Polyolefin Elastomer Blends as an Alternative to Poly(vinyl chloride) Flooring

Nikhil Vyas

A Thesis

in

The Department

of

Building, Civil and Environmental Engineering

Presented in Partial Fulfillment of the Requirements

for the Degree of Master of Applied Science at

Concordia University

Montreal, Quebec, Canada

May 2002

0-612-72901-X

ABSTRACT

Polyolefin Elastomer Blends as an Alternative to Poly(vinyl chloride) Flooring

Nikhil Vyas

Poly(vinyl chloride) (PVC) flooring products in the form of flexible sheets and tiles dominate the resilient flooring market. These flooring products are produced by calendering compounds based on vinyl chloride-vinyl acetate copolymer filled with calcium carbonate, essentially with plasticizers and other additives. Plasticizers have become matter of concern from indoor air quality (IAQ) point of view as they are suspected to be the one of the sources of volatile organic compound (VOC) emissions, considered harmful to human health.

In the research work reported here, polyolefin elastomers (POE) filled with calcium carbonate filler are prepared and their mechanical properties are evaluated as an alternative to poly(vinyl chloride), PVC matrix for flooring products. POEs are olefin copolymers synthesized using metallocene technology and does not require plasticizers for processing, yet can provide similar flexibility to the finished product as that of plasticized PVC. Also, POE can incorporate relatively higher amounts of post consumer polyethylene (PC-PE) while maintaining adequate properties. The POE used in this study is Engage-8440, which is an ethylene-octene copolymer. Two types of PC-PE are studied in this research: the first one is a 50-50 mixture of linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) and the second is a high density polyethylene (HDPE). The mechanical and thermal properties, as well as the technique is used to study the difference in thermal properties of the two recycled resins. Further, heat and UV stabilizers are added and the tensile properties of POE/PC-PE blend composites are tested for accelerated weathering effects.

As a result of the present study, an alternative flooring material is attempted with appreciable properties, such as Young's modulus, tensile strength at break and yield point, elongation at break, impact, hardness and static load limit values.

TO MY FAMILY

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to my supervisor, Dr. Dorel Feldman, Professor Emeritus at the Department of Building, Civil and Environmental Engineering for his valuable guidance and encouragement throughout the course of this study.

I am highly grateful to Mrs. Dorina Banu, Research Associate, for her valuable suggestions, criticism, assistance and continuous encouragement at every step of this research work.

Special thanks to Mr. Joseph Hrib for his help in setting the research experiment.

The financial support of the EJLB Foundation is gratefully acknowledged.

Thanks to my friends – Ramanee, Deep, Jatin and Jeet for their continuous support and encouragement throughout the course of this study. Special thanks to Sanjeev for proofreading the manuscript and his valuable suggestions.

I am forever indebted to my wife, Archana for her understanding, encouragement and patience throughout course of this study.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

BBP	Butyl benzyl phthalate
$CaCO_3$	Calcium carbonate
DOP	Dioctyl phthalate
DSC	Differential Spectral Calorimetry
EMA	Ethyl methylacrylate
EPDM	Ethylene propylene diene monomer
ESCR	Environmental stress crack resistance
EVA	Ethyl vinyl acetate
HCl	Hydrochloric acid
HDPE	High-density polyethylene
Hf	Hafnium
HMWPE	High molecular weight polyethylene
HV	Homogenous vinyl
IAQ	Indoor air quality
LCB	Long chain branches
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MDPE	Medium-density polyethylene
MOD	Macromolecular organic dust
MPa	Mega Pascal
MW	Molecular weight

MWD	Molecular weight distribution
Nm	Nanometre
OBPA	Oxybisphenoxyarsine
PC-HDPE	Post consumer high density polyethylene
PC-LDPE	50-50 Mixture of post consumer linear and low density polyethylene
PC-PE	Post consumer polyethylene
PE	Polyethylene
Phr	Per hundred parts resin
POE	Polyolefin elastomer
POP	Polyolefin plastomer
PP	Polypropylene
PP	Polypropylene
PVC	Poly (vinyl chloride)
RH	Relative humidity
SA	Stearic acid
SBS	Sick building syndrome
SCB	Short chain branches
SV	Sheet vinyl
T_g	Glass transition temperature
T_m	Melting temperature
TXIB	2, 2, 4 –trimethyl –1, 3 – pentanediol-di-isobutyrate
UHMWPE	Ultra high molecular weight polyethylene
UV	Ultraviolet

VA	Vinyl acetate
VAT	Vinyl asbestos tile
VC	Vinyl chloride
VCT	Vinyl composition tile
VLDPE	Very-low-density polyethylene
VOC	Volatile organic compound
Zr	Zirconium

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Construction industry in North America in the year 2000, consumed almost 22% of total polymeric resins production. Polyethylene (PE) was the highest selling resin with sales in North America of 22.2 million tons followed by poly(vinyl chloride) (PVC) at 6.52 million tons. While the current PE applications in the building and construction sector is limited to pipes, conduits and some other specialty products, almost 75% of the total PVC produced in the year 2000 was consumed by building and construction industry [1].

PVC offers a combination of versatile performance and low cost. One of the major applications in construction is its use as resilient flooring material. Other indoor applications include wall coverings, baseboards, blinds, profile for doors and windows [2].

The resilient flooring market is dominated by vinyl flooring products. PVC has been used as a principal component for resilient flooring since 1934, when vinyl flooring was first introduced [3].

Vinyl flooring is available in three different product groupings: sheet vinyl (SV), vinyl composition tile (VCT) and homogenous vinyl (HV). These flooring materials are generally made by calendering compounds based on vinyl chloride-vinyl acetate (VC-VAc) copolymer filled with calcium carbonate (CaCO3) [3].

The PVC copolymers and homopolymers are quite stiff and rigid. These physical characteristics can be altered through the addition of plasticizers, which are low molecular weight additives that act to reduce molecular binding forces and increase flexibility. Plasticizer facilitates the processing and forming of PVC-based compositions. The use of such plasticizing additives also facilitates the incorporation of high level of fillers and pigments and affords finished composition with an acceptable degree of flexibility and resilience. Plasticizers such as phthalates and benzoates are used in formulation along with stabilizers and other additives, pigments and lubricants [2, 4].

Studies suggest that plasticized PVC products can be a source of volatile organic compounds (VOCs) in buildings leading to poor indoor air quality [5].

Plasticizers are also subjected to microbial degradation, which leads to VOC emission and to unsightly fungal growth in many flooring products in humid environment [5]. Some studies also suggest that they may act as endocrine disruptors i.e. hormone mimic [6]. These considerations point to the need for research into more sustainable alternatives to PVC-based indoor building materials.

PVC resins generally require the use of stabilizing additives to prevent discoloration resulting from thermally induced decomposition of resin during processing and also during the service life of the product. These stabilizing additives typically include metal containing compounds such as barium, zinc, and cadmium salts of organic acids and organotin compounds. As a result, the waste management of PVC is also being questioned [4, 6].

In fact, PVC is the only building material to come under harsh scrutiny where the entire life cycle of the product is questionable and target to objections and scientific criticism. Opposition to the material can be found in manufacturing processes, recycling and disposal.

Much of the issue deals with the fact that it is not economically feasible to convert PVC to pellets; and, consequently, it is the least recycled of the six common plastics used to make household, consumer and construction materials. Also, PVC is manufactured with chlorine and other additives. The process of breaking down the material is costly and can release harmful chemicals into the environment [6].

Recent advances in the synthesis of polyolefins based on metallocene catalysis can render similar flexibility for formulation as available in PVC. Polyolefin copolymers are considered to be one of the possible replacements to PVC. 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. This flexibility in polymer synthesis enables metallocene-based resins to have a wider range of physical properties, which can also be tailored to suit applications. For this reason, the new resins are making quick inroads into packing, wire and cable, and some specialty markets [7].

Polyolefin based composites can have important advantage over PVC-based ones. The first advantage is that POE can be processed without the use of plasticizers, thus avoiding problems associated with VOC emissions and microbial degradation. The second advantage in using POE is its potential for incorporating post-consumer resins. Post-consumer polyolefins, which can be used as extenders to lower the cost and for better waste management and environmental sustainability.

1.2 RESEARCH OBJECTIVES

The main objective of this research is to develop and evaluate a new polyolefin based flooring material with post-consumer component as an alternative to plasticized poly(vinyl chloride) flooring.

1.3 METHODOLOGY

In order to achieve this objective, polyolefin elastomer (POE) and blends of POE and post-consumer polyethylene (PC-PE) were formulated with calcium carbonate ($CaCO_3$) as filler and tested for key mechanical and thermal properties.

1.4 ORGANIZATION OF THE THESIS

The next chapter presents the literature review related to resilient flooring, vinyl flooring, indoor air quality problems due to vinyl flooring, polyolefin and polyolefin as a potential substitute to vinyl flooring.

Chapter 3 presents the detailed research program including the different phases of this research, formulations and experimental procedures as well as description of testing equipments.

Chapter 4 consists of experimental results presented in order of different phases of the research program. The analysis and explanation of the results of mechanical, thermal and processability properties are provided.

Finally, conclusions and recommendations for further research on this topic are provided in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 RESILIENT FLOORING

Resilient flooring is featured by its ability to deform and recover from the compressive forces caused by the dynamic action of footsteps, cartwheels, and casters, or static load of appliances and furnishings. Resilient flooring refers to a family of flooring products that include such materials as linoleum, asphalt tile, rubber and vinyl flooring. Resilience distinguishes this group from carpeting, wood, ceramic and stone [3].

The resilient flooring produced today evolved from painted fabric or floor cloth that was laid over the board flooring to provide a decorative, washable surface and to keep out drafts from the cracks between floor-boards. Several attempts, dating back as far as the 1600's were made to establish an industry to manufacture floor cloth and oil coated cloth. In 1844, a floor cloth made from India rubber, sawdust, and cork became quite popular. In 1864, linoleum was first introduced in England. This was essentially regarded as the beginning of the modern resilient flooring industry. The earlier resilient flooring products included linoleum, rubber and asphalt tiles [3, 8].

Today, resilient flooring has advanced a long way from early linoleum and asphalt tile products. Flooring structures and compositions have continuously changed to take advantages of advancement in raw materials. Consumer sophistication in defining perceived and absolute needs has accelerated the process of change.

2.2 POLYMERIC FLOORING

Polymeric flooring can be broadly classified into homogenous and heterogeneous flooring. Homogenous flooring is generally viewed as a system that is of constant composition throughout its whole structure, as shown in Figure 2.1. Homogeneous composition with thin top-coat also fit into this broad category. Homogenous flooring has the advantage of wear layer being the full depth of construction and is used in industrial or commercial settings where fashionable appearance is secondary to economy and functionality. Heterogeneous flooring, as the name implies, consists of multiple components. The simplest construction consists of a reverse printed, transparent, top layer bonded to a base layer. Heterogeneous flooring may also contain additional layers, one of which is often foamed, as shown in Figure 2.1. Vinyl flooring materials are available in homogeneous as well as heterogeneous forms [9].

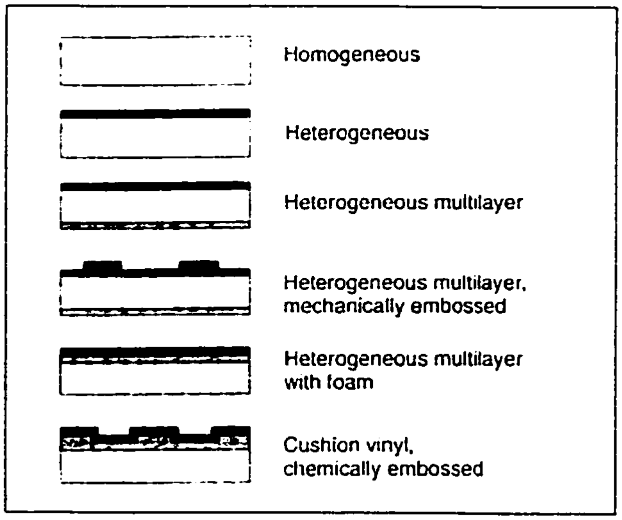

Figure 2.1: Polymeric flooring construction [9]

2.3 RESILIENT FLOORING MARKET

In terms of commercial applications, the uses of resilient flooring include those in housing, mercantile, health care, light industry, office and bank buildings [3]. Globally, over a billion Sqm per year of polymeric flooring are sold. In Western Europe, over 300 million Sqm per year are sold, of which 80% is PVC, 12% linoleum and 8% cross linked rubber [9]. Table 2.1 shows the Canadian Floor Covering Market as in 1993. As indicated in Table 2.1, PVC-based floor covering commands the second highest market share, after carpet/area rugs which are not essentially regarded as resilient flooring materials [10].

Table 2.1: Canadian floor covering market in the year 1993 [10]

Floor Covering Material	Volume (0,000,000 Sqm)	Market Share (%)
Carpet/area rugs	57	61
PVC-based (sheet, VCT)	26	28
Hardwood	5	6
Ceramic Tile	1	1
Other	4	4
Total	93	100

2.4 VINYL FLOORING

Dynamit Nobel AG introduced vinyl or PVC flooring in Europe in 1934 under the trade name of Nipolan. In the USA, the same was manufactured by Carbide and Chemical Corporation 1931 as Vinylite [3, 8].

Sheet vinyl (SV) is the most common form of PVC flooring. It is slightly spongy, composite-layered material most often used on residential surfaces such as kitchens and bathrooms. Sheet vinyl flooring products are available in two varieties i.e., cushioned rotovinyls and inlaid sheet vinyl flooring [3, 8, 10].

Rotovinyl or rotogravure flooring is composed of several layers of vinyl plastisol coatings, usually applied by reverse roll coating. Plastisols are dispersions of emulsion-polymerized PVC, blending resins, pigments, stabilizers and other additives in a plasticizer system. Typical rotogravure sheet flooring structure comprises of a backing layer, foam interlayer (for cushioning) with rotogravure print and a clear wear layer. Each layer can be custom made depending upon the specific user requirement. It is available in virtually unlimited design patterns because of versatility of rotogravure printing [3, 8, 10].

Inlaid SV may have felt composition backing with an inlaid vinyl wear layer of varying thickness depending on intended end use. Compared to rotovinyls, these are relatively stiff and heavy. It may have alternate layer of filled and unfilled vinyl matrix. The filled component of the wear layer is a suspension of PVC homopolymer. Copolymers are also used to have better color and graining effect in the design pattern. The primary plasticizers are phthalates and calcium carbonate is used as a filler. They are widely used in high-traffic residential applications such as dormitories as well as schools, health care facilities and other institutional buildings [3, 8, 10].

The second most widely used type of vinyl flooring is Vinyl Composition Tile (VCT). It has superseded vinyl asbestos tile (VAT). A majority of VCT is used in commercial flooring such as supermarkets and large department stores. It is an economy grade, commercial flooring material, typically composed of 6-13 wt % of PVC resin. The vinyl resins normally used are copolymers of VC-VAc, in which a high level of calcium carbonate filler is added. PVC homopolymer may also be blended for processablity. The processing aid is usually a low-melting hydrocarbon. The plasticizers may consist of blends of phthalates. VCTs are available in several gauges, sizes, often embossed and may contain surface applied pattern and graining [3, 8, 10].

Homogeneous vinyl (HV) or solid vinyl tiles are commonly used in institutional buildings such as hospitals and schools. It is a PVC compound typically containing 30% binder (PVC resin and plasticizer) with the balance being filler. It is normally manufactured by a combination of calendering, consolidating, and laminating. The formulation for solid vinyl tiles is similar to those discussed for inlaid vinyl flooring [3, 8, 10].

The weight average molecular mass (MW) of the resins, which are most useful in flooring, ranges from 40,000 to 200,000. The higher the molecular mass the greater are the ultimate tensile strength and abrasion resistance; such products are generally used in flooring wear layerwhereas, the polymer with lower softening temperatures are most useful in producing foams for cushioned flooring [3].

2.4.1 RAW MATERIALS FOR VINYL TILES

Materials for the manufacturing of composite vinyl flooring products include PVC resin. fillers and additives such as plasticizers. heat and light stabilizers. antimicrobial. lubricants, pigments, UV stabilizers and processing aids [3].

2.4.1.1 PVC RESINS

The versatility of PVC to be compounded in wide range of flexibilities makes it material of choice for the manufacturing of various products. resilient flooring being one of them. PVC has several attributes that make it well suited for flooring application:

1. It can tolerate high levels of inert filler. thus reducing cost
2. It is clear and colorless (design and colors can be added)
3. It is inherently fire resistant and
4. It can be effectively plasticized to a wide range of flexibilities [3]

PVC also 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) [3. 11].

Both vinyl chloride homopolymer (PVC) or VC-VAc copolymers can be employed in the binder system in the vinyl flooring manufacturing depending upon the characteristics necessary for the end product. 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 [3].

Flooring manufacture employs suspension and modified bulk-polymerized PVC in processes requiring intensive mixing and emulsion-polymerized resin in processes involving liquid coating of plastisols [3].

2.4.1.2 HEAT STABILIZERS

Heat stabilizers are essential ingredients of any PVC formulation. These are added with a prime objective of inhibiting thermal degradation of PVC during processing and in service. The thermal degradation in PVC is evident by the presence of colored patches. Thermal degradation of PVC occurs during processing at high temperature and also due to exposure to high temperature while in service. The thermal degradation results into loss of hydrogen and chlorine atoms from adjacent carbons in the polymer chain, with the formation of hydrogen chloride. The resulting C=C double bond weakens the adjacent C-Cl bond leading to the loss of further HCl and the formation of a second double bond. The released HCl acts as a catalyst for further dehydrochlorination [12].

Heat stabilizers thus have two functions viz., - to prevent dehydrochlorination by interrupting the reaction sequence and to bind the released HCl so as to stop autocatalytic effect [12].

While most stabilizer systems used in commercial PVC formulations contain two or more components acting synergistically, some single product stabilizing systems are also available [13].

The most common stabilizers used in vinyl flooring formulations are soaps of barium, calcium and zinc and certain organotin compounds. Soy-bean oils, tallate esters and other partially unsaturated oils, are frequently used as co-stabilizers with the primary organometallic compounds [3, 12].

2.4.1.3 PLASTICIZERS

Plasticizers are essential ingredient of any plasticized vinyl product. Plasticizers are the materials added to a polymer to increase flexibility and workability brought about by reducing intermolecular forces. The addition of plasticizers also results in the lowering of glass transition temperature ($T_{g.}$) of the polymer. It is expected that a plasticizer would provide the required flexibility and process workability based on the product specification, be soluble and compatible with resins [13]. Plasticizers are responsible for imparting stain resistance to the product, which is important for flooring applications [14].

The selection of a plasticizer may vary from product to product. In case of sheet vinyl flooring which is generally made up of four layers of plastisols, with each layer designed to perform a different task, three basic types of the plasticizers in various combinations are used. A plasticizing system consist of:

a) A general purpose plasticizer, usually Di-octyl phthalate (DOP)
b) A fast fusing/stain resistant plasticizer, such as butyl benzyl phthalate (BBP)
c) A low viscosity component, for example Kodaflex TXIB (2, 2, 4 – trimethyl –1, 3 – pentanediol-di-isobutyrate) [15]

In vinyl floor tiles, calcium carbonate is the major component, which is dispersed in plasticized PVC matrix. Here, the plasticized PVC functions as a binder. It is required to achieve maximum dispersion of the filler particles in the formulation. This can be achieved by using a general-purpose phthalate such as DOP, which has relatively low cost, good permeance, and lack of color. Chlorparaffin may also be incorporated in the formulation for further cost reduction. DOP is the most commonly used plasticizer for flooring because of its DOP is also used in more flexible (less highly filled) tiles or continuous calendered sheet flooring [3, 15].

2.4.1.4 FILLERS

Fillers are used to reduce the cost of a resin. The inclusion of fillers in the formulation can improve the important properties such as dimensional stability, water resistance, weathering, surface smoothness, stiffness and temperature resistance of the compounded product. It has been observed that filled resins shrink less than unfilled resins. Fillers are also used to improve electrical insulation properties, to control gloss and to reduce tackiness of highly plasticized compounds. However, most fillers have tendency to absorb plasticizer resulting into increased stiffness of the plasticized PVC product [16, 17].

For flooring applications, inorganic mineral fillers, mostly calcium carbonate ($CaCO_3$) is used because of its low cost, general lack of color, and low plasticizer absorption properties. $CaCO_3$ provides mass and thickness at lower cost compared to other fillers. It also has less toxicity, easy coating ability, and the acid-acceptance capability providing a degree of secondary stabilization for PVC during processing. $CaCO_3$ also improves resistance to cigarette burns and flame spreading ratings and reduces smoke generation. Other fillers such as clay or talc are rarely used due to their significant stiffening effect on plasticized PVC [6, 12].

$CaCO_3$ is available in five forms – water ground, dry ground, ultra fine ground, precipitated and surface treated. Flexible PVC compounds often contain 100-300 phr of $CaCO_3$ [6, 12].

2.4.1.5 PIGMENTS AND COLORANTS

Organic and inorganic pigments are used to impart colors to plasticized PVC product. Pigment selection should be based on the pigment's ability to withstand process conditions, its effect on stabilizer and lubricants and its effect on end-use properties. Organic pigments are preferred because of their higher color strength though inorganic pigments have better opacity. Carbon black and titanium dioxide are the most common pigments used in PVC formulations [18].

2.4.1.6 FLAME-RETARDANTS AND SMOKE SUPPRESSANTS

In plasticized PVC product, the type and level of plasticizer influences the fire resistance properties. Specific compounds may be added to the formulation to reduce flame spread and smoke generation. Antimony trioxide, aluminum oxide trihydrate, phosphate esters or chlorinated hydrocarbon plasticizers, zinc oxide and boron compounds are used as flame retardants. Molybdenum trioxide is most widely used as a smoke suppressant [18].

2.4.1.7 BLOWING AGENTS

Specific to cushion flooring, blowing agents are used to form expanded foam layer. Blowing agents are additives, which decompose during the processing of the composition with the evolution of gas bubbles, resulting a cellular end product [18].

2.4.1.8 ANTI-MICROBIALS

Anti-microbial agents, also called biostabilizers are added to formulations to inhibit the growth of microorganisms on the surface of PVC. They impart protection against mould, mildew, fungi and bacterial growth.

In absence of organic additives such as plasticizers, PVC is resistant to microbiological attack. However, addition of plasticizers and other additives with similar characteristic structures can act as nutrient source for microorganisms. The surface growths can cause allergic reactions, unpleasant odors, embrittlement and premature product failure. The effectiveness of anti-microbials depends upon their ability to migrate to the surface of the product where the attack first occurs. However this can pose problems of toxicity and leaching. Ideally, anti-microbial agents should be toxic to their targets and benign to all others. However, this balance is difficult to achieve in practice. Also, most anti-microbials are supplied as suspensions in plasticizers. Plasticizers are highly mobile and migrate throughout the product, sometimes resulting into leaching. Significant leaching can render a product susceptible to microbial attack. For flexible PVC, most common anti-microbial is oxybisphenoxyarsine (OBPA), commercially available in the diluted form as Vinyzene (Morton Thiokol) [18].

2.4.1.9 UV ABSORBERS

Photodegradation is one of the attributing factors to the weathering with detrimental effects. Photodegrdation occurs when plasticized PVC is exposed to solar radiation in the wavelength band of 290-400 nm composed of ultraviolet (UV) rays. Absorption of such energy leads to macromolecular bond fracture and the formation of free radicals. The free radicals initiate and participate in destructive chain reaction. The oxygen present in the environment accelerates the photodegradation [19].

The UV absorber additives absorb the UV radiation and dissipate its energy as heat before degradation initiates. They are polymer soluble materials having high absorption coefficients for wavelengths in the damaging UV range. Carbon black and TiO_2, widely used as colorants for plastics can act as UV absorbers and are often called as "light screens". They act as physical barriers to both UV and visible range of radiation [18].

2.5 PVC FLOORING AND INDOOR AIR QUALITY

Building materials can be considered as emission sources in buildings due to large surface areas exposed to indoor air [20]. Emissions of VOCs from floor covering are mentioned as one of such sources responsible for poor Indoor Air Quality in buildings. Interest in potential health effects has resulted primarily from complaints investigated in Nordic countries. Many investigations have been carried out to assess the role of PVC flooring products as a potential cause of health complaints in specific problem building environments or risk factors for Sick Building Syndrome (SBS) symptoms in general [5].

Floor coverings are considered as a potential risk to IAQ because, they

1. are used in large quantities and have a large surface to volume ratio
2. are for the most part composite materials
3. require adhesion to a substratum
4. require periodic cleaning.

Due to these factors, floor coverings can have potentially significant effect on IAQ and possibly human health and comfort as well [5].

Effects may be either direct or indirect. In the former case, floor coverings may themselves release toxic contaminants, which may affect the health and well being of building occupants. In the latter case, a variety of air contamination problems can be anticipated to occur. These include toxic emissions from bonding agents used to apply floor coverings, shampoos and waxes used in cleaning, and reservoir effects involving VOCs and/or immunological macromolecular organic dust (MOD) [5].

The ideal plasticizer would show zero loss from the plasticized product and would remain chemically unchanged despite prolonged exposure to heat, humidity, light, aggressive chemicals, microorganisms and contact with wide variety of extracting media. However in reality, since external plasticizers are not chemically bound to the polymer, they are subject to loss by migration to the surrounding environment. Plasticizer exudation and evaporation occurs continuously in time, even at low temperatures although it may be undetected even by sensitive analytical techniques [21].

The potential consequences of loss of plasticizers are hardening of the product, with considerable shrinkage in extreme cases and deleterious effect of plasticizer vapor on adjacent materials or may pose risk to health, safety and environment [22].

Evaporation of plasticizer from plasticized PVC is the most ubiquitous form of plasticizer loss. Plasticizers can also migrate to other solids, liquids and to the surface coating. Various organic liquids can extract plasticizers, as they are miscible with them. Extraction actually occurs after the migration of the plasticizer to the surface. Plasticizer migrated to the surface can as well be extracted by water and water plus surfactant. Exudation of plasticizer can also be induced by high level of humidity. Water can reduce the compatibility of a plasticizer with PVC. The extraction is resisted by hydrophobic molecular structure of the plasticizer, however the surfactant in water disperses the plasticizer as it arrives at the surface followed by progressive extraction. Research has indicated that plasticizers can migrate to the non-plasticized wear layer, that is the top coating of the PVC flooring product [21].

