins and composites. The objective of the Izod impact test is to measure the relative susceptibility of a standard test specimen to the pendulum-type impact load. The results are expressed in terms of kinetic energy consumed by the pendulum in order to break the specimen. The specimen used in the test is usually notched. The reason for notching the specimen is to provide a stress concentration area that promotes a brittle rather than a ductile failure. A plastic deformation is thus prevented in the specimen.

Exposure to ultraviolet light can lead to fading and yellowing of the flooring tiles over time. The ASTM D5208 [29] test is used to study resistance to discoloration upon exposure to UV light.

Tensile and elongation behavior of virgin PVC and composites is evaluated in ASTM D 638[30]. Tensile strength, elongation and tensile modulus measurements are among the most important indications of strength in a material and are the most widely specified properties of plastic materials. Tensile test, in a broad sense, is a measurement of the ability of a material to withstand forces that tend to pull it apart, and to determine to what extent the material stretches before breaking. Tensile modulus, an indication of the relative stiffness of a material, can be determined from a stress-strain diagram. Different types of plastic materials are often compared on the basis of tensile strength, elongation, and tensile modulus data.

Tables 2.4, 2.5 and 2.6 show the mechanical, thermal, physical, and processing properties of typical calcium carbonate-filled PVC composites, respectively.

Table 2.4: Mechanical properties:[31].

1. Tensile strength at break, MPa	7 - 24
2. Elongation at break, %	200 - 400
3. Compressive strength (rupture or yield), MPa	7 - 12

Table 2.5: Processing properties:[31]

1. Processing Temperature Range , ^{0}C	140 - 176
2. Molding Pressure Range, MPa	7 - 14
3. Compression Ratio	2.0

Table 2.6 :Thermal and physical properties:[31]

Thermal conductivity, 10^{-4}cal.- cm./sec.-cm^2.-^{0}C.	3-4
Specific gravity	1.3-1.7
Water absorption(0.32 cm.thick specimen),% 24hr	0.5-1.0
Dielectric strength (0.32 cm..thick specimen)v./mil	250-300

2.3.2 Materials

Materials used for the manufacturing of the composite floor tile include PVC, fillers and additives such as plasticizers, antimicrobials, heat stabilizers, lubricants, and processing aids. Each of these components is discussed in greater detail below.

2.3.2.1 PVC Resins

Both vinyl chloride homopolymers (PVC) and vinyl chloride-vinyl acetate copolymers are used in the production of resilient flooring. As a general rule, vinyl chloride homopolymers are used primarily in sheet flooring and vinyl tiles, whereas vinyl composition tiles usually contain copolymers of vinyl chloride and vinyl acetate. Copolymers are used in place of PVC homoploymers because the internal plasticizing effect of the vinyl acetate makes it easier to process on conventional equipment. The vinyl acetate also gives pigment wetting characteristics when high levels of filler are to be used.

Flooring manufacture employs suspension and modified bulk-polymerized PVC in processes requiring intensive mixing, and emulsion polymerized resin in processes involving liquid coating plastisols[32].

PVC is one of the highest-volume thermoplastics currently in use. It is the most versatile commercial polymer in terms of both the manner it can be processed and the large number of final applications for which it can be used as shown in Table 2.7. From a processor's point of view, PVC is versatile for its ability to accept large amounts of "modifiers" that can alter its properties considerably. While unmodified PVC homopolymer is stiff and relatively brittle (rigid PVC), when suitable plasticizers are added it can show rubber -like behavior (flexible PVC). The role of the plasticizer can be interpreted roughly in terms of a lowering of the glass transition temperature, T_g , due to the decrease of intermolecular forces.

Table 2.7: Applications of PVC [2].

Type of application	**Percentage of PVC used**
Building and construction	53%
Packaging	16%
Wire cable and electrical	9 %
Leisure	4 %
Transport	3 %
Furniture/office equipment	3 %
Clothing and footwear	3 %
Domestic appliances	1 %
Other uses	8 %

PVC has good general chemical resistance. However, some polar organic solvents will attack the resin. Weatherability can be excellent with incorporation of suitable additives. The presence of chlorine atoms in the repeat unit is associated with an intrinsic resistance to combustion. High temperatures cause degradation with formation of hydrochloric acid, which is toxic and can cause severe equipment corrosion. Heat stabilizers are generally used to prevent this degradation[33].

2.3.2.2 Fillers

Fillers can be added to lower the cost of the compound and to improve dimensional stability, stiffness, and impact strength. Calcium carbonate (limestone) is the filler of choice in flooring formulations because of its low cost, general lack of color and low plasticizer absorption properties. Talc and clay are rarely used because of their significant stiffening effect on plasticized vinyl. Asbestos was used in the past in vinyl asbestos and asphalt tiles and in some homogeneous sheet flooring[32].

Calcium carbonates are mineral type fillers. They generally are categorized as fillers or extenders since they are used for cost reduction, and provide little reinforcement. Calcium carbonates are supplied in five particulate forms : water -ground, dry-ground, ultra fine ground, precipitated, and surface treated. Flexible PVC compounds often contain 100 to300 phr of calcium carbonate[33].

2.3.2.3 Plasticizers

A plasticizer may be defined as a low molecular weight substance which, when added to a polymer, changes the physical and chemical properties of that polymer in such a manner that the finished product is more useful. More specifically, a plasticizer serves to alter such physical properties as flexibility, hardness, tensile strength and elasticity. In many cases, a plasticizer serves another important function: it reduces the melt viscosity of the plastic and permits easy fabrication of the end product. PVC is especially well-suited for plasticization and accounts for about 80% of all plasticizer use. It can thus be obtained in a wide range of stiffness from rigid and somewhat brittle types, to very flexible rubber-like types.

PVC is semi-crystalline with 5-10 % crystallinity, consisting of crystallites surrounded by amorphous areas. Even these amorphous areas are tightly bound by strong polar attractions between chlorine and hydrogen atoms in proximity. Given opportunity (compounding) and motivation (heat and shear), a plasticizer can penetrate the amorphous areas of rigid vinyl and disrupt intermolecular attractions. When enough plasticizer has entered this matrix a general relaxation ensues, and partial mobility is imparted to the polymer chain.

The number of commercial plasticizers is extremely large and recourse to the experience of polymer manufacturers and plasticizer suppliers is advisable to obtain best results at optimum cost. Common plasticizers used with PVC are phthalate derivatives. These compounds have excellent compatibility with PVC and low cost, which provides users with a breadth of processing and service properties[33].

2.3.2.4 Antimicrobials

Antimicrobials impart protection against mold, mildew, fungi, and bacterial growth to materials. Without antimicrobials, PVC can experience surface growths, causing allergic reactions, unpleasant odors, embrittlement, and premature product failure. The effectiveness of an antimicrobial depends on its ability to migrate to the surface of the product where microbial attack first occurs. Most antimicrobials are carried in plasticizer, which are highly mobile and migrate throughout the end product. This mobility results in the gradual leaching of the additives. If significant leaching occurs, the product is left unprotected. Another major concern in the use of antimicrobial is toxicity. The majority of all antimicrobial additives are used in PVC applications such as flooring, garden hose, pool liners, and wall coverings[33].

2.3.2.5 Heat stabilizers

These additives are used primarily to protect PVC from thermal degradation during processing. The development of effective heat stabilizers is one of the major breakthroughs which allowed PVC to be commercialized in such a wide variety of applications. At elevated temperatures of processing, PVC is subject to dehydrochlorination which leads to an " unzipping" effect and causes degradation. To complicate the problem, the HCl given off during dehydrochlorination is a catalyst to further dehydrochlorination. Heat stabilizers for PVC must essentially perform two functions. First, they must prevent the dehydrochlorination from occurring initially. Secondly, the stabilizer must react with the HCl formed, thereby slowing the autocatalytic effect. Some stabilizers perform both functions with a single product while other stabilization systems require two or more additives to perform the entire task. The types of materials available for heat stabilization include organotin compounds, mixed metal systems consisting of barium-cadmium, barium-zinc or calcium-zinc, and finally, lead-based systems. The type of heat stabilizer used depends on the application. Organotin stabilizers are the common compounds used for PVC sheets. The tin content varies depending upon the end-use. It can contain sulfur, such as the mercaptides, or not, such as the maleates[33].

2.3.2.6 UV Absorbers

UV radiation of wavelength 310nm is often considered the most damaging to PVC. This wavelength range excites the PVC macromolecules in the sense of imparting excess energy sufficient to break bonds in the molecular chains. The free radicals formed as a result initiate and participate in the degradation process which is accelerated by the presence of oxygen.

The UV-protective additives which are frequently included in PVC for outdoor use afford additional and complementary protection. They absorb and dissipate the incident UV radiation essentially before it can initiate degradation. Carbon black and titanium dioxide widely used as pigments for plastics, have a light stabilizing effect on many polymers including PVC. They are often referred to as "light screens". Each compound functions as a physical barrier to both UV and visible radiation. Carbon black absorbs the radiation over both these wavelength ranges and emits the energy in the infrared region. It is also believed to act as an antioxidant by capturing free radicals. TiO_2 has some UV absorption capacity but its screening action is principally due to reflection and scattering of radiation (infrared, visible and UV) [33].

2.3.2.7 Lubricants

Lubricants control the frictional and adhesive properties of plastics during processing and in service. Lubricants also improve the dispersion of pigments and fillers in plastics. Better dispersion of fillers improves flow limits and material properties.

Internal lubricants reduce friction between polymer particles and molecules during the melting of plastics and transport of the melt. They thus reduce energy consumption on melting, lower melt viscosity, improve flow properties and increase output of processing machinery.

External lubricants reduce the friction and adhesion of polymer melts on hot metal surfaces of processing machinery. This reduces abrasion between the polymer melt and the metal, and improves melt flow. It also improves the gloss, smoothness and regularity of the surface of the plastic [33].

2.3.3 Processing of PVC to Produce Tiles

Processing of flooring tiles includes several steps, which are summarized below. The first operation is compounding, which is the mixing of raw materials in batch mixers, or in screw extruders. Single- and twin-screw extruders, Figure 2.5 and Figure 2.6, respectively, are the systems most often specified, since they offer more consistent product quality and lower operating costs. Raw materials such as PVC, fillers and additives in pellet or powder form enter a twin screw extruder . The reason for choosing this type of extruder is because PVC is a shear-sensitive material that must be processed under carefully controlled conditions. The function of the extruder is to convert solid feedstock into a homogeneous melt and to pump it through a die at a uniform rate. Following the die, a train of equipment handles the molten extrudate in order to insure that it cools to precisely the right shape and with the required molecular orientation.

The second operation is calendering. In this stage a fast production of the sheet occurs . Material from the extruder is fed between two counter- rotating, heated cylinders or rolls and squeezed in the wedge as illustrated in Figure 2.7. A layer of a thickness corresponding to the shortest distance between the roll surfaces, or gap, is formed through the nip, and entrained on the surface of one of the rolls. An excess of material forms the bank. The plasticated material undergoes very severe deformations in the nip region, and the viscoelastic character of polymeric materials imposes limitations on the speed of deformation and on the thickness of the sheet formed. The material normally goes through one or more additional roll nips, where the gap becomes progressively smaller, and the roll temperature becomes progressively lower, in order to attain the desired sheet thickness and a solid-like consistency in the product.

The final operation is stamping. In this step the tiles are cut by knives into the required dimensions for the final product. For floor tiles, the usual dimensions are squares of 1ft×ft (30.5 cm×30.5 cm).

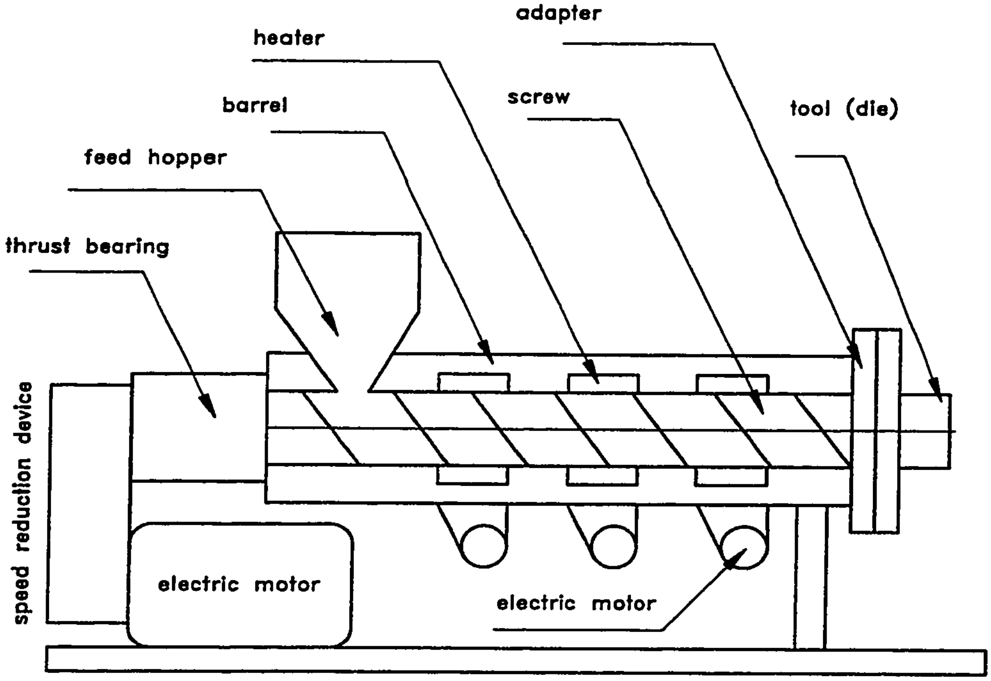

Figure 2.5 : Single screw extruder [23].

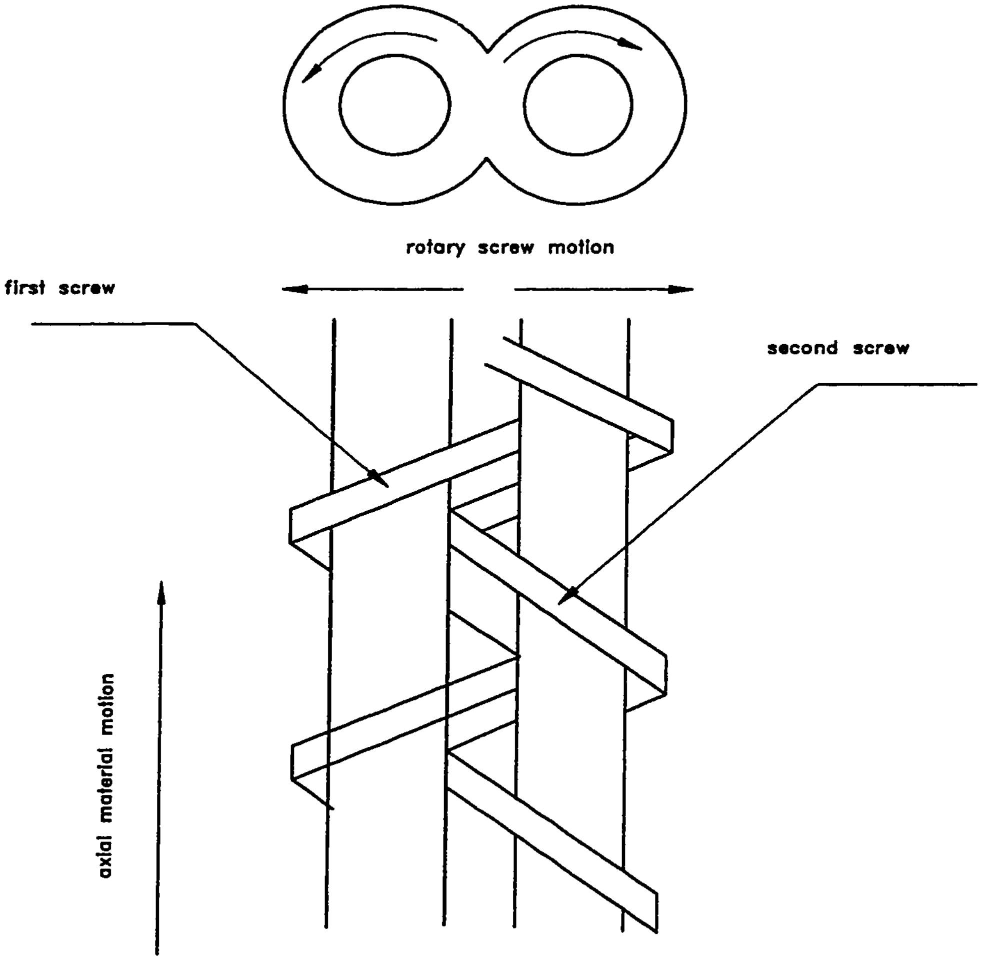

Figure 2.6: Twin screw extrusion [23].

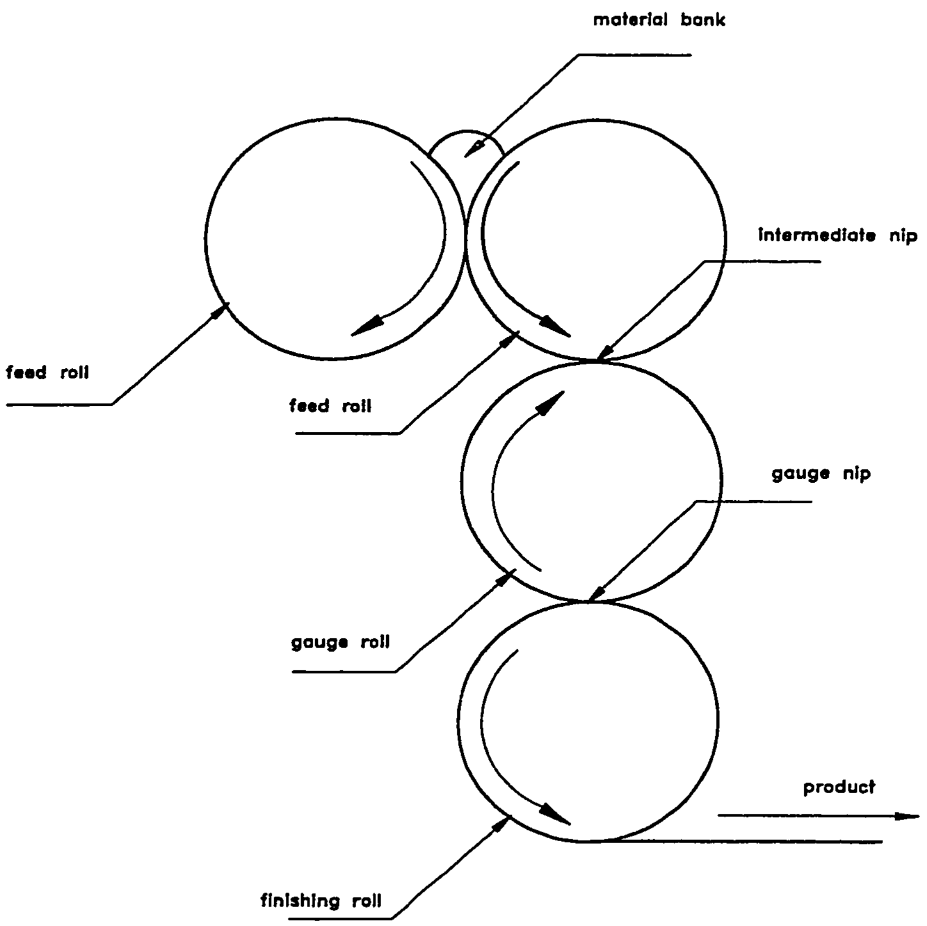

Figure 2.7: Calendering equipment [23].

3

EXPERIMENTAL PROGRAM

3.1 OBJECTIVES:

The overall objectives of the research project are described below. A principal goal is to evaluate POP's as potential replacements for PVC in composites used for flooring tiles. Most commercially available floor tiles are currently made from PVC filled with calcium carbonate . This work aims to study the use of metallocene-based polyolefinic plastomers as the matrix resin for floor tiles. By replacing PVC as the matrix resin, it will be possible to achieve the elimination of the use of plasticizers, currently used in PVC composites.

Plasticizers suffer from a number of serious drawbacks that have made them the targets of several environmental groups. Plasticizers are known to exude to the surface of a PVC product over time. At the surface, they may become volatilized, or subjected to microbial degradation. This kind of degradation is especially prevalent in humid environments. As a result, plasticized PVC flooring products often suffer from discoloration due to unsightly bacterial and fungal growths. In addition to the esthetic drawbacks, microbial growth on plasticizers also presents a number of risks to human health and well-being. The microorganisms break down the plasticizer molecule into more volatile components, which are subsequently released into the enclosed building environment. Inhabitants may thus be subjected to long-term exposure of low-level VOC. These organisms may also increase the susceptibility of the polymer chain itself to biodegradation, leading to the possibility of volatilizing halogenated organics. Finally, the plasticized surfaces may provide a breeding ground for microorganisms, which can then spread throughout the building. Moreover the exudation of the plasticizer to the surface will lead to a loss in mechanical properties of the material such as toughness and elongation. Polyolefinic plastomers to be studied do not require plasticizers.

The incorporation of post consumer plastics into the tiles to replace part of POP will also be studied. A number of benefits can be obtained from this incorporation. The chief benefit is a cost reduction due to the use of cheaper raw materials. A marketing edge will also be gained due to improved public perception of the product. Since PE is widely available as a post-consumer resin, and is also compatible with POP, recycled PE will be examined in this work.