Fungi have been shown to produce esterases, the enzymes capable of breaking ester linkages. The fragment molecules so produced, can be metabolized both by fungi and bacteria causing further degradation [4, 6]. Major problems of substratum damage may occur when plasticized PVC is colonized by microorganisms in many different environmental situations. It has long been established that this susceptibility results from the presence of plasticizers [22, 23].

Webb et. al [22] observed that, plasticizers may accelerate the bio-degradation processes occurring on plasticized PVC by enhancing fungal adhesion. They investigated the effect of plasticizer on the adhesion of the deteriogenic fungus Aureobasidium pullulans to PVC.

Aging of articles made from plasticized PVC under real use conditions is often controlled by its diffusional desorption of plasticizing additives from the material [24, 25]. The desorption of phthalate plasticizers, widely used in PVC and readily accumulated by microorganisms, may contribute to biodegradation of PVC [26].

Gumargalieva et. al [25] have reported the influence of bio-degradation on the loss of DOP plasticizer from PVC by the microscopic fungus Aspergillus niger. They concluded that loss of a plasticizer from PVC under influence of surface bio-degradation is much faster than loss without fungal overgrowth. The fungus acts like a leaching solvent, presumably because it effectively removes plasticizer from the surface of the material by bio-degradation.

Jaakkola et.al. [27] in a study published in American Journal of Public Health has linked occurrence of bronchial obstruction in young children to PVC flooring. In a matched case-control study conducted in Oslo, they observed that children with bronchial obstruction were more likely to have PVC flooring in their homes than were children without bronchial obstruction.

In a separate study, Jaakkola et.al. [28] also observed that plasticizer migrate from PVC floor to sedimented house dust. Since plasticizer have high affinity for particles, in this case to the house dust, the risk of bronchial obstruction is more likely due to PVC flooring than PVC wallpaper [29].

Rittfeldt et al. [30] in Sweden proposed that vinyl floor coverings may contribute to "temporary sick buildings" due to emission of benzyl and benzal chloride associated with the plasticizer butyl benzyl phthalate (BBP). These compounds cause irritation to eyes, respiratory mucosa and are also carcinogenic. In addition to benzyl and benzal chloride, emission of many other compounds was also observed.

Gustafsson [31] reported association of unpleasant odor with vinyl floor covering for large number of cases in Sweden. Odor was associated with the formation of higher alcohols (e.g., 2-ethylhexanol) produced from the hydrolysis of phthalate plasticizers in contact with alkaline concrete in the presence of moisture. Self-leveling floor-topping compound was also found responsible for the hydrosis of phthalic esters.

The occurrence of low volatile compounds such as phthalates, PCB and TXIB in the indoor air is due to adsorption on dust and airborne particles. Adsorbed compounds can be released when dust is heated to 70° C or more on electric bulbs, radiators, and cooling panels on refrigerators [31].

Rosell [32] has reported significant levels of "TXIB" in the air of 8 so-called sick buildings (2-7 years old) in concentrations ranging from $100\text{-}1000 \mu g/m^3$. TXIB is a common plasticizer in PVC floor covering where it comprises 7-8% of product weight. TXIB is semi-volatile with a molecular weight of 286 and a boiling point of 280° C.

Andersson et al. [33] identified 2-ethylhexanol in indoor air investigation for an office building. The study was initiated following complaints about irritation caused by indoor air and occurrence of symptoms of irritation of eyes, nose, throat, unnatural tiredness and headaches. Phthalate esters, mostly DOP used as plasticizer in vinyl floor coverings are considered to be the origin of 2-ethylhexanol.

Saarela and Sundell [34] reported results of emission testing of various flooring materials including unused PVC. They observed that emissions vary widely, in some cases, from PVC floor coverings, which decreased relatively slowly with time. The outgassing depends partly on emitting compounds. Traces of substances based on aliphatic hydrocarbons used as viscosity modifier, frequently used as a processing aid were encountered.

2.6 ALTERNATIVE POLYMERIC MATERIALS TO PVC FLOORING

The problems associated with PVC and PVC flooring products has prompted the researchers and manufacturers to look for a substitute to PVC flooring materials. Rubber and polyolefin based flooring materials are regarded as alternative polymeric materials to PVC flooring. Linoleum is considered as a natural alternative material to PVC as a flooring material.

For any new material to be accepted as a flooring material, it should have at least equal or better properties in terms of traffic and durability, resilience for static and impact loads and rolling loads, moisture resistance, colorfastness, fire and smoke spread, stain reagent resistance, light reflectance, acoustics and most importantly no emission of VOCs. At the same time, it should be suitable for underfloor heating, easy in installation and maintenance.

2.6.1 RUBBER FLOORING

Rubber tile and sheet flooring were introduced in the 1920s and widely used through the 1950s, particularly for applications unsuited to linoleum or asphalt tile. Its popularity declined through 1960s and 1970s because of the relative success of vinyl tiles and sheet flooring. In the mid 1980s, it made a comeback in certain applications, primarily because of the popularity of raised-disk design. Several companies produce rubber floor coverings. Particularly in situations such as airports or sports stadiums where floor coverings have to meet great demands in durability, rubber floor coverings have proven effective [3,8].

Earlier rubber floor tiles were made from sheets of calendered (rolled) rubber strengthened by vulcanization before being die-cut into smaller pieces. Rubber tiles offered many advantages over linoleum: They were resilient, sound-deadening, water-resistant, relatively easy to clean, and easy to install. On the down side, rubber picked up oily stains, and it deteriorated over time from exposure to oxygen, ozone, and solvents. Like linoleum, it was a poor choice for installation in basements because it deteriorated in the presence of alkaline moisture [3, 8].

Natural rubber was replaced by synthetic rubber polymer such as SBR, EPDM. Rubber flooring available today employs styrene-butadiene rubber (SBR) as the primary binder. Other rubbers that may be incorporated with SBR include neoprene and nitrile rubbers as well as Ethylene propylene diene (EPDM). EPDM is recommended by the Danish Environmental Protection Agency as an alternative to PVC [3, 35].

2.6.2 POLYOLEFIN FLOORING

Polyolefin represents group of thermoplastic polymers comprising basically of various grades of polyethylene, polypropylene and polymeric derivatives of butadiene. Polyolefin are also the highest produced and sold resins in thermoplastic resin market [1].

Polyolefin based composites can have the following important advantages over PVC-based ones.

1. They can be processed without use of plasticizers.
2. The potential for incorporating post-consumer resins into the composites. Incorporation of these materials into PVC flooring tiles would lead to reductions of physical properties because of poor miscibility between PVC and polyolefins. POP, on the other hand, is compatible with post-consumer polyolefins, which could, thus be used as extenders at lower costs [11].
3. Polyolefin also has lower energy consumption during polymerization and melt processing.
4. Scrap generated during processing and fabrication can be recycled or reused.

In fact, polyethylene is the highest recycled thermoplastic. Polyolefins consist of carbon and hydrogen atoms and its combustion results into exclusive release of CO_2 and H_2O. Considering environmental aspects, clean disposal can be achieved by burning or pyrolysis. Modern gas phase and liquid phase polymerization technologies do not require solvents for polymer purification [2, 36]. Thus, polyolefins offer economical and ecological advantages over other polymeric resins [36, 37].

Polyolefins are produced by polymerization of basic olefins in presence of catalysts by commercialized processes. Conventional polyolefin produced by Ziegler-Natta catalyst technology provided limited flexibility in properties desired for various applications. The new families of polyolefin polymers based on metallocene-based catalyst provide the balance of properties required for application such as flooring [2, 11, 38].

Manar et.al. [11] in their study of filled polyolefin composites with postconsumer polyolefin found favorable results for tensile and impact properties as compared with PVC based flooring material. $CaCO_3$ was used as filler at 200 phr loading. For both post-consumer LLDPE and HDPE (PC-LLDPE and PC-HDPE) 50/50 blends with POP are found to retain satisfactory elongation and impact properties when compared to PVC formulations.

Betso, Kale and Hemphill have described the benefits of using Constrained Geometry Catalyst (CGC) ethylene copolymers in flooring applications. According to them, given the flexibility in designing the molecular architecture using CGC technology, novel homogenous and heterogeneous flooring systems can be designed. They tested Affinity POP-formulations and concluded that Affinity based POPs offer distinct advantages over traditional raw materials in flooring applications. Figure 2.2 shows typical flooring structure using "Affinity-based POP". Figure 2.3 depicts the surface resistance of POP as compared to that of PVC and linoleum [9].

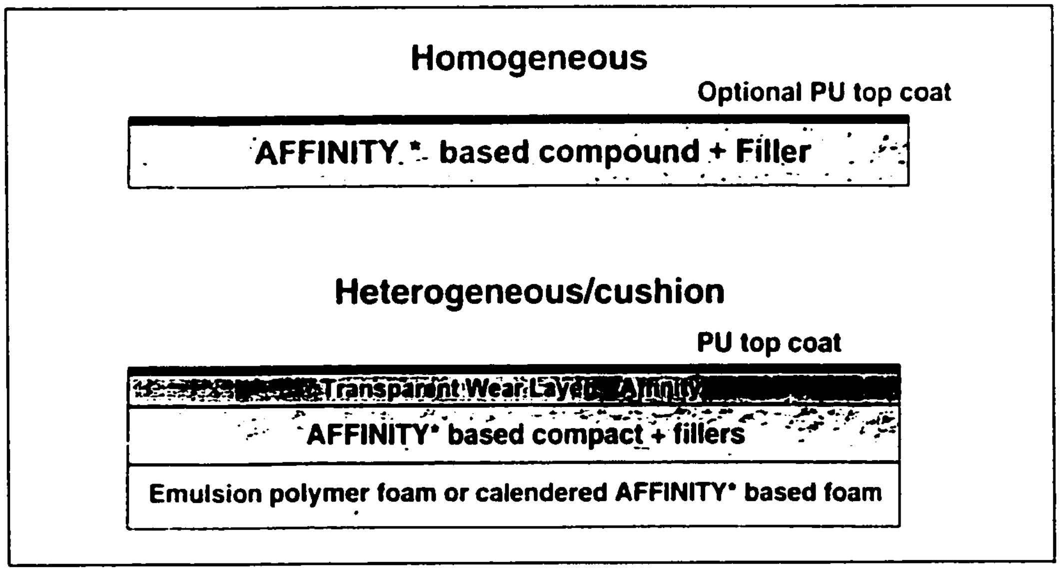

Figure 2.2: Typical flooring structure with "Affinity-based POP" [9]

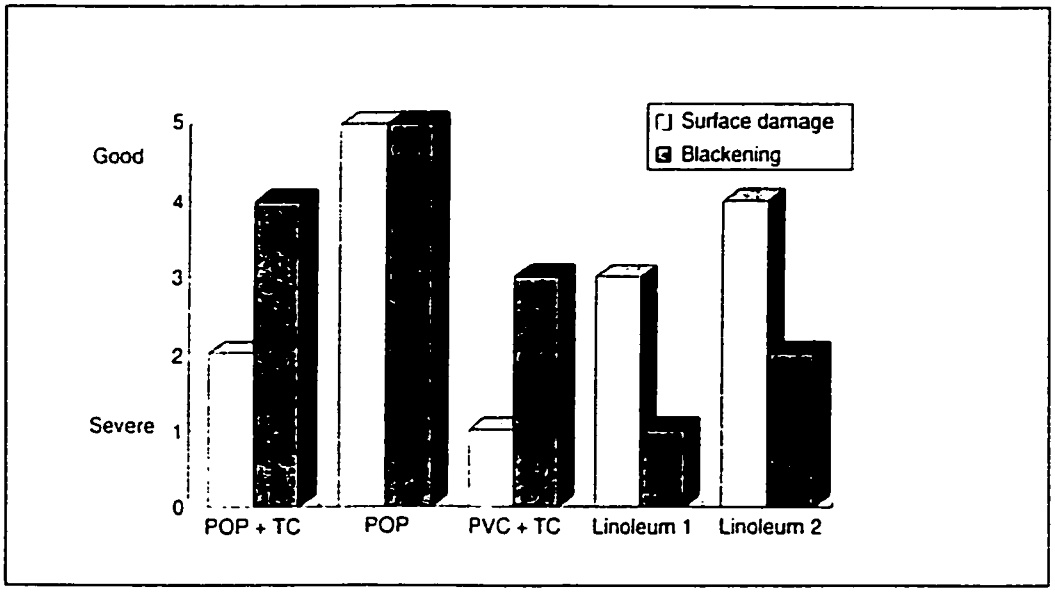

Figure 2.3: Resistance of POP to cigarette damage. TC= with Top Coat [9]

Johnson patented formulation for "Halogen Free Resilient Flooring". He claims that resilient flooring material can be made from a halogen-free, filled, thermoplastic polymer composition, which utilizes copolymers of ethylene and methacrylic acid. The ethylene/(meth)acrylic acid should be from about 40% to about 95% by weight. The floor coverings may be highly filled having about 60% to about 90% by weight of filler or extender such as calcium carbonate, clays, fumed silica and aluminum hydroxide alumina trihydrate [39].

Thoen et.al. [40] have patented formulation of filled polymer compositions. They claim that the articles fabricated from it can be used as sound insulating or energy absorbing films or sheets or as floor, wall or ceiling coverings. They report that thermoplastic substantially random copolymers which have been prepared by polymerizing one or more α-olefin monomers with one or more vinylidene monomers, and optionally with other polymerizable ethylenically unsaturated monomer(s) can be blended with high levels of one or more inorganic fillers. The fabricated articles made from filled polymer composition comprising one or more of such thermoplastic copolymers and one or more inorganic fillers have a substantially improved hardness and tensile modulus while generally maintaining good elongation properties, such as strain at break, stress at break and energy at break, as compared to fabricated articles made from a corresponding thermoplastic copolymer without inclusion. The α-olefin/vinylidene aromatic copolymers display a high level of compatibility with inorganic fillers.

Viet Dao [41] claims that film/sheets made out of LDPE, LLDPE, HDPE and/or PP mix with the other polymer and containing between 20~1000 phr filler with at least 65 phr of metallocene polymer can be used as floor/wall covering with good sound insulation properties. As metallocene copolymer, they have used ethylene with octene or ethylene with hexane, pentene or butene. Metallocene copolymer shall have density between 0.87 - 0.935, melt index between 0.1 and 30, preferably 0.5 and 5. Films and sheets can also be made after adding post-consumer polyolefin in the above formulation, with inert filler such as $CaCO_3$ or $BaSO_4$. Plasticizing agent such as mineral oil and/or fatty acid salt or amide can be added.

Simpson et al. [42] have patented formulation and manufacturing process for sheet material suitable for floor covering. The said sheet material comprises a polyalkene resin of relatively narrow molecular weight distribution (MWD) in intimate admixture with at least one additive comprising a filler.

Naoyuki et al. [43] claim in their patent of a polyolefin resin composition suitable for use as flooring material. Its composition is characterized by: (A) 70 to 98 wt.% ethylene/C4-8 alpha -olefin copolymer having a melting point as determined by DSC of

80 to 110° C, an enthalpy of melting of 60 to 120 J/g, and a density of 0.87 to 0.925 g/cc and (B) 30 to 2 wt.% polymer having at least one polar group selected from the groups consisting of unsaturated, carbonyl, ether, and hydroxyl. The composition is fully satisfactory in material properties including flexibility and load bearing properties (dent resistance) and can be molded by a method such as calendering or extrusion molding.

Thoen et al. [44] claim formulation for PVC-free foamed flooring and wall coverings. The invention pertains to a multilayer foamed flooring and wall product. The product is a resilient cushion foam flooring and wall product that is free of poly(vinyl chloride) (PVC), plasticizers and heavy metal stabilizer. It is made of a multilayer top layer which is integrated with a latex or polyolefin polymer foam back layer. The product has particular utility in the heterogeneous flooring market and can be prepared using ordinary PVC melt processing equipment.

Boldizar et al. [45] studied simulated recycling of post-consumer high density polyethylene material. The material was evaluated in terms of mechanical properties, such as elongation at break and tensile strength. The results indicate that after simulated recycling the HDPE had considerable resistance against thermal degradation and even after repeated recycling and accelerated aging the stability of material was high.

2.7 POLYOLEFIN STRUCTURE-PROPERTY RELATIONSHIP

Polyolefins can be classified on the basis of densities with all of them having density little less than that of water. Density is generally a reflection of polyolefin linearity and crystallinity. Density governs the characteristics and performance properties of polyolefins. Higher the density, higher is the chain linearity, stiffness, tensile strength, softening temperature and brittleness. On the other hand, polyolefin failure properties such as impact strength, flexural strength, and Environmental Stress Crack Resistance (ESCR) decreases as the polyolefin density increases. The catalyst used during polymerization of polyolefins strongly influences the structure and properties of polyolefin as shown in Figure 2.4. A classification of polyolefins and their corresponding densities are presented in Table 2.2 [38, 46].

The wide range of resin characteristics of polyolefins allows them to be used in various applications. The end-product properties, particularly processability and physical and mechanical properties are highly dependent on average MW and MWD. As in the case of PE, the degree and type of chain branching strongly influences the MWD, degree of crystallinity, lamellar morphology, density and rheology [38].

According to Kim et al., real PE molecules 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 into a lower modulus [47].

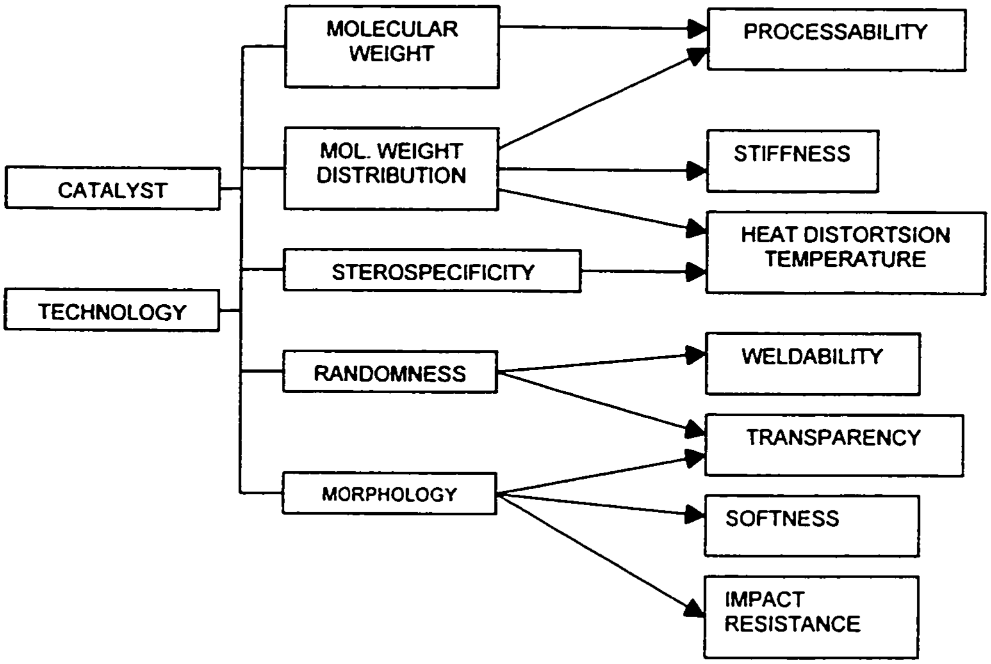

Figure 2.4: Catalyst technology and property relationship of polyolefins [46]

The use temperature of the different polyolefins are limited by the T_g at the lower 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 temperatures or Vicat softening points. The specific heat of polyolefins are in the order polyethylene > polypropylene > polybutene-1, but polypropylene has about the lowest thermal conductivity and thermal expansion coefficient. Polyolefins generally have good ESCR, with PP being better than PE, but all polyolefins require a degree of stabilization against all forms of degradation [46].

Table 2.2: Polyethylene classification based on their densities [46]

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)	Copolymer	0.941-0.959
High-density polyethylene (HDPE)	Homopolymer	0.960 and higher
HMW polyethylene (HMWPE)	Homopolymer	0.947-0.955
HMW 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)	Homopolymer	0.830

2.7.1 LINEAR LOW DENSITY POLYETHYLENE (LLDPE)

LLDPE is a semi-crystalline ethylene copolymer containing 8-10% of α-olefins produced in catalytic polymerization reactions. α-olefins comonomers such as butene-1, hexene-1, or octene-1 are generally added in commercial LLDPE resins, and it has a nonrandom broad comonomer distribution with density ranges between 0.900 and 0.945 g/cm^3. The situation is however different in the case of very-low-density-polyethylene (VLDPE) produced with emerging single site catalyst (SSC) technology. The VLDPE has a density between 0.89 and 0.915 g/cm^3 and is structurally very similar to LLDPE [38, 46].

Densities and crystallanities of LLDPE mostly depend on their composition. There is an inverse relationship between comonomer content and LLDPE density and between molecular weight and density. An increase in molecular weight generally results into significant improvement in mechanical properties, particularly dart impact strength [46].

The primary advantages of LLDPE over LDPE arising from its backbone linearity and the presence of SCB are as follows: higher tensile strength, impact strength, toughness, stiffness, film gloss, puncture resistance, tear strength, ESCR, permeability to water vapor and CO_2 [46].

LLDPE is generally non-reactive with both organic and inorganic acids. At room temperature, LLDPE resins are not soluble in any known solvent. It is also stable in alkaline and salt solutions. However, at elevated temperatures, it forms sulfo-compounds with concentrated solution of H_2SO_4 and also be nitrated with concentrated solution of HNO_3 [38].

LLDPE is usually stable to heat. Thermal degradation starts at temperatures above 250°C and results into gradual decrease in MW and formation of double bonds in polymer chain [38].

Oxidation reaction can occur during processing of LLDPE resins. To protect molten resins from oxygen attack, antioxidants must be used. These antioxidants are added to LLDPE resins in concentrations of 0.1-0.5 wt.% and may be naphtylamines or phenylenediamines, substituted phenols. However, inhibitor based on hindered phenols are preferred [38].

2.7.2 LOW DENSITY POLYETHYLENE (LDPE)

Traditionally, LDPE is defined as a homopolymer product having a density of 0.915 – 0.940 g/cm^3, and 45-60% crystallinity. The unique feature LDPE as opposed to HDPE or LLDPE is the presence of both LCB and SCB along the polymer chain. Another important feature of LDPE is its ability to incorporate a wide range of comonomers that can be polar in nature along the polymer chain. One disadvantage of LDPE lies in its higher energy and production cost. They are available in the form of waxy products with molecular weight of 500 to tough products with molecular weight of 60,000 [38, 46].

The mechanical properties of LDPE falls somewhere between those of rigid polymers such as polystyrene and soft materials such as polyvinyls. Physical properties depend upon MW, MWD and frequency and distribution of SCB and LCB [38].

With increase in MW, certain properties increase such as: melt viscosity, abrasion resistance, tensile strength, resistance to creep, flexural stiffness, resistance to brittleness at low temperatures, shrinkage, warpage and film impact strength [38].

LDPE is highly resistant to penetration by most chemically neutral or reactive substances. It is also highly impermeable to polar liquids like water thus making it an ideal material for packaging and storage containers [38].

2.7.3 HIGH DENSITY POLYETHYLENE (HDPE)

HDPE is a linear polymer with chemical composition of polymethylene, $(CH_2)n$. The name polyethylene really reflects the principal production method of ethylene polymerization by various processes. ASTM defines HDPE as a product of ethylene polymerization with a density of 0.940 g/cm^3 or higher and crystallinity as high as 95%.

This range includes both homopolymers of ethylene and its copolymers. Density and crystallinity both depend primarily on the extent of SCB in polymer chains and, to a lesser degree, on MW [38].

Depending on application, HDPE molecules either have no branches at all, as in certain injection molding and blow molding grades, or contain a small number of braches introduced by copolymerizing ethylene with α-olefins. Commercially available HDPE contains 1-3 wt. % of butene-1, hexane-1, or octane-1; it has few SCB. The range of MWs commercially produced HDPE is wide, from several hundreds for PE waxes to several millions for ultra high molecular weight polyethylene (UHMWPE) [38, 46].

HDPE exhibits very low chemical reactivity due to its highly crystalline structure and low permeability. At room temperature, it is insoluble in any known solvent. HDPE is relatively stable under heat. Chemical reactions at high temperature in the absence of oxygen become noticeable only above 290-300°C [38, 46].

The thermal degradation results in reduction of the resin MW and produces low MW hydrocarbons. At elevated temperatures, oxygen attacks HDPE molecules in a series of radical reactions with reduction of MW [38, 46].

The photooxidative degradation of HDPE is a slow reaction and resembles thermooxidative degradation. Light with a wavelength of 400nm initiates radical reactions that result into reduction of MW, formation of double bonds and organic peroxides in polymer chains and evolution of low MW compounds such as alcohols, aldehydes and ketones. Although HDPE itself absorb UV light poorly, the polar products of its degradation are able to react faster with oxygen and accelerate additional radical reaction [38, 46].

Photooxidative degradation of HDPE results in aging, development of surface cracks, brittleness, change in color, and drastic deterioration of mechanical and dielectric properties. The reaction can be slowed down or prevented by utilizing UV stabilizers such as carbon black [38, 46].

2.8 METALLOCENE BASED POLYOLEFINS

The manufacture of polyolefins by metallocene catalysts represents a revolution in the polymer industry [48]. These newest type of catalysts for polymerization has variously been termed Kaminsky type, single site, constrained geometry or metallocene catalysts [49].

Polymerization of olefin monomers with single site metallocene catalysts allows the production of polyolefins (such as polyethylene or polypropylene) with a highly defined structure and superior properties. Furthermore, the structure of these metallocene catalysts can be varied to tune the properties of polymer, making it possible to tailor carefully the desired properties for large-volume commodity polymers such as PE and PP [48].

Metallocene polymerization catalysts generally have a constrained transition metal (usually a group 4b metal such as Ti, Zr, or Hf) which is sandwiched between cyclopentadienyl ring structures to form a sterically hindered site [50].

While the term metallocene classically described compounds with π -bound cyclopentadienyl ring structures, today's catalysts are better described as being "single-site catalysts". They differ from traditional olefin polymerization catalysts by the fact that catalytically active metal atom is generally in a constrained environment. By confining the polymerization reaction to a single site instead of multiple sites, these catalysts permit close control over monomer placement, side chain length and branching. The resulting polymer has the following characteristics:

1. Narrower MWD, thereby improved ECSR, low extractables and better optical properties
2. Improved strength and toughness
3. Enhanced sealing properties
4. Increased elasticity and cling performance

Table 2.3 provides a comparison of properties of metallocene based ethylene copolymers vs. conventional materials [50].

Table 2.3: Metallocene-based ethylene copolymers vs. conventional materials [50]

Property	LLDPE	High-E EVA	Plasticized PVC	Ionomers	Metallocene Copolymer
Density, (g/cc)	0.92-0.93	0.94-0.95	1.2-1.4	0.95-0.97	0.87-0.92
Melting Point, (°C)	122-128	67-97	-	66-88	60-120
Flexural Modulus (Kpsi)	40-100	1-14	1-25	4-52	2-15
Tensile Strength (Kpsi)	1.9-4	0.6-2.4	1.5-35	1.8-4.8	1.6-4.0
Thermal Stability	Good	Poor	Fair	Good	Excellent
Off taste/odor	Slight	Yes	Yes	Yes	No

Commercially, metallocene based polyolefins are manufactured by almost all major petrochemical companies. Exxon was the first company to commercialize the metallocene process. Dow, also an early entrant in this area, produces metallocene-based polyolefins using their INSITE technology. Dow markets its metallocene-based products under the trade name of "Affinity" POP and "Engage" POE. Apart from these two major players, host of other companies such as BASF, BP Chemicals, Mobil, Mitsui, and Philips have either converted existing olefin capacity to the metallocene process or are in the midst of developing commercial-scale metallocene polyolefins [50].

2.8.1 METALLOCENE BASED OLEFINIC ELASTOMER AND PLASTOMERS

Metallocenes have a good ability to incorporate different comonomers, including higher α-olefins, such as octane into polymer. When ethylene is copolymerized with up to 20% of higher α-olefins, new materials called plastomers (Polyolefin Plastomer – POP) is produced. POP are flexible thermoplastics and have better properties than conventional polyolefins, at much lower densities [51, 52].

Copolymers containing more than 20% of comonomer are called polyolefin elastormer (POE) POE materials are not pure elastomers, but have elastomeric properties [52].

POP/POE can be used for plastic or rubber applications depending on the application requirement. POE/POE has improved elasticity, optical properties and tensile strength has allowed them to replace traditional thermoplastics such as PVC, EVAc, EMA and styrene block copolymers as well as EPR and EPDM. Improved processability is claimed, attributed to controlled-engineered molecular architecture. They also offer clarity, low modulus, superior low-temperature toughness, low level of extractable material and extractable plasticizer has allowed them to replace plasticized PVC for medical applications [52].

2.9 COMMERCIAL POLYOLEFIN FLOORING PRODUCTS

Polyolefin floor coverings are now offered by leading flooring manufacturers such as the DLW, Amtico and Tarkett.

Stratica is manufactured by Amitco. Stratica consists of two different layers of polymers. The bottom layer is a resin called "Lotryl", which is described as an ethylene copolymer, or combination of several types of polyethylene. This layer also includes chalk and clay as filler materials. The pattern is printed on top of this layer of material. [53]. The surface or "wear" layer of Stratica is a polymer resin from DuPont named "Surlyn." Surlyn is based on copolymers such as ethylene/methacrylic acid, processed with zinc, solium, lithium, or other metal salts to create ion clusters within the polymer matrix. This material is durable enough that it is used on the surface of golf balls, among many other things. Amtico claims that a 26 mil (0.65 mm) layer of Surlyn provides the durability of a PVC layer twice as thick, without the need for plasticizers [53, 54].

In terms of indoor air quality impacts, test results from Europe show emissions below the detection limit of 10 microgram/m^2/hr. Amtico sells a "solvent-free" adhesive for use with Stratica in most conditions, and an epoxy adhesive for wet conditions [53].

Supernova is a polyolefin based resilient flooring material made by Tarkett, which was introduced in commercial and institutional market in August 1996. The material is a homogeneous combination of polyethylene and polypropylene resins (patented formula), with a small amount (<6%) of pigments and processing additives. A thin coating of a non-scuff polyurethane surface provides durability. The current product has not been approved for wet environments, and so it is not sold in the residential market [55].

CHAPTER 3

EXPERIMENTAL PROGRAM

3.1 OBJECTIVES

This research program is a contribution towards testing the feasibility of blends of POE as potential replacements for PVC in composites used for flooring tiles. Based on this principal purpose, the program is divided into following phases.

1. Laboratory scale production of POE-based composites, selection of optimum lubricant
2. Determination of physical and mechanical properties of obtained composites
3. Incorporation of post-consumer recycled resins, effects on physical and mechanical properties
4. Incorporation of UV and heat stabilizers in the POE/PC-PE composites made in Phase 1 and 3 with optimum amount of lubricant and determining the effects on physical and mechanical properties
5. Subjecting the heat and UV stabilized POE/PC-PE composites to weathering and testing its effect on physical and mechanical properties

3.2 MATERIALS AND EXPERIMENTAL PROCEDURES

This section covers the materials, formulations, compounding processes and experimental description and methodology adopted to achieve the specific research objectives.

3.3 MATERIALS

In order to evaluate the performance of POE and PC-PE as a resin in flooring tile, formulations presented in the Table 3.1 without introduction of heat and UV stabilizers, were evaluated. Table 3.2 presents the formulation for selected POE/PC-PE blends with UV and heat stabilizers.

Table 3.1: POE and POE/PC-PE formulations

Component	**Formulation**
	Concentration, (phr)
Resin	100
Filler, $CaCO_3$	200
Lubricant, Stearic Acid	3 or 4
PC-PE	20, 40, 50, 60, 80 and 100% of total resin content

Table 3.2: POE and POE/PC-PE formulations with UV and heat stabilizers

Component	**Formulation**
	Concentration, (phr)
Resin	100
Filler, $CaCO_3$	200
Lubricant, Stearic Acid	3
PC-PE	40, 50, 60 and 100% of total resin content
Heat Stabilizer, Hostavin N-30	0.8
UV Stabilizer, Hostavin ARO8	0.5

3.3.1 POLYOLEFIN ELASTOMER (POE)

The POE resin, "Engage 8440" was obtained from Dupont Dow Elastomers (USA). It is synthesized from ethylene and octene monomer [56]. Table 3.3 provides the key physical properties of Engage 8440.

Table 3.3: Physical Properties of Engage 8440 POE [56]

Comonomer, octene content (%)	23*
Melt Index, (deg/min)	1.6*
Density, (g/cc)	0.897*
DSC Melting Point, (°C)	94.6**

* Provided by manufacture

** Determined in laboratory

3.3.2 FILLER

Calcium carbonate is used as filler for the formulations. It was obtained from Steep Rock Resources Inc., Perth, Ontario. The grade used was "Snowhite-12". The particle size distribution is provided in Figure 3.1. This grade is often used in PVC-based composites because of finer particle size yields better physical properties. The physical properties of "Snowhite-12" is provided in Table 3.5 [57].

Table 3.4: Properties of Snowhite-12 $CaCO_3$ [57]

Typical Physical Properties	
Bulk density – Loose, (g/cm^3)	0.8
Bulk density – Packed, (g/cm^3)	1.4
Specific Gravity	2.71

Table 3.4 continue..

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

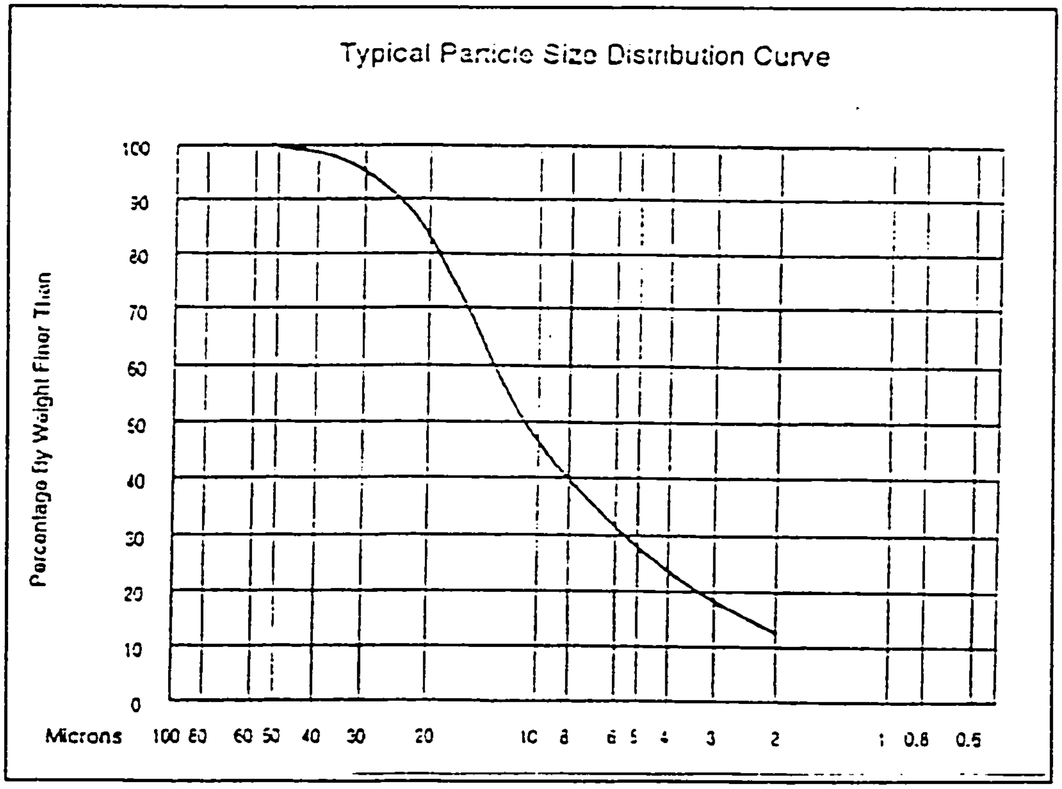

Figure 3.1: Typical Particle Size Distribution of Snowhite-12 [57]

3.3.3 POST CONSUMER POLYETHYLENE (PC-PE)

The research involves incorporation of post-consumer polyethylene with the POE. PC-PE was obtained from Enviroplast Inc., of Montreal, Quebec. Two kinds of PC-PE were used in this research

(a) HDPE (represented as PC-HDPE) and

(b) 50-50 mixture of LLDPE and LDPE (represented as PC-LDPE)

Their properties are presented in the following Table 3.5. These recycle resins were obtained primarily from manufacturing scraps.

Table 3.5: PC-PE Properties

Recycle Resin	Specific Gravity*	Melting Temperature (°C)**
PC-HDPE	0.987	128.6
PC-LDPE	0.938	124

* Determined in the lab in accordance with ASTM D 792 [58]

** Determined in lab by Differential Scanning Calorimetry

3.3.4 LUBRICANT

Stearic acid (SA), obtained from Fisher Scientific was used as lubricant.

3.3.5 UV STABILIZER

Since polyolefins are vulnerable to photochemical degradation, it is necessary to add UV absorbers in the formulations. The UV stabilizer used in this case is HostavinARO8 powder, manufactured by Clariant GmbH (Germany). Also available in granular form, ARO8 is a benzophenone derivative, widely used as UV absorber for different kinds of plastics [59].

ARO8 is a benzophenone derivative, widely used as UV absorber for different kinds of plastics [59].

3.3.6 HEAT STABILIZER

To prevent the heat induced degradation of polyolefins during processing and in service, heat stabilizers are added. Hostavin N30 powder is used in this case, also manufactured by Clariant GmbH (Germany). N30 is a high molecular weight sterically hindered amine HAL and is used as antioxidant [60].

3.4 EXPERIMENTAL PROCEDURES

All the blends were prepared by melt compounding and then, compression molded.

3.4.1 MIXING USING A TORQUE RHEOMETER

All the blends were prepared by melt compounding in a Haake Rheomix 600, consisting of a batch mixer equipped with pair of roller blades and a set of 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 condition is as mentioned 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 of the chamber is 70% of a net chamber volume of 69 cm^3.

Table 3.6: Operating Conditions for blend preparation using Rheomix 600

Formulation	T (°C)	Roller Speed (rpm)	Mixing Time (min)
POE	175	60	10.5
POE/PC-PE	175	60	10.5
POE/PC-PE, ARO8, N30	175	60	10.5

3.4.2 COMPRESSION MOLDING

The compounded material from the mixer was cut into small chips, when still warm. These chips were weighed and placed in a mold to make sheets of 3 mm thickness. Carver laboratory press equipped with temperature controllers, as shown in Figure 3.3 was used for molding. The whole assembly of mold was placed between platens of the press, set at desired temperature. The press was heated with no pressure for initial 7 min. Then the pressure was applied for 4 min, followed by cooling for 5 min at a pressure as indicated in Table 3.7.

Table 3.7: Conditions for Compression Molding

Formulation	Platen Temp. (°C)	Pressure (MPa)		Time (min)		
		Melting	Cooling	Melting*	Pressure	Cooling
POE	178	6.86	4.58	7	4	5
POE/PC-PE	178	6.86	4.58	7	4	5
POE/PC-PE, Stabilizers	178	6.86	4.58	7	4	5

* *Without pressure*

3.4.3 SPECIMEN PREPARATION

From the molded samples, specimens were prepared for the tensile, impact. hardness and static load limit tests. Specimens for tension tests were cut as shown in Figure 3.4 in accordance wtih ASTM D638 [61], specimens for impact tests were cut as shown in Figure 3.5 as per ASTM D250 [62], and for durometer as per ASTM D2240 [63].

3.4.4 CONDITIONING

Specimens were conditioned at 23°C and 50% RH at least for 40 hours before testing according to ASTM D618.

3.5 TESTING

3.5.1 MECHANICAL PROPERTIES

Tensile and impact tests were performed for the blend composites.

3.5.1.1 TENSILE TEST

The tensile tests were carried out in accordance with the procedures as outlined in ASTM D638 [61], using Instron Universal Testing Machine, Model 1125 as shown in Figure 3.6. The machine is of the cross-head movement type, comprising of fixed member carrying one grip and a movable member carrying second grip. Self-aligning grips are employed for holding the test specimen between the fixed member and the movable member to prevent alignment problems. A controlled velocity device mechanism is used and a load-indicating mechanism capable of indicating the 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.

For the POE specimen, cross head speed of 5mm/min was selected. Tensile strength at 5% strain, at yield point, break point and total elongation at break was recorded. In the case of other specimens, the tests were done at high and low speeds. A speed of 15 mm/min was selected to determine tensile strength at yield point, break point and total elongation. For low speed, cross head speed was kept at 1 mm/min and tensile strength at 3% strain and at yield point was calculated.

3.5.1.2 IMPACT TEST

Impact tests were carried out using notched Izod procedure as outlined in ASTM D256 [62] with a Tinius Olsen Model 92T shown in Figure 3.7. In the Izod impact test, a specimen is held as a vertical cantilever beam, and is broken by a swing of the 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.

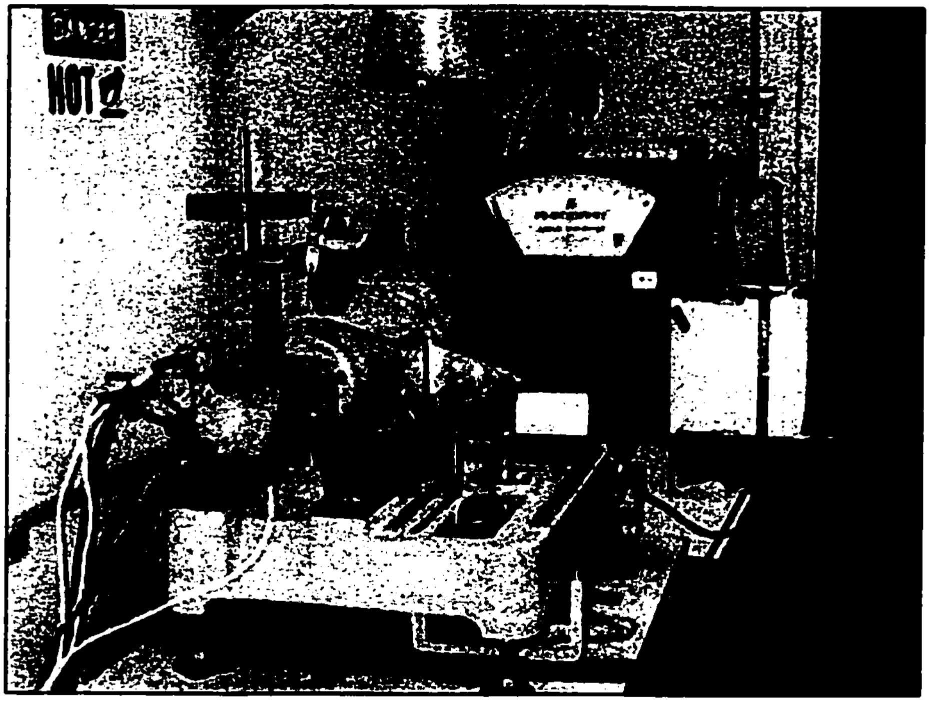

Figure 3.2: Haake Rheomix 600 for mixing

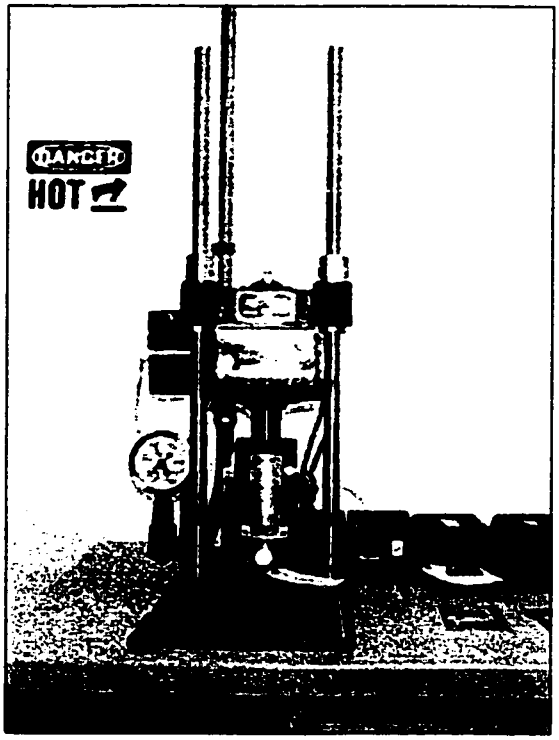

Figure 3.3: Carver Laboratory Press for compression molding

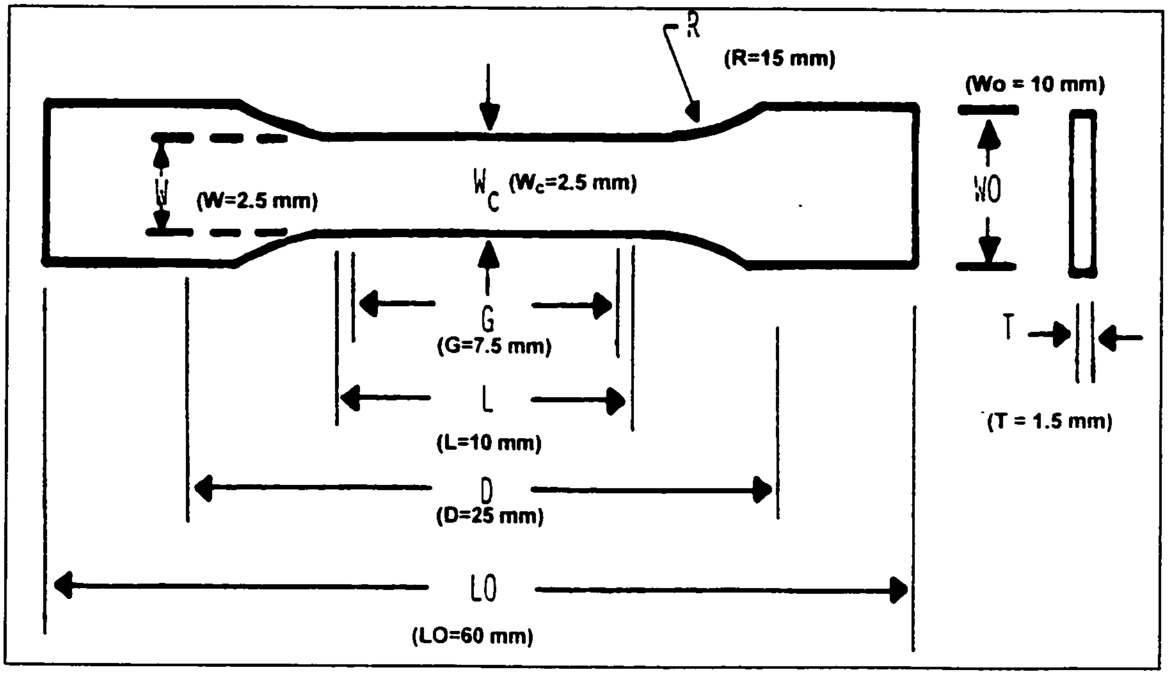

Figure 3.4: Illustration of specimen for tensile tests [61]

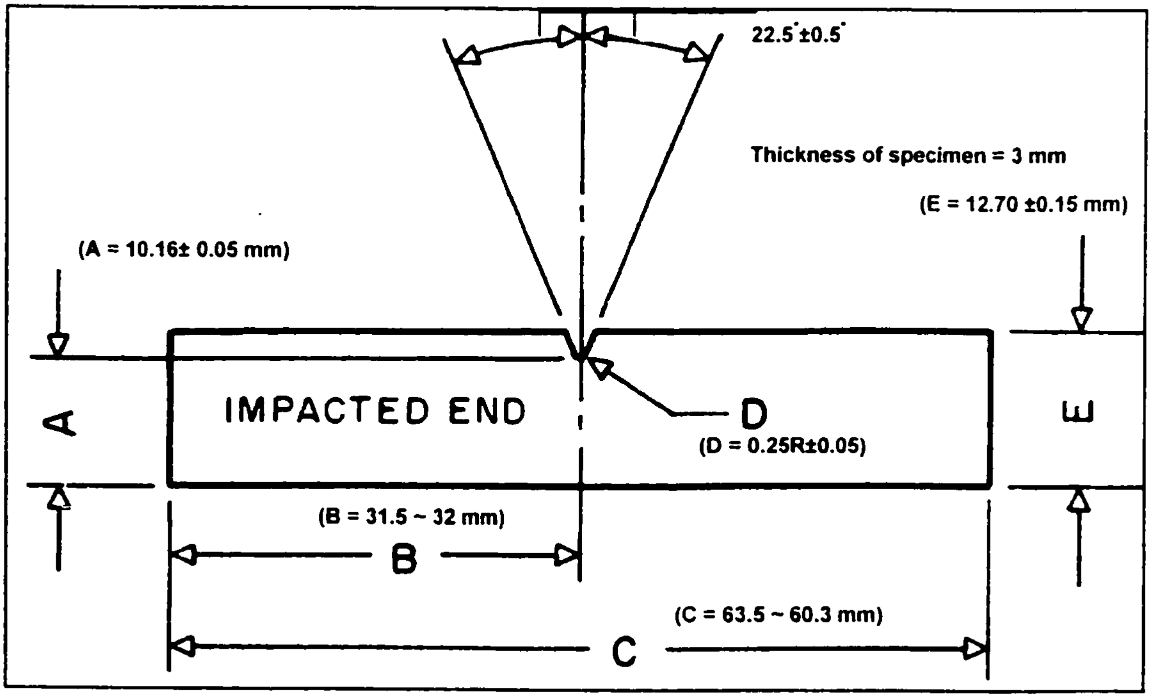

Figure 3.5: Illustrations for specimens for impact test [62]

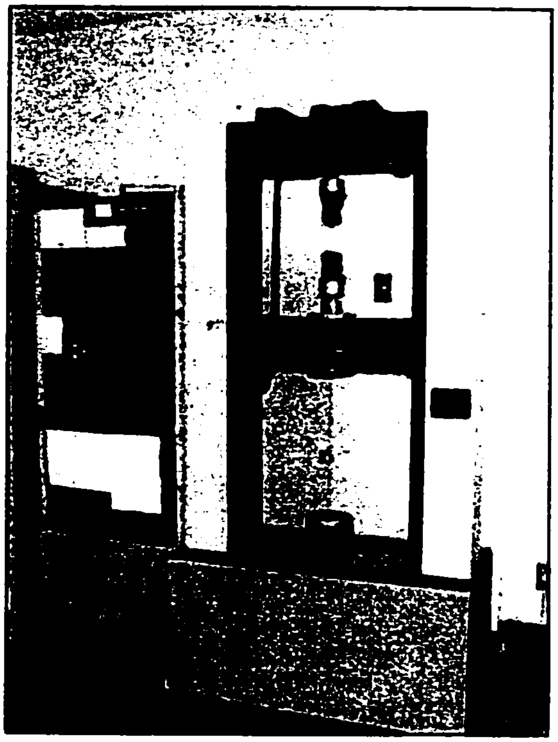

Figure 3.6: Instron Universal Testing Machine

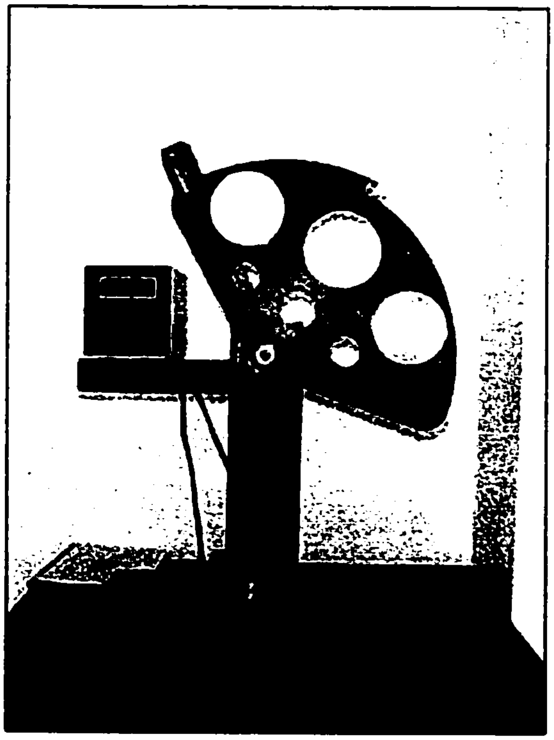

Figure 3.7: Notched Izod Impact Testing Machine

3.5.1.3 HARDNESS TEST

Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation or scratching. Hardness is purely a relative term and should not be confused with wear and abrasion resistance of a plastic material. Durometer hardness test – Type A was performed in order to evaluate the hardness of POE and POE/PC-PE [63].

Durometer hardness test method is based on the penetration of a specified indentor forced into the material under specified conditions. The durometer hardness tester consists of a pressure foot, an indentor and an indicating device. The specimens in the form of sheets piled together of at least 10mm thickness were placed on a hard, flat surface. The pressure foot of the instrument was pressed onto the specimen, making sure that it is parallel to the surface of the specimen. The durometer hardness was read within 1 second after the pressure foot was in firm contact with the specimen [63].