The specific research objectives to be met in this thesis are:

☐ Lab-scale production of POP-based composites,

☐ Determination of physical and mechanical properties of the composites,

☐ Incorporation of recycled resins, and the effects on physical and mechanical properties,

☐ Comparison of the POP and PVC- based composites.

3.2 METHODOLOGY

The methodology section is divided into a description of the materials used, and of the experimental procedures used for compounding, specimen preparation and testing.

3.2.1 Materials

In order to evaluate POP relative to PVC as a resin for flooring tile applications, formulations were prepared using both types of resins. These formulations are indicated in Table 3.1. The basic vinyl polymer tile formulations presented in Table 2.3 were used, and the formulation of POP tile was established at the laboratory scale.

3.2.1.1 PVC

The PVC resin, Oxy 1810, was obtained from the Occidental Chemical Corporation (USA). It is a VC-VAc copolymer. The resin properties are presented in Table 3.2. Oxy 1810 is a common flooring-grade resin.

Table 3.1: PVC and POP-based formulations prepared and tested.

Component	PVC Formulations	POP Formulations
	Concentration, phr	Concentration, phr
Resin	100	100
Filler, $CaCO_3$	200	200
Plasticizer, DOP	35	-
Stabilizer, DBTL	3	-
Lubricant, stearic acid	2	2
PC-PE	0	20, 50, 80, 100% of total resin content

Table 3.2: Properties of Oxy 1810 PVC Copolymer.

K value	57*
Specific Gravity	1.37
Bulk Density, g/cm^3.	0.63
Particle Size	
% Retained, mesh 40	10
% Through, mesh 200	
Comonomer VAc content, %	9.7

*Corresponding MW ≈ 100,000.

3.2.1.2 POP

The POP resin, Affinity PF 1140, was obtained from Dow Plastics (USA). It is a copolymer synthesized from ethylene and octene monomers. Key physical properties are summarized in Table 3.3.

Table 3.3. Physical Properties of Affinity PF 1140 POP copolymer.

Comonomer, octene content,%	14
Specific Gravity	0.895
Melt Index, dg/min.	1.6
DSC Melting Point, ^0C	94

3.2.1.3 Calcium Carbonate

The calcium carbonate was obtained from Steep Rock Resources in Perth, Ontario. The grade used was Snowhite 12. Typical particle size distribution is provided in Figure 3.1. This grade is often used in PVC-based composites because finer particle size yields better physical properties. Table 3.4 summarizes the properties of the calcium carbonate.

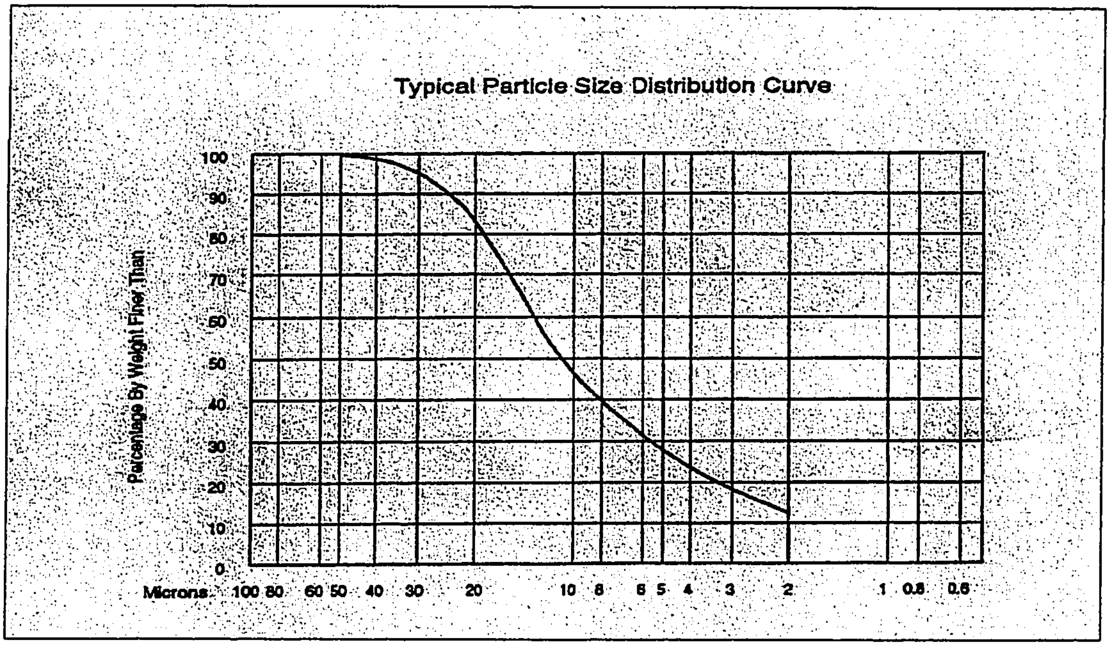

Figure 3.1: Typical Particle Size Distribution Curve of Snowhite 12 [44].

Table 3.4: Properties of Snowhite 12 $CaCO_3$.

Typical Physical Properties	
Bulk density(Loose), g/cm^3	0.8
Bulk density(Packed), g/cm^3	1.4
Specific Gravity	2.71
Typical Particle Size	
% Retained, 325 mesh	0.1
Mean Particle Size	12 microns
Typical Chemical Analysis	
$CaCO_3$ (%)	96.0
$MgCO_3$ (%)	2.0
Acid Insolubles (%)	2.0

3.2.1.4 Additives

For PVC formulations, a technical grade of DOP was used as a plasticizer, and DBTL was used as a heat stabilizer. For both polymers, a technical grade of stearic acid was used as an external lubricant. Both stearic acid and DOP were obtained from Fisher Scientific. DBTL was obtained from American Chemicals Ltd.

3.2.1.5 PC-PE

Some formulations were prepared with post-consumer polyethylene (PC-PE),obtained from Enviroplast Inc. of Ville d'Anjou, Quebec. Two types of recycle have been studied. The first one was a LLDPE and the second was a HDPE. Their properties are presented in Table 3.5. The recycle resins were obtained primarily from packaging sources.

Table 3.5: PC- PE, Properties.

Recycle Resin	specific gravity*	melt index (dg/min.) **	melting temp. (^oC)***
PC-LLDPE	0.931	1.0	124.8
PC-HDPE	0.949	0.5	128.1

* Determined in the lab in accordance with ASTM D 792 [34].

** Provided by the supplier.

*** Determined in the lab by Differential Scanning Calorimetry.

3.2.2 Experimental Procedures

(A) Mixing Using A Torque Rheometer:

All the blends were prepared by melt compounding in a Haake Rheomix 600. The apparatus consists of a batch mixer equipped with roller blades and accurate temperature controllers which maintain constant temperature in each mixer zone. The mixer is electrically heated and air cooled. The temperature was measured by a thermocouple connected to a temperature recorder as shown in Figure 3.2. The operating conditions for

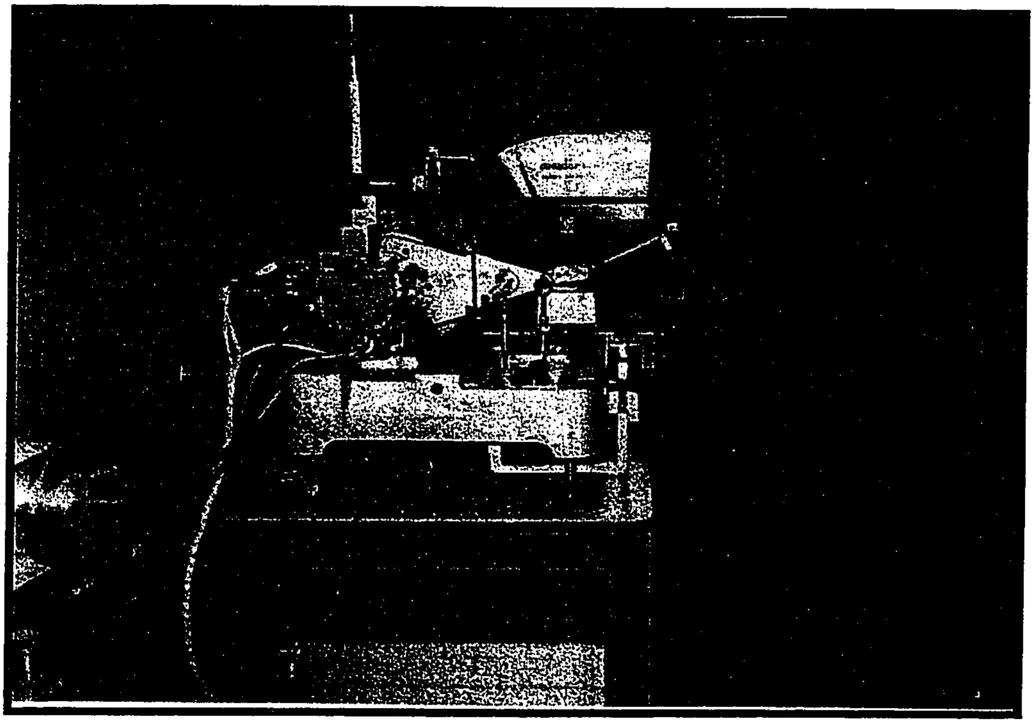

Figure 3.2: Haake torque rheometer.

the mixer are summarized in Table 3.6. The components of the blends were carefully weighed, manually dry mixed for a standard period of time and then introduced in the mixer for melt compounding. The filling coefficient was 67 % for a net chamber volume of 60 cm^3.

Table 3.6: Operating conditions in the laboratory mixer.

Formulation	T, °C	Roller speed (rpm)	Mixing time (min)
PVC-based	140	40	6
POP-based	175	60	10

(B) Compression Molding:

The compounded material from the mixer was cut when still warm into small chips. Then sheets of about 3 mm thick were molded by compression in a Carver Laboratory Press equipped with temperature controllers as shown in Figure 3.3. The weighed amount of material was placed in the mold and the mold was placed between the platens of the press which were set at the desired temperature. A heating period with no pressure was allowed. Then the pressure was applied for a determined period of time, followed by cooling with air at a rate of 10 ^{0} C/min. The conditions of compression molding for each type of material are indicated in Table 3.7.

Table 3.7: Conditions for Compression Molding.

Formulation	platen temp., ^{0}C	Pressure, Pa	Time, min.		
			melting	pressure	cooling
PVC-based	158	320	5	3	10
POP-based	178	320	5	3	10
POP/PC-PE	178	427	7	4	10

(C) Specimens Preparation:

From the molded samples, specimens were prepared for the tensile and impact tests. Specimens for tensile tests were cut with the Type V die specified in ASTM D638 and shown in Figure 3.4, and specimens for impact test were cut in accordance with ASTM D250 specifications.

(D) Conditioning:

Specimens were conditioned at 23±2 ^{0}C and 50±5 % RH for 48 hours before testing according to ASTM D 638.

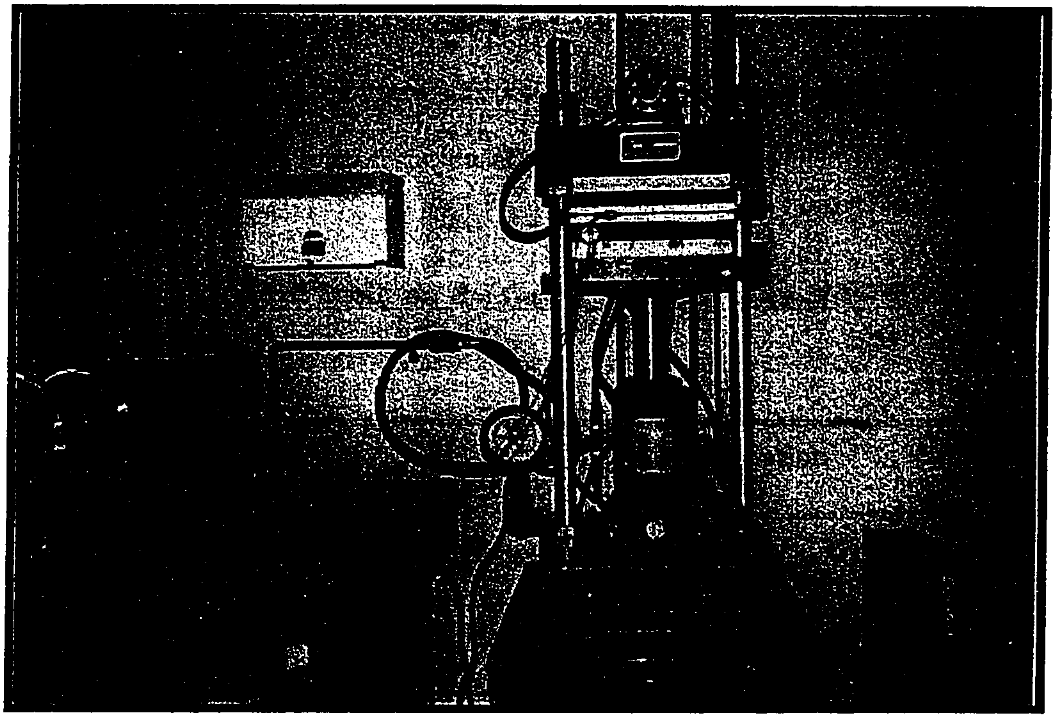

Figure 3.3: Carver laboratory press for compression molding.

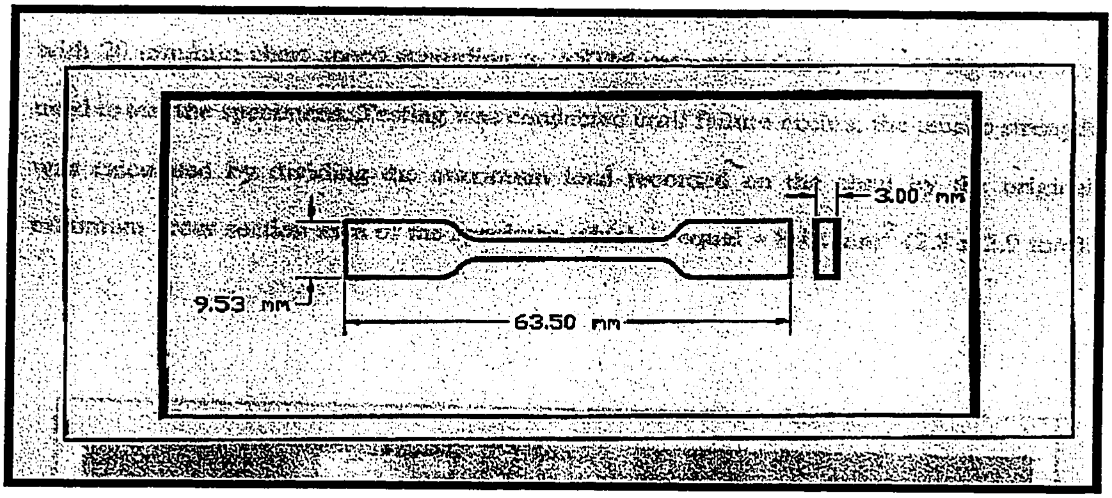

Figure 3.4: Tensile test specimen.

(E) Testing

1. Mechanical Properties

Tensile and impact tests were performed for all PVC and POP-based formulations. The tensile tests were carried out in accordance with the procedures outlined in ASTM D638, using an Instron universal testing machine model 1125 (Figure 3.5). The machine is of the cross head movement type, comprising of a fixed member carrying one grip and a movable member carrying a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and the movable member prevent alignment problems. A controlled velocity drive mechanism is used. A load-indicating mechanism capable of indicating total tensile load is used. An extension indicator, commonly known as the extensometer, is used to determine the distance between two designated points located within the gauge length of the test specimen as the specimen is stretched. The speed of testing that produces rupture of specimens in 5 min. was selected for each type of formulation. The tensile strength at yield was calculated by dividing the load at yield recorded on the chart by the cross sectional area of the specimen. Tensile strength at break was calculated by dividing the load recorded at break on the chart by the cross sectional area of the specimen. Percent elongation at break was calculated by dividing the extension at break from the chart (change in the gage length) by the original gage length and multiplying by 100.

Impact tests were carried out using the notched Izod procedure given in ASTM D256 with a model 92T Tinius Olsen impact tester illustrated in Figure 3.6. In the Izod impact test the specimen is held as a vertical cantilever beam, and is broken by a single swing of the

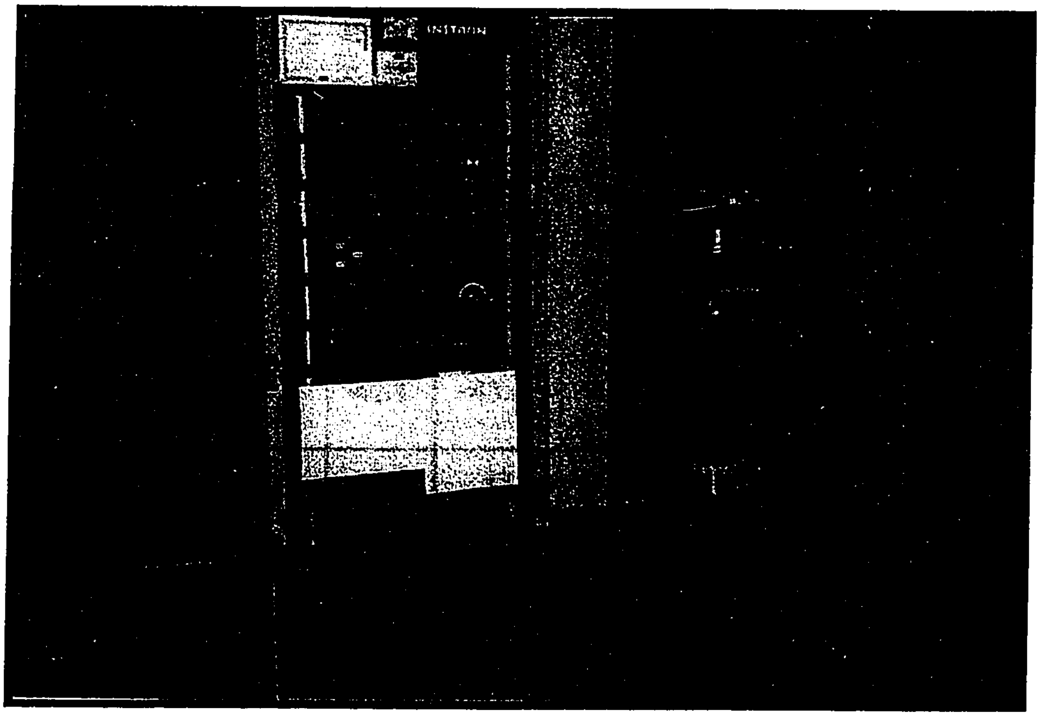

Figure 3.5: Instron universal testing machine.

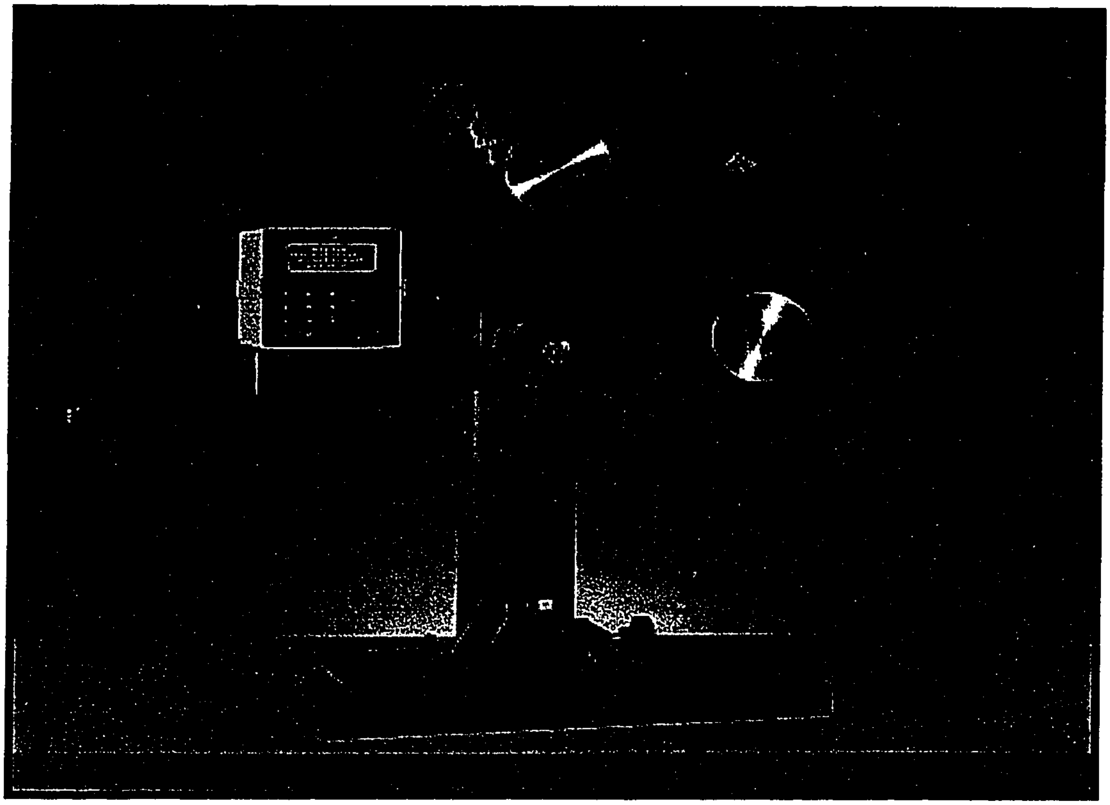

Figure 3.6: Notch Izod impact testing machine.

pendulum with the line of initial contact at a fixed distance from the specimen clamp, and from the centerline of the notch and on the same face as the notch. The impact strength is read directly in J/m from the calibrated scale on the instrument.