3.5.1.4 STATIC LOAD LIMIT TEST

Static load limit test was conducted in accordance to ASTM F970 [65], in order to determine the recovery properties of the POE/PC-PE blend composites. The test was carried out by measuring the residual compression on the surface of the material after subjecting it to a load of 55 kgs for 24 hours. The indentation was made by indentor plates measuring 28.6mm in diameter.

3.5.1.5 ACCELERATED WEATHERING TEST

Most data on the aging of plastics are acquired through accelerated tests and actual outdoor exposure. The latter being a time-consuming method, accelerated tests are often used to expedite screening the samples with various combinations of additive levels and ratios. A variety of artificial light sources are used to simulate the sunlight such as carbon arc lamps, fluorescent sun lamps and mercury lamps. These light sources, except fluorescent lamp generate a much higher intensity light than natural sun light. A condensation apparatus is used to simulate the deterioration caused by sunlight and water as rain or dew. In this case, the specimens were subjected to exposure to fluorescent lamps and condensation as per ASTM D5208 [66] as shown in Figure 3.8. "QUV accelerated weathering tester" made by Q-Panel Lab Products was used.

The test apparatus basically consists of series of UV lamps, a heated water pan, and test specimen racks. The equipment uses UV-A340 type lamps made by Q-Panel Company. The UVA-340 simulates sunlight in the critical short wavelength UV region between 365 nm and the solar cut-off of 295 nm. The temperature and operating times are independently controlled for UV and condensation effect. The test specimens are mounted in specimen racks with test surfaces facing the lamps.

The test conditions are selected based on requirements and programmed into the unit. The specimens are removed for inspection at a pre-determined time to examine color loss, chalking, and cracking [64, 66].

The specimens were exposed to UV radiation for a period of 20 hours per day for 7 days. Condensation cycle was set for 4 hours per day for 7 days.

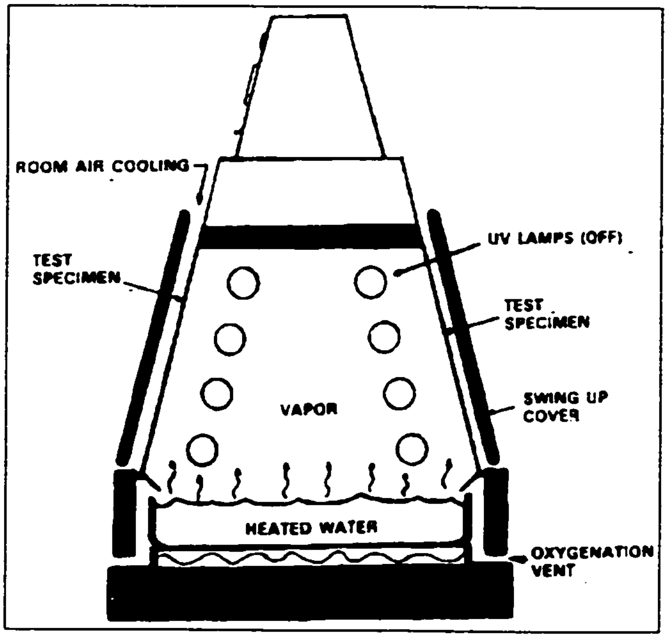

Figure 3.8: Accelerated weathering tester [64]

3.5.2 THERMAL PROPERTIES

Differnetial Scanning Calorimetry (DSC) and dimensional heat stability tests were performed on all formulations.

3.5.2.1 DIFFERENTIAL SCANNING CALORIMETRY TEST

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 Dupont 912 Differential Scanning Calorimeter connected to a Dupont

2100 Thermal Analyzer. The DSC data were analyzed with the Dupont DSC standard Data Analysis Program version 4.0 [66, 67].

Samples of about 10 mg weighed with an accuracy of +/-0.002 mg were tested for each blend. In order to obtain good heat transfer between sample and samples's pan, films of 0.25mm were prepared from each blend using Spectra-Tech Universal Film Maker, then disks with the same diameter that of sample's pan were punched from each film. All samples were heated from room temperature to 150° C at a heating rate of 10° C/min kept isothermally at 150° C for 10 mins. to ensure the complete melting of the crystals, then cooled from 150° C to room temperature at a cooling rate of 10°C/min, then heated again from -20° C to 160° C at a heating rate of 10°C/min. The melting temperature and latent heat of melting were measured in the second heating cycle as specified in ASTM D 3417 [67, 68]. The DSC cell shown in Figure 3.9 was carefully calibrated for temperature and latent heat using Indium etalon sample which has a latent heat of melting at 28.42 J/g and melting temperature of 156.61°C. The Indium sample was scanned at the same heating rate of 10° C/min. All the scans were done under nitrogen atmosphere at the flow rate of 20ml/min [67, 68].

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 [68].

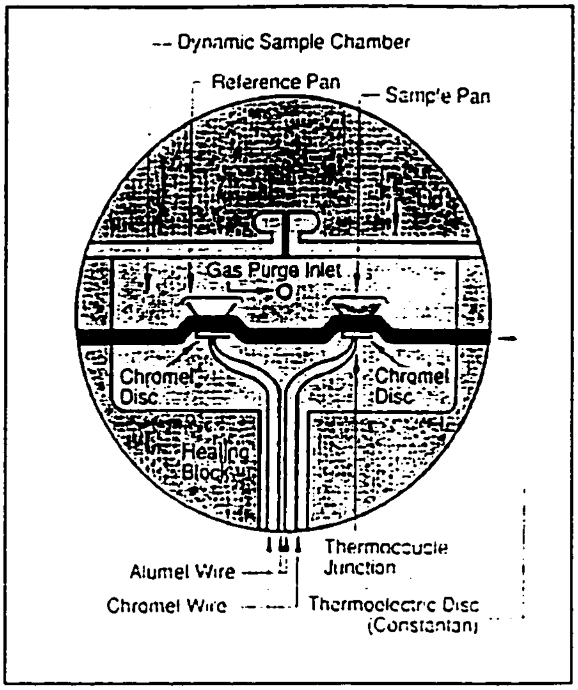

Figure 3.9: DSC Cell

3.5.2.2 DIMENSIONAL HEAT STABILITY TEST

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 A126.10. 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 in the form of smooth flat steel plate approximately 13 mm thick and 25 mm smaller than the sheet, on top of the tests 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 hrs. at 65±1 °C. At the end of the heating period, the sheets on their supporting plate were removed from the oven and conditioned at 23±1 °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 [69].

3.6 STATISTICAL ANALYSIS

All the indicated values for mechanical and thermal tests 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.

CHAPTER 4

RESULTS AND DISCUSSION

Mechanical and thermal properties of formulations of POE, PC-PE and composites of POE/PC-PE were tested at three stages.

Stage-1 consisted of testing for selection of suitable lubricant and its amount in the formulation and also selection of POE/PC-PE blends with better results.

Stage-2 involved testing of selected blend formulations with UV and heat stabilizers.

Stage-3 consisted of testing the blend formulations prepared at stage-2 after subjecting them to accelerated weathering effect.

4.1 SELECTION OF LUBRICANT

Stearic acid (SA), obtained from Fisher Scientific was used as lubricant. Prior to selection of SA as lubricant, other lubricants such as Naftonic oil - shelflex 371 and hostalub FA1 were tested. They were rejected as a lubricant because formulation was not easily released from the mixing chamber of Rheomix after the end of mixing period.

4.2 MECHANICAL PROPERTIES OF POE AND PC-PE FORMULATIONS

Table 4.1 shows break strength, elongation at break and impact strength of formulation prepared with sole matrix of POE, PC-LDPE and PC-HDPE. The data show that both PC-PE exhibit no elongation but are very hard as indicated by higher break strength values. However the loss of elasticity is also reflected as reduction in toughness with very low impact strength values and brittle failure during impact testing. These also indicate that the PC-PE matrix is not functioning as an effective binder. Thus to improve the mechanical properties of PC-PE formulations, blends of PCPE with POE were prepared as per Table 3.1, 3.2 and tested.

Table 4.1: Break strength, elongation at break and impact strength of compounded POE and PC-PE with 3 phr and 4 phr SA

Sample Identification	Break Strength (MPa)	Elongation at Break (%)	Impact Strength (J/m)
Formulations with 3 phr SA			
POE	6.64	1587	266.6
PC-HDPE	6.68	-	104
PC-LDPE	8.09	-	41.5
Formulations with 4 phr SA			
POE	6.82	1667	275.7
PC-HDPE	6.62	-	101.2
PC-LDPE	7.95	-	43.1

4.3 MECHANICAL PROPERTIES OF POE/PC-PE BLEND COMPOSITES

Mechanical properties in terms of break strength, elongation at break and impact strength were determined for POE/PC-PE blend composites with PC-PE contents of 20, 40, 50, 60 and 80%. These results are presented in Table 4.2 through 4.7. Calculated values assuming the additivity of each component are also presented along with the experimental values. Figures 4.1 through 4.6 show the normalized tensile and impact strength values, so that the data for unblended POE represents 100%.

4.3.1 MECHANICAL PROPERTIES OF POE/PC-LDPE BLEND COMPOSITES

As indicated in Table 4.2, the experimental break strength of POE/PC-LDPE blend composites decreases with the addition of 20% recycled content. The experimental values show a non-uniform downward trend upon further addition. This is in contrary to the calculated values, which follows additivity rule and an upward trend is expected. As shown in Figure 4.1, the blend composites made with 3 phr SA and 40 to 60% recycled content, the variation in the experimental break strength values is within 10%. Overall, the blend composites made with 3 phr SA, have higher break strength than those made with 4 phr SA, especially at 50% and more recycled polymer content in the blends.

The elongation data presented in Table 4.3 indicates that both blend composites of POE/PC-LDPE, as expected, lose elasticity with the incorporation of recycled content. Though the experimental values are higher than the calculated values, as shown in Figure 4.2, the influence of the recycled component is noticeable. There is a steady drop in the elasticity with incorporation of PC-LDPE from 20% to 60% level. At 80% PC-LDPE contents, the blend composites suffered complete loss of elasticity. In this case too, blends made with 3 phr SA exhibited better results than their 4phr counterparts.

The loss in elasticity is usually accompanied by loss in the toughness which in turn should also reduce the impact strength of the material. Table 4.4 and Figure 4.3 present results of the impact tests for POE/PC-LDPE blend composites.

Surprisingly, in case of POE/PC-LDPE blend composites, the impact strength increases upon addition of the PC-LDPE to POE formulations. As indicated in Figure 4.3, only the 20/80 blend composites with 3 phr SA exhibit about 3% lower and blend composites with 4 phr SA show about 9% higher experimental impact strength as compared to calculated values.

As shown in Figure 4.3, the normalized experimental impact strength of POE/PC-LDPE blends steadily increases by almost 8% ~ 10% for both 3 phr SA and 4 phr SA blends upon incorporation of 20% to 60% of recycled content. This may be attributed to the similarity in chemical structure of LLDPE component present in PC-LDPE and the POE macromolecule. The increase in impact strength may also be due to difference in the melt rheology during the compounding of $CaCO_3$ filled blends. The final blend viscosity will depend on the ratio of higher viscosity PC-LDPE to lower viscosity POE present in the formulation. Melt viscosity affects the dispersion of filler particles, which in turn, affects the impact strength. Here, too the blends composites made with 3 phr SA perform better as compared to 4 phr SA blend composites.

Table 4.2: Break strength of POE/PC-LDPE blend composites with 3 phr and 4 phr SA

PC-LDPE (%)	Break strength with 3 phr SA			
	Experimental Value (MPa)	Normalized Value (%)	Calculated Value (MPa)	Normalized Value (%)
0	6.64	100	6.64	100
20	6.06	91.3	6.93	100.4
40	6.34	95.5	7.22	108.7
50	5.84	88.0	7.37	111.0
60	6.16	92.8	7.51	113.1
80	6.83	102.9	7.80	117.5
100	8.09	121.8	8.09	121.8
	Break strength with 4 phr SA			
0	6.82	100	6.82	100
20	6.07	89.0	7.05	103.3
40	6.35	93.1	7.27	106.6
50	5.60	82.1	7.39	108.3
60	5.43	79.6	7.50	109.9
80	6.44	94.4	7.72	113.3
100	7.95	116.6	7.95	116.6

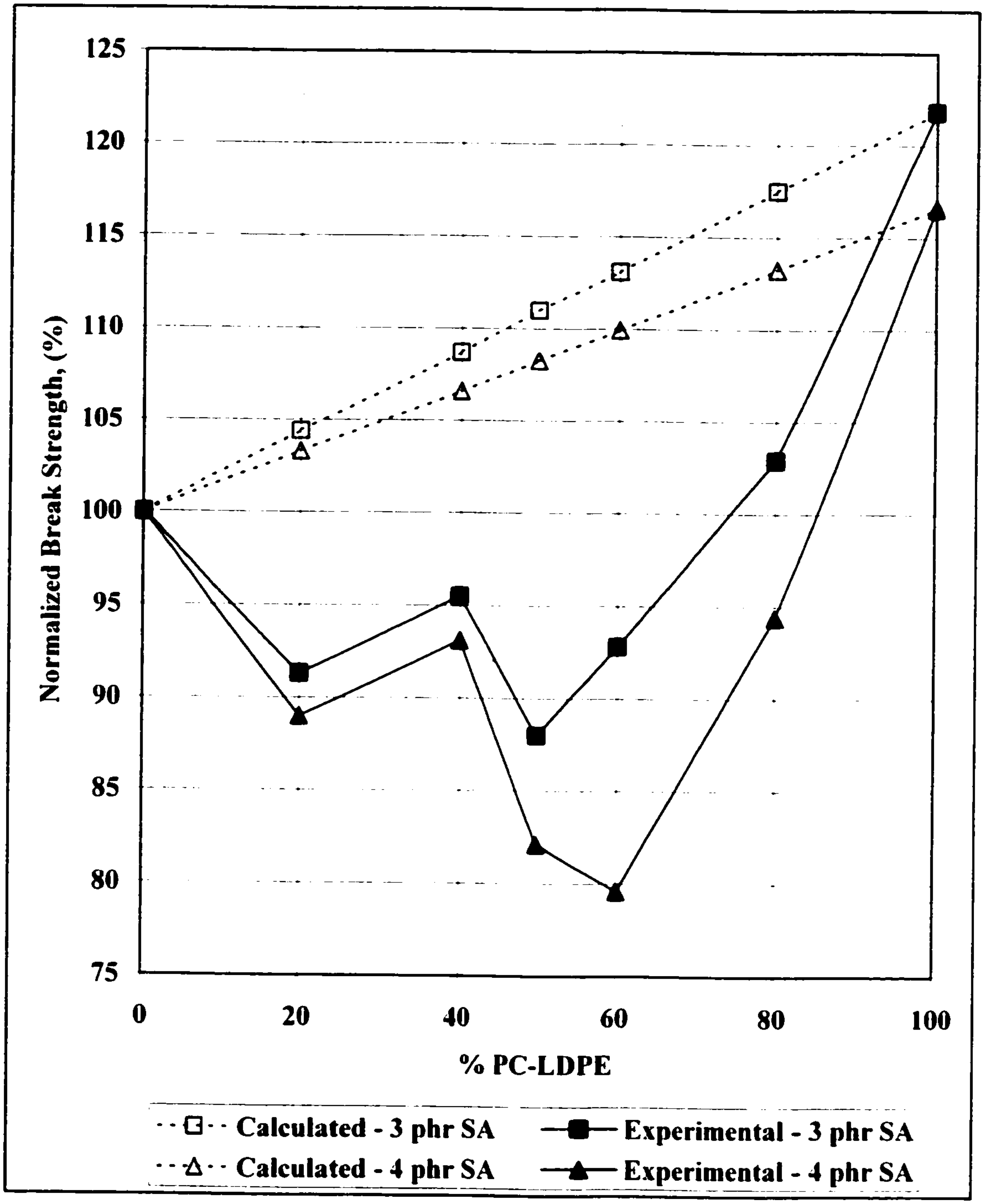

Figure 4.1: Normalized break strength of POE/PC-LDPE blend composites with 3 and 4 phr SA, as a function of PC-LDPE content

Table 4.3: Elongation at break of POE/PC-LDPE blend composites with 3 phr and 4 phr SA

PC-LDPE (%)	Elongation at break with 3 phr SA			
	Experimental Value (%)	Normalized Value (%)	Calculated Value (%)	Normalized Value (%)
0	1587	100	1587	100
20	1337	84.25	1269.60	80
40	1225	77.19	952.20	60
50	1037	65.34	793.50	50
60	1012	63.77	634.80	40
80	0	0	317.40	20
100	0	0	0	0
	Elongation at break with 4 phr SA			
0	1667	100	1667	100
20	1321	79.24	1333.60	80
40	1232	73.91	1000.20	60
50	926	55.55	833.50	50
60	753	45.17	666.80	40
80	0	0	333.40	20
100	0	0	0	0

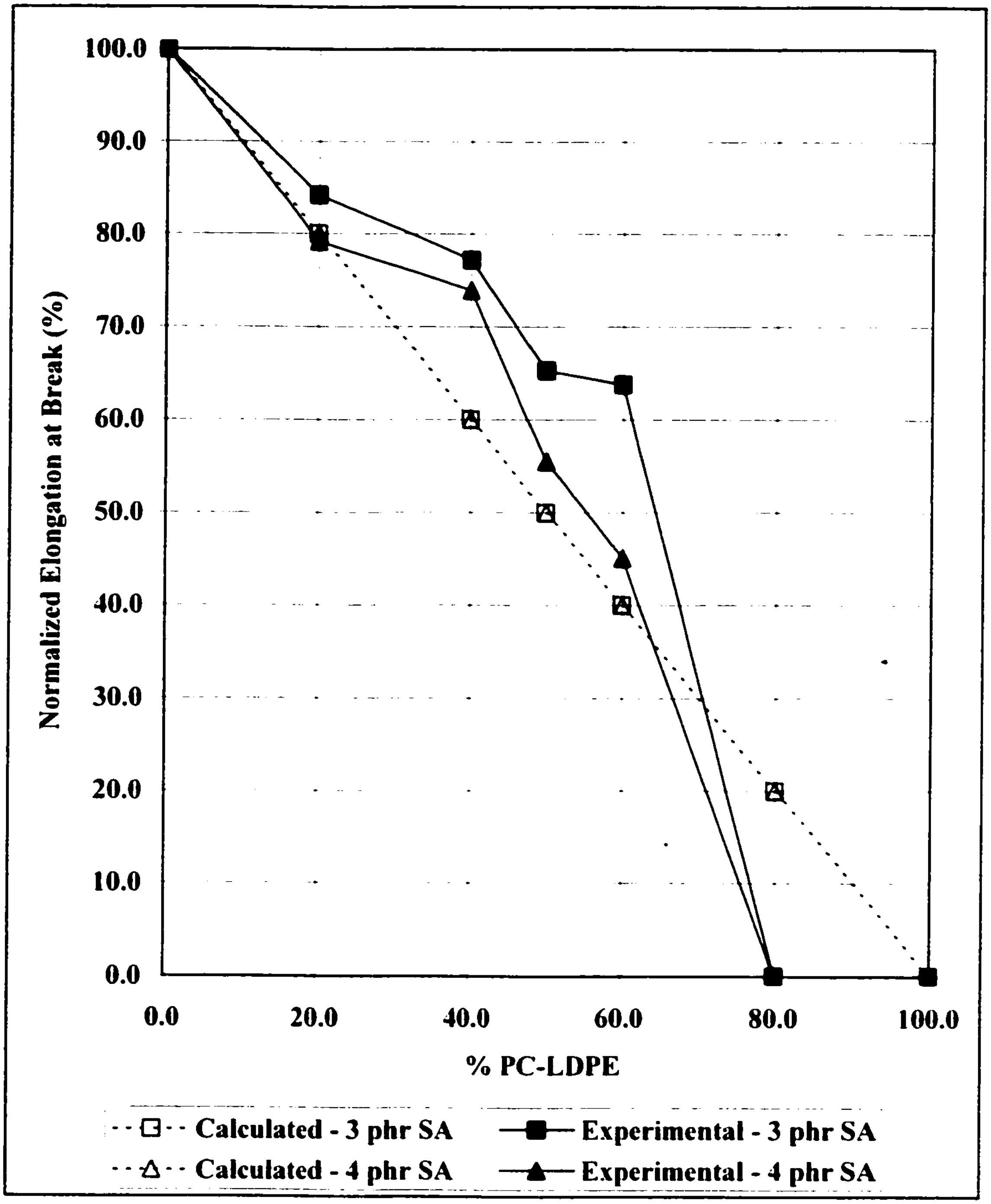

Figure 4.2: Normalized elongation at break of POE/PC-LDPE blend composites with 3 and 4 phr SA, as a function of PC-LDPE content

Table 4.4 : Impact strength of POE/PC-LDPE blends composites with 3 phr and 4 phr SA

PC-LDPE (%)	Impact Strength with 3 phr SA			
	Experimental Value (J/m)	Normalized Value (%)	Calculated Value (J/m)	Normalized Value (%)
0	266.60	100	266.60	100
20	289	108.40	221.58	83.11
40	342.10	128.32	176.56	66.23
50	346	129.78	154.05	57.78
60	368	138.03	131.54	49.34
80	78.6	29.48	86.52	32.45
100	41.5	15.57	41.50	15.57
	Impact Strength with 4 phr SA			
0	275.70	100	275.70	100
20	305.20	110.7	229.18	83.10
40	332.50	120.60	182.66	66.30
50	335.80	121.80	159.40	57.80
60	359.10	130.25	136.14	49.30
80	114.30	41.46	89.62	32.50
100	43.10	15.63	43.10	15.60

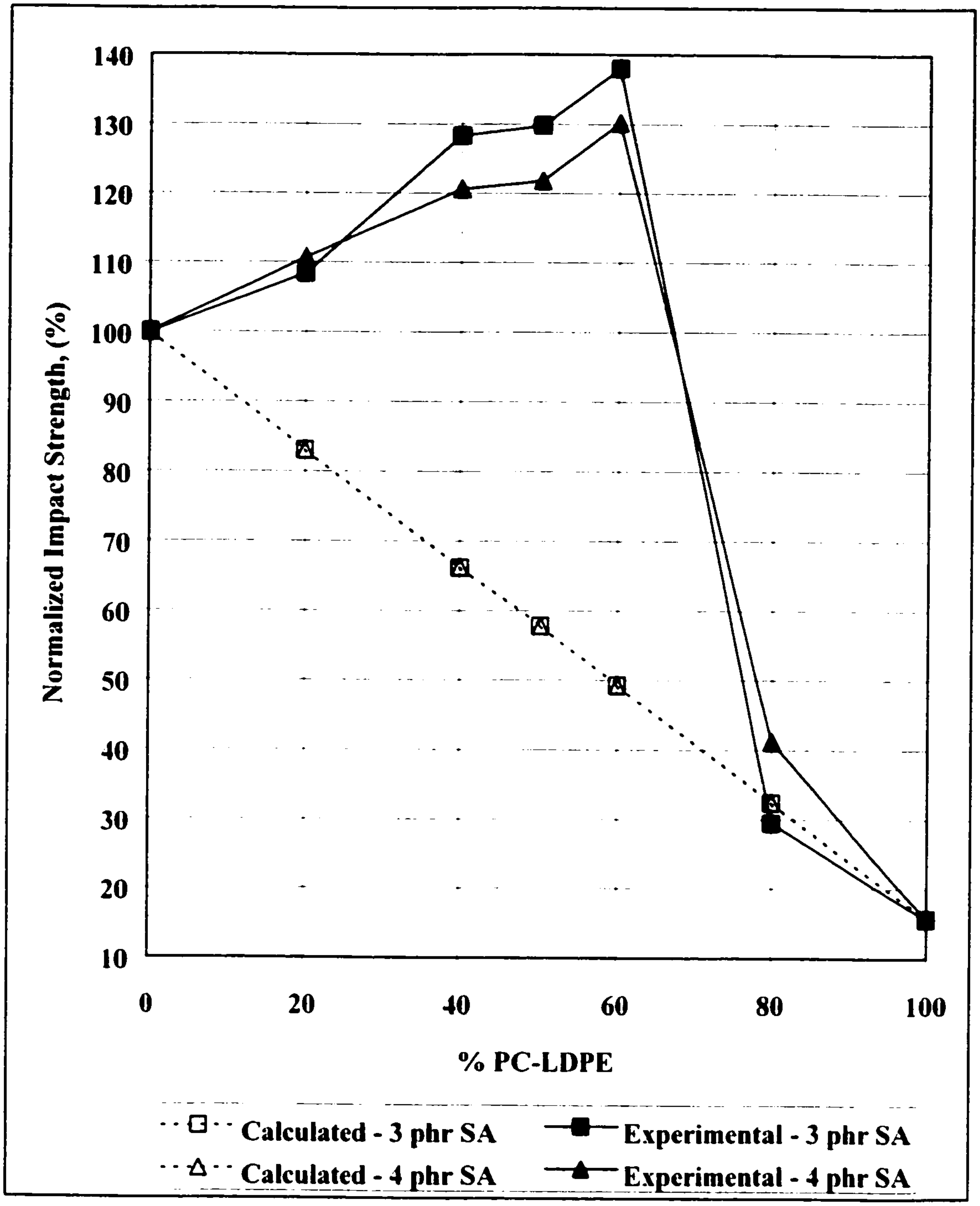

Figure 4.3: Normalized impact strength of POE/PC-LDPE blend composites with 3 and 4 phr SA, as a function of PC-LDPE content

4.3.2 MECHANICAL PROPERTIES OF POE/PC-HDPE BLEND COMPOSITES

For PC-HDPE blend composites, a similar trend in mechanical behavior is observed as that in POE/PC-LDPE blend composites. Table 4.5 through 4.7 present the tensile and impact strength properties of POE/PC-HDPE blend composites with 3 and 4 phr SA lubricant. Figure 4.4 through 4.6 present the normalized calculated and experimental values for POE/PC-HDPE blend composites.

As shown in Table 4.5 and Figure 4.4, the break strength shows a similar non-uniform downward trend as POE/PC-LDPE blend composites. Also the elongation at break values presented in Table 4.6 and Figure 4.5 decreases as in case of POE/PC-LDPE blend composites. However, the effect in case of PC-HDPE is more pronounced than PC-LDPE. This may be attributed to the fact that HDPE is more crystalline than PC-HDPE which adversely affects the elongation.

The impact strength also exhibits similar trend as that of POE/PC-LDPE blends with dramatic reduction of impact values of 20/80 POE/PC-HDPE blend composites. In this case too, blend composites made with 3 phr SA performed better than 4 phr SA blend composites.

Based on the results obtained at this stage, blends with 3 phr SA as lubricant and 40%, 50% and 60% PC-PE contents were selected for weathering effects with incorporation of UV and heat stabilizers.

Table 4.5 : Break strength of POE/PC-HDPE blend composites with 3 phr and 4 phr SA

PC-HDPE (%)	Break strength with 3 phr SA			
	Experimental Value (MPa)	**Normalized Value (%)**	**Calculated Value (MPa)**	**Normalized Value (%)**
0	6.64	100	6.64	100
20	5.57	83.89	6.65	100.12
40	5.69	85.69	6.66	100.24
50	5.53	53.28	6.66	100.30
60	5.45	82.08	6.66	100.36
80	5.72	86.14	6.67	100.48
100	6.68	100.60	6.68	100.60
	Break strength with 4 phr SA			
0	6.82	100	6.82	100
20	5.74	84.16	5.74	99.41
40	5.43	79.62	5.43	98.83
50	5.55	81.38	5.55	98.53
60	5.41	79.33	5.41	98.24
80	5.68	83.28	5.68	97.65
100	6.62	97.07	6.62	97.07

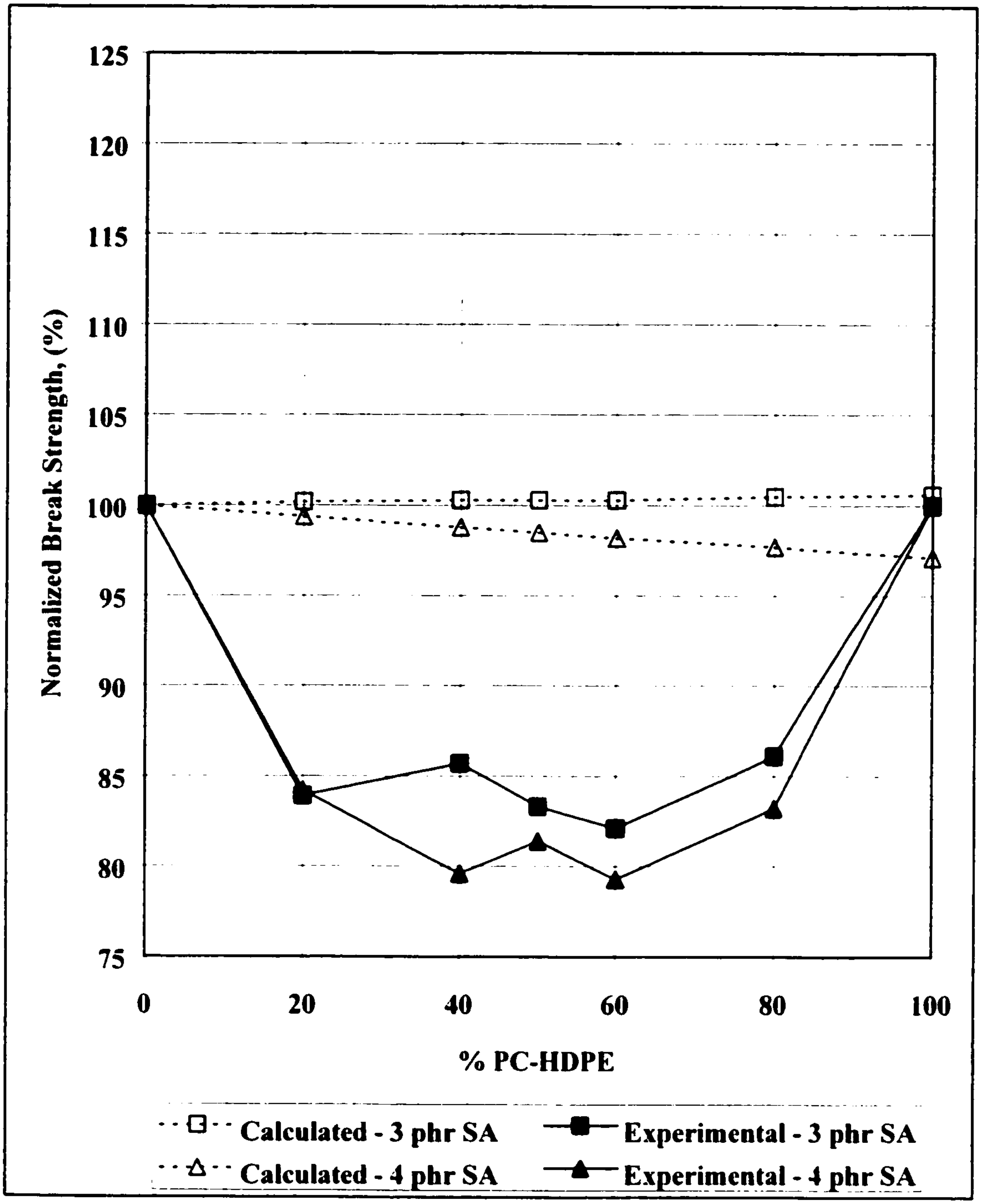

Figure 4.4: Normalized break strength of POE/PC-HDPE blend composites with 3 and 4 phr SA, as a function of PC-HDPE content

Table 4.6: Elongation at break of POE/PC-HDPE blend composites with 3 phr and 4 phr SA

PC-HDPE (%)	**Elongation at break with 3 phr SA**			
	Experimental Value (%)	**Normalized Value (%)**	**Calculated Value (%)**	**Normalized Value (%)**
0	1587	100	1587	100
20	1118	70.45	1269.60	80
40	817	51.29	952.20	60
50	726	45.75	793.50	50
60	590	37.18	634.80	40
80	265	16.70	317.40	20
100	0	0	0	0
	Elongation at break with 4 phr SA			
0	1667	100	1667	100
20	1115	66.89	1115	80
40	773	46.37	773	60
50	636	38.15	636	50
60	496	29.75	496	40
80	88	5.28	88	20
100	0	0	0	0

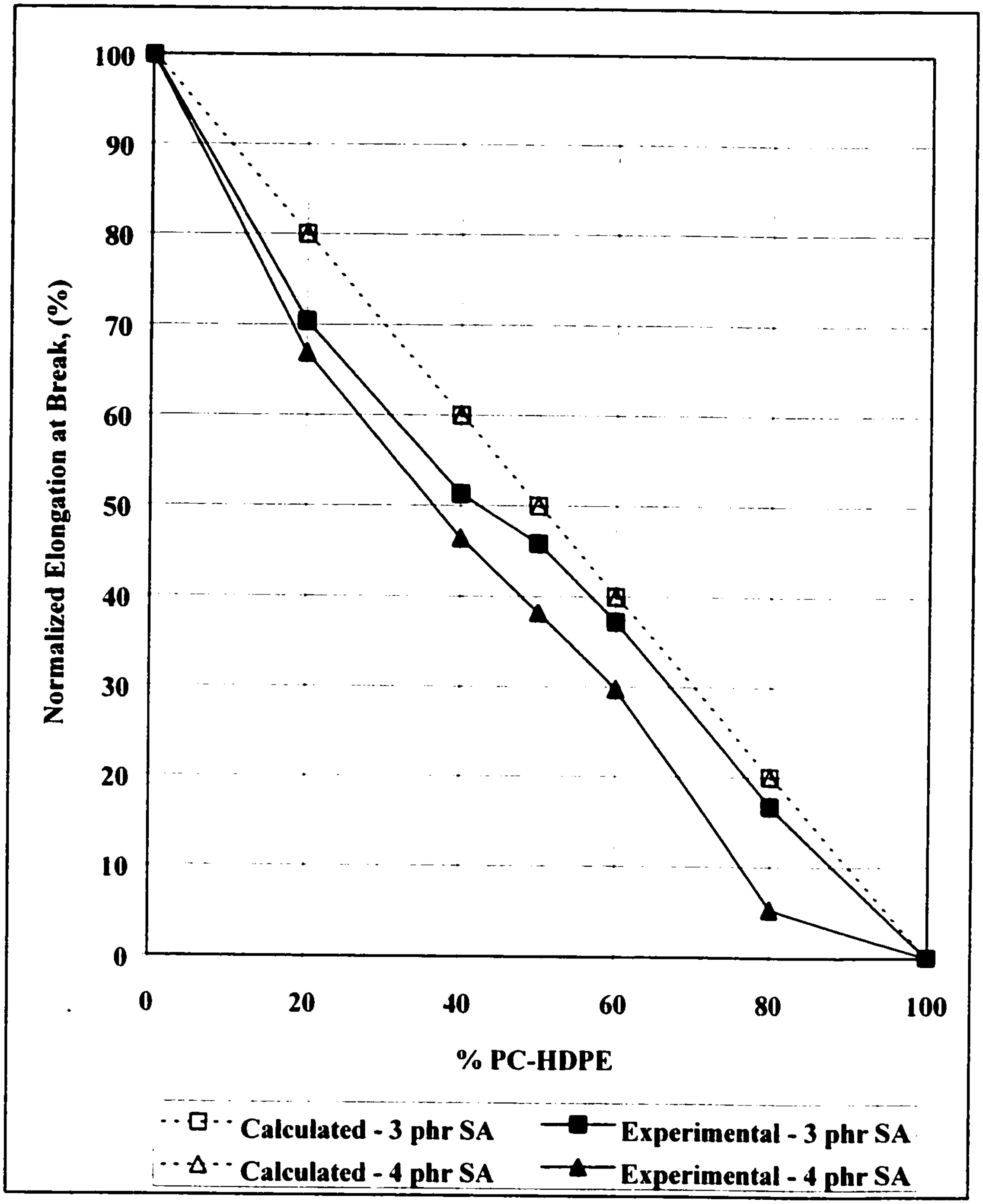

Figure 4.5: Normalized elongation at break of POE/PC-HDPE blend composites with 3 and 4 phr SA, as a function of PC-HDPE content

Table 4.7 : Impact strength of POE/PC-HDPE blend composites with 3 phr and 4 phr SA

PC-HDPE (%)	**Impact Strength with 3 phr SA**			
	Experimental Value (J/m)	**Normalized Value (%)**	**Calculated Value (J/m)**	**Normalized Value (%)**
0	266.60	100	266.60	100
20	306.70	115.04	234.08	87.80
40	361.70	135.67	201.56	75.60
50	365.20	136.98	185.30	69.50
60	359.60	134.88	169.04	63.41
80	235.10	88.18	136.52	51.21
100	104	39.01	104	39.01
	Impact Strength with 4 phr SA			
0	275.70	100	275.70	100
20	315.50	114.44	240.80	87.34
40	345.60	125.35	205.90	74.68
50	376.70	136.63	188.45	68.35
60	344.80	125.06	171	62.02
80	267.40	96.99	136.10	49.37
100	101.20	36.71	101.2	36.71

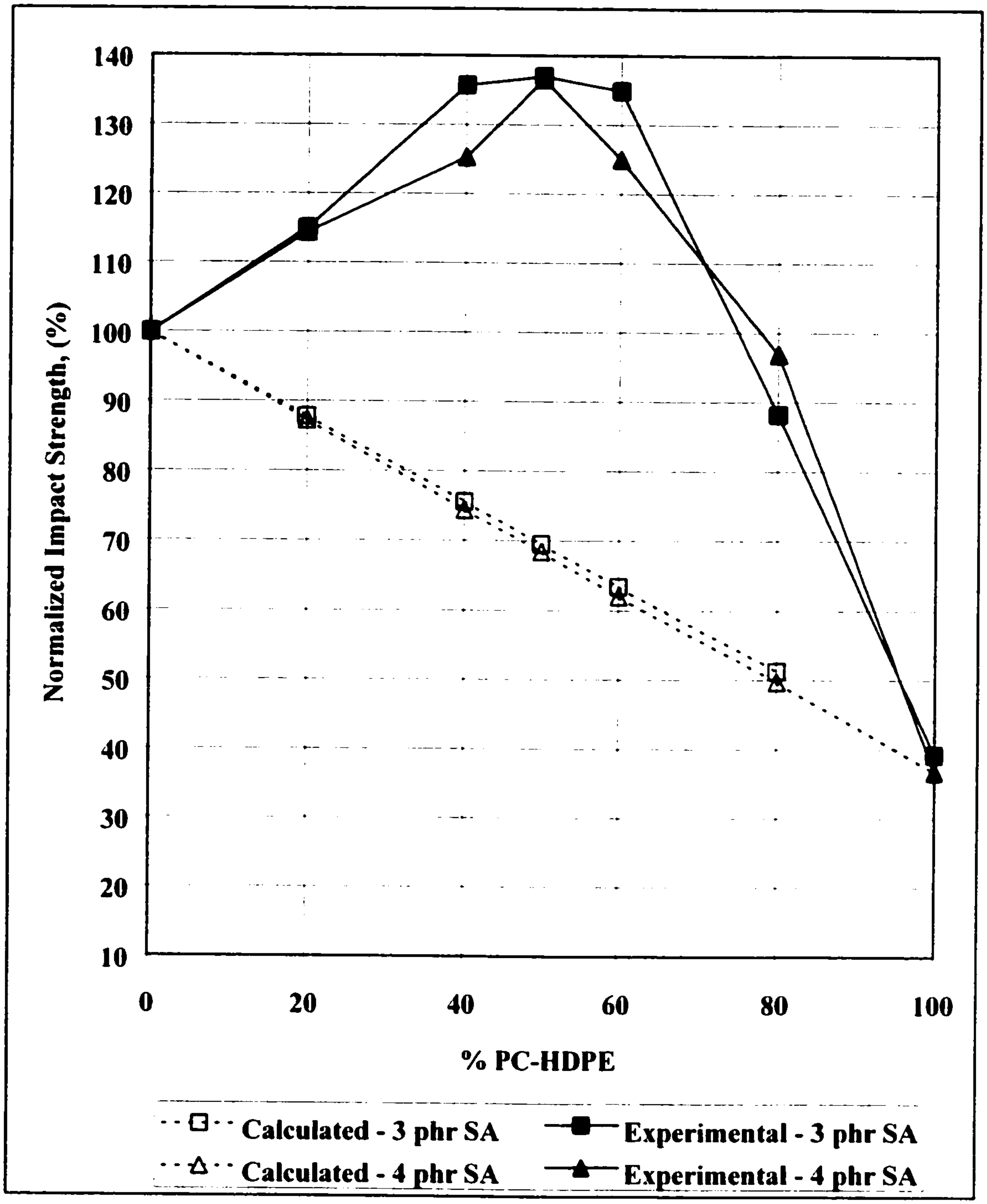

Figure 4.6: Normalized impact strength of POE/PC-HDPE blend composites with 3 and 4 phr SA, as a function of PC-HDPE content

4.4 EFFECTS ON TENSILE PROPERTIES DUE TO WEATHERING

Table 4.8 and 4.9 and Figure 4.7 through 4.10 present the tensile properties in terms of Young's modulus, yield strength, break strength and elongation at break measured for heat and UV stabilized POE formulation and POE/PC-PE blend composites containing 40%, 50% and 60% PC-PE before and after subjecting them to accelerated weathering effect.

Young's modulus and yield strength of the POE and POE/PC-PE blend composites are presented in Table 4.8 and Figure 4.7. As shown in the Table 4.8, the modulus of unweathered sole POE formulation is very low at 560 MPa, owing to the elastomeric property of the POE. Upon addition of PC-PE to the POE formulations, the Young's modulus increases steadily for both the blend composites of POE/PC-PE.

In case of POE/PC-LDPE blend composites, the increase in Young's modulus is a steady rise in value from 877 MPa for 60/40 unweathered compositions to 1107 MPa for 40/60 blend compositions. However, the composition with sole matrix of PC-LDPE exhibit 66% increase in Young's modulus value to 1842 MPa.

Similar upward trend in Young's modulus values is observed in the POE/PC-HDPE blend compositions. However, due to highly crystalline macromolecular structure of HDPE, there is almost 125% increase to 1265 MPa in Young's modulus values upon addition of 20% PC-HDPE to the POE formulation. An increase in the Young's modulus values upon further addition of PC-HDPE is gradual except for 100% PC-HDPE formulation, which exhibit almost 70% increase similar to PC-LDPE formulation.

Weathered POE formulation exhibit almost 22% increase in Young's modulus as compared to unweathered POE formulation. This may be attributed to the morphological changes in the macromolecular structure due to photooxidative effect resulting into degradation and cross-linking due to exposure to accelerated weathering effect.

The weathered POE/PC-LDPE blend composite also experience an increase of almost 35% in Young's modulus values for 60/40 POE/PC-LDPE blend. The upward trend continues for entire range of composition, owing to the stiffening of the specimen due to development of cross-linked structure as a result of thermal and UV exposure.

Similarly, the weathered POE/PC-HDPE composite exhibits increase in Young's modulus values, though not as pronounced as PC-LDPE. This is probably due to the relatively stable crystalline morphological structure of HDPE macromolecules.

The yield strength values are also presented in Table 4.8 and Figure 4.7. The yield strength values of unweathered POE formulation increases upon incorporation of PC-PE components due to higher yielding of the PEs compared to the elastomeric POE, which is more ductile. Upon incorporation of the PC-LDPE to POE/PC-LDPE blend composites, the yield strength increases by about 40% and does not experience much variation with increasing of PC-LDPE content suggesting almost similar adhesion between the matrix and $CaCO_3$ filler in all the cases. In contrast, the formulation with 100% PC-LDPE matrix is very brittle and break without yielding and elongation. The unweathered POE/PC-HDPE blend composites show almost 75% increase in the yield strength values. The upward trend continues such that at 100% PC-HDPE content the yield strength is not measurable due to continuous increase in stiffness and as a result of highly crystalline HDPE macromolecular structure.

The weathering effect on the formulation of POE shows a slight reduction in the yield strength values and not much notable change is observed for the POE/PC-LDPE blend composites. Similarly for weathered POE/PC-HDPE blend composites also, no significant change in yield strength values is observed, with slight increase in the values as shown in Figure 4.8 and Table 4.8.

Table 4.9 presents the break strength and elongation at break of unweathered and weathered POE formulation and blend composites of POE/PC-PE. Figure 4.9 shows the break strength and elongation at break for unweathered and weathered PC-LDPE blend composites, while Figure 4.10 displays that of PC-HDPE blend composites.

As indicated in Table 4.9 and Figure 4.9, the break strength values of the unweathered POE/PC-LDPE blend composites displays non-uniform trend. However, the elongation data reveals that upon addition of PC-LDPE, the formulation starts losing elasticity such that, 100% PC-LDPE formulation displays no elasticity at all. Similarly, unweathered POE/PC-HDPE blend composites also exhibit non-uniform trend in the break strength. As in the case of PC-LDPE blends, the elasticity reduces upon addition of PC-HDPE content and is totally lost for 100% PC-HDPE formulation. However the loss in elasticity is more noticeable in PC-HDPE blend composites. The weathering does not much affect the break strength for either of PC-PE blend composites, however, there is further reduction in the elongation values for both blend composites upon weathering.

Table 4.8: Young's modulus and yield strength of unweathered and weathered POE and POE/PC-PE composites

Sample Identification	Young's Modulus (MPa)		Yield Strength (MPa)	
	Unweathered	Weathered	Unweathered	Weathered
POE	560	683	3.04	2.65
POE/PC-LDPE (%)				
60-40	877	1180	4.25	4.19
50-50	970	1206	4.17	4.29
40-60	1107	1295	4.23	4.68
100	1842	1940	-	-
POE/PC-HDPE (%)				
60-40	1265	1405	5.29	5.39
50-50	1467	1602	5.86	6.16
40-60	1662	1753	6.65	6.8
100	2144	2299	-	-

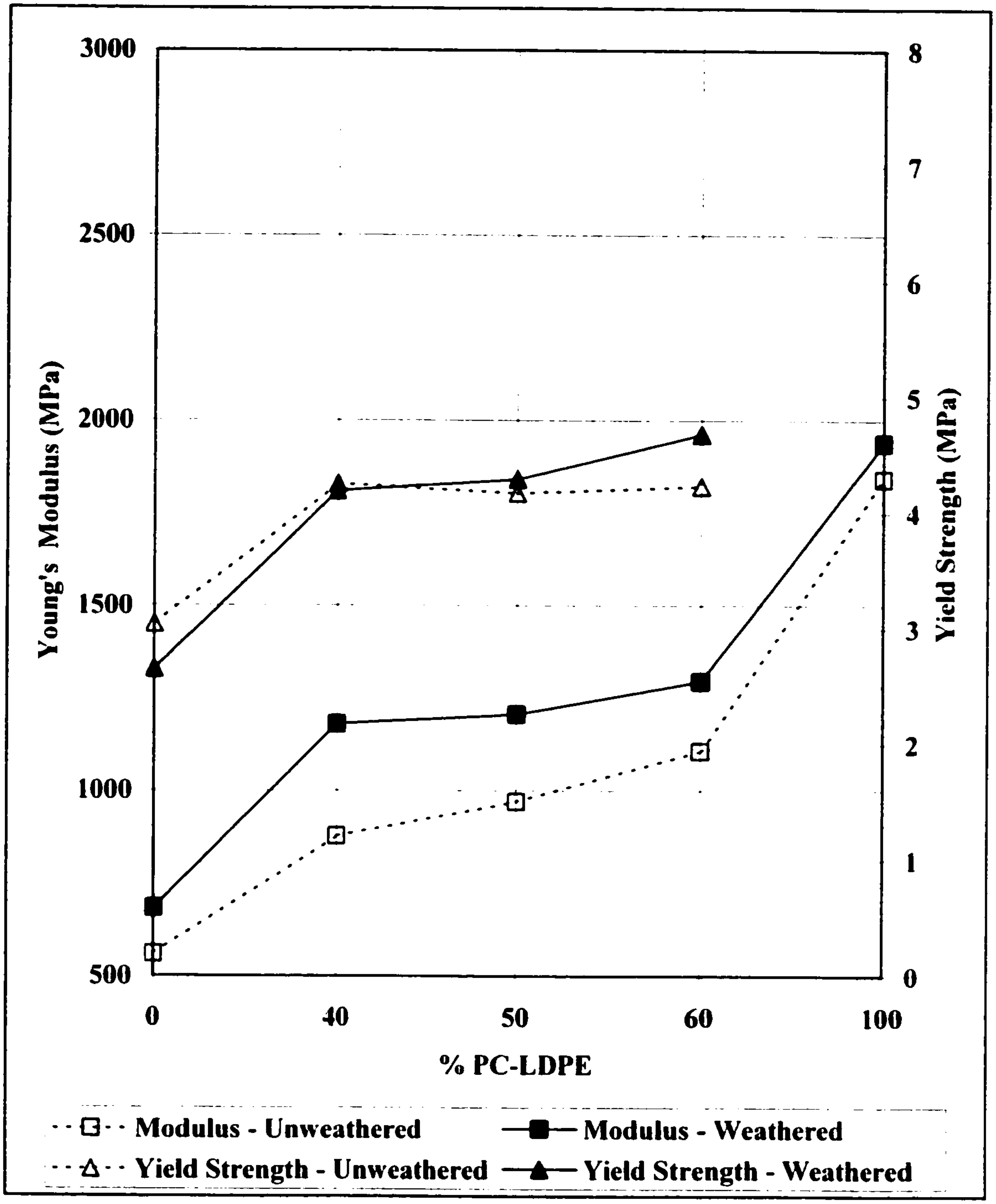

Figure 4.7: Young's modulus and yield strength of unweathered and weathered POE/PC-LDPE composites with 3 phr SA

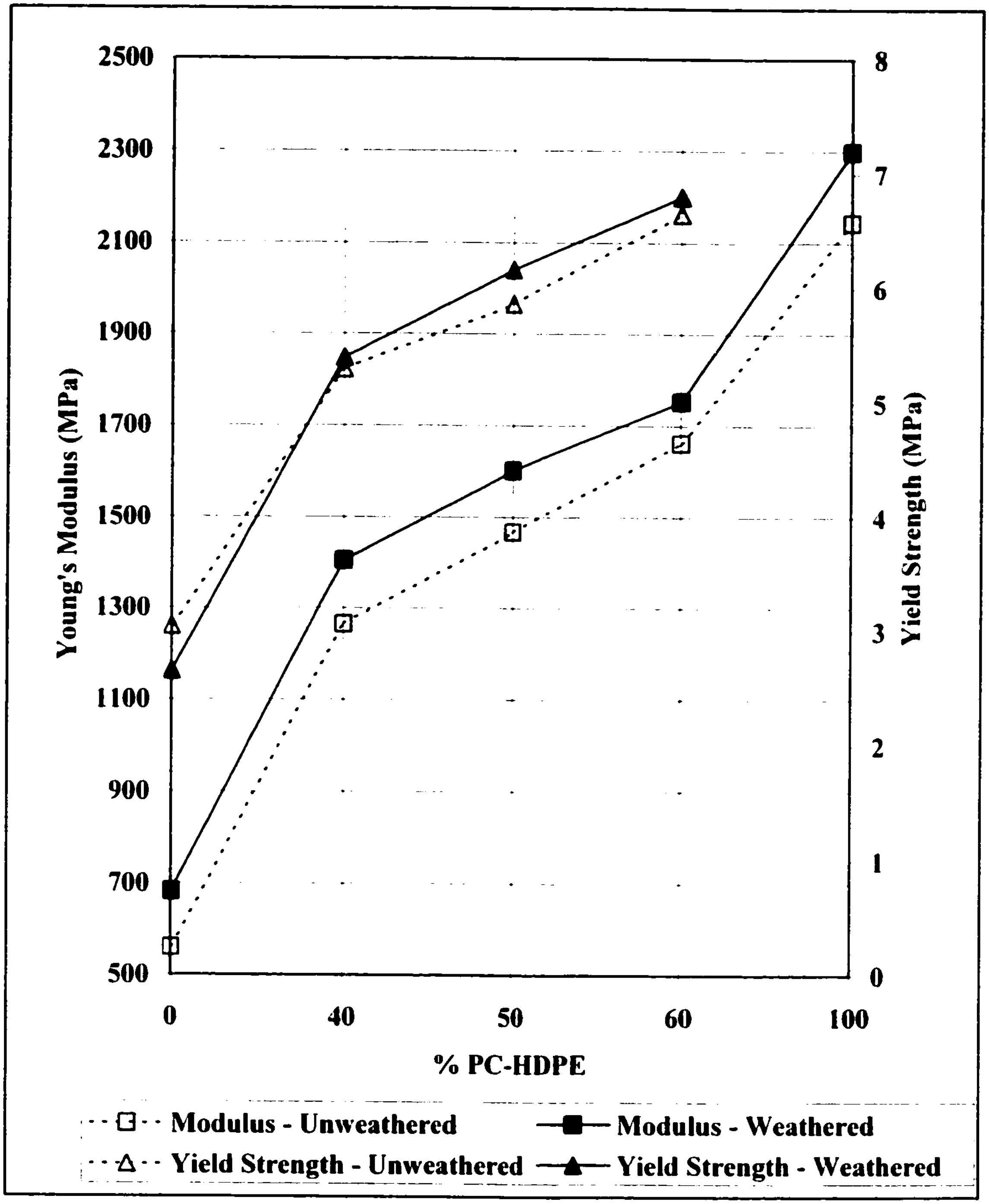

Figure 4.8: Young's modulus and yield strength of unweathered and weathered POE/PC-HDPE composites with 3 phr SA