All the specimens for tensile and impact strength were tested within one week of their preparation after conditioning. All of the indicated values are an average of at least five determinations. The coefficients of variation inferior to 10% were taken into account for each set of specimens tested.

2. Thermal Properties:

Differential scanning calorimetry (DSC) was carried out on POP formulations and dimensional heat stability tests were carried out on both PVC and POP formulations.

DSC is a thermal analysis technique that measures the quantity of energy absorbed or evolved by a sample as its temperature is changed. This is accomplished by heating a sample and an inert reference material and measuring the difference in energy required to heat the two at a programmed rate. Initially, constant energy input is required to heat both the sample and the reference at a constant rate. At a transition point, the sample requires either more or less energy than the reference, depending on whether the change is endothermic or exothermic. The thermal properties of raw materials and blends were measured using a 912 DuPont differential scanning calorimeter connected with a 2100 Du Pont Thermal Analyzer. The DSC data were analyzed with the Du Pont DSC Standard Data Analysis Program version 4.0. Samples of about 10 mg weighed with an accuracy of ± 0.002 mg were tested for each mixture. In order to obtain a good heat transfer between sample and sample's pan, films of 0.25 mm were prepared from each mixture using Spectra-Tech Universal Film Maker, then disks with the same diameter as that of sample's pan were punched from each film. All samples were heated from room temperature to 150 ^{0}C at a heating rate of 10 ^{0}C/ min. kept isothermally at 150 ^{0}C for 10 min. to ensure the complete melting of the crystals, then cooled from 150 ^{0}C to room temperature at a cooling rate of 10 ^{0}C/ min and then heated again from -20 ^{0}C to 160 ^{0}C at a heating rate of 10 ^{0}C/ min. The melting temperature and the latent heat of melting were measured in the second heating cycle as specified in ASTM D 3417 [35]. The DSC cell shown in Figure 3.7 was carefully calibrated for temperature and latent heat using an Indium etalon sample which has a latent heat of melting of 28.42 J/g and a melting temperature of 156.61 ^{0}C. The Indium sample was scanned at the same heating rate of 10 ^{0}C/ min. All the scans were done under nitrogen atmosphere at the flow of 20 ml/ min.

The latent heat of melting represents the area under the DSC curve integrated between selected start and end linear baseline limits. The temperature of melting, or melting point, is represented by the peak temperature in the melting range as specified in ASTM D3418.

Five different samples of Affinity 1140, POP, were scanned in order to determine the method's precision. The average results are: latent heat of melting is 74.8 J/g with a standard deviation of 1.7 J/g, and a peak melting temperature of 93.6 ^{0}C with a standard deviation of 0.5 ^{0}C .

DSC analysis was done on:

1. Raw materials: POP, PC-LLDPE, PC-HDPE and lubricant(stearic acid).

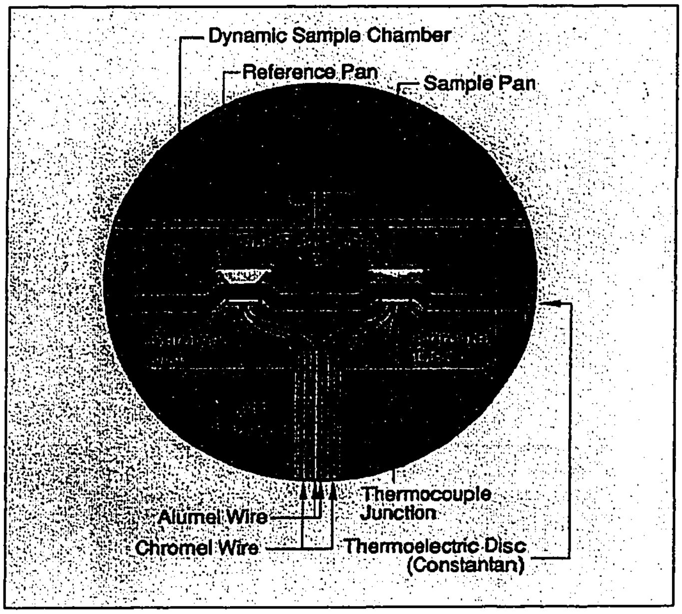

Figure 3.7:DSC cell.

2. Compounded products with the $CaCO_3$ and lubricant, in order to ascertain the influence of the filler and lubricant on the crystallization of POP and recycled PE's.
3. POP/ PC-PE formulations containing 20, 50 and 80% recycle, 200 phr $CaCO_3$., and 2 phr lubricant.

Dimensional heat stability is the ability of a plastic material to retain the precise shape in which it was molded or fabricated under conditions of variable temperature. Tests were carried out in accordance with Clause 3.14 of CSA Standard A 126.10[36]. First, sheets of around 150 mm length of each formulation were prepared and placed on a supporting plate. They were kept flat by placing a weight, which is a smooth flat steel plate approximately 13 mm thick and approximately 25 mm smaller than the sheet, on top of the test sheets. After removing the weight, the sheets' length was measured to a precision of 0.025 mm. Subsequently, each sheet was placed on the supporting plate, and the sheets and the supporting plates were heated in an air circulating oven for a period of 6 h at 65±1 ^{0}C. At the end of the heating period, the sheets on their supporting plate, were removed from the oven and conditioned at 23±1 ^{0}C and 50±4% RH for 16 hrs. At the end of the conditioning period, the sheets were removed and their lengths were measured again.

4

RESULTS AND DISCUSSION

1. Mechanical properties of PVC tile formulation

In order to evaluate POP relative to PVC as a resin for flooring tile applications, a PVC formulation was prepared and tested at the laboratory scale. A typical PVC tile formulation (in phr) was used according to data presented in Table 3.1. The formulation was tested for tensile properties and impact strength and the results are presented in Table 4.1.

Table 4.1: Results of tensile and impact testing of PVC tile formulation.

Yield Strength, MPa	2.77
Break Strength, MPa	5.55
Elongation, %	336
Impact Strength, J/m	154

2. Effect of filler($CaCO_3$) loading on the tensile properties of the POP formulation.

Formulations with POP alone and filler loadings of 100, 150 and 200 phr were prepared and tested for tensile strength. The same amount of lubricant used in PVC formulation was utilized in POP formulations.

In Table 4.2 and Figures 4.1 through 4.4 there are indicated the average tensile properties of POP formulations for 0, 49.5, 59.5, and 66.2% filler loadings. It can be seen that filler concentration has a pronounced effect on the tensile properties. As the concentration of filler increases, all mechanical property values decrease. This is to be expected, since the incorporation of filler into an elastomeric material has an adverse effect on its mechanical properties and no reinforcing effect is observed. However, the magnitude of the decrease is much less than expected for traditional polyolefins [37].

As can be seen in Table 4.2, even at a filler loading of 200 phr the mechanical properties of POP formulation are still superior to those of the PVC formulation tested. Consequently, this filler loading was considered appropriate and was utilized for further experiments.

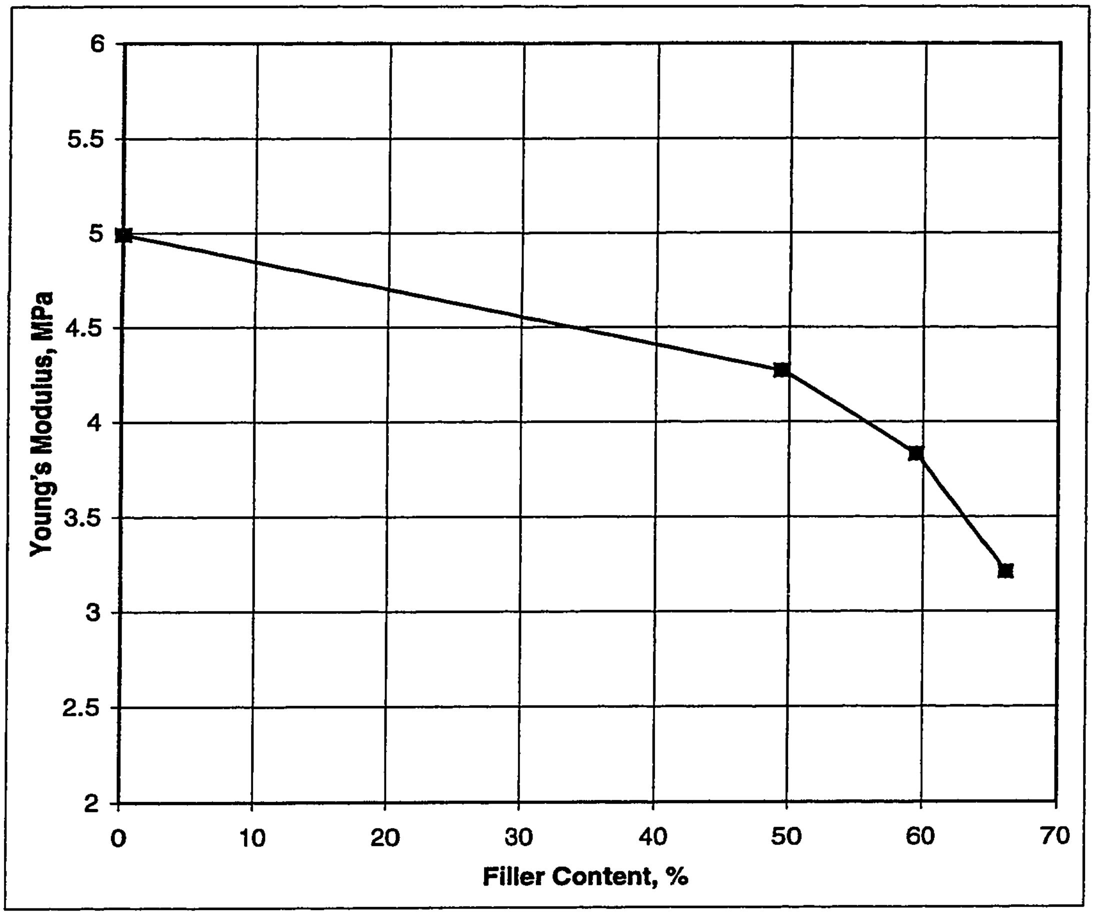

Figure 4.1: Effect of filler ($CaCO_3$) content on Young's Modulus for POP formulations.

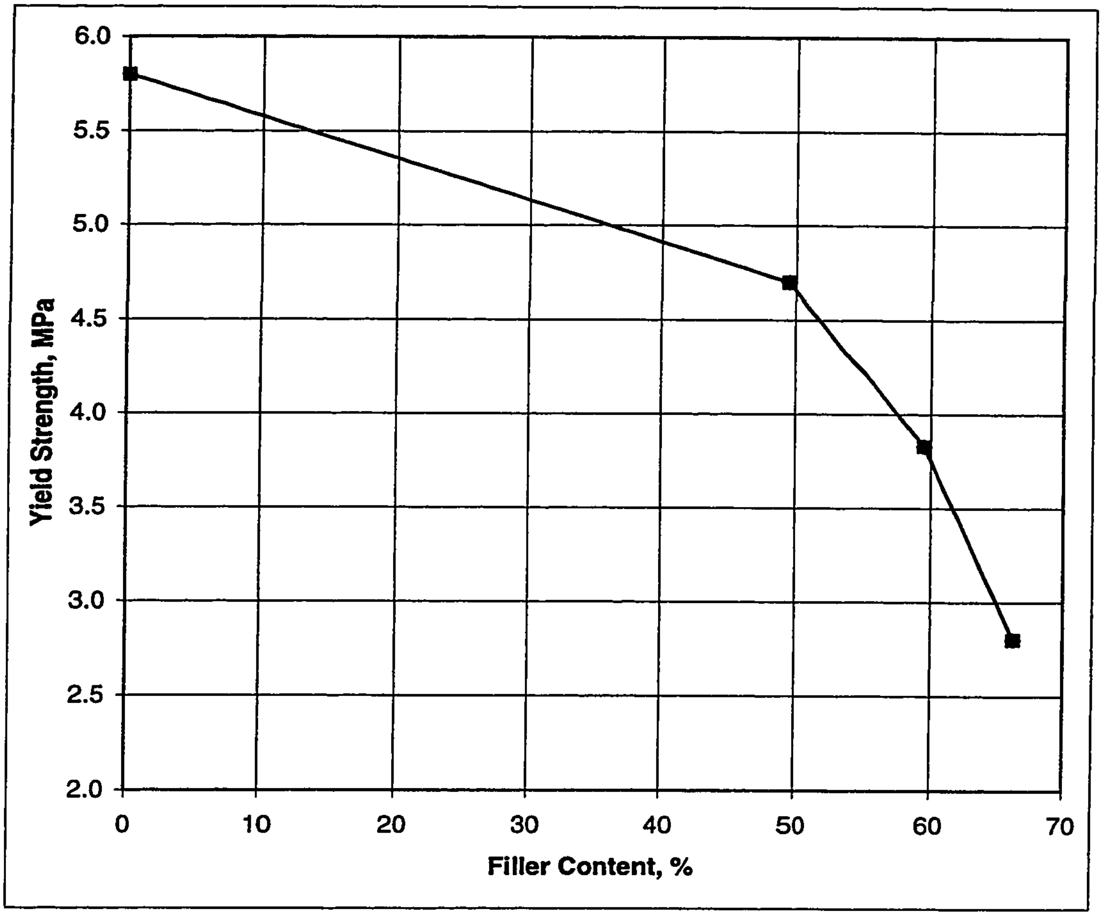

Figure 4.2: Effect of filler ($CaCO_3$) content on the yield strength for POP formulations.

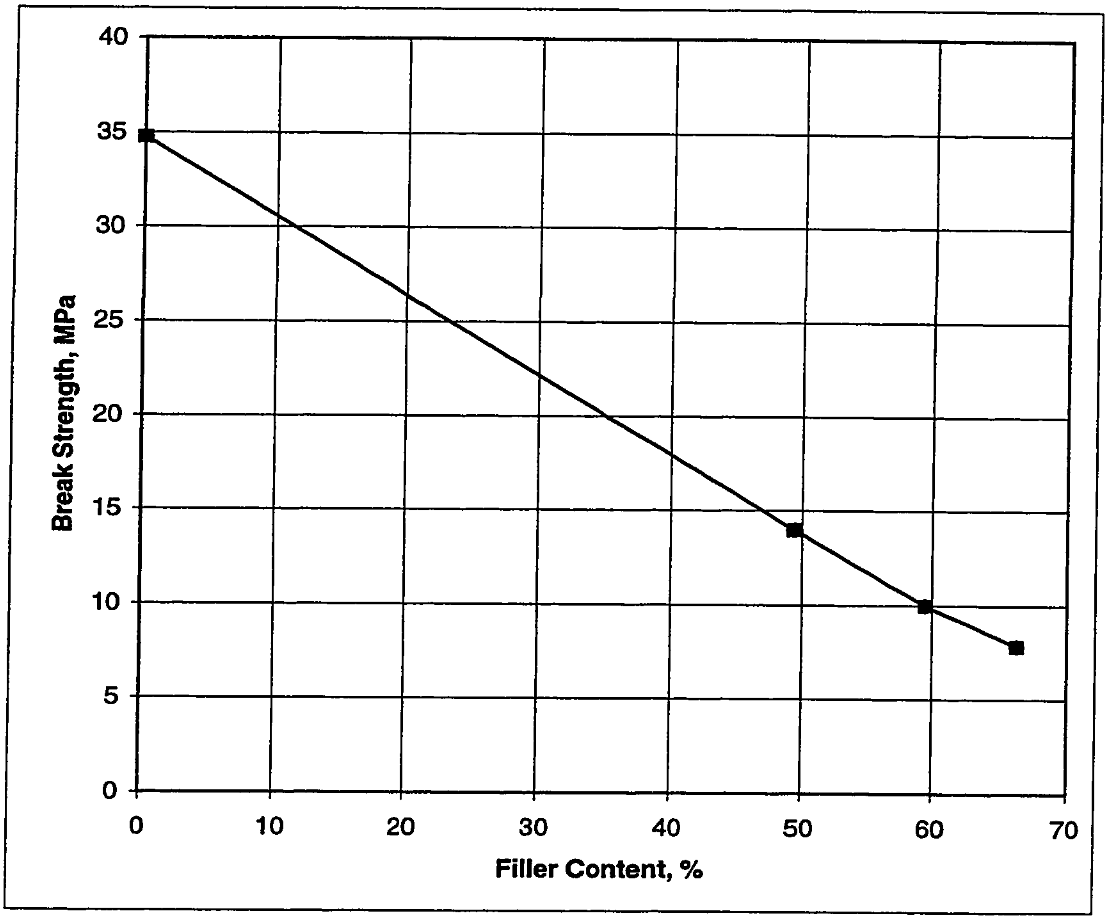

Figure 4.3: Effect of filler ($CaCO_3$) content on the break strength for POP formulations.

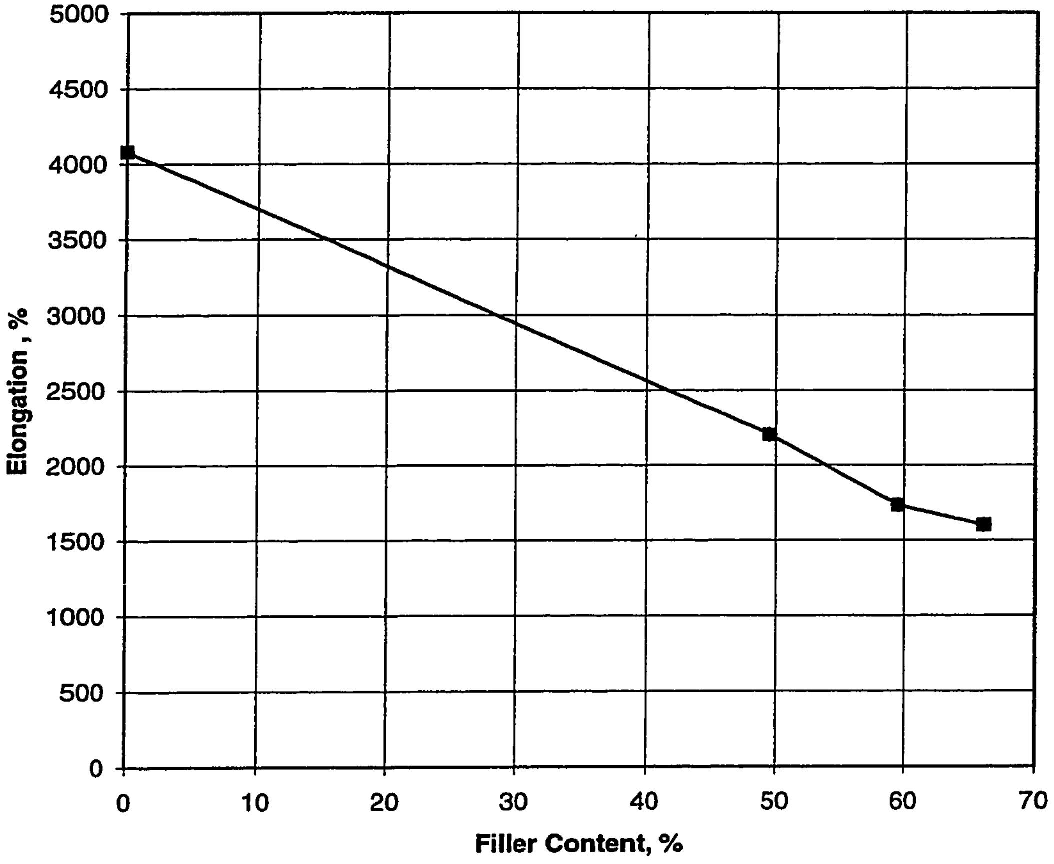

Figure 4.4: Effect of filler ($CaCO_3$) content on the elongation for POP formulations.

Table 4.2: Results of tensile testing for POP formulations for different filler loadings.

Filler content,		Young's Modulus, MPa	Yield Strength, MPa	Break Strength, MPa	Elongation, %
%	phr				
0	0	4.99	5.8	34.76	4080
49.5	100	4.27	4.7	13.97	2204
59.5	150	3.83	3.83	9.99	1733
66.2	200	3.21	2.80	7.82	1601

3. Comparing the tensile and impact properties for PVC and POP formulations

Table 4.3 summarizes the results obtained in the tensile and impact tests for PVC and POP formulations described in Table 3.1, with 200 phr filler and 2 phr lubricant.

Table 4.3. Results of tensile and impact testing for PVC and POP tile formulations.

Resin	Yield Strength, MPa	Break Strength, MPa	Elongation, %	Impact Strength, J/m
PVC	2.77	5.55	336	154
POP	2.80	7.82	1601	278.3

The tabulated data show that the physical properties of the POP-based formulations compare very favorably to the PVC-based ones. In particular, the higher values in elongation and impact strength point to superior toughness in the POP samples. This point is significant since high filler loadings have large adverse effects on the toughness of composites made with conventional polyolefin resins. The results also indicate that the POP resin can likely accommodate calcium carbonate loadings in excess of 200 phr while maintaining adequate mechanical properties.