Table 4.9: Break strength and elongation at break of unweathered and weathered POE and POE/PC-PE composites

Sample Identification	Break Strength (MPa)		Elongation at Break (%)	
	Unweathered	Weathered	Unweathered	Weathered
POE	6.87	6.64	1557	1567
POE/PC-LDPE (%)				
60-40	7.02	6.76	1320	1278
50-50	6.5	6.56	1282	1205
40-60	6.46	6.1	1040	970
100	7.52	5.41	-	-
POE/PC-HDPE (%)				
60-40	5.92	6.14	857	894
50-50	6.02	5.95	858	767
40-60	5.89	5.53	674	514
100	8.4	8.47	-	-

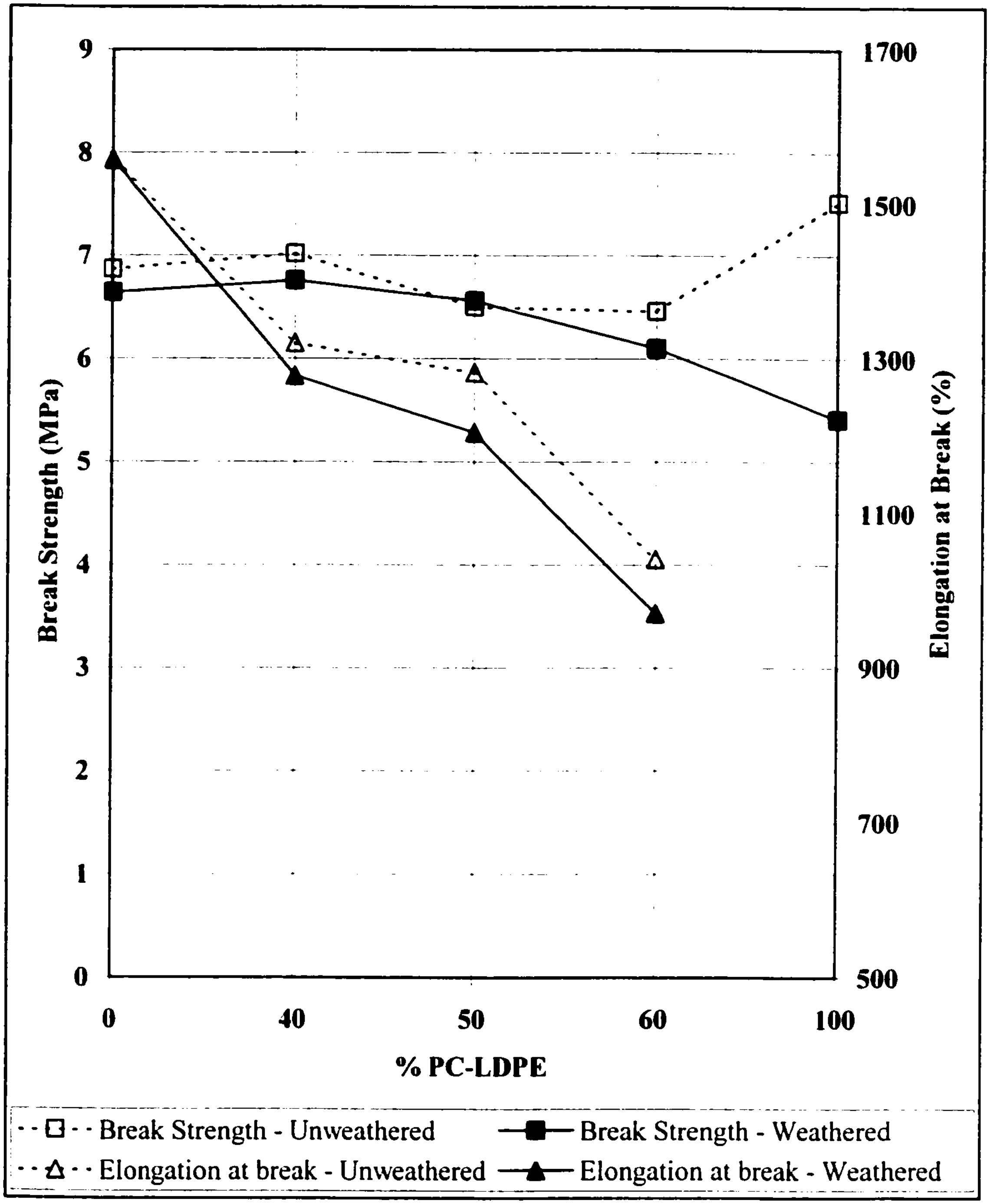

Figure 4.9: Break strength and elongation at break of unweathered and weathered POE/PC-LDPE composites with 3 phr SA

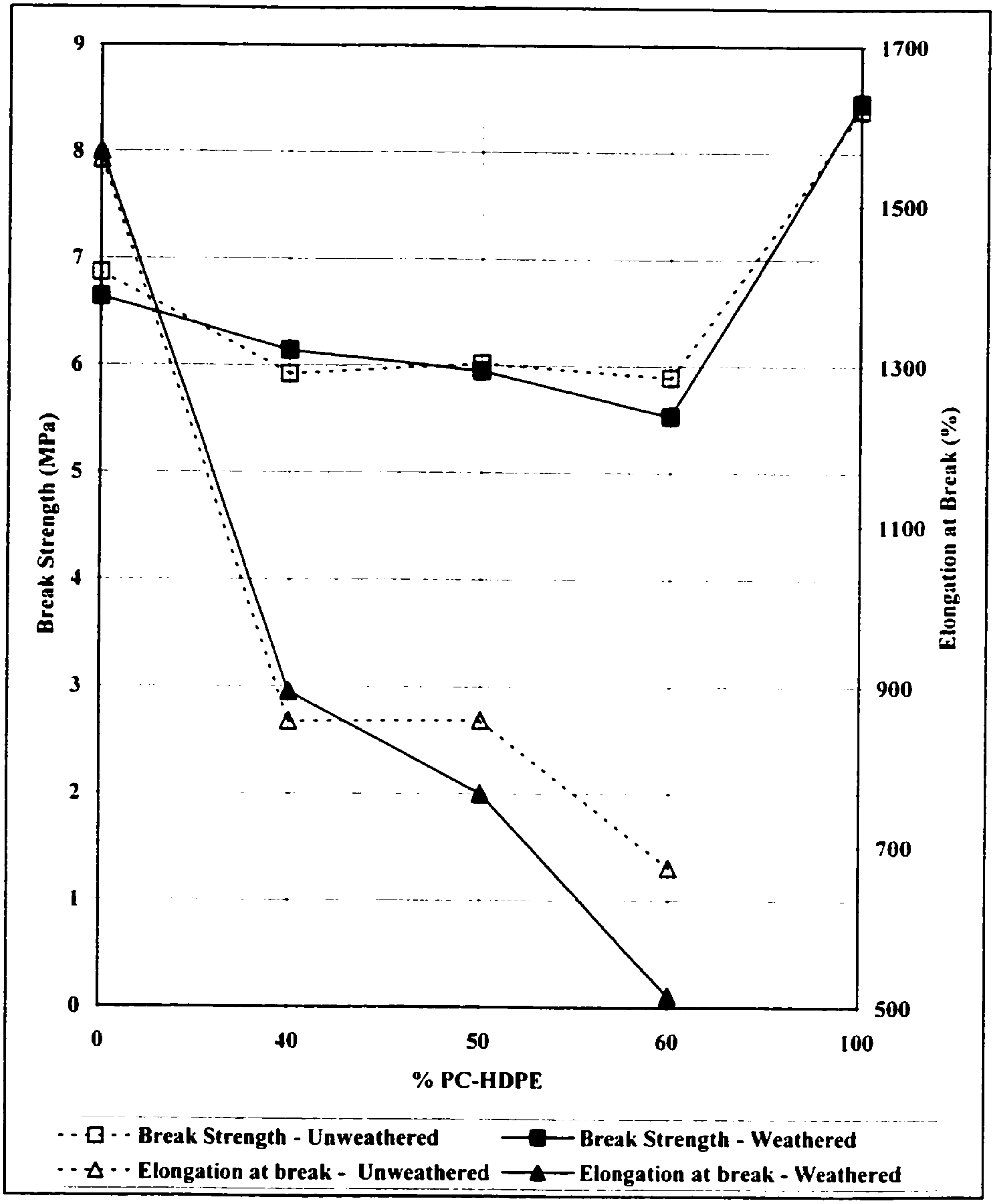

Figure 4.10: Break strength and elongation at break of unweathered and weathered POE/PC-HDPE composites with 3 phr SA

4.5 STATIC LOAD LIMIT TEST OF POE/PC-PE BLEND COMPOSITES

Table 4.10 presents the static load limit test results. The residual compression recorded for 50/50 POE/PC-LDPE and 40/60 POE/PC-HDPE blend composites is less than 1%. Overall, the data indicates that no significant residual compression was observed in any of the blend composites after subjecting them to a load of 55 kg for 24 hrs.

Table 4.10: Static load limit data of POE/PE-PE blend composites

Sample Identification	Initial Thickness (mm)	Final Thickness (mm)	Residual Compression (mm)
POE/PC-LDPE (%)			
60-40	1.585	1.585	0.000
50-50	1.51	1.495	0.015
40-60	1.455	1.455	0.000
POE/PC-HDPE (%)			
60-40	1.585	1.585	0.000
50-50	1.515	1.515	0.00
40-60	1.435	1.43	0.005

4.6 HARDNESS OF POE/PC-PE BLEND COMPOSITES

The hardness test for POE/PC-PE composites were carried out by Type A Shore Durometer. The indentation hardness is inversely related to the penetration and is dependent on the elastic modulus and viscoelastic behavior of the material. Table 4.11 shows the scale reading for each blend composites, which is an inverse function of the indentor extension. As shown in Table 4.11, the hardness decreases with increase in POE content in the blend formulation.

Table 4.11: Hardness of POE/PC-PE blend composites as a function of PC-PE content

POE/PC-LDPE (%)	Hardness Value	POE/PC-HDPE (%)	Hardness Value
100-00	94.8	100-00	94.8
60-40	93	60-40	92.5
50-50	90.8	50-50	96.2
40-60	86.2	40-60	88.2

4.7 PROCESSABILITY

The data presented in Table 4.12 represents the values of constant torque, which occurs during the last two minutes before the end of the mixing.

The values indicated in Table 4.12 show the forces involved in mixing the viscous melt, which are measured as the torque acting on the rotors and can be co-related with melt viscosity.

Table 4.12: Steady state torque as a function of PC-PE contents

POE/PC-PE %	Steady state torque (g m)			
	POE/PC-LDPE		POE/PC-HDPE	
	3 phr SA	4 phr SA	3 phr SA	4 phr SA
100/00	1000	1000	1000	1000
80/20	1025	1025	1050	1050
60/40	1280	1150	1125	1050
50/50	1300	1250	1150	1100
40/60	1350	1300	1162	1150
20/80	1750	1650	1200	1150
00/100	1850	1700	1300	1200

4.8 THERMAL ANALYSIS OF POE AND PC-PE FORMULATIONS USING DSC TECHNIQUE

DSC analysis data of uncompounded and compounded polyolefin is presented in Table 4.13, 4.14 and Figures 4.11 through 4.16.

The DSC melting thermogram of POE – "Engage 8440" presented in Table 4.13 and Figure 4.11 show a broad melting range with a peak at 94.5° C diffusing into a long, low temperature tail. The DSC melting temperature provided by the producer of "Engage 8440" is 94°C.

The uncompounded and compounded PC-LDPE shown in Table 4.13 and Figure 4.13 exhibit a broad melting range characterized by two melting peaks with first peak at about 114°~115°C and second peak occurring at 124°C. This can be attributed to the presence of LLDPE component in the PC-LDPE, which may contain non-uniform distribution of α-olefin comonomer, resulting into segregation during crystallization.

The uncompounded and compounded PC-HDPE shown in Figure 4.15 exhibit a single sharp peak and high latent heat value as compared to that of PC-LDPE, due to the highly crystalline nature of the HDPE.

For compounded polyolefin, as shown in Table 4.13 and Table 4.14, experimental latent heat of melting and crystallization respectively are compared with calculated values. Calculated values were obtained by an additivity relationship taking into account the weight fractions of each component of the formulation.

The latent heat data presented in Table 4.13 and 4.14 show good agreement between the calculated and experimental values. This suggests that within the compound, the ability of individual polymers to crystallize is not hindered by the presence of calcium carbonate filler and other ingredients of the formulation. The same conclusion is obtained when the transition temperatures of compounded and uncompounded polyolefins are compared.

The crystallinity data, as expected shows an increasing trend in the following order: POE<PCLDPE<PCHDPE i.e. crystallinity increases from semi-crystalline POE and LDPE to highly crystalline HDPE.

It should be noted that the crystallization and melting thermograms are similar, depicting the same morphological features in melting and crystallization. As was expected, there is a difference of about 10°C ~ 12°C between melting and crystallization temperatures, because for polymers in the molten state, a significant degree of supercooling, usually of about 10°C below melting point is required before crystallization.

The thermal characteristics of POE blends with PC-PE are described in the following section.

Table 4.13: DSC melting data of polyolefins and compounded polyolefins

Sample Identification	Latent Heat (J/g)		Crystallinity (%)		T_m (°C)	
	Calculated	Experimental	Calculated	Experimental	Peak	
					I	II
Without additives						
POE	-	75.6	-	25.8	-	94.6
PC-LDPE	-	126.3	-	43.1	114.9	124.0
PC-HDPE	-	173.0	-	59.0	-	128.6
Compounded polyolefins with 200phr $CaCO_3$ and 3phr SA						
POE	26.8	26.1	9.1	8.9	-	94.9
PC-LDPE	43.6	45.2	14.9	15.4	114.7	123.9
PC-HDPE	59	59.6	20.1	20.3	-	128.0
Compounded polyolefins with 200phr $CaCO_3$ and 4phr SA						
POE	27.4	27.1	9.4	9.2	-	95.2
PC-LDPE	44.0	44.2	15.0	15.1	114.7	123.7
PC-HDPE	59.4	59.4	20.3	20.3		127.9

Table 4.14: DSC crystallization data of polyolefins and compounded polyolefins

Sample Identification	Latent Heat (J/g)		Crystallinity (%)		T_c (°C)	
	Calculated	Experimental	Calculated	Experimental	Peak	
					I	II
Without additives						
POE	-	75.5	-	25.8	-	76.9
PC-LDPE	-	127.1	-	43.4	102	111.0
PC-HDPE	-	172.8	-	59.0	-	115.6
Compounded polyolefins with 200phr $CaCO_3$ and 3phr SA						
POE	26.8	26.7	9.1	9.1	-	80.5
PC-LDPE	43.6	44.8	14.9	15.3	100.7	112.6
PC-HDPE	59	60.0	20.1	20.5	-	115.6

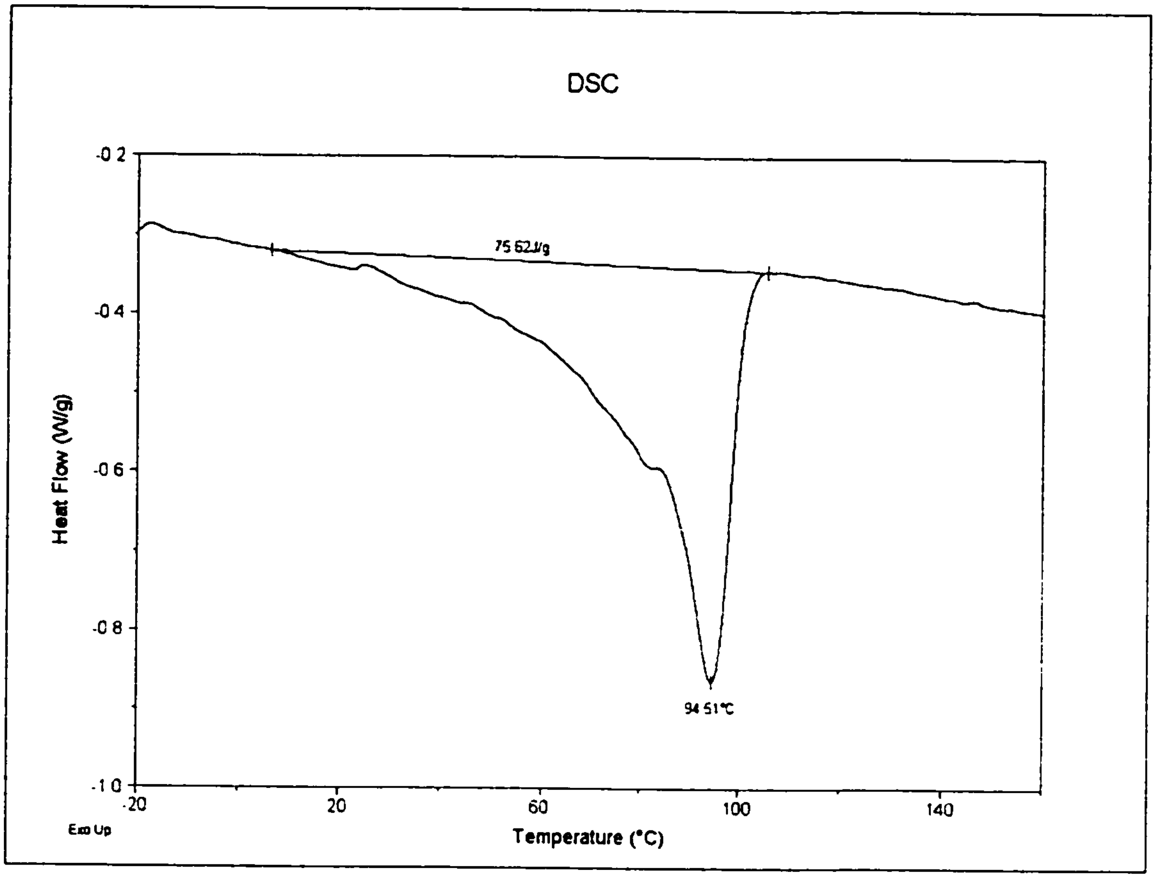

Figure 4.11: DSC melting curve for POE "Engage 8440"

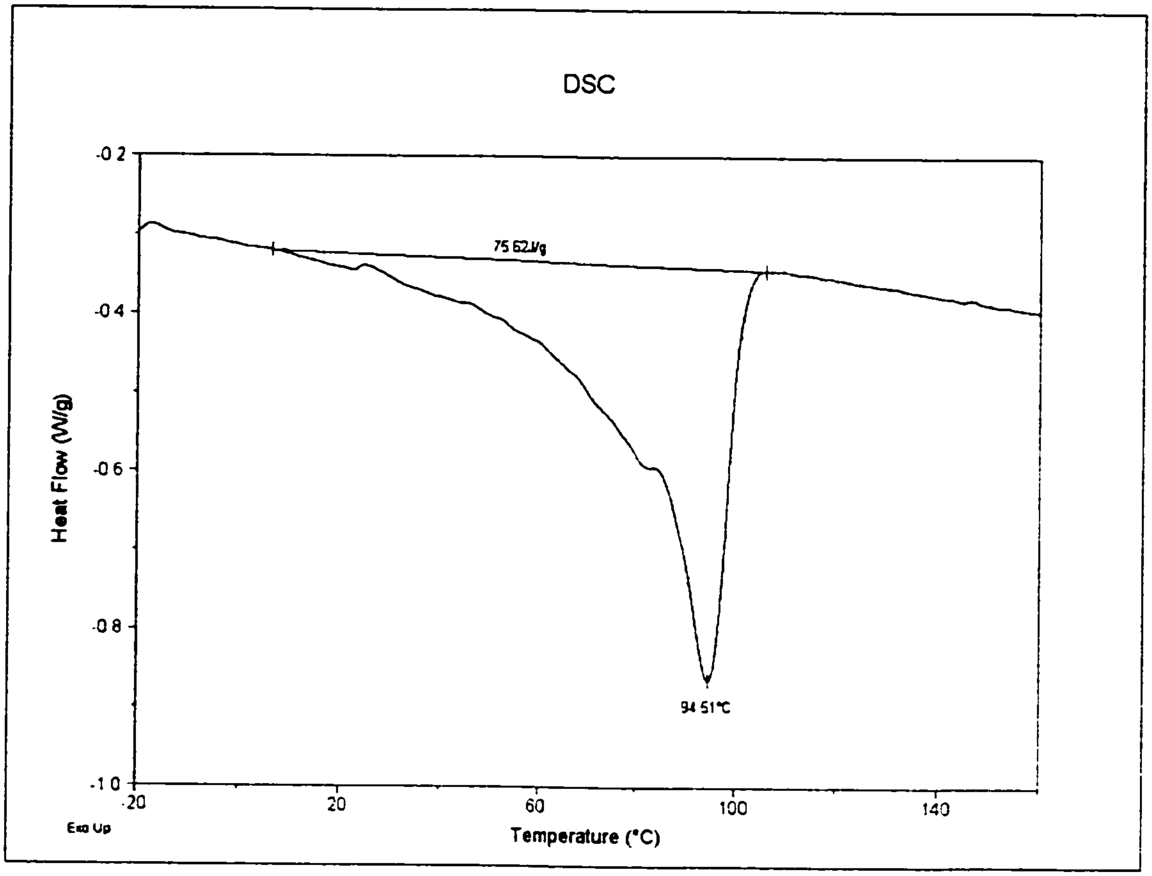

Figure 4.12: DSC crystallization curve for POE "Engage 8440"