4. Effect of recycle incorporation on tensile and impact properties.

Table 4. 4 shows that formulations containing solely PC-PE as the matrix resins have very poor mechanical properties. The calcium carbonate loading of 200 phr is clearly much too high for the PC-PE to function as an effective binder. Formulations using a blend of POP and PC-PE resins were therefore prepared and tested. Mechanical properties were determined for the POP and PC-PE formulations with recycle contents of 20%, 50% and 80% of the total polymer concentration, and 200 phr filler loading, as indicated in Table 3.1. These results are presented in Table 4.5 and in Figures 4.5 through 4.14. As can be seen from Table 4.5, the blends with 80% PC-LLDPE have lost their elasticity to a large extent. All the specimens of these blends fail at the point of highest stress. However, it appears that for the blends with 20 and 50% PC-LLDPE, POP has a greater influence on the mechanical properties than the recycled resin. Figure 4.5 shows the effect of PC-LLDPE concentration on Young's modulus of the blend. For 20 and 50% PC-LLDPE, the modulus increases by 8 and 33% respectively, and this provides evidence that PC-LLDPE imparts a measurable

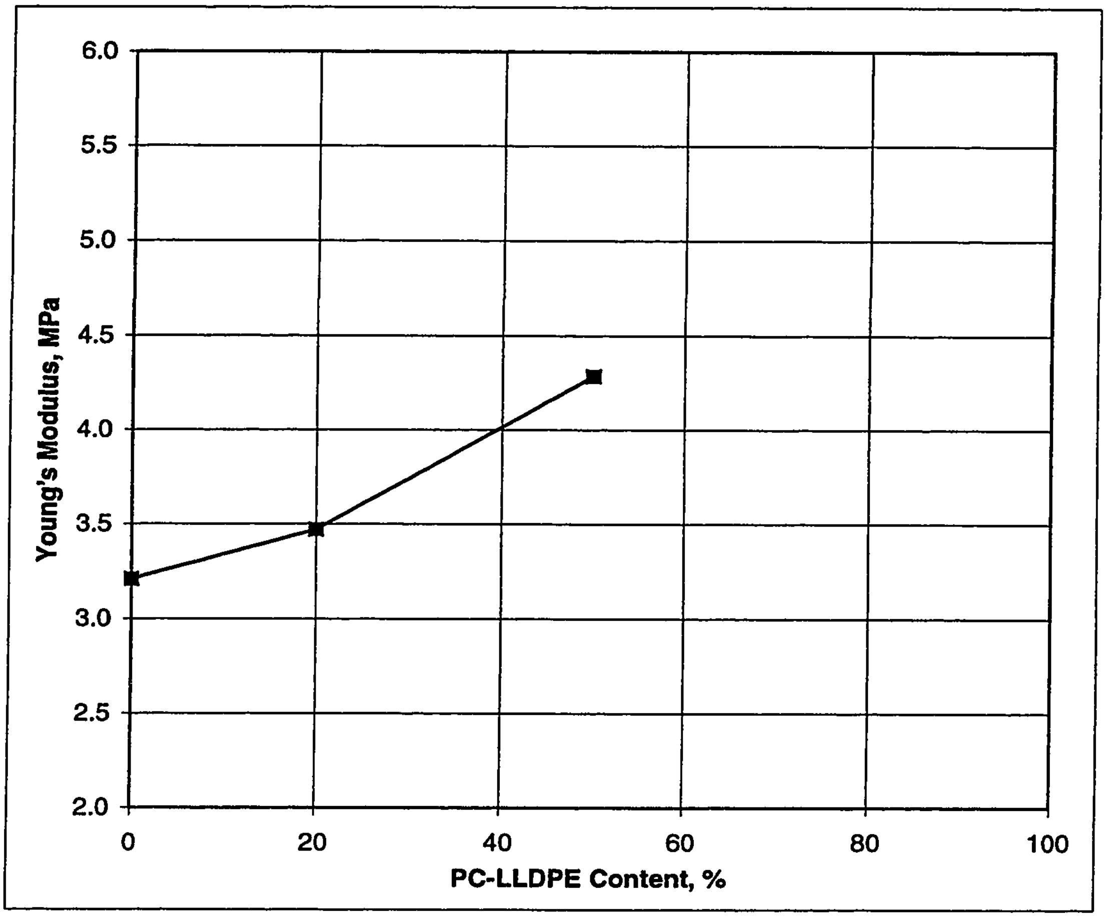

Figure 4.5: Effect of PC-LLDPE content on Young's Modulus of POP formulations containing 200 phr $CaCO_3$.

reinforcing effect. Figure 4.6 shows an increase in yield strength with increasing recycle content. This is to be expected taking into account the high value of yield strength of PC-LLDPE, 7.42 MPa, in comparison to that of POP, which is only 2.80 MPa. From Table 4.5 and Figure 4.7 it can be seen that the break strength decreases by only 7 and 13% for each of the 20 and 50% PC-LLDPE blends, respectively, and by 36 % for 80% PC-LLDPE blends. The elongation at break, shown in Figure 4.8, decreases by only 13 and 29% for each of the 20 and 50% PC-LLDPE blends, respectively. This behavior is characteristic of a loss in the elasticity of the blend upon addition of the recycle resin, and is to be expected. The loss of elastic properties due to the incorporation of recycled resins is well documented, and is frequently translated into a decrease in toughness. However, for the case of POP containing PC-LLDPE there is an almost 27 % increase in the impact strength when 50% of this recycle resin is incorporated into the POP formulation as shown in Figure 4.9. This surprising result is due to the close chemical similarity of the LLDPE and POP macromolecules. Thus, the PC-LLDPE appears to act as an impact modifier in increasing toughness. For the 80% PC-LLDPE blends a dramatic decrease in the impact strength is observed, indicating that at very high levels the recycled resin affects adversely the impact strength of the blend.

For PC-HDPE a similar trend in mechanical behavior is observed. There is an increase in Young's modulus, shown in Figure 4.10, an increase in yield strength, shown in Figure 4.11, and a decrease in the elongation, shown in Figure 4.13. In fact, the decrease in elongation is more dramatic in the case of POP/PC-HDPE blends, and this is explained by the fact that HDPE has high crystallinity which adversely affects elongation. The impact

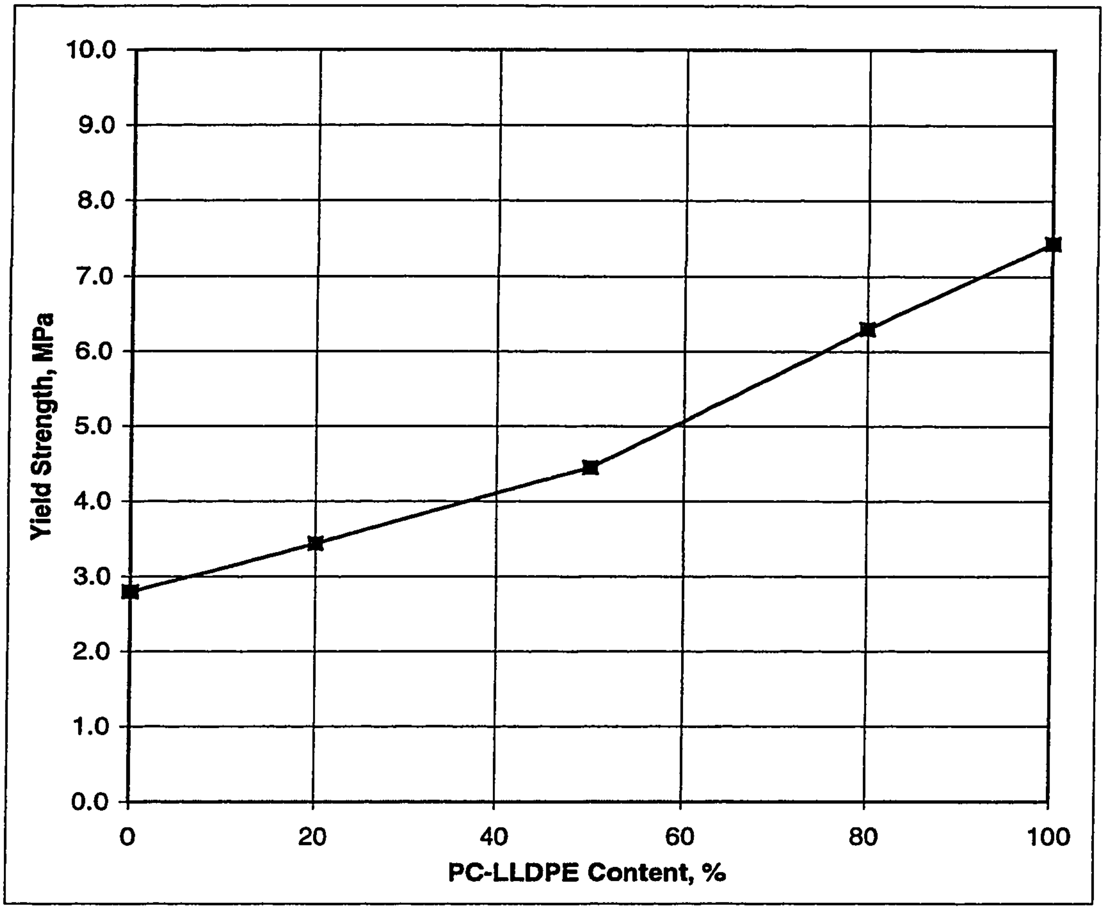

Figure 4.6: Effect of PC-LLDPE content on the yield strength of POP formulations containing 200 phr $CaCO_3$.

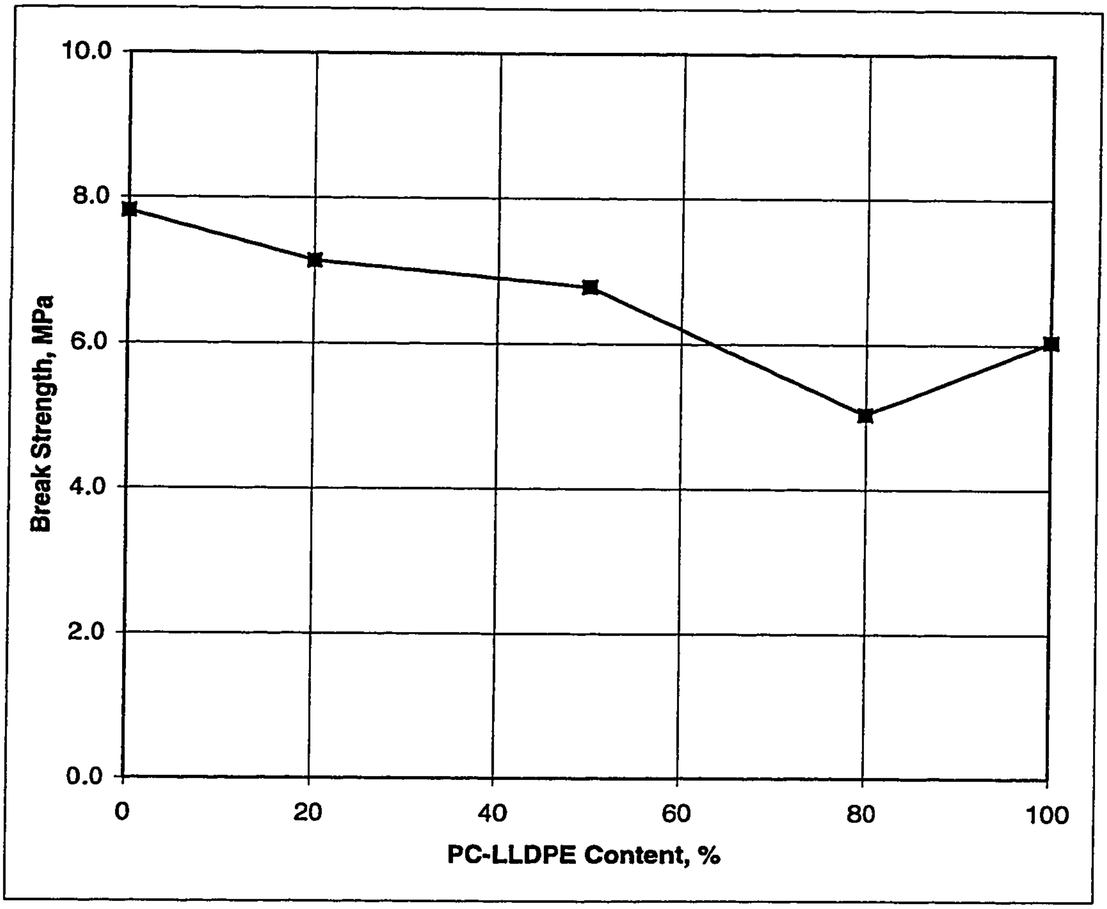

Figure 4.7: Effect of PC-LLDPE content on the break strength of POP formulations containing 200 phr $CaCO_3$.

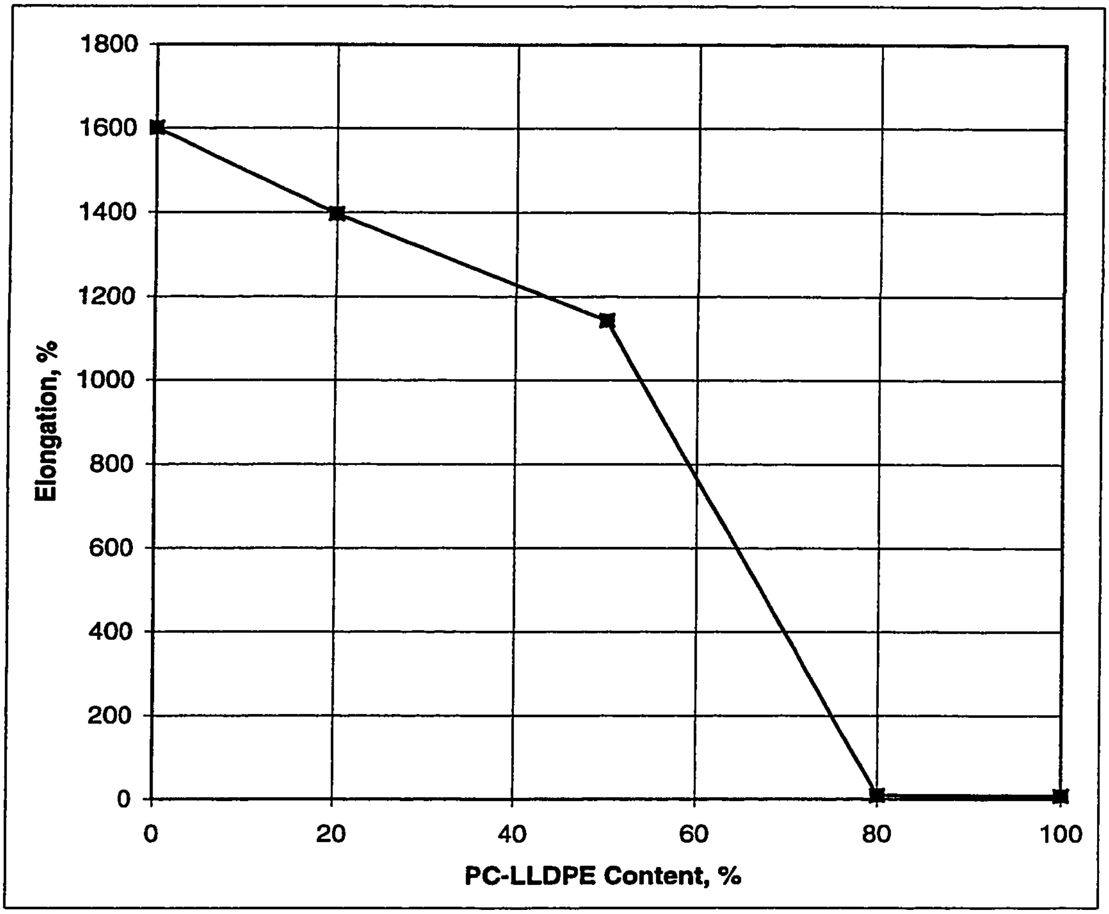

Figure 4.8: Effect of PC-LLDPE content on the elongation of POP formulations containing 200 phr $CaCO_3$.

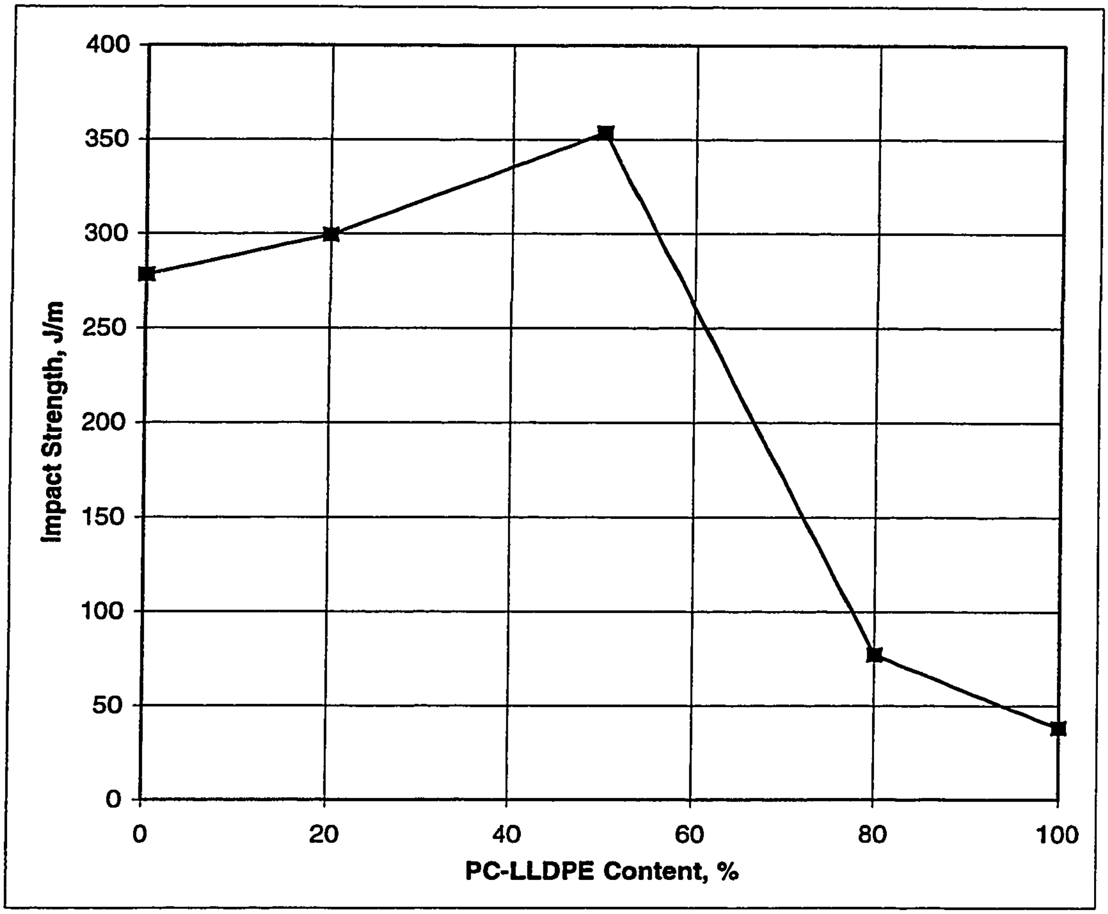

Figure 4.9: Effect of PC-LLDPE content on the impact strength of POP formulations containing 200 phr $CaCO_3$.

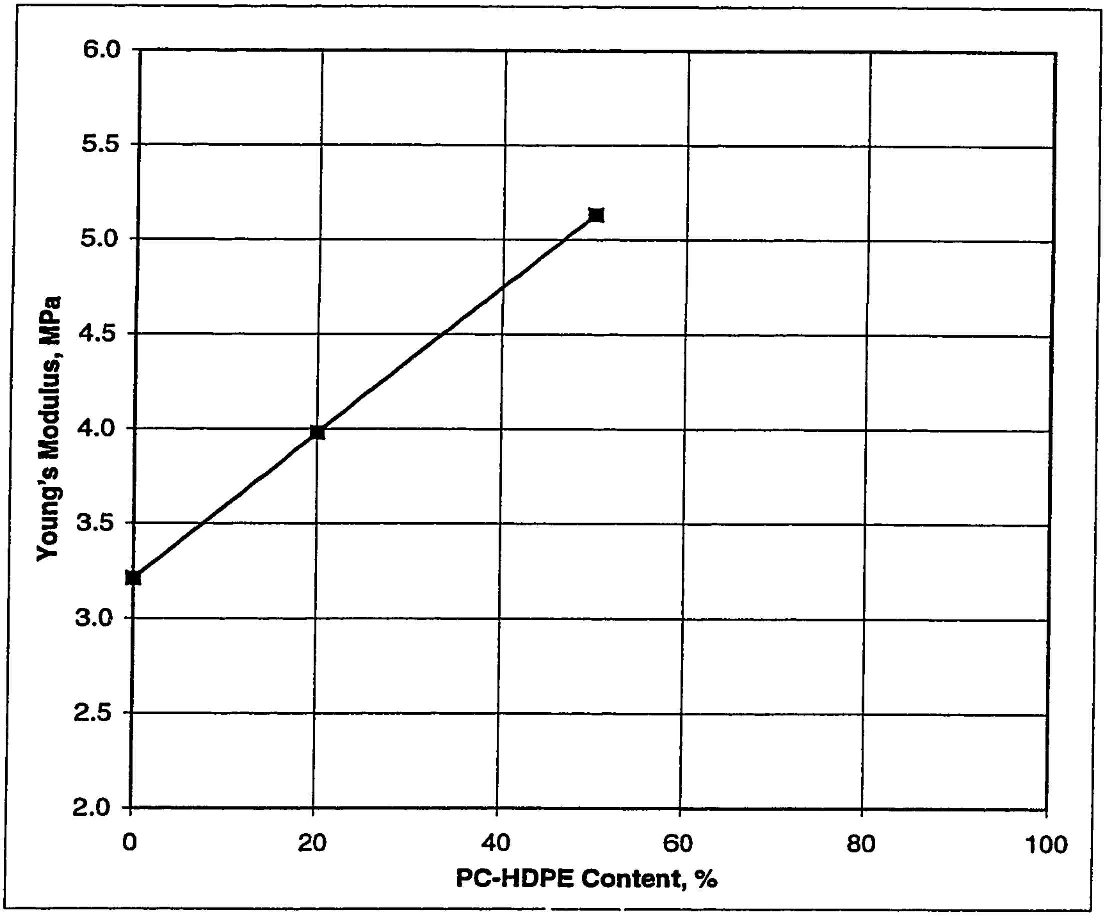

Figure 4.10: Effect of PC-HDPE content on Young's Modulus of POP formulations containing 200 phr $CaCO_3$.

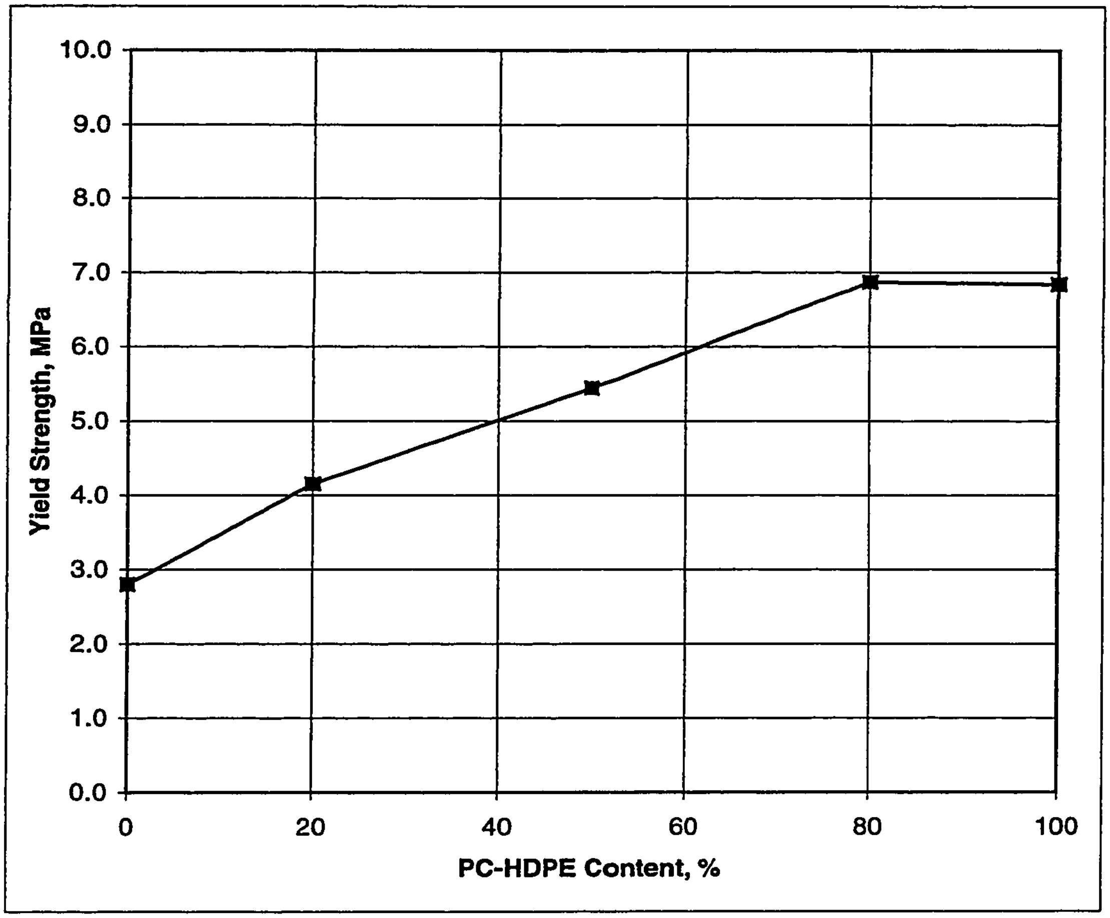

Figure 4.11: Effect of PC-HDPE content on the yield strength of POP formulations containing 200 phr $CaCO_3$.

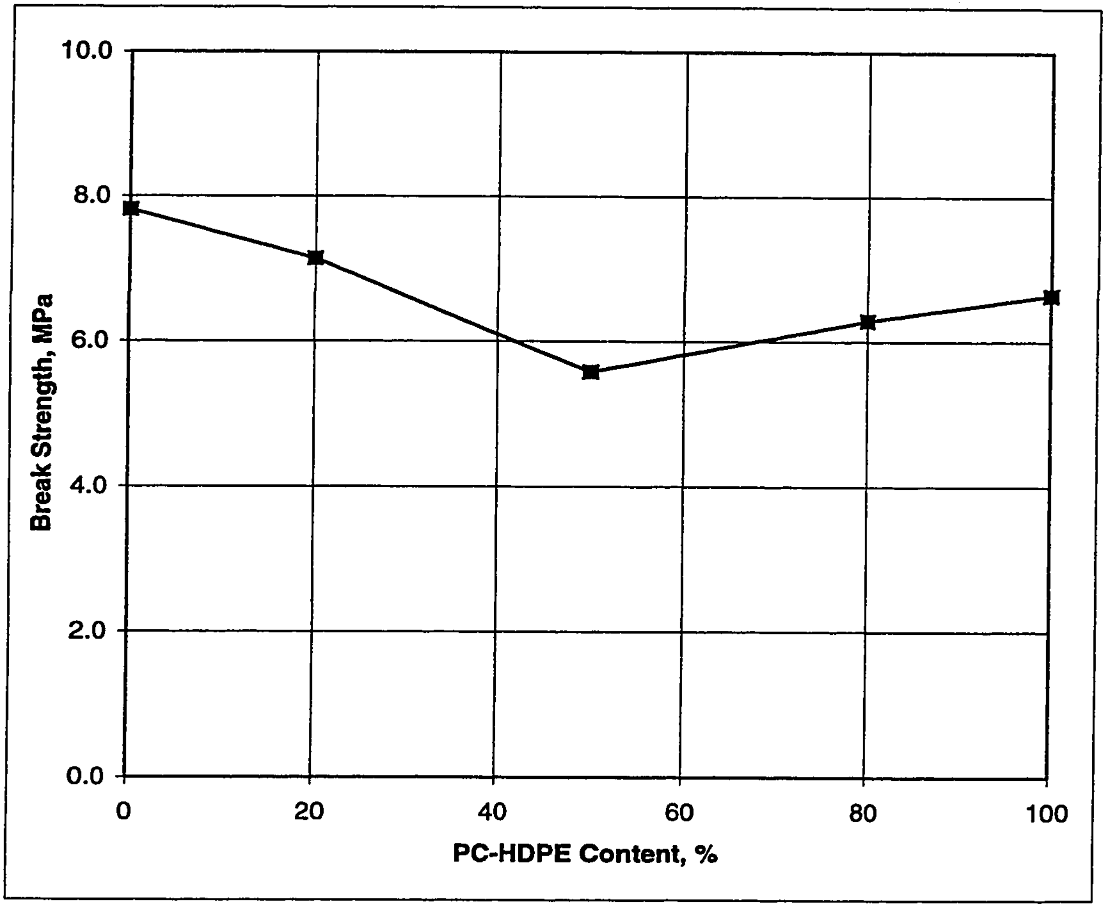

Figure 4.12: Effect of PC-HDPE content on the break strength of POP formulations containing 200 phr $CaCO_3$.

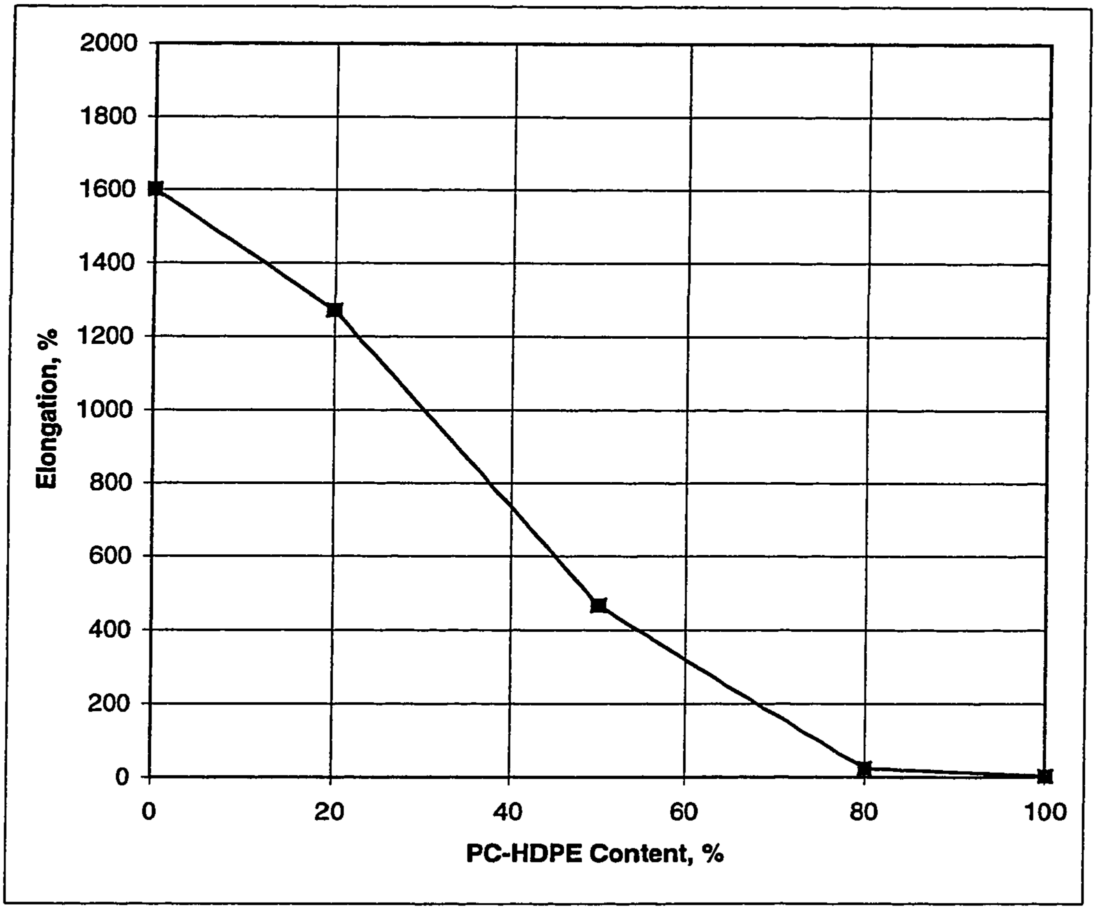

Figure 4.13: Effect of PC-HDPE content on the elongation of POP formulations containing 200 phr $CaCO_3$.

strength is increased for 20 and 50% recycle content as shown in Figure 4.14. But for 80% recycle content, the impact strength is reduced dramatically as before. This behavior is explained in greater detail in a subsequent section on DSC analysis. The incorporation of post-consumer recycle into POP-based flooring tile formulations at fairly high loadings appears to be quite feasible based on this study of mechanical properties alone. As can be seen from the data presented in Table 4.5, the mechanical properties of blends formulated with 50% PC-LLDPE or PC-HDPE are still comparable with the mechanical properties of PVC formulation presented in Table 4.3.

Table 4.4: Results of tensile and impact testing of recycled resins after compounding with 200 phr $CaCO_3$.

Resin	Yield Strength, MPa	Break Strength, MPa	Elongation %	Impact strength, J/m
PC-LLDPE	7.42	6.04	8	40
PC-HDPE	6.84	6.64	3	110

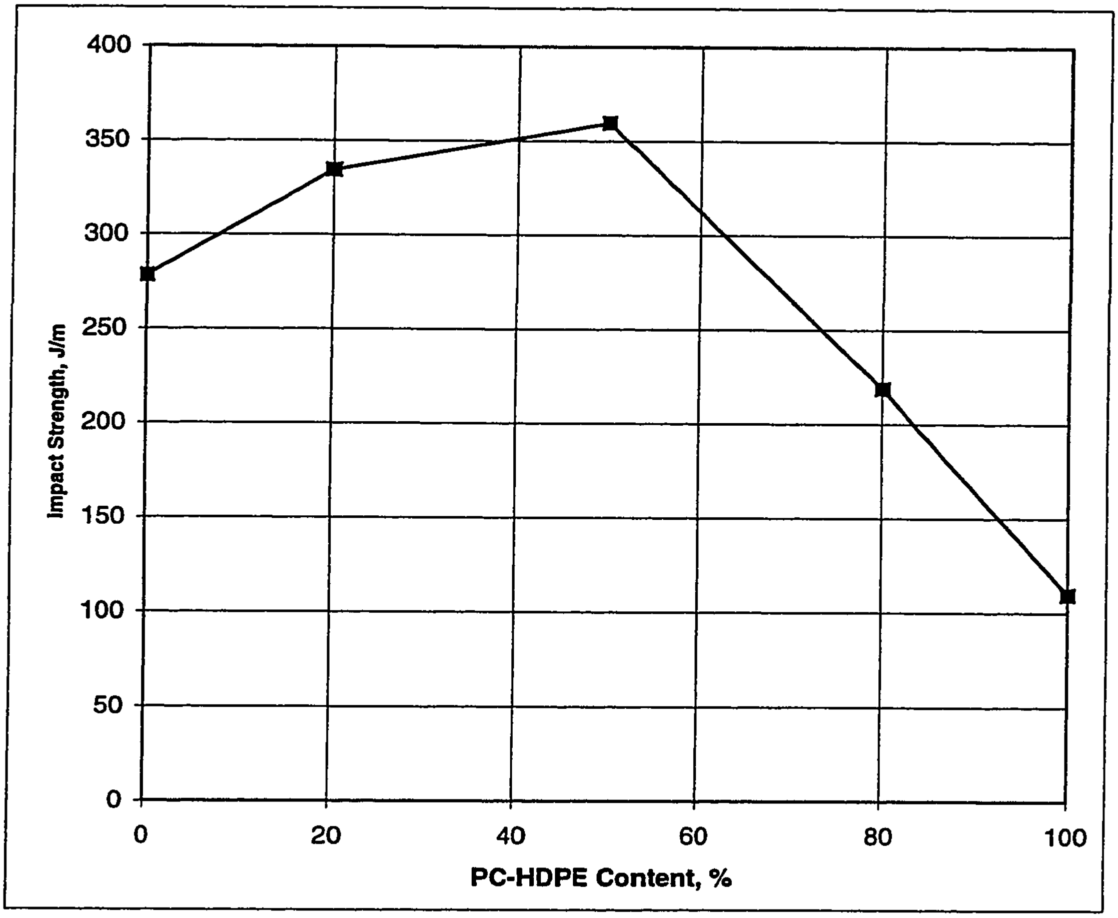

Figure 4.14: Effect of PC-HDPE content on the impact strength of POP formulations containing 200 phr $CaCO_3$.

Table 4.5: Results of tensile and impact testing of POP/PC-PE composites after compounding with 200 phr CaCO$_3$.

		POP /PC-LLDPE			POP/PC-HDPE		
Mechanical Properties	**POP**	**20%**	**50%**	**80%**	**20%**	**50%**	**80%**
Yield Strength, MPa	2.8	3.44	4.45	6.3	4.15	5.44	6.87
Break Strength, MPa	7.82	7.13	6.78	5.04	7.14	5.58	6.29
Modulus at 100% elong.	3.21	3.47	4.28	------	3.98	5.13	------
Elongation, %	1601	1396	1143	9	1272	467	24
Impact Strength, J/m	278	299	354	77	334.4	360	219

5. Thermal analysis using the DSC technique.

The DSC results for raw materials and compounded resins containing 200 phr CaCO$_3$ are presented in Table 4.6 and Figures 4.15 through 4.21. The results for blends are found in Table 4.7 and Figures 4.22 through 4.27.

As can be seen from Table 4.6 and Figure 4.15 the DSC melting peak of Affinity 1140 is 93.6± 0.5 ^{0}C which encompasses the value of 94 ^{0}C given in the Dow Plastics Product Specification[45].

The DSC curve of PC-LLDPE , shown in Figure 4.17, is characterized by a broad melting range with two melting peaks: one located at 111.4 ^{0}C, and the other at 124.9 ^{0}C. Literature data indicates indeed a broad range of melting for LLDPE with a lower melting peak at around 106-110 ^{0}C, and a higher one in the range of 120-124 ^{0}C. This occurrence is a result of molecular segregation during crystallization, due to the heterogeneous distribution of α-olefin comonomer in different molecules [38,39].

For PC-HDPE , the melting peak in the DSC curve, shown in Figure 4.18, is quite sharp and is located at 128.7 °C. Since HDPE has a linear molecular structure, it crystallizes to a higher degree than LLDPE, with up to 70% by weight of the molecules present as crystals. However, the degree of crystallinity depends on several factors, and most of the commercial products have a melting peak in the range 125-130 °C, with a latent heat of melting of about 160-200 J/g [37].

For compounded POP (Affinity 1140), as well as for compounded PC-LLDPE and PC-HDPE, Table 4.6 shows that the respective locations of the melting peaks are practically unchanged. With respect to the matrix resins moreover, the latent heat of each compounded material is proportional to the content of the respective polymer. It seems that within the composite, the ability of the polymer to crystallize is not prevented by the presence of a large proportion of filler, nor by the presence of lubricant.

Thermal characteristics of POP/PC-LLDPE blends present some interesting features. Two melting peaks are present for these blends: a broad one located at a lower temperature and a sharp one located at a higher temperature. The location of the first peak increases from about 92.5 °C for 20% PC-LLDPE to about 113 °C for 80% PC-LLDPE. This represents a difference of about 20 °C. The location of the second peak changes within only a few degrees from about 122.6 °C for 20% PC-LLDPE, shown in Figure 4.22, to about 124.6 °C for 80% PC-LLDPE(see Figure 4.24). The total latent heat of the blends was determined by measuring the area under the melting curves obtained from DSC scans. This can also be calculated by the additivity relationship, defined by the following equation:

$$\Delta H_m = \sum w_i x_i \tag{4.1}$$

where w_i is the weight fraction of component i, and x_i is the latent heat of component i [40,41]. The accuracy of this equation is very good as evidenced by differences between experimental and calculated results in Table 4.6, which were less than 5 %. It was shown earlier that PC-LLDPE exhibits a double melting behavior. The sharp high temperature peak, located at about 125 ^{0}C, corresponds to the crystallization of the longest and usually less branched molecule, while the broad low temperature peak, located at 112.8 ^{0}C, reveals the crystallization of the shorter and highly branched molecules[39,42] . The POP/PC-LLDPE blends also exhibit a double melting endotherm. For 20% PC-LLDPE the first peak temperature is located around 92.5 ^{0}C and its temperature is increased up to around 113 ^{0}C , as the concentration of PC-LLDPE is increased. Changes in the second peak location are less important, varying from 122.6 ^{0}C for 20% PC-LLDPE to 124.6 ^{0}C for 80% PC-LLDPE. The change in the first melting peak location can be taken as evidence of a partial cocrystallization between the shorter and branched molecules of LLDPE and molecules of POP of adequate length [38,43]. This is evident for the 20 and 50% PC-LLDPE composites.

The increase of tensile strength at yield, and of the impact strength of POP with 20% and 50% PC-LLDPE composites discussed earlier, provides evidence that good interfacial adhesion is achieved, which is consistent with the partial cocrystallization taking place in these blends. The gradual reinforcing effect of PC-LLDPE as expressed by increased modulus can be explained by gradual increase in total latent heat of the blends, which represents an increase in crystallinity as can inferred from Table 4.7.

Thermal characteristics of POP/PC-HDPE blends differ from those of POP/PC-LLDPE blends. The blend with 20% PC-HDPE, shown in Figure 4.25, presents two well-defined melting peaks . The first one is located at around 92 ^{0}C, and can be attributed to the POP . The second one at 124 ^{0}C is sharper, and can be attributed to HDPE. There is a very good agreement between the experimental and calculated latent heats, an indication that the presence of one material does not affect the crystallization behavior of the other. The position of the higher melting peak is lowered from about 128 ^{0}C for 100% compounded PC-HDPE to around 124 ^{0}C in the 20% blend with POP. Similarly, the position of the lower melting peak is lowered from about 95 ^{0}C in compounded POP to around 92 ^{0}C. As in the case of POP/PC-LLDPE blends, the changes in the positions of the melting peak are consistent with the mechanism of partial cocrystallization . Literature data reported on the basis of a detailed x-ray analysis of HDPE indicates that the unit cell of HDPE could accommodate a limited amount of branched polyethylene [42]. Therefore , a limited range of cocrystallization is possible for the system. More detailed investigations are required to confirm this explanation for the POP/PC-HDPE formulations.

In the blends with 50% PC-HDPE, shown in Figure 4.26, the first melting peak is not well defined, and it appears like a shoulder. In the blends with 80% PC-HDPE, shown in Figure 4.27, the first peak is practically non- identifiable and there is practically only one peak located at high temperature, 127.6 ^{0}C, which is very close to the melting point of PC-HDPE. From the data presented in Table 4.7 it can be seen that the latent heats of the blends formulated with PC-HDPE are higher than those of the blends formulated with PC-LLDPE. This means that the total amount of crystallinty is higher in PC-HDPE blends. An increase in crystallinity brings about an increase in modulus and yield strength, but a decrease in elongation.