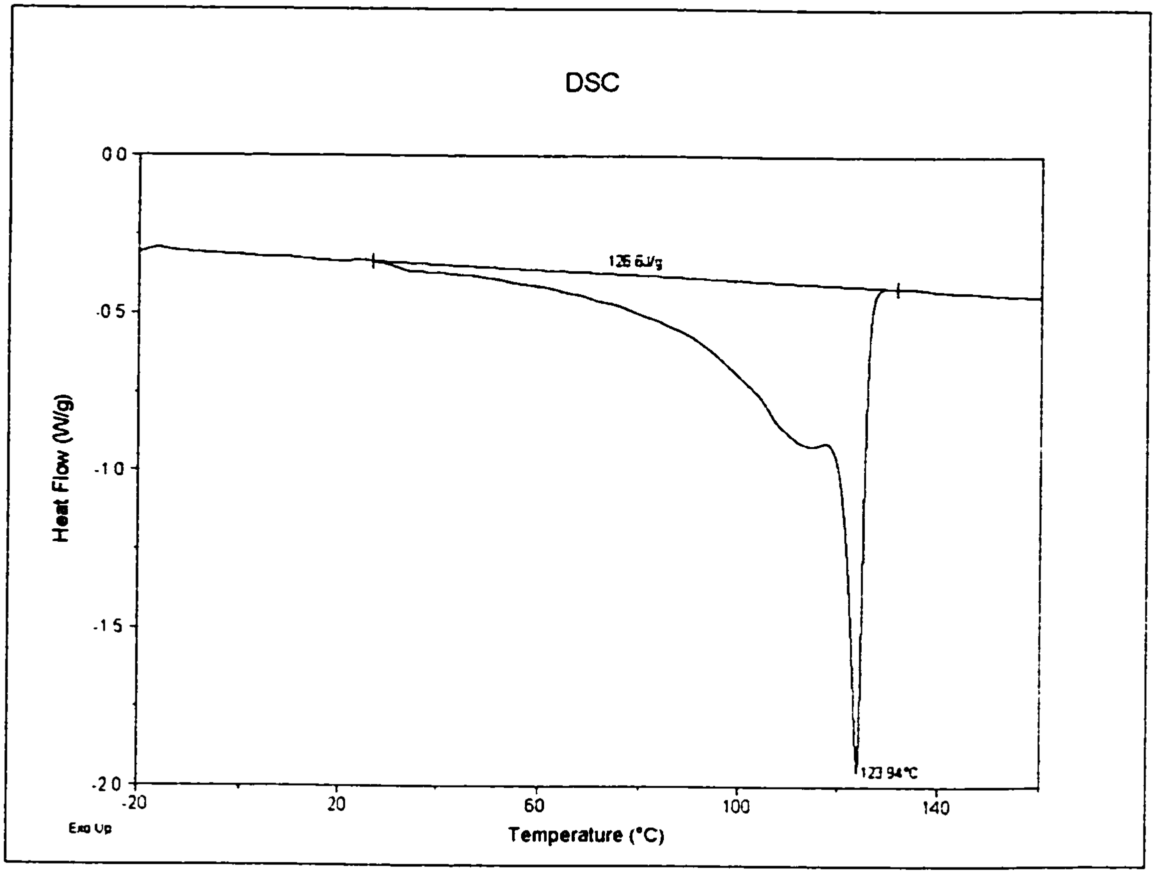

Figure 4.13: DSC melting curve for PC-LDPE

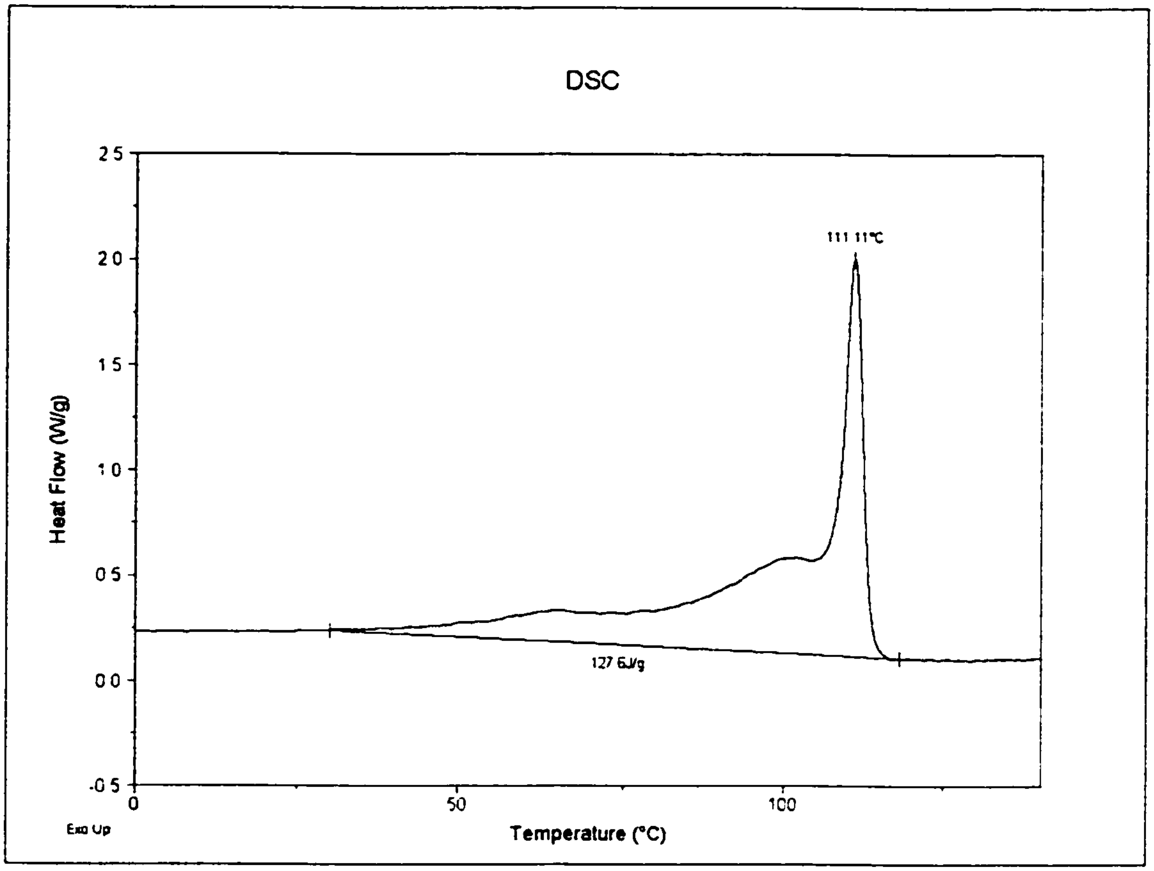

Figure 4.14: DSC crystallization curve for PC-LDPE

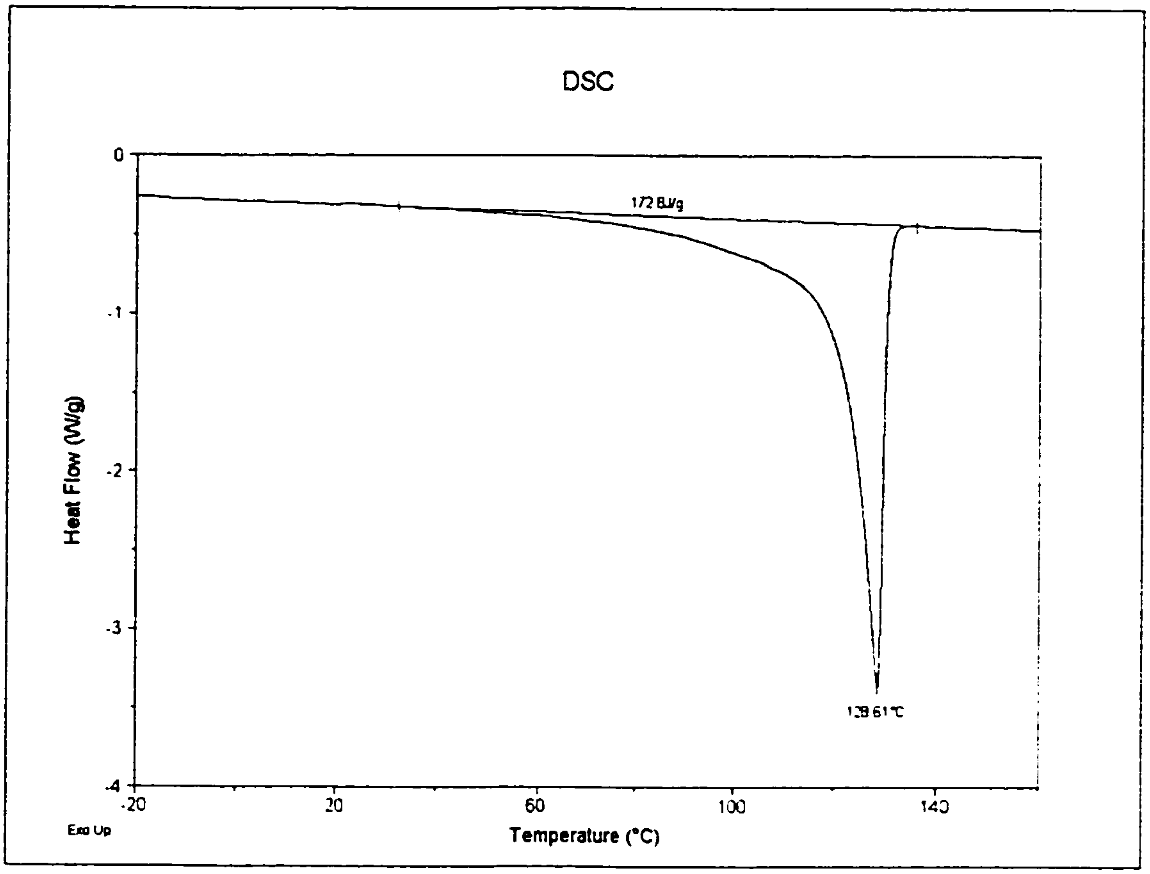

Figure 4.15: DSC melting curve for PC-HDPE

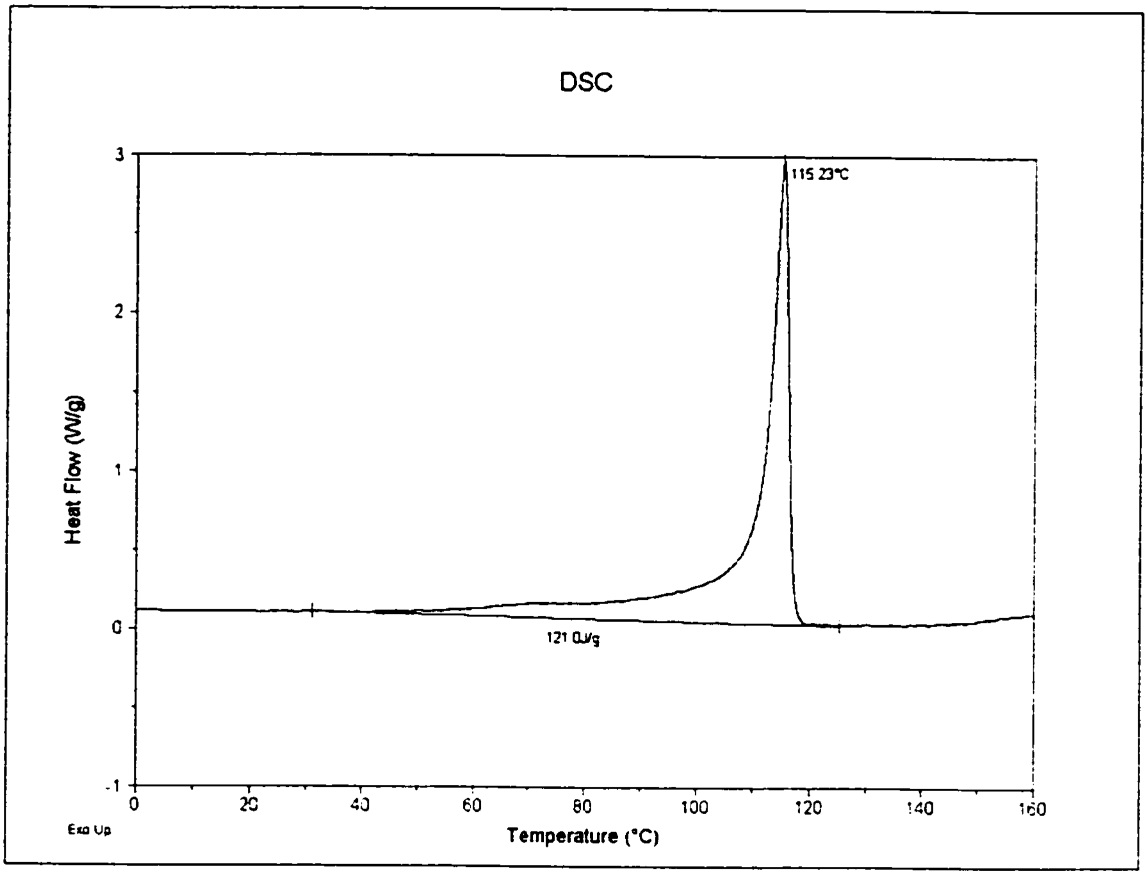

Figure 4.16: DSC crystallization curve for PC-HDPE

4.8.1 THERMAL ANALYSIS OF POE/PC-LDPE BLEND COMPOSITES

The melting and crystallization behavior of these blends over the entire range of composition is presented in Table 4.15 and 4.16 respectively. Figures 4.17 and 4.18 show the DSC thermograms in melting and crystallization for these blends.

In melting, all the blends show two melting peaks, the first broad peak at lower temperature related to POE and the second sharp peak at higher temperature related to PC-LDPE, except 20/80 POE/PE-LDPE blend presented in Figure 4.17. The location of first melting peak changes from 92°C for 80/20 POE/PC-LDPE blend to 107°C for 40/60 POE/PC-LDPE blend, while the temperature of the second peak varies by only few degrees. The 20/80 POE/PC-LDPE blend exhibits just one melting peak with a diffusing second peak, which appears as a tail. Similar behavior is exhibited by these blends in crystallization too, as shown in Table 4.16.

The crystallinity increases with the increase in the PC-PE contents, making the specimens more rigid, which explains the decrease in elongation. The crystallinity as a function of blend composition for POE/PC-LDPE blends with 3 phr and 4 phr SA is shown in Figure 4.19.

Although the calculated and experimental values are quite close, the differences between these values are not uniform within the entire range of composition depicting a slight degree of inhomogeneity of the recycled polymer, which is normal. This characteristic of PC-LDPE may explain some slight unexpected variations in tensile properties of the blends.

Table 4.15: DSC melting data of POE/PC-LDPE blend composites

Sample Identification %	Latent Heat (J/g)		Crystallinity (%)		T_m (°C)	
	Calculated	Experimental	Calculated	Experimental	Peak	
					I	II
POE/PC-LDPE blends with 200phr $CaCO_3$ and 3phr SA						
80 – 20	30.2	25.8	10.3	8.8	92.1	121.0
60 – 40	33.5	32.4	11.4	11.1	96.1	121.8
50 – 50	35.2	33.7	12.0	11.5	102.3	122.3
40 – 60	36.9	37.6	12.6	12.8	107.2	122.6
20 – 80	40.2	41.1	13.7	14.0	Tail	123.5
POE/PC-LDPE blends with 200phr $CaCO_3$ and 4phr SA						
80 – 20	30.7	29.2	10.5	10.0	92.8	120.3
60 – 40	34.0	32.2	11.6	11.0	97.5	121.7
50 – 50	35.6	34.8	12.2	11.9	102	122.1
40 – 60	37.3	36.3	12.7	12.4	106.4	122.1
20 – 80	40.7	42.0	13.9	14.3	Tail	124.0

Table 4.16: DSC crystallization data of POE/PC-LDPE blend composites

Sample Identification (%)	Latent Heat (J/g)		Crystallinity (%)		T_c (°C)	
					Peak	
	Calculated	Experimental	Calculated	Experimental	I	II
POE/PC-LDPE blends with 200phr $CaCO_3$ and 3phr SA						
80 – 20	30.2	29.9	10.3	10.2	83.5	108.6
60 – 40	33.5	33.9	11.4	11.6	85.2	109.7
50 – 50	35.2	34.0	12.0	11.6	87.2	110.5
40 – 60	36.9	37.3	12.6	12.7	90.2	110.9
20 – 80	40.2	41.3	13.7	14.1	-	112.1

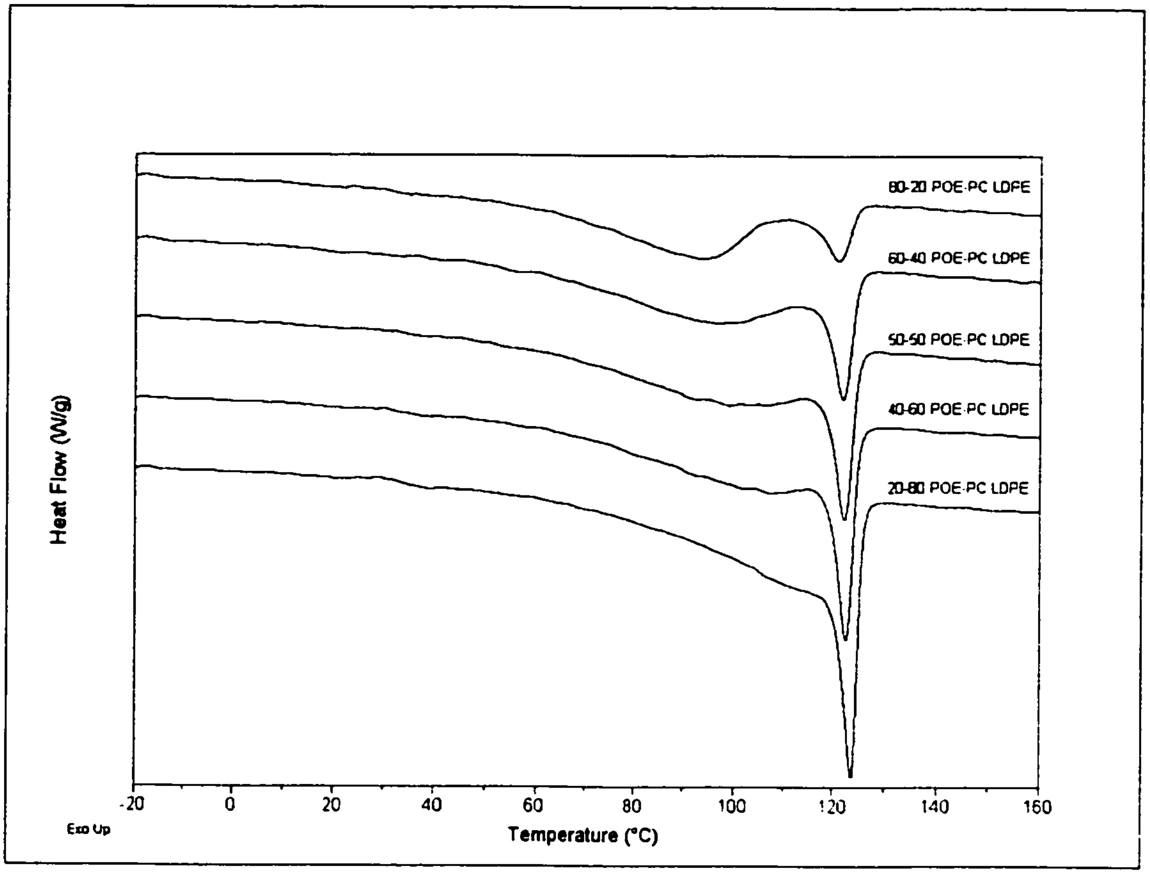

Figure 4.17: DSC melting curves for entire range of POE/PC-LDPE composition

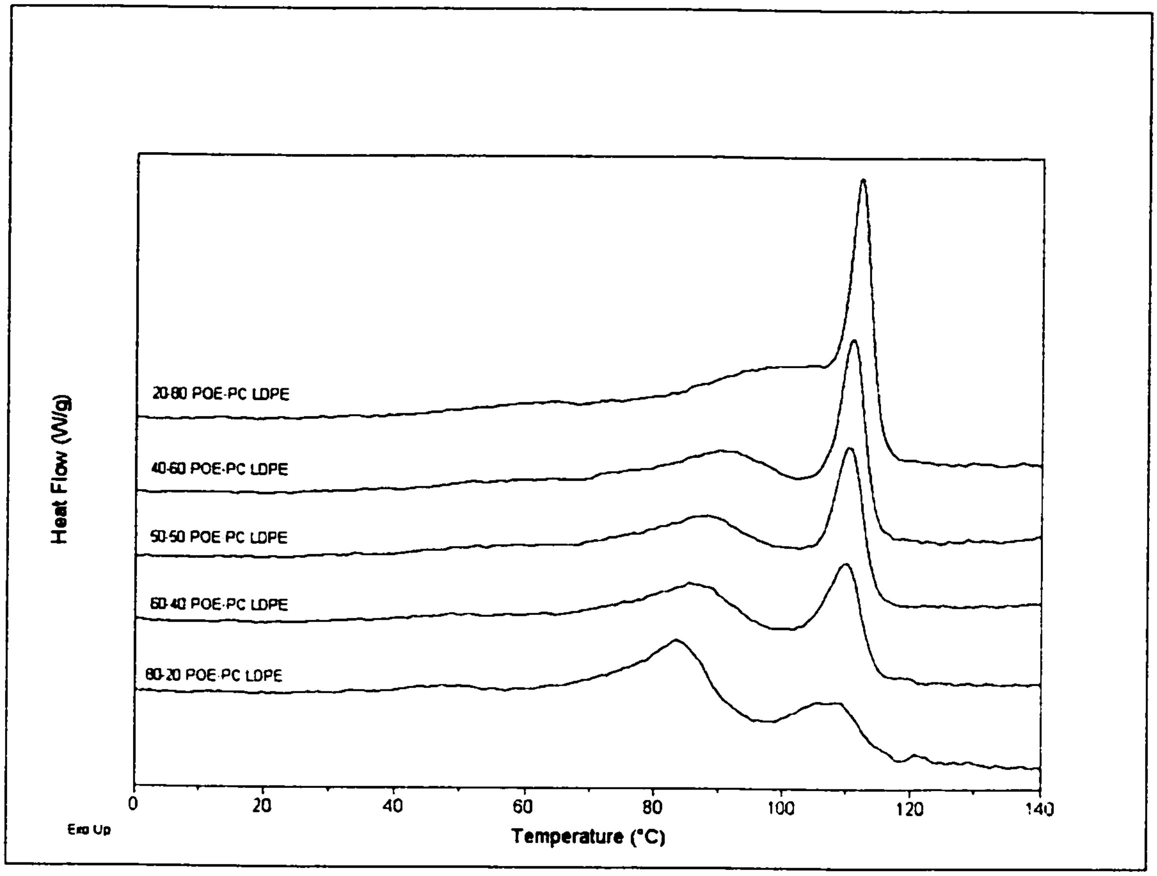

Figure 4.18: DSC crystallization curves for entire range of POE/PC-LDPE composition

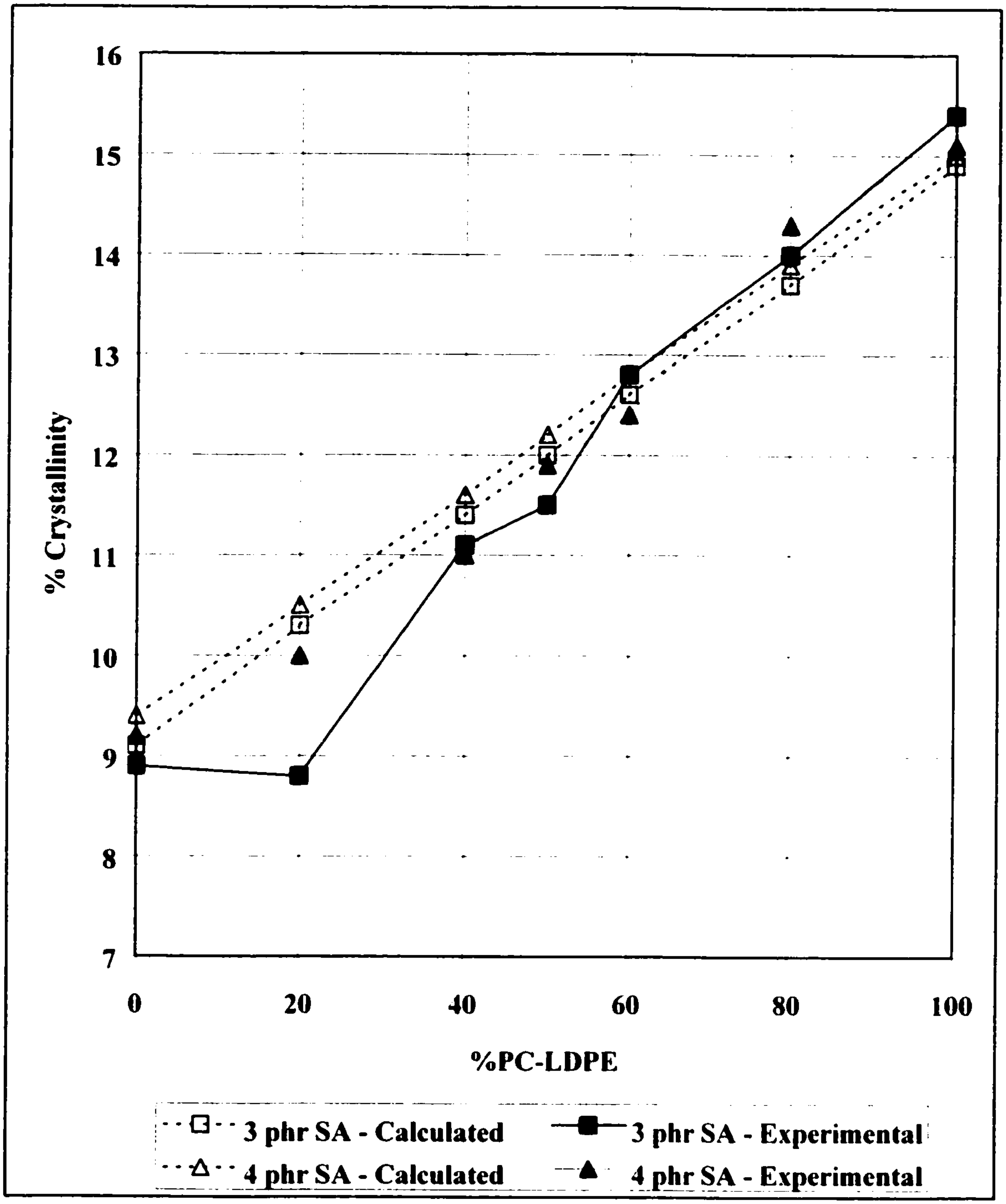

Figure 4.19: Crystallinity as a function of blend composition for POE/PC-LDPE blends

4.8.2 THERMAL ANALYSIS OF POE/PC-HDPE BLEND COMPOSITES

The melting and crystallization behavior of POE/PC-HDPE blends over the entire range of composition is presented in Table 4.17 and 4.18 respectively. Figure 4.20 and 4.21 show the DSC thermograms in melting and crystallization respectively for these blends.

They also show two melting peaks, one broad low temperature melting indicating melting of the POE and a sharp high temperature melting peak of HDPE component. There is not much of a shift in the peaks temperatures with the increase in PC-HDPE % in the blends. The data also shows that the difference in low and high temperature melting peaks is almost 30°C. However, the low temperature melting peak diffuses to a tail for blends containing 40/60 and 20/80 POE/PC-HDPE. The single melting peak shows the temperature of 126.3°C and 127°C for these two blends respectively, which is very much closer to the melting point of PC-HDPE of 127°C.

The latent heat of melting in case of POE/PC-HDPE blend is higher compared to PC-LDPE blends, showing higher crystallinity. Throughout the range of composition, these blends show an increase in crystallinity values upon addition of PC-HDPE content, which is expected due to the crystalline nature of HDPE. The crystallinity as a function of blend composition for POE/PC-HDPE blends with 3 phr and 4 phr SA is shown in Figure 4.22.

In this case too, there is good agreement between the calculated and experimental values, even better than in the case of POE/PC-LDPE blends due to the fact that PC-HDPE is a more homogenous material than PC-LDPE.