DSC analyses data for POP/PC-LLDPE and POP/PC-HDPE correlate quite well with most of their mechanical properties. However, it is difficult to explain the high values of impact strength for the POP/PC-HDPE blends. In semicrystalline polymers, the impact strength decreases with increasing degree of crystallinity, because the amorphous regions between crystallites provide higher impact strength. Thus, the miscibility between the POP and PC-HDPE crystallites and the amorphous areas in these polymers could explain the high impact strength of these blends. It is also possible that the POP/PC-HDPE blend is capable of achieving superior dispersion of the $CaCO_3$ filler during compounding. Impact strength is known to be very sensitive to the quality of dispersion in highly-filled composites.

Table 4.6: DSC analyses of raw materials and products after compounding with 200 phr $CaCO_3$.

Sample	Integration limits, ^0C	Peak T_m, ^0C	ΔH_m, J/g	ΔH_m, calculated by the additive rule, J/g
POP (Affinity 1140)	8.1-106	93.2	74.2	
	8.1-105	93.3	72.5	
	8.1-107	94.5	77.3	
	8.1-107	93.7	75.2	
	8.1-107	93.5	74.9	
Average		93	74.8	
Stearic acid	33-77.2	61.2	188.2	
(lubricant)	33-77.2	61.2	189.4	
Average		61.2	188.8	
Affinity 1140+200phr	8.1-105	94.4	26.4	0.33×74.8+0.0066×188.8=26.01
$CaCO_3$	8.1-105	94.5	26.1	Difference = 2.25 %
	8.1-105	94.5	27.1	
Average		94.5	26.6	
PC-LLDPE	8.1-133	124.8	124.4	
	7.72-133	125.0	125.9	
Average		125	125.2	
PC-LLDPE +200phr	8.1-133	124.5	46.7	0.33×125.2+0.0066×188.8=42.7,
$CaCO_3$	8.1-1333	124.8	43.2	difference=0.5%
Average		124.7	42.9	
PC-HDPE	25-135	128.6	163.1	
	25-136	128.6	163.1	
Average		128.7	163.1	
PC-HDPE +200phr	30.2-136	128.1	54.3	0.33×163.1+0.0066×188.8=54.3,
$CaCO_3$	30.2-136	128.1	54.2	difference=1.7%
Average		128.1	54.3	

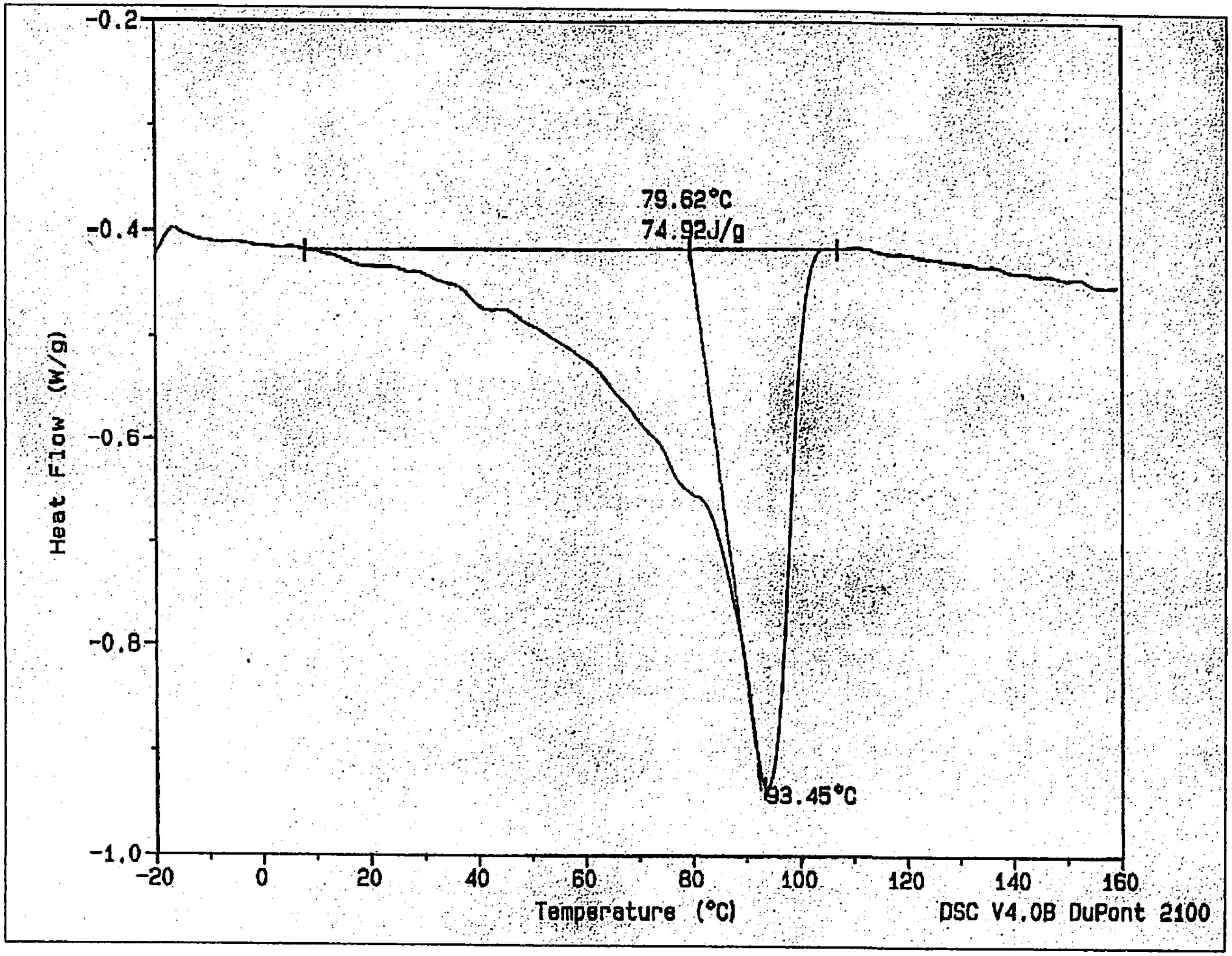

Figure 4.15: The DSC curve for POP (Affinity 1140).

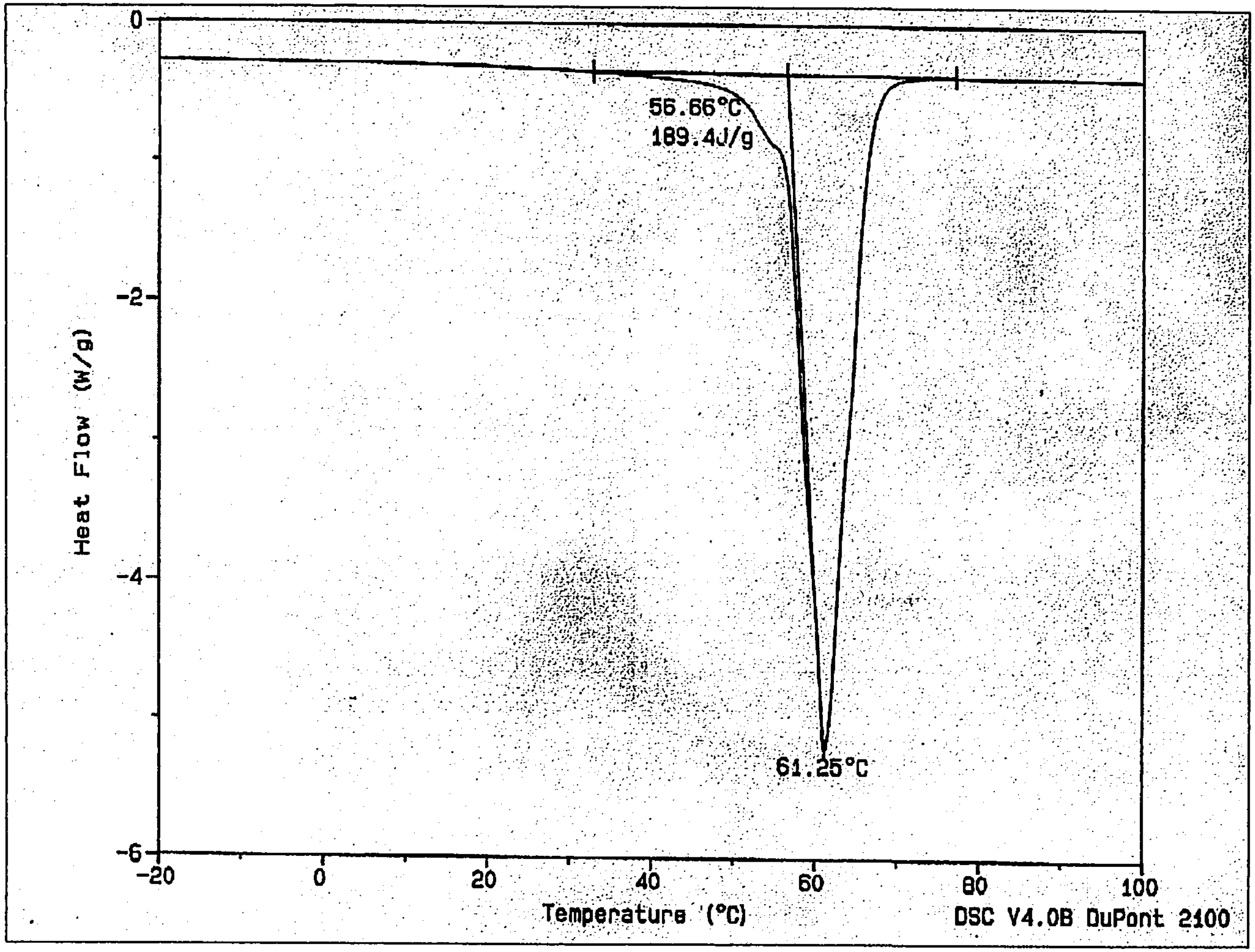

Figure 4.16: The DSC curve for stearic acid.

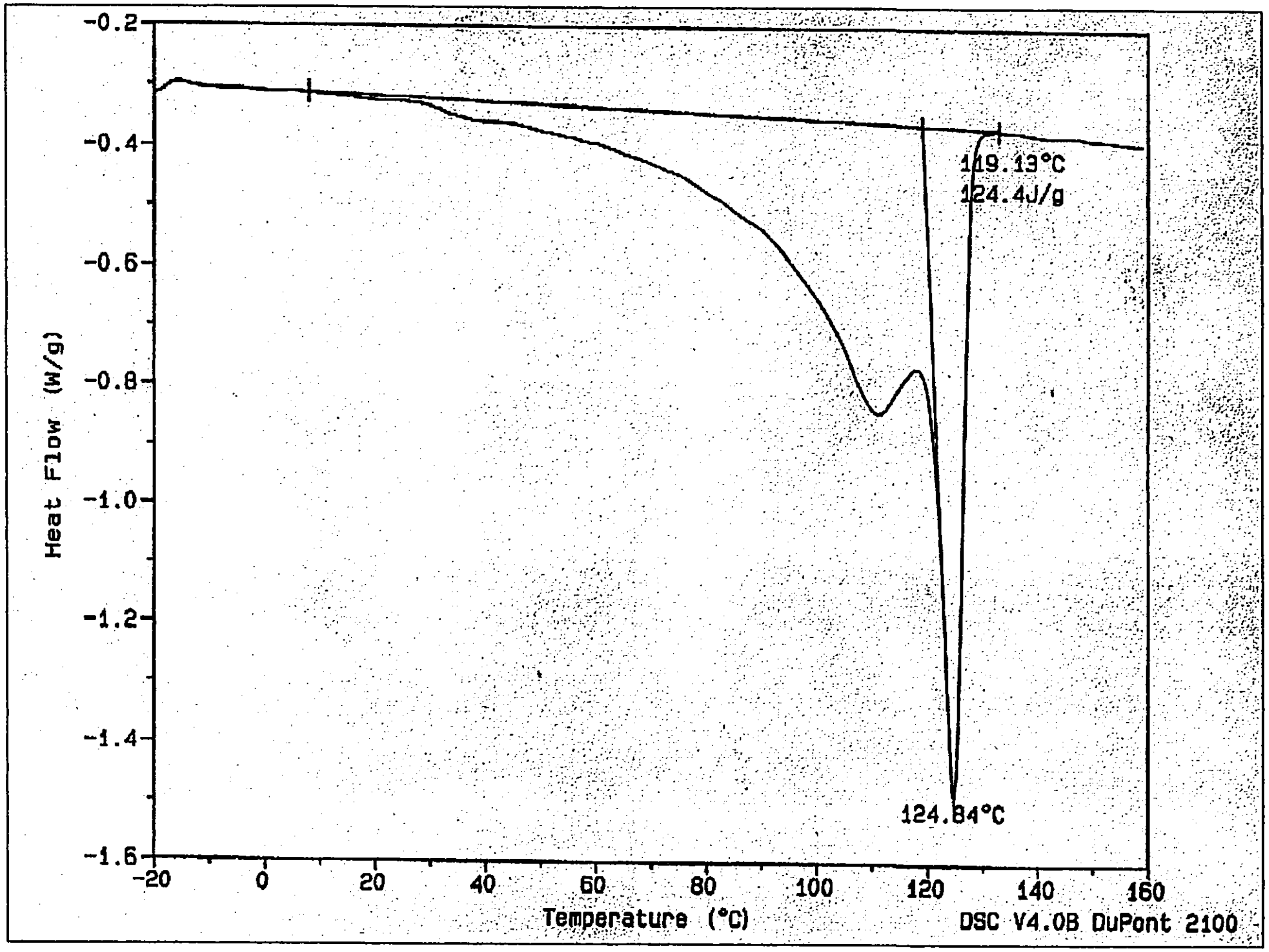

Figure 4.17: The DSC curve for PC-LLDPE.

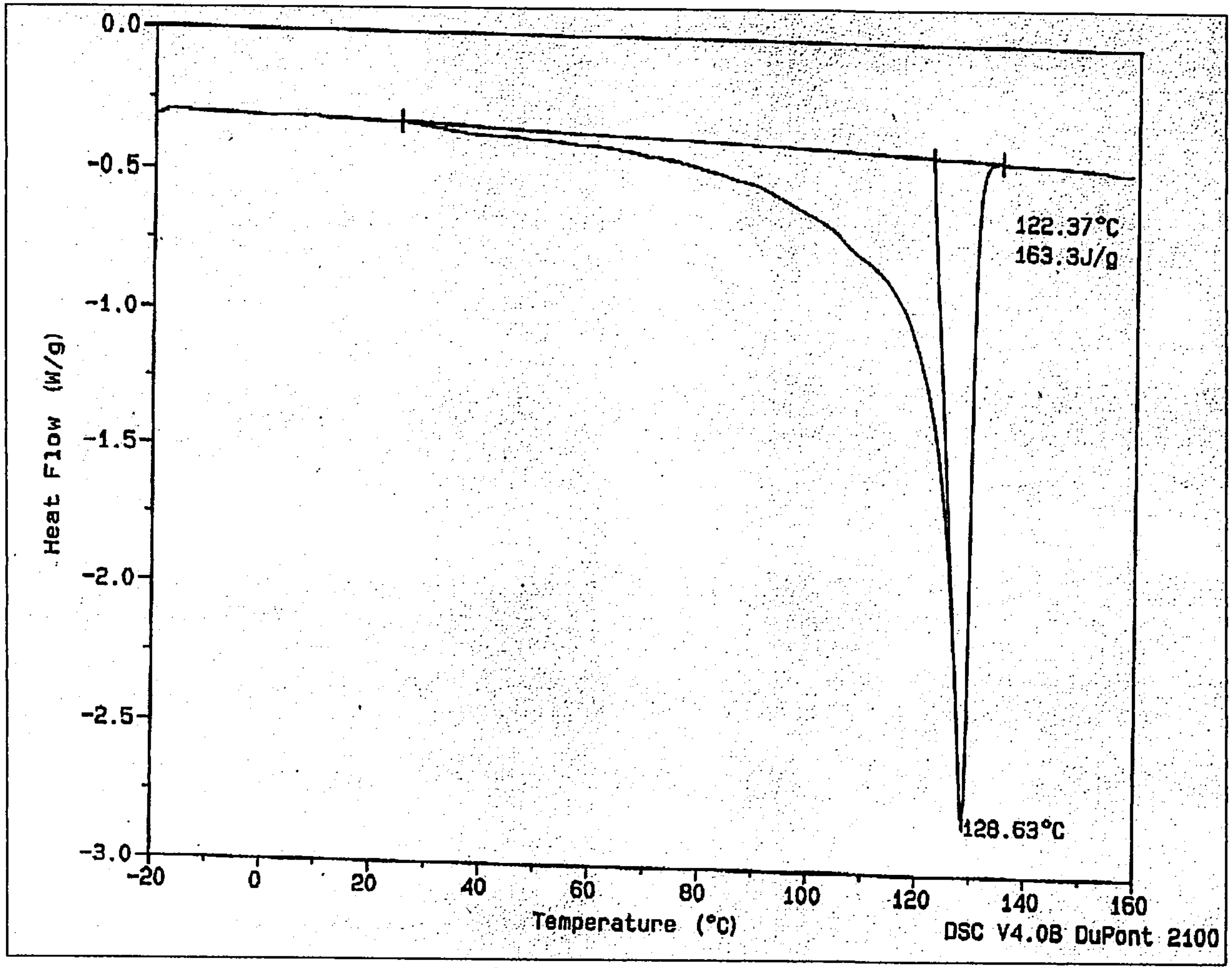

Figure 4.18: The DSC curve for PC-HDPE.

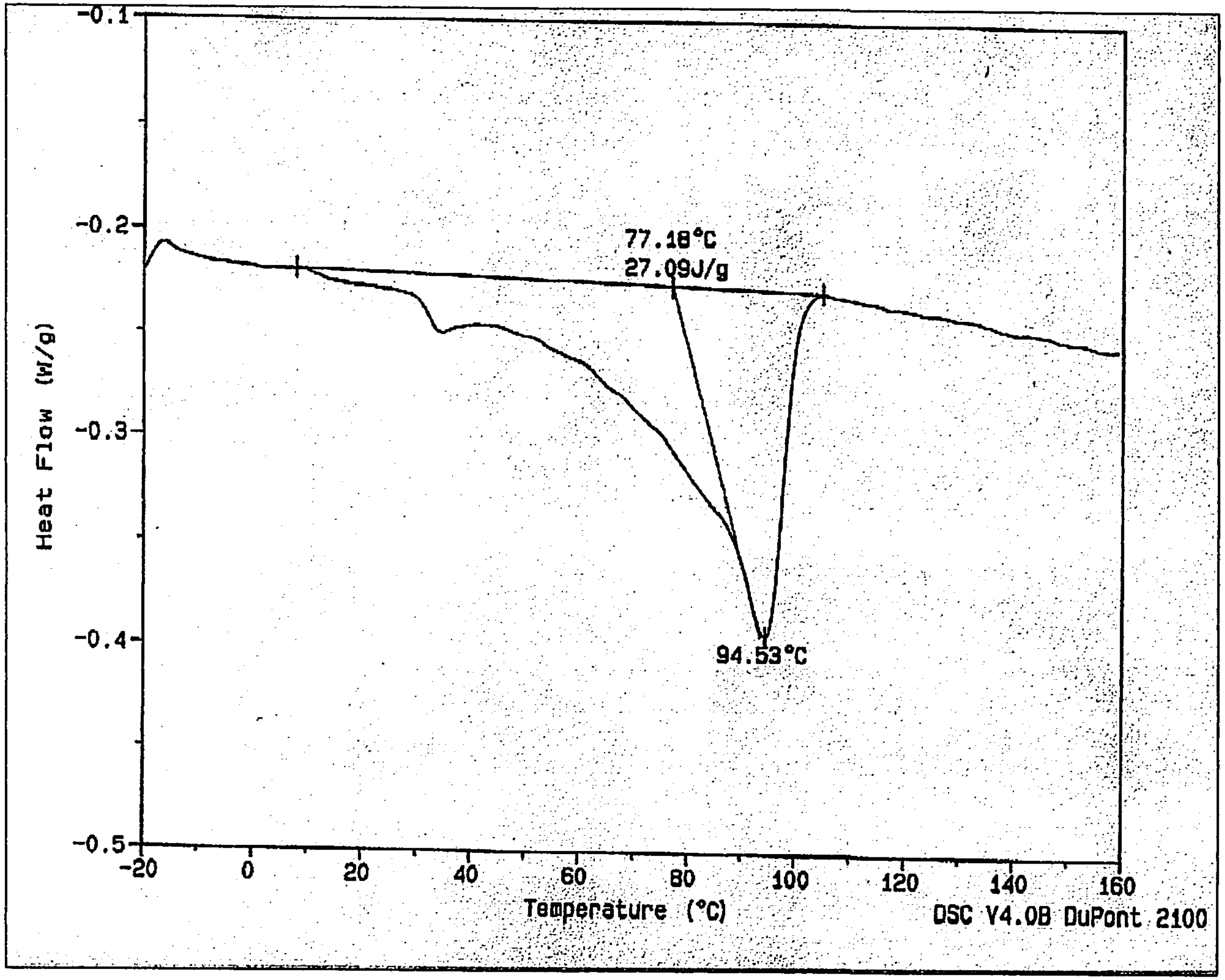

Figure 4.19: The DSC curve for POP formulation containing 200 phr $CaCO_3$.

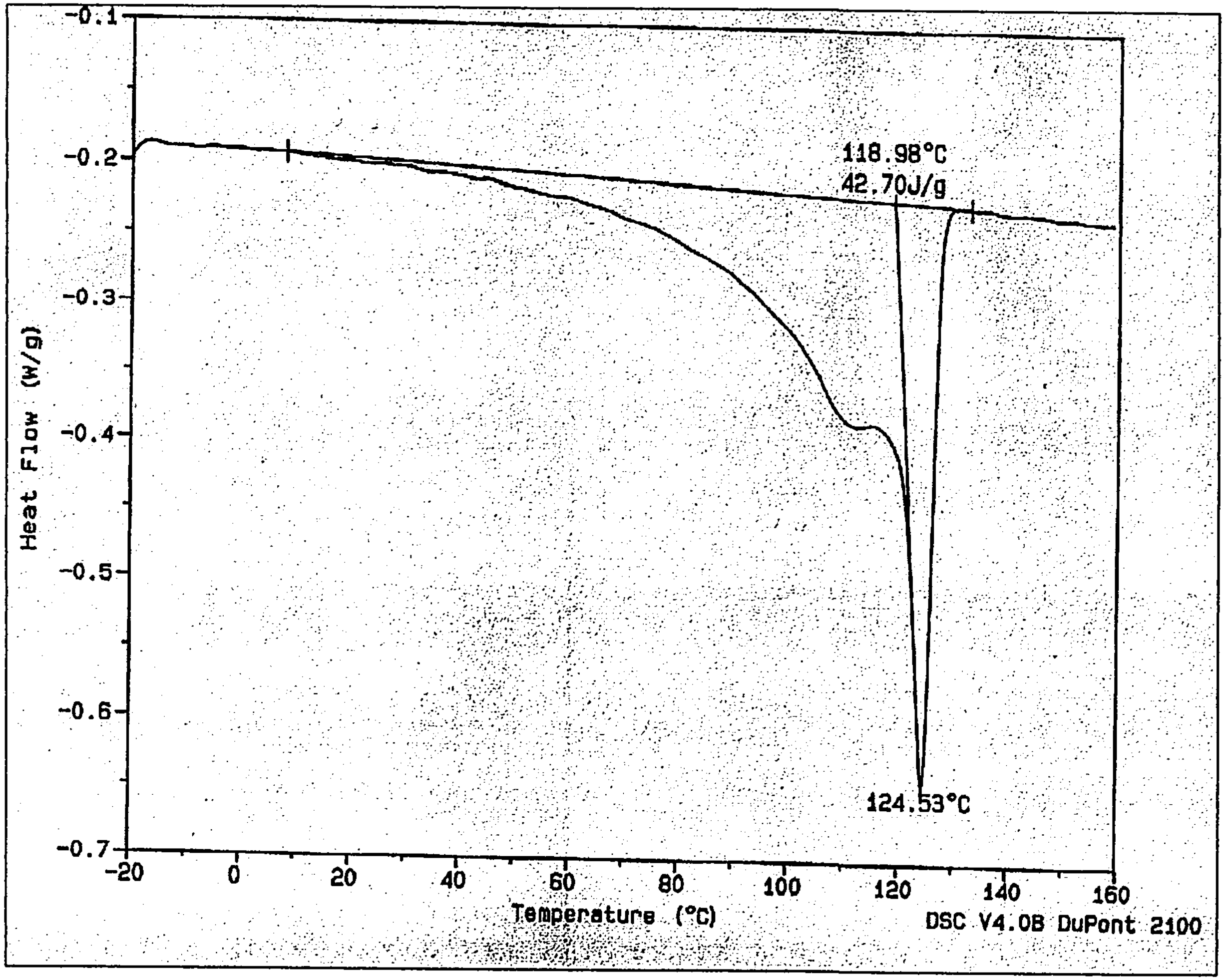

Figure 4.20: The DSC curve for PC-LLDPE formulation containing 200 phr $CaCO_3$.

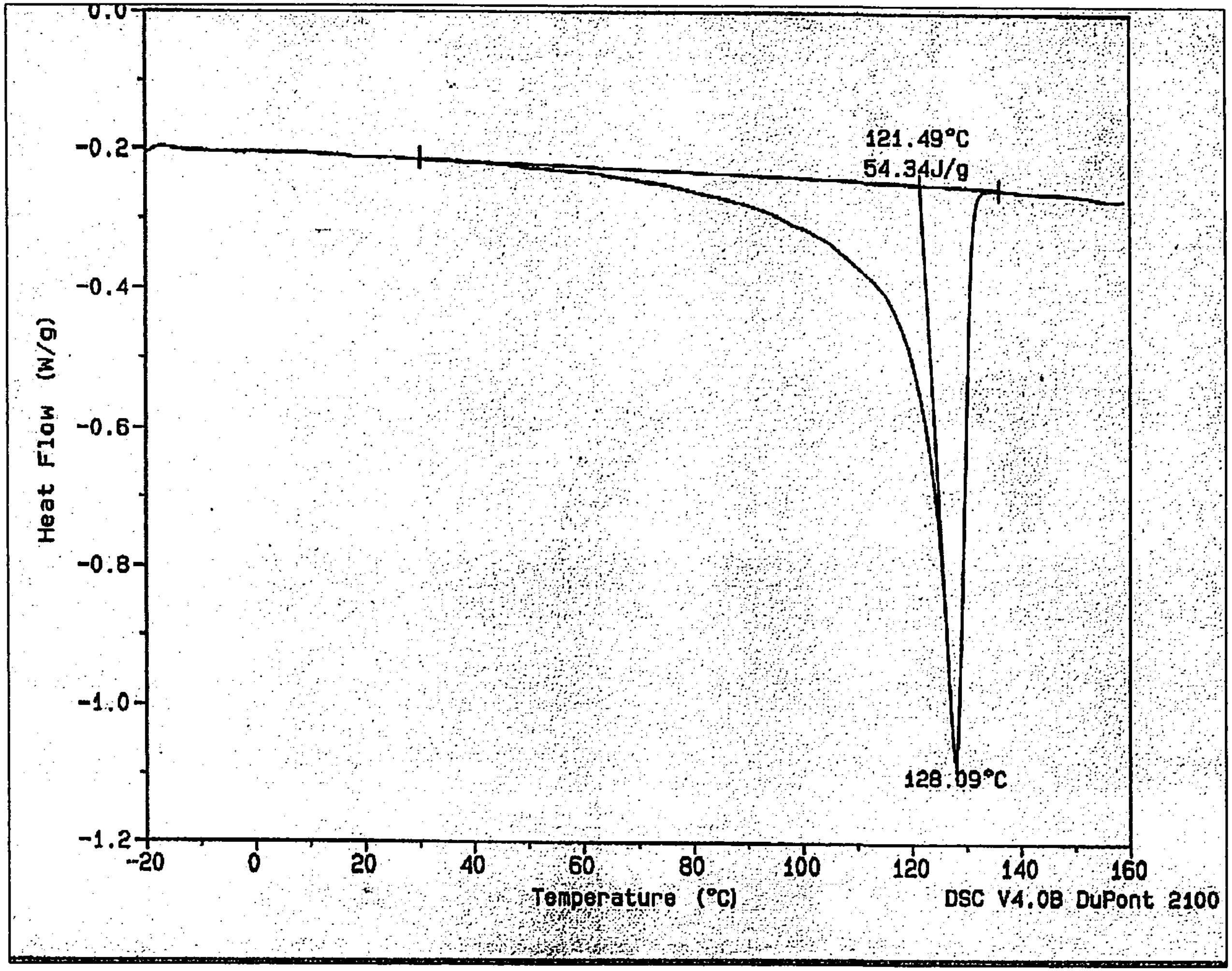

Figure 4.21: The DSC curve for PC-HDPE formulation containing 200 phr $CaCO_3$.

Table 4.7: DSC analyses of POP/PC-LLDPE and POP/PC-HDPE blends.

Sample	Integration limits,^{0}C	T_m, ^{0}C		ΔH_m ,J/g	
		I peak	II peak	Experimental	Calculated
20% PC-LLDPE					
#1	8.1-130	92.7	122.5	30.0	29.9
# 2	6.9-132	92.2	122.7	30.8	
Average		92.5	122.6	30.4	
50% PC-LLDPE					
#1	6.52-132	98.7	123.9	36.32	34.8
# 2	6.52-130	97.2	123.9	36.42	
Average		98	123.9	36.3	
80%PC-LLDPE					
#1	8.1-132	112.8	124.6	41.5	39.6
# 2	7.3-132	112.8	124.5	41.2	
Average		112.8	124.6	41.3	
20% PC- HDPE					
#1	8.1-132	92.1	123.8	32.1	32.2
# 2	8.1-132	92.0	124.2	31.4	
Average		92	124	31.8	
50% PC- HDPE					
#1	12.5-133	------	125.6		40.5
# 2	12.5-133	------	125.9		
Average			125.8		
80% PC- HDPE					
#1	8.4-135	------	127.5		48.7
# 2	8.9-135	------	127.6		
Average			127.6	48.5	

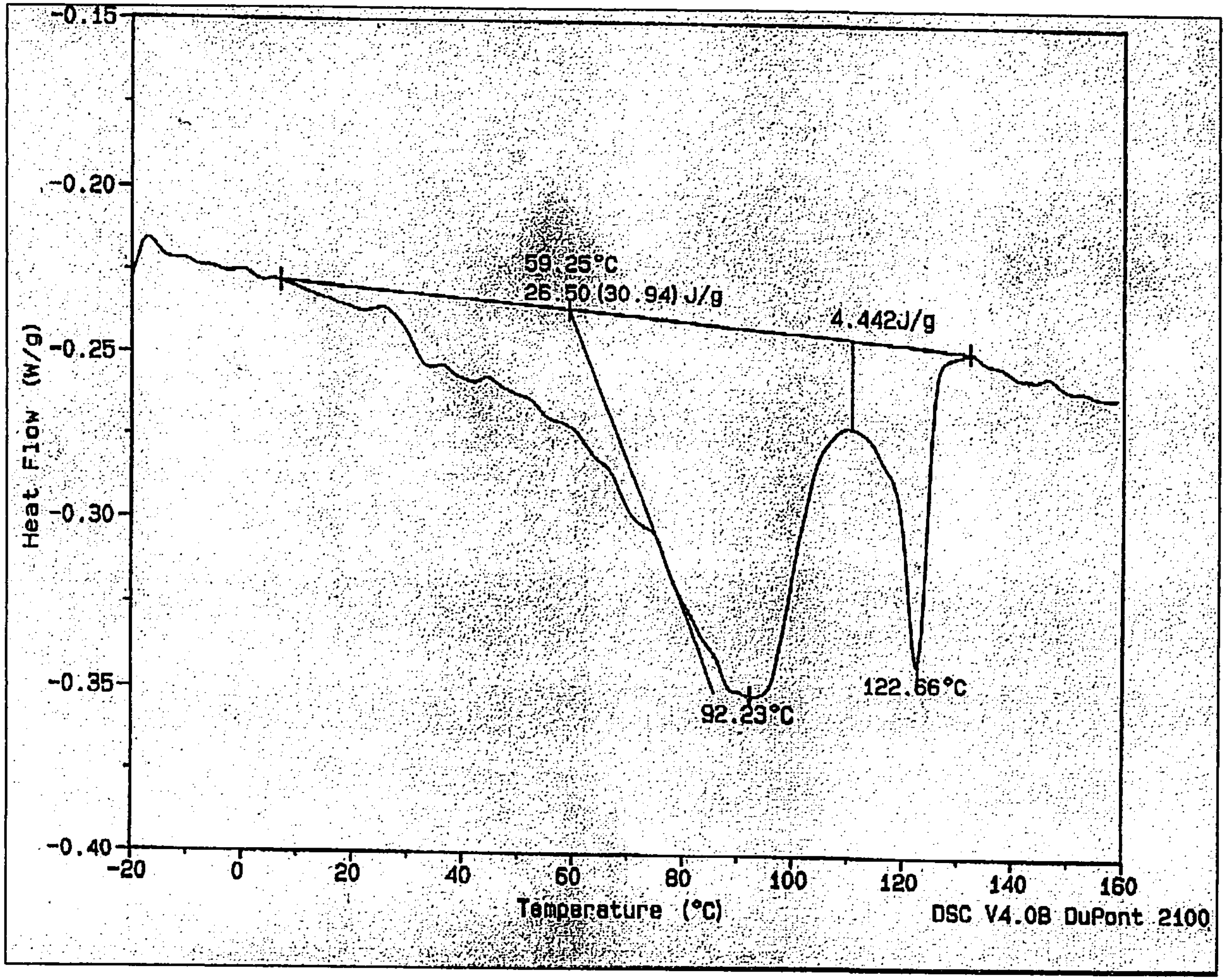

Figure 4.22: The DSC curve for POP/ PC-LLDPE formulation containing 20% recycle and 200 phr $CaCO_3$.

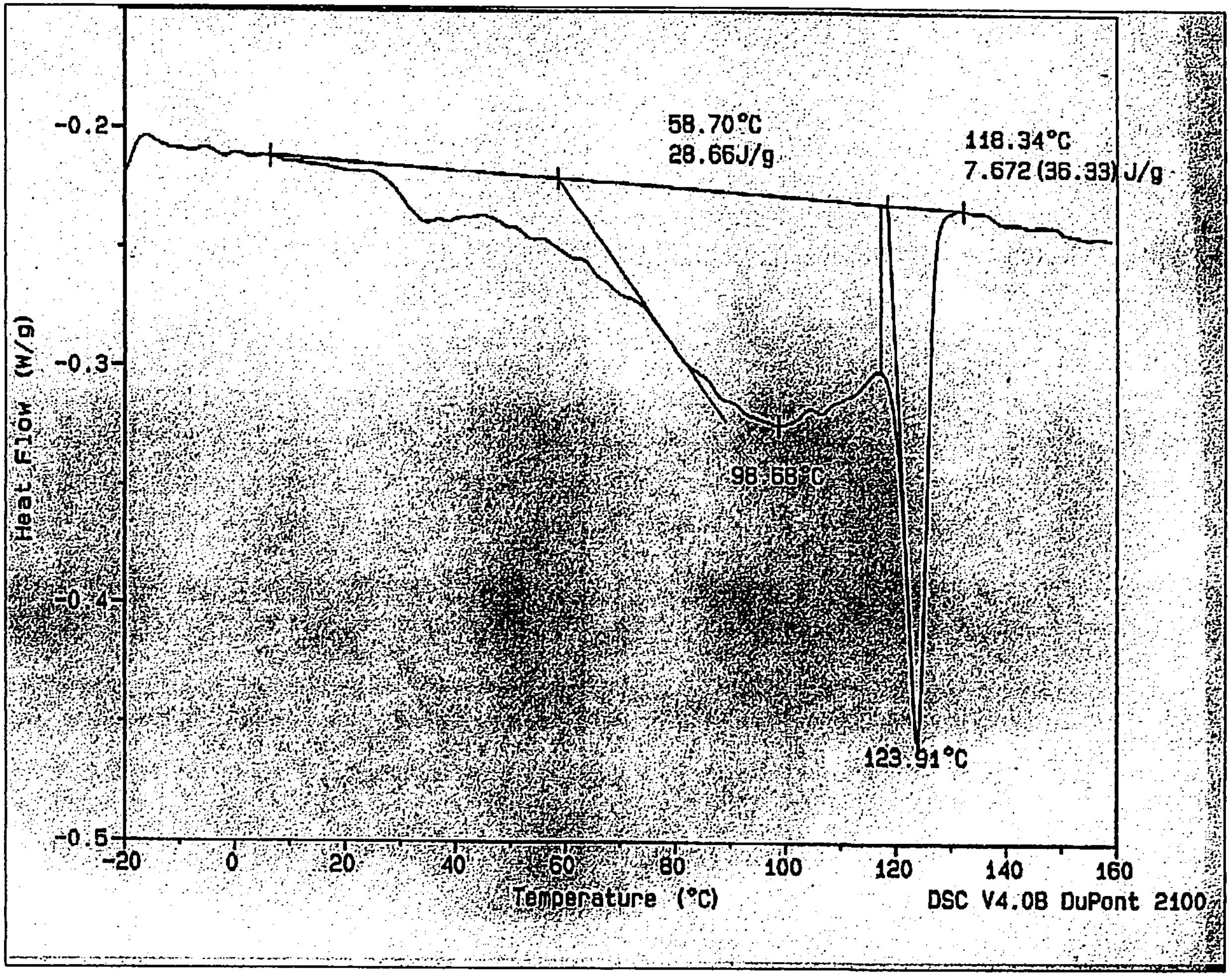

Figure 4.23: The DSC curve for POP/ PC-LLDPE formulation containing 50% recycle and 200 phr $CaCO_3$.

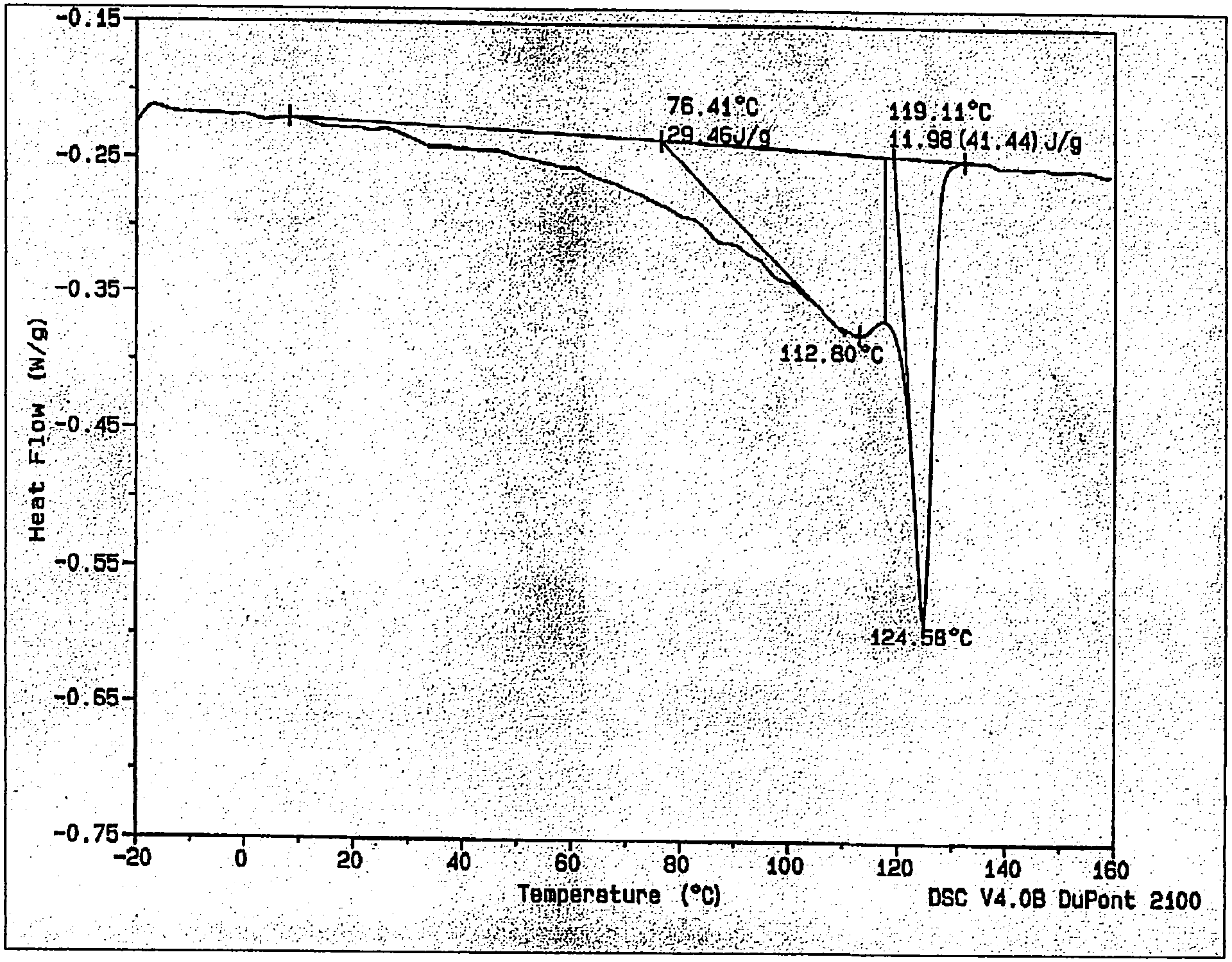

Figure 4.24: The DSC curve for POP/ PC-LLDPE formulation containing 80% recycle and 200 phr $CaCO_3$.

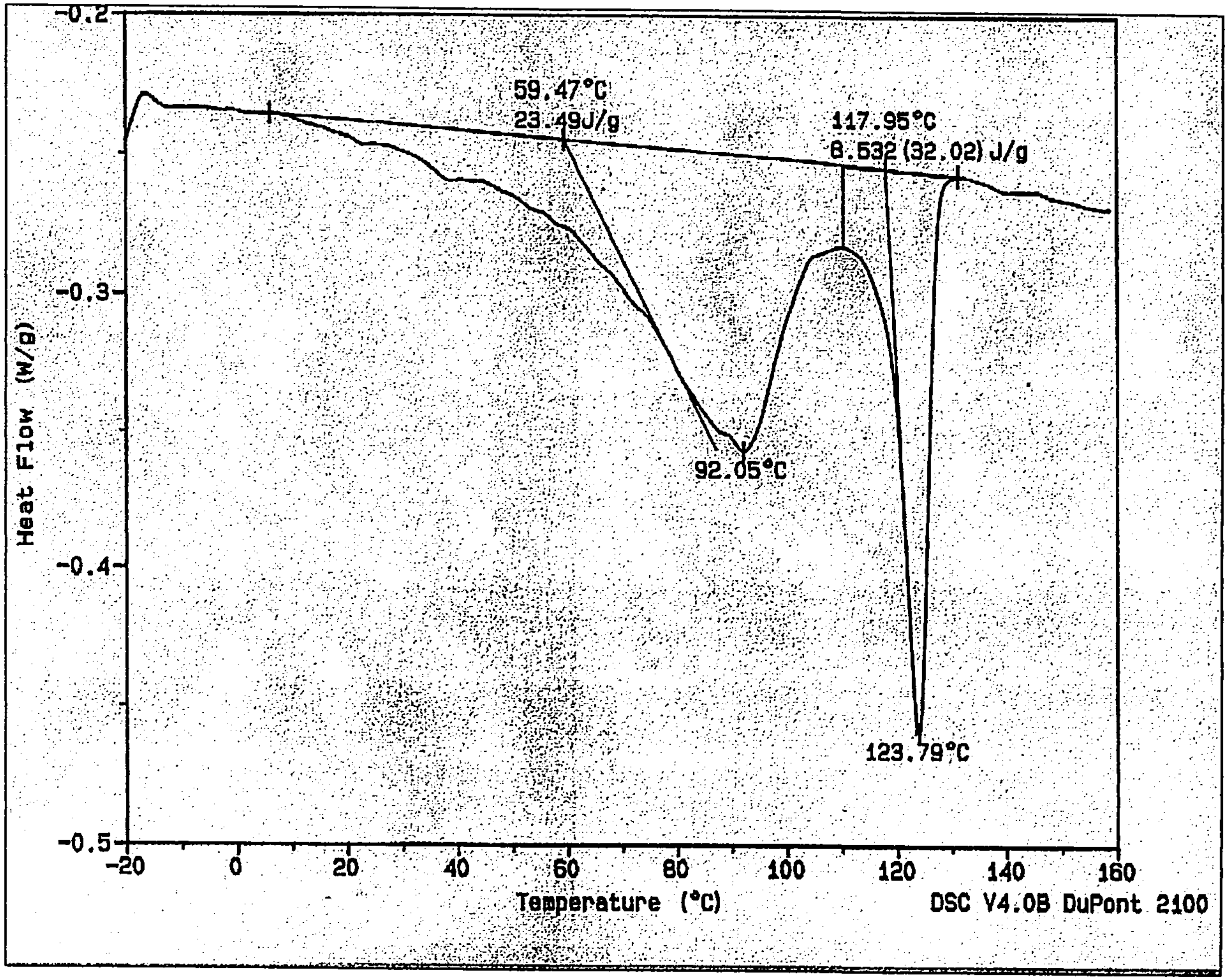

Figure 4.25: The DSC curve for POP/ PC-HDPE formulation containing 20% recycle and 200 phr $CaCO_3$.

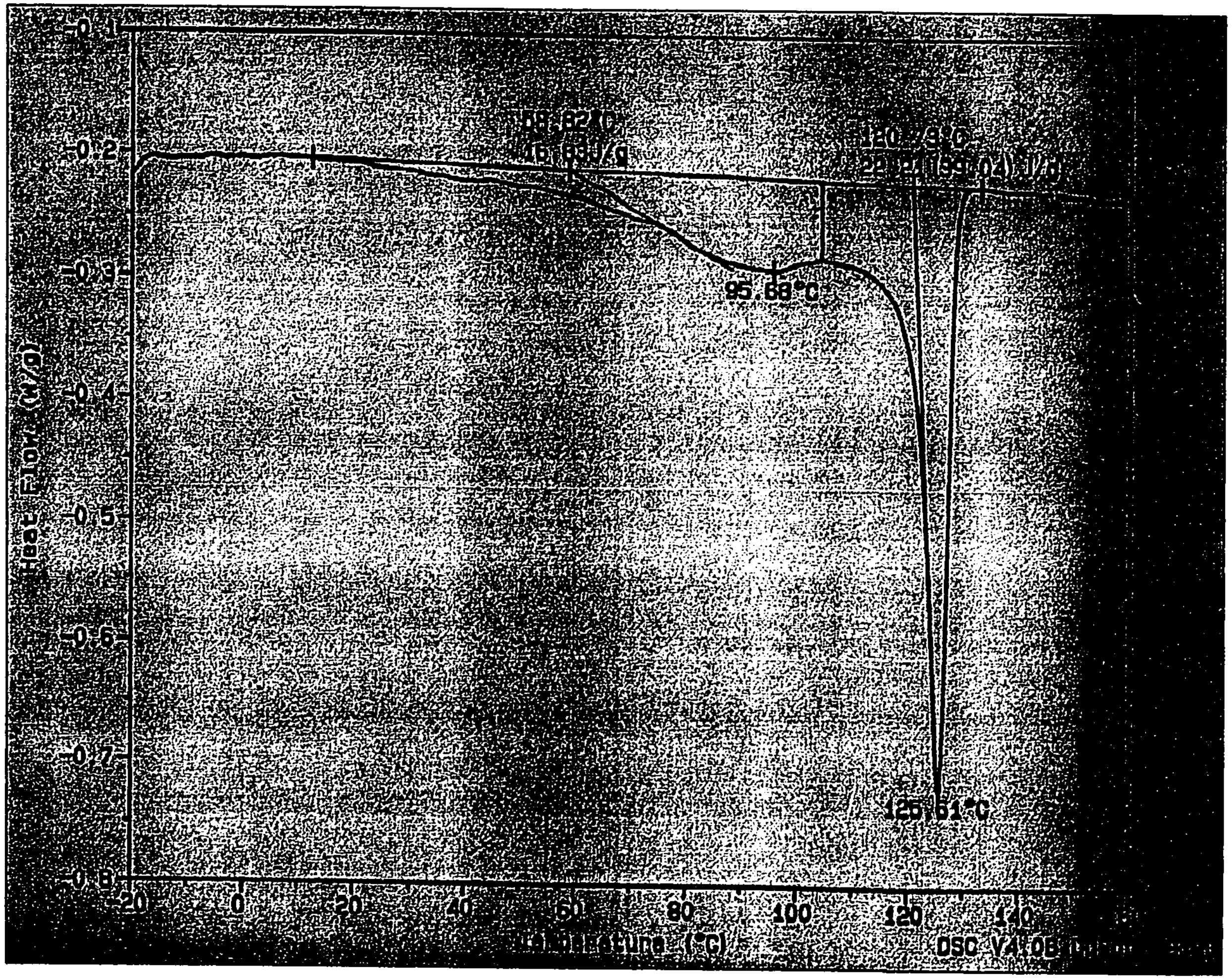

Figure 4.26: The DSC curve for POP/PC-HDPE formulation containing 50% recycle and 200 phr $CaCO_3$.

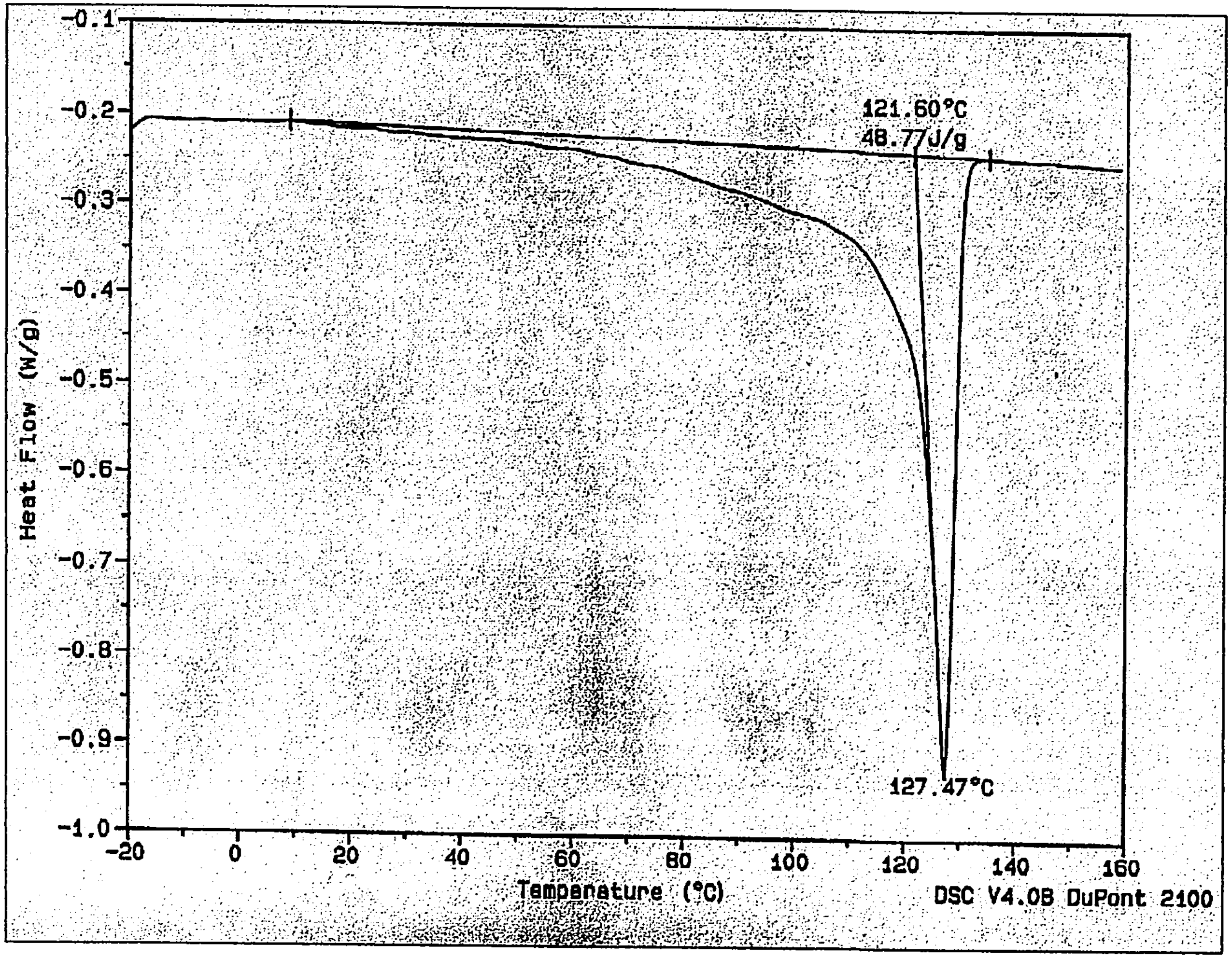

Figure 4.27: The DSC curve for POP/PC-HDPE formulation containing 80% recycle and 200 phr $CaCO_3$.

6. Dimensional stability.

Results of dimensional stability at heating tests are shown in Table 4.8. It can be seen that POP composites contract slightly more than the PVC-based ones. This is to be expected, since an elastomeric material is more affected by heat ageing. However, the amount of change in length is reduced by 54% for formulations containing 50% PC-HDPE. Thus, the introduction of HDPE may be a convenient way of enhancing the dimensional stability of POP formulations. The same effect is not noted for POP formulations containing recycled LLDPE, since its macromolecular structure is similar to POP.

Table 4.8: Results of dimensional stability.

Formulation	Initial length	Final length	% Change
POP-based	15.81	15.63	1.1
PVC-based	16.24	16.17	0.4
100% PC-HDPE	14.49	14.5	0.07
80% PC-HDPE	14.7	14.66	0.27
50% PC-HDPE	15.24	15.15	0.59
20% PC-HDPE	15.76	15.45	1.9
100% PC-LLDPE	15.64	15.34	1.9
80% PC-LLDPE	15.83	15.4	2.7
50% PC-LLDPE	15.32	15.14	1.17
20% PC-LLDPE	15.77	15.14	4

5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 CONCLUSIONS

This research was carried out to test and evaluate POP plastomers as matrix resins for composites for flooring applications, in order to explore their suitability as alternatives for plasticized PVC.

A polyolefin plastomer, Affinity 1140, has been used to produce formulations containing 200 phr calcium carbonate. Similar formulations based on PVC copolymers are typically used in the flooring industry for flexible tiles and sheets. The POP-based formulations were found to have mechanical properties superior to those of the PVC-based formulations in terms of tensile strength, elongation and impact strength. In addition, the POP-based formulations offer two significant advantages over PVC:

1. No plasticizers are required in their production, thereby eliminating a hazardous class of chemicals currently used in PVC-based flooring products.
2. POP formulations were shown to be capable of incorporating large amounts of post-consumer polyethylene with acceptable reductions in key mechanical properties. In fact, the impact strength of recycle-containing POP formulations was found to increase up to loadings as high as 50% recycle. Such a result would not be possible for the incorporation of recycled polyethylene into PVC-based formulations.

Two types of PC-PE have been tested in this research work: the first one was a LLDPE, and the second was a HDPE. The first gave better properties when blended with POP to make the composites. The DSC analysis technique was used to study the difference in behavior between PC-LLDPE and PC-HDPE in the POP formulations. It was found that due to the macromolecular structure similarity between the LLDPE and POP, a partial cocrystallization between the shorter and branched molecules of LLDPE and molecules of POP can occur especially for the 20 and 50% recycle loadings. For PC-HDPE ,on the other hand, the decrease in elongation was more dramatic, and this was explained by the fact that HDPE has high crystallinity, which adversely affects elongation and break strength. But the same trend of increase in impact strength with formulations containing up to 50% PC-HDPE has been noted. Formulations containing solely PC-LLDPE and PC-HDPE as the matrix resins have very poor mechanical properties. The calcium carbonate loading of 200 phr is clearly much too high for the PC-PE to function as an effective binder.

According to dimensional stability testing, it was found that POP composites contract slightly more than the PVC-based ones. However, for formulations containing PC-HDPE , the amount of change in length was reduced by 54% for a recycle loading of 50% PC-HDPE. Thus, the introduction of HDPE may be a convenient way of enhancing the dimensional stability of POP formulations. The same effect is not noted for POP formulations containing recycled LLDPE.

It can thus be concluded that the incorporation of post-consumer recycle into POP-based flooring tile formulations at fairly high loadings appears to be quite feasible based on this study of physical properties alone. POP resins therefore warrant further detailed investigation as more sustainable alternatives to PVC in formulations for flooring products.

5.2 RECOMMENDATIONS FOR FUTURE WORK

In this study, mechanical and thermal testing were used to evaluate POP relative to PVC. Other important tests performed on flooring tiles should be included in future studies. These tests include resistance to common household substances, exposure to UV light and resilience.

Future studies should also focus on adhesion of the composites to a polyurethane wear layer commonly used in flooring applications. Dynamic contact angles between the wear layer and the composite must be determined in order to study the coatability of the composite. Emission of volatile organic compounds,VOC's, should be tested as well, as these compounds are of growing concern for any product used within a confined space.

Formulating composites using new grades of POP's, as well as POE's, may prove extremely useful to other building products, and it is recommended here that a variety of applications be investigated in studies similar to the work presented here.

REFERENCES

1. Summers, J.W. (1997) *J. Vinyl Additive Technol.*, Vol. 3, No. 2, p.130
2. http://www.compulink.co.uk/~plasticsdata/pvc/pvcuse.hti
3. Morfini, L., Dessy, P. and Nironi, L. (1997) *Proc. 2nd Int. Conf. Buildings and Environment*, Vol. 1, Paris, June 9-12, p.181
4. Brockmeier, N., Arzoumanidis, G., Karayannis, N. and Stein, N. (1996) *Chemical Engineering*, Vol. 103, No. 9, p.90
5. Zamora, M., Miller, T. and Brennan, A. (1997) *Plastics Engineering*, Vol. 53, No. 5, pp.75
6. Wigotsky,V., "Metallocenes" (1995) *Plastics Engineering*, Vol. 51, No. 7, pp.16
7. Olabisi O.," Conventional Polyolefins" *Handbook of Thermoplastics*, Marcel Dekker, Inc., (1997), pp.1,18

8. Kim Y. S. et al, "Melt Rheological and Thermodynamic Properties of Polyethylene Homopolymers and Poly(ethylene/α- olefin) Copolymers with Respect to Molecular Compostion and Structure",(1996) *Journal of Applied Polymer science*, Vol.59, pp.125-137

9. ASTM D 648, "Tests for Deflection Temperature of Plastics" Vol.08.01, American Society for Testing and Materials, book of Standard(1983).

10. ASTM D, "Tests Method for Vicat Softening Temperature of Plastics", Vol.08.01, American Society for Testing and Materials, book of Standard(1983).

11. http://www.cm.utexas.edu/courses/CH380L/ig.html

12. MacAdams J., "Polyethylene, Markets expanding very rapidly and technology growing at unequalled rate "*Modern Plastics* ,Mid-November, 1995, B-5

13. Eckstut.M. et.al "Polyolefin Catalysts", Chemical Engineering, September 1996, pp.92

14. Feldman D. and Barbalata A., "Synthetic Polymers: Technology, properties, applications", (1996) Chapman & Hall, pp.15

15. Leaversuch R. D., "Exxon adapts metallocene catalysts for slurry PE process", *Modern Plastics*,V 73, July 1996, pp. 25,26

16. Leaversuch R. D., et. al., " Licensing alliances aim to speed metallocene PE use in processing", *Modern Plastics*, September 1996, pp. 30, 31

17. Kates D.F.," Metallocene Products in The Spotlight at Polyolefins" *Plastics Engineering* , April 1995, pp. 17

18. Anonymous, " DSM to Produce Metallocene-catalyzed EPDM", *Modern*

Plastics,August 1996, p.16

19. Anonymous, "DuPont Dow plans launch of a metallocene-EPDM grade" *Modern Plastics* , November 1996, p. 34

20. Leaversuch R. D., " Metallocenes versatile PE s take on large-volume applications" *Modern Plastics*, January 1997 pp. 59

21. Leaversuch R. D., " Metallocenes, volume is beginning to build as end-users assess resins' benefits", *Modern Plastics* , January 1996, pp. 57

22. Anonymous, "Metallocene Catalysts Push Polymer Production", Process Engineering",April 1996, pp.27

23. Charrier J.M.," Polymeric Materials and Processing"(1990), Hanser Publisher

24. Rosato D. V., Fallon W. k., Markets for Plastics,(1969) Van Nostrand Reinhold Company

25. Feldman D. , "Polymeric Building Materials",1989, Elsevier Applied Science, pp 490-493.

26. Dunbar P. R. "Vinyl and allied polymers", 1968, V. 2, pp.154

27. ASTM D1044, "Test Method for Resistance of Transparent Plastics to Surface Abrasion", Vol. .08.02, American Society for Testing and Materials, book of Standards.

28. ASTM D256-93a,"Standard Test Methods for Determining The Pendulum Impact Resistance of Notched Specimens of Plastics, Notched Izod Impact ",Vol. 8.01, pp.1, American Society for Testing and Materials, book of Standards (1993)

29. ASTM D 5208-91, " Practice for operating fluorescent (UV) condensation apparatus

for exposure of photodegredable plastics", Vol. 08.03, American Society for Testing and Materials, book of Standards (1993)

30. ASTM D 638-82,"Standard Test for Tensile Properties of Plastics"Vol. 8.01, pp. 65, American Society for Testing and Materials ,book of Standards (1993)

31. Anonymous, "Resins and Compounds", Modern Plastics, Mid November 1995,B-20

32. Ullman's Encyclopedia of Industrial Chemistry, Fifth Edition, Vol.A :11(1985)VCH, pp.271

33. Titow W.V., "PVC Technology", Fourth Edition (1984), pp. 10-11

34. ASTM D792, "Test Method for Density and Specific Gravity(Relative Density) of Plastics by Displacement", Vol.08.02, American Society for Testing and Materials.

35. ASTM D3417, "Standard Test Method for Heats of Fusion and Crystallization of Polymers by Thermal Analysis", Vol.08.02, pp.81, American Society for Testing and Materials

36. CSA Standard A126.1-M 1984,"Test Method for Resilient Flooring", 3.14:Dimensional Stability

37. Vasile C. and Seymour R.B., Handbook of Polyolefins-Synthesis and properties, Marcel Dekker (1993) pp759-777, pp235-236.

38. Prasad A., "A Quantitative analysis of LDPE/LLDPE Blends Composition By DSC and FTIR Methods", (1997) SPE Annual Technical Conference 55th pp 2310-2314.

39. Muller A.J. and Balsamo V., "Thermal Characterization of LDPE and LLDPE Blends", (1994), Advanced Polymer Blends Alloys Technology No.5, pp 1-21.

40. Donatelli A.A., "Characterization of Multicompenent Polyethylene Blends by DSC"

(1979) J.Applied Polymer Science Vol. 23, pp 3071-3.

41. Shishesaz M.R. and .Dontelli A.A., "Tensile Properties of Polyethylene Blends", Polymer Engineering Science (1981) vol 21 pp 869-872.

42. DATTA N.K. and Birley A.W. , "Thermal Analysis of Polyethylene Blends", Plastic and Rubber Processing and Applications, (1982) No.2, pp 237-245.

43. Starkweather H.W., "Cocrystallization and Polymer Miscibility, J.Applied Polymer Science 1980. V.25, PP 139-147.

44. Steep Rock Resources Inc. Technical Information Sheet, Snowhite 12, 1997.

45. Dow Plastics Technical Information Sheet, Polyolefin Plastomers, Affinity 1140, 1997.