Table 4.17: DSC melting data of POE/PC-HDPE blend composites

Sample Identification (%)	**Latent Heat (J/g)**		**Crystallinity (%)**		**T_m (° C)**	
	Calculated	**Experimental**	**Calculated**	**Experimental**	**Peak**	
					I	**II**
POE/PC-HDPE blends with 200phr CaCO3 and 3 phr SA						
80 – 20	33.3	31.6	11.4	10.8	92.1	123.7
60 – 40	39.7	38.4	13.5	13.1	92.6	124.8
50 – 50	42.9	40.6	14.6	13.9	94.6	125.5
40 – 60	46.1	42.7	15.7	14.6	Tail	126.3
20 – 80	52.5	51.7	17.9	17.8	Tail	127.0
POE/PC-HDPE blends with 200phr CaCO3 and 4 phr SA						
80 – 20	33.7	32.0	11.5	10.9	92.1	123.7
60 – 40	40.2	39.1	13.7	13.3	92.8	125.0
50 – 50	43.2	41.6	14.7	14.2	96.3	125.5
40 – 60	46.5	44.7	15.9	15.3	Tail	126.0
20 – 80	52.9	50.6	18.1	17.3	Tail	126.7

Table 4.18: DSC crystallization data of POE/PC-HDPE blend composites with 3phr SA

Sample Identification (%)	Latent Heat (J/g)		Crystallinity (%)		T_c (°C)	
	Calculated	Experimental	Calculated	Experimental	Peak	
					I	II
80 – 20	33.3	32.0	11.4	10.9	82.7	113.0
60 – 40	39.7	38.4	13.5	13.1	83.4	114.3
50 – 50	42.9	40.3	14.6	13.6	83.3	114.8
40 – 60	46.1	43.2	15.7	14.7	86.5	115
20 – 80	52.5	52.8	17.9	18.0	Tail	115.4

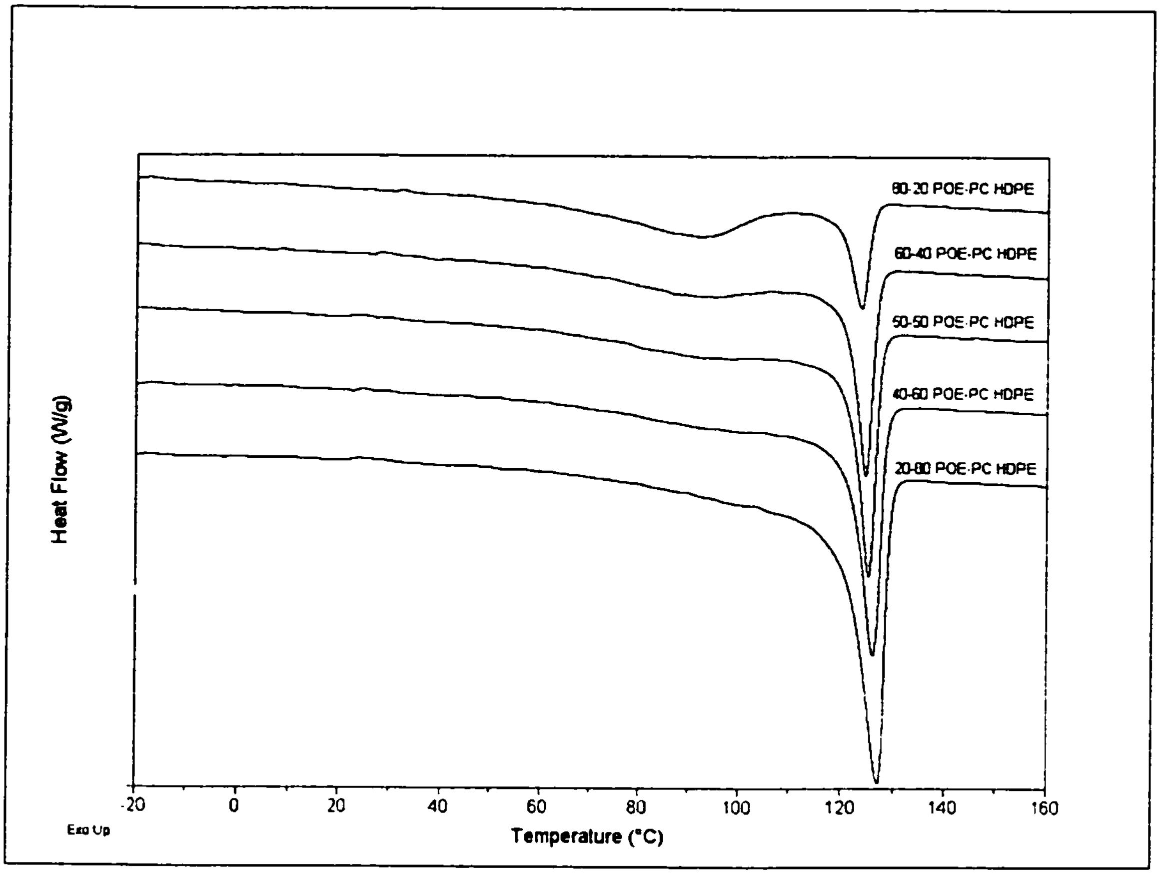

Figure 4.20: DSC melting curves for entire range of POE/PC-HDPE composition

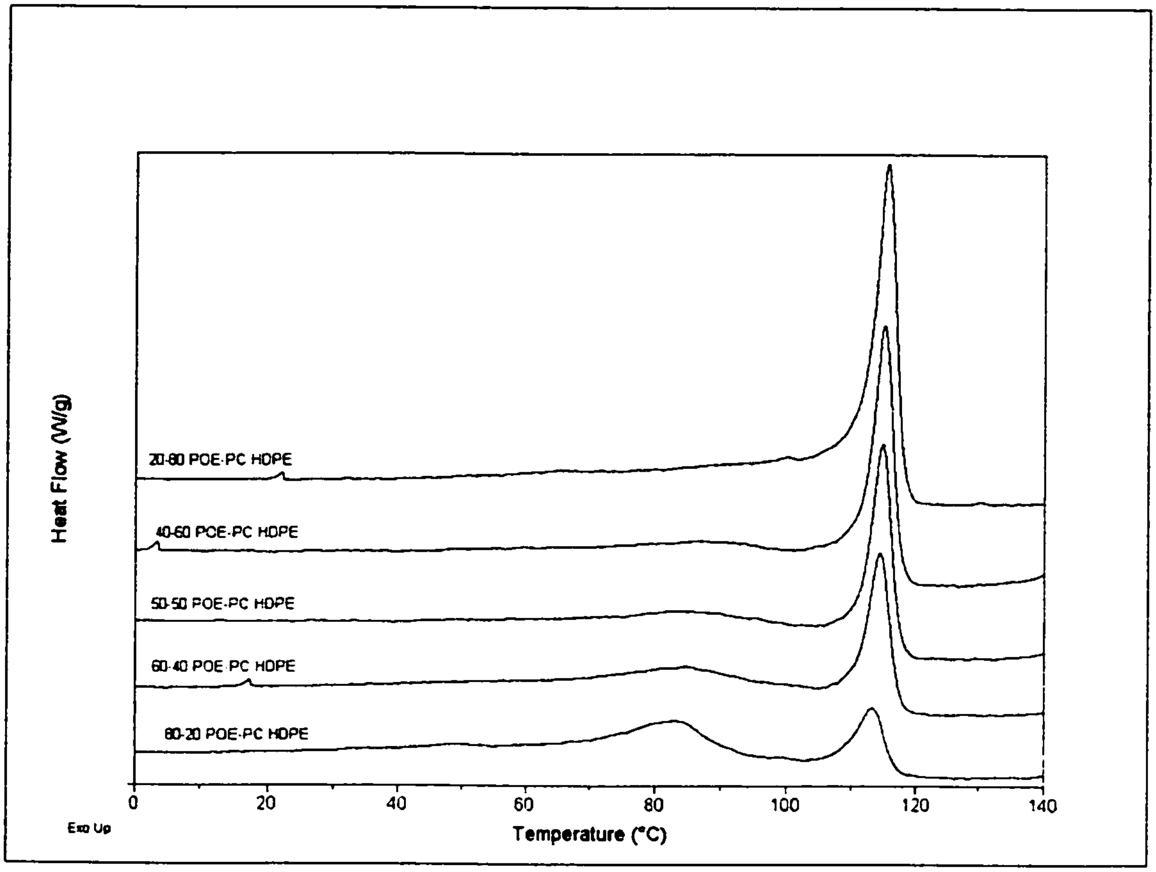

Figure 4.21: DSC crystallization curves for entire range of POE/PC-HDPE composition

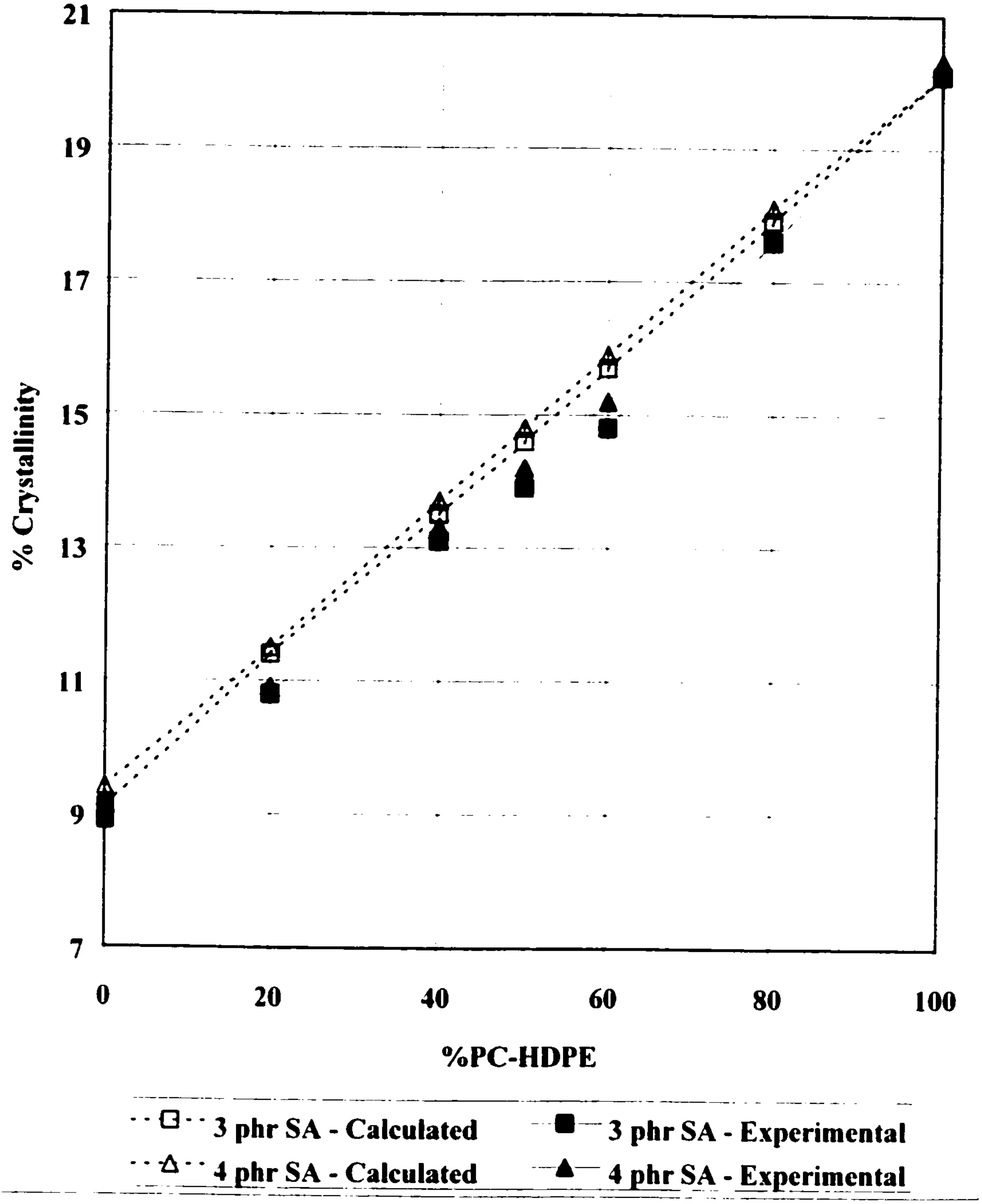

Figure 4.22: Crystallinity as a function of blend composition for POE/PC-HDPE blends

4.8.3 THERMAL ANALYSIS OF HEAT AND UV STABILIZED COMPOUNDED POLYOLEFINS AND POE/PC-PE BLEND COMPOSITES

Table 4.19 shows the thermal analysis of heat and UV stabilized compounded polyolefin and POE/PC-PE blend composites. Figures 4.23 and 4.24 show the DSC melting thermogram from entire range composition of POE/PC-LDPE and POE/PC-HDPE respectively.

The data indicates that for compounded polyolefin and blend composites of POE/PC-PE, the latent heat values, crystallinity as well as melting temperature values do not show significant change from their unstabilized counterparts.

This essentially means that within the compound, the ability of individual polymers to crystallize is not hindered by the presence of other ingredients of the formulation.

Table 4.19: DSC melting data of heat and UV stabilized compounded polyolefins and POE/PC-PE blend composites

Sample Identification	Latent Heat (J/g)		Crystallinity (%)		T_m (° C)	
	Calculated	Experimental	Calculated	Experimental	Peak	
					I	II
Compounded polyolefins with 200phr $CaCO_3$, 3phr SA, 0.5 phr heat and 0.8phr UV stabilizer						
POE	26.7	27.2	9.1	9.3	-	95.0
PC-LDPE	43.4	44.1	14.8	15.1	114.8	122.7
PC-HDPE	58.7	59.2	20.0	20.2	-	127.4
POE/PC-LDPE blends with 200phr CaCO3, 3phr SA, 0.5 phr heat and 0.8phr UV stabilizer						
60 – 40	33.4	33.9	11.4	11.6	94.5	122.2
50 – 50	35.0	35.6	12.0	12.2	101.5	122.0
40 – 60	36.7	37.5	12.5	12.7	108	122.3
POE/PC-HDPE blends with 200phr CaCO3, 3phr SA, 0.5 phr heat and 0.8phr UV stabilizer						
60 – 40	39.5	39.6	13.5	13.5	93	124.5
50 – 50	42.7	43.1	14.6	14.7	95.1	125.0
40 – 60	45.9	46.7	15.7	15.9	Tail	125.5

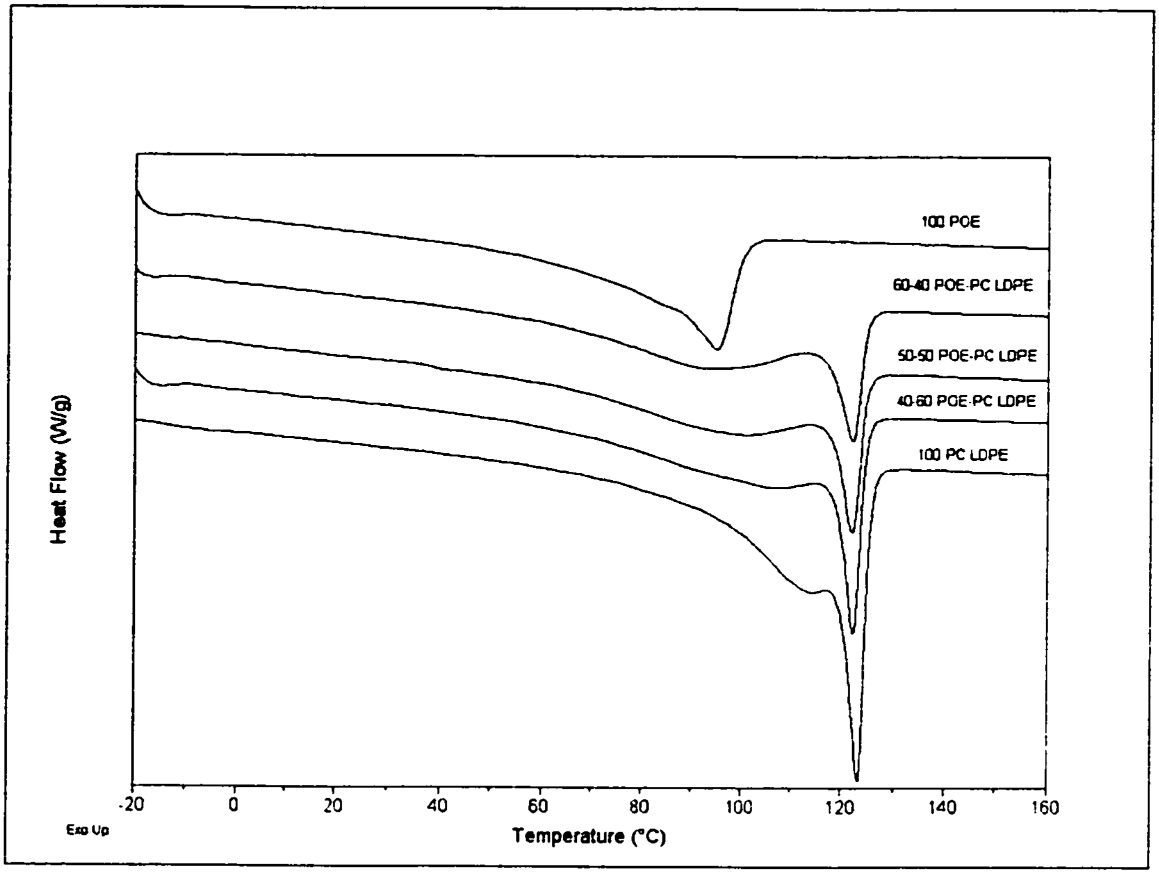

Figure 4.23: DSC melting curves of POE/PC-LDPE blend composites with UV and heat stabilizers

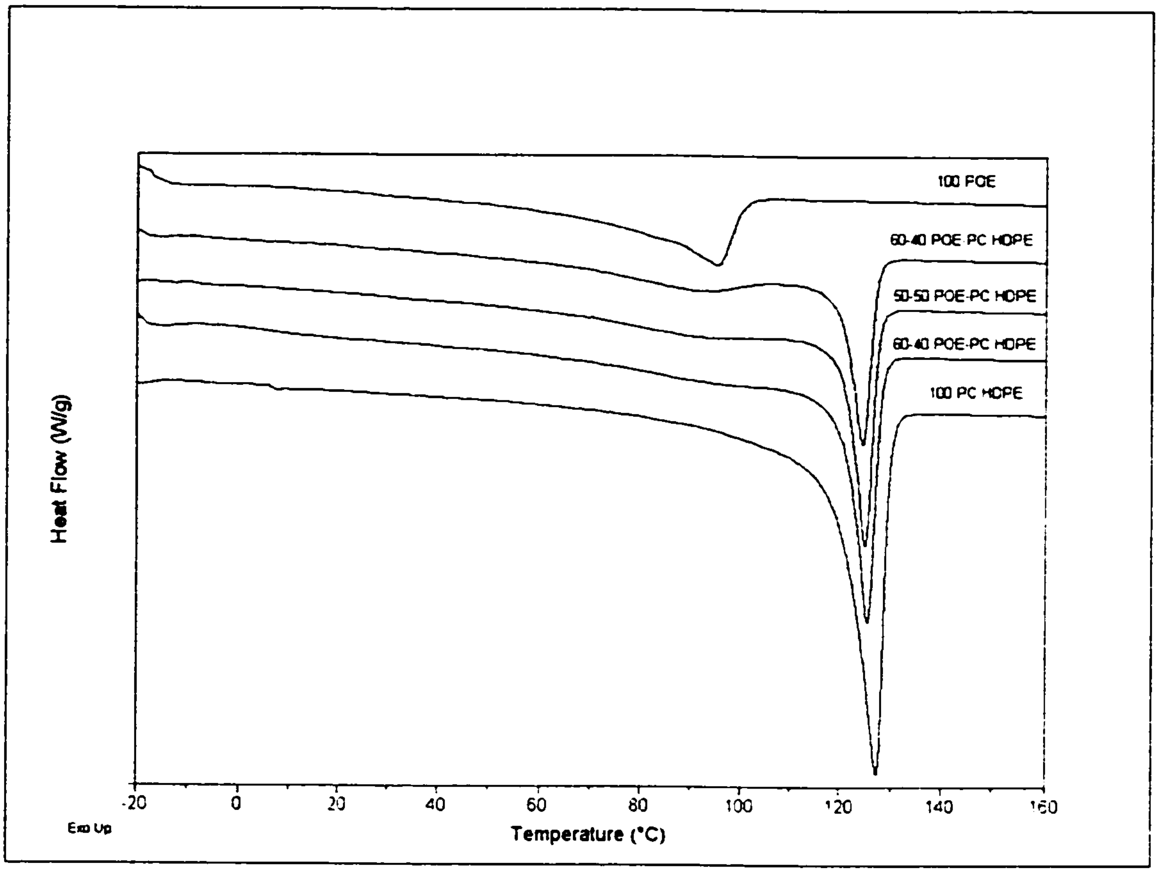

Figure 4.24: **DSC melting curves of POE/PC-HDPE blend composites with UV and heat stabilizers**

4.9 DIMENSIONAL HEAT STABILITY

Results of dimensional stability due to heat aging of POE/PC-PE blend composites are presented in Table 4.20. As can be seen in the Table 4.20, the formulations of sole matrix of PC-HDPE were the most stable followed by PC-LDPE and then by POE. This can be explained due to the degree of crystallinity of these respective polymers.

Table 4.20: Dimensional heat stability of POE/PC-PE composites

Formulation	Initial Length (mm)	Final length (mm)	% Change
POE	63.705	63.61	0.150
POE/PC-LDPE (%)			
60-40	63.65	63.57	0.126
50-50	63.69	63.58	0.173
40-60	63.62	63.52	0.165
100	63.63	63.50	0.102
POE/PC-HDPE (%)			
60-40	63.65	63.47	0.283
50-50	63.625	63.54	0.134
40-60	63.61	63.52	0.141
100	63.625	63.575	0.078

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

5.1 CONCLUSIONS

The present research was carried out to obtain and evaluate POE/PC-PE blends as a matrix for composites for flooring applications, such as flexible sheets and tiles.

Blends of polyolefin elastomer- Engage 8440 with PC-LDPE and PC-HDPE were used to produce formulations containing 200phr calcium carbonate filler and tested for key mechanical and thermal properties. 3 phr Stearic acid was added to the formulation as lubricant. Similar formulations based on PVC copolymers are typically used in the flooring industry for flexible tiles and sheets.

A comparison of POE/PC-PE blend composites with 40%, 50%, 60% and 100% PC-PE with a typical PVC flooring formulation [70] in terms of break strength, elongation at break, impact strength and hardness is presented in Table 5.1 and Figures 5.1 through 5.4.

As indicated in Table 5.1, the break strength of all the blend composites of POE/PC-LDPE showed higher values as compared to PVC, except that with 50% PC-LDPE. However, all blend composites of POE/PC-HDPE exhibited lower break strength than that of PVC. This may be attributed to the highly crystalline structure of HDPE. Also, the blends with sole matrix of PC-PE were very hard as indicated by very high break strength values.

Elongation at break of POE/PC-LDPE and POE/PC-HDPE blend composites exhibited higher values than PVC. This characteristic may be attributed to the presence of elastomeric component in the POE/PC-PE blends. However, composites with sole matrix of PC-LDPE and PC-HDPE failed to show any elongation. This loss of elasticity is also reflected as reduction in toughness with very low impact strength values and brittle failure during impact testing. Impact values of POE/PC-LDPE and POE/PC-HDPE blend composites exhibited higher values compared to PVC.

Hardness values show slight reduction in values in case of POE/PC-PE blend composites indicating POE/PC-PE as softer materials compared to PVC composites.

Further, heat and UV stabilizers were incorporated into POE/PC-PE blend composites with 40%, 50%, 60% and 100% PC-PE contents and were subjected to accelerated weathering effects. A comparison of weathered POE/PC-PE blend composites with 40%, 50%, 60% and 100% PC-PE with a typical unweathered PVC flooring formulation [70] in terms of yield strength, break strength, Young's modulus and elongation at break is presented in Table 5.2 and Figures 5.5 through 5.7.

As indicated in Table 5.2 and Figures 5.5 through 5.7, the Young's modulus increases for the PC-PE blend composites, in comparison to PVC based formulation. The modulus of PC-HDPE is higher than that of PC-LDPE due to the higher crystalline structure of the former making it stiffer material.

Yield strength values were higher for PC-PE blend composites in comparison to PVC. The break strength and elongation at break of POE/PC-PE blend composites also exhibited higher values than PVC composites.

Table 5.1: Comparison of key mechanical properties of PVC [70] and POE/PC-PE blend composites

Sample Identification	Break Strength (MPa)	Elongation at Break (%)	Impact Strength (J/m)	Hardness
PVC [70]	6.01	336	152.9	96.3
POE	6.64	1587	266.6	94.8
POE/PC-LDPE (%)				
60-40	6.34	1225	342.1	93
50-50	5.84	1037	346	90.8
40-60	6.16	1012	368	86.2
0-100	8.09	-	41.5	-
POE/PC-HDPE (%)				
60-40	5.69	814	361.7	92.5
50-50	5.53	726	365.2	96.2
40-60	5.45	590	359.6	88.2
0-100	6.68	-	104	-

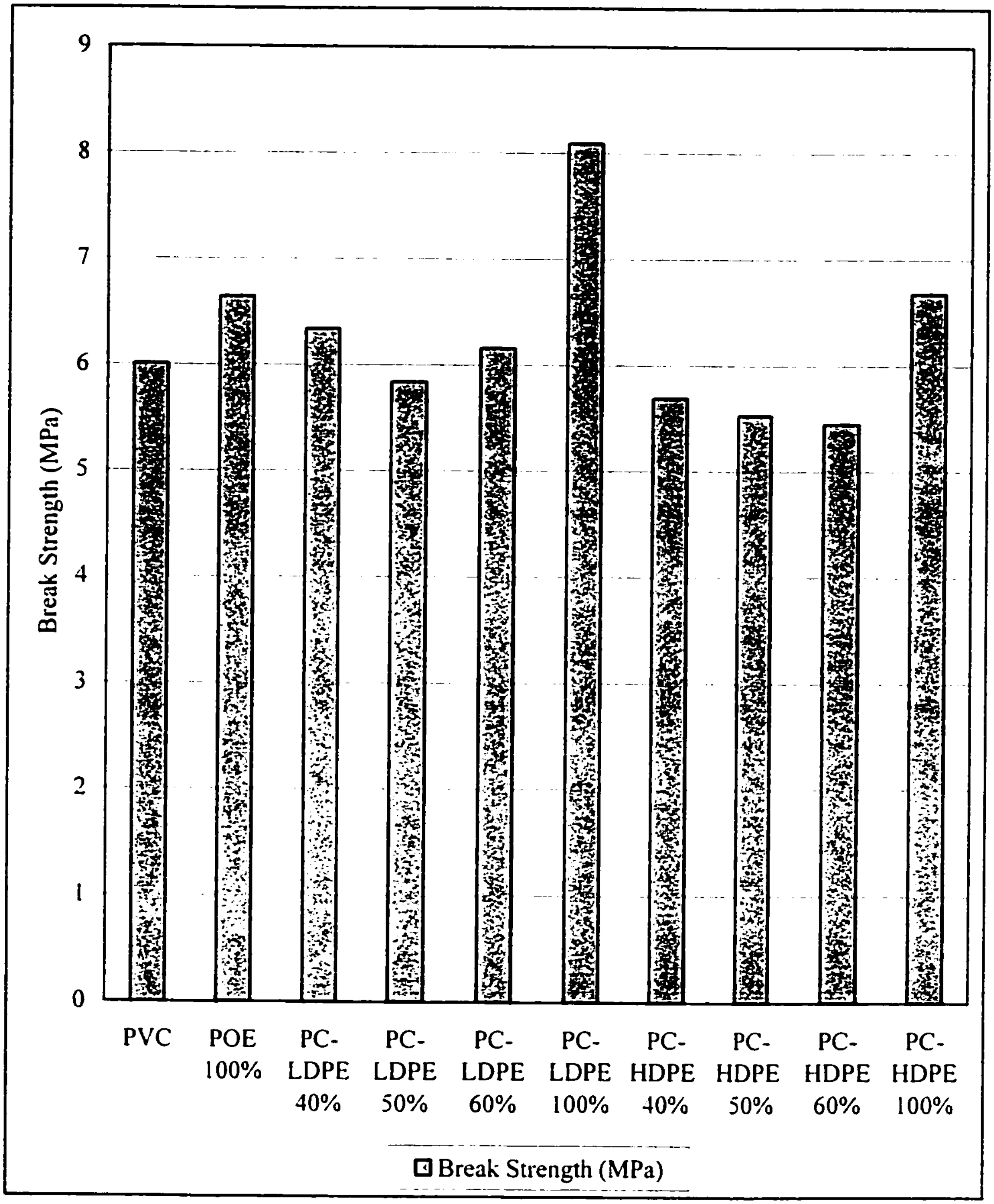

Figure 5.1: **Comparison of break strength of PVC [70] and POE/PC-PE blend composites**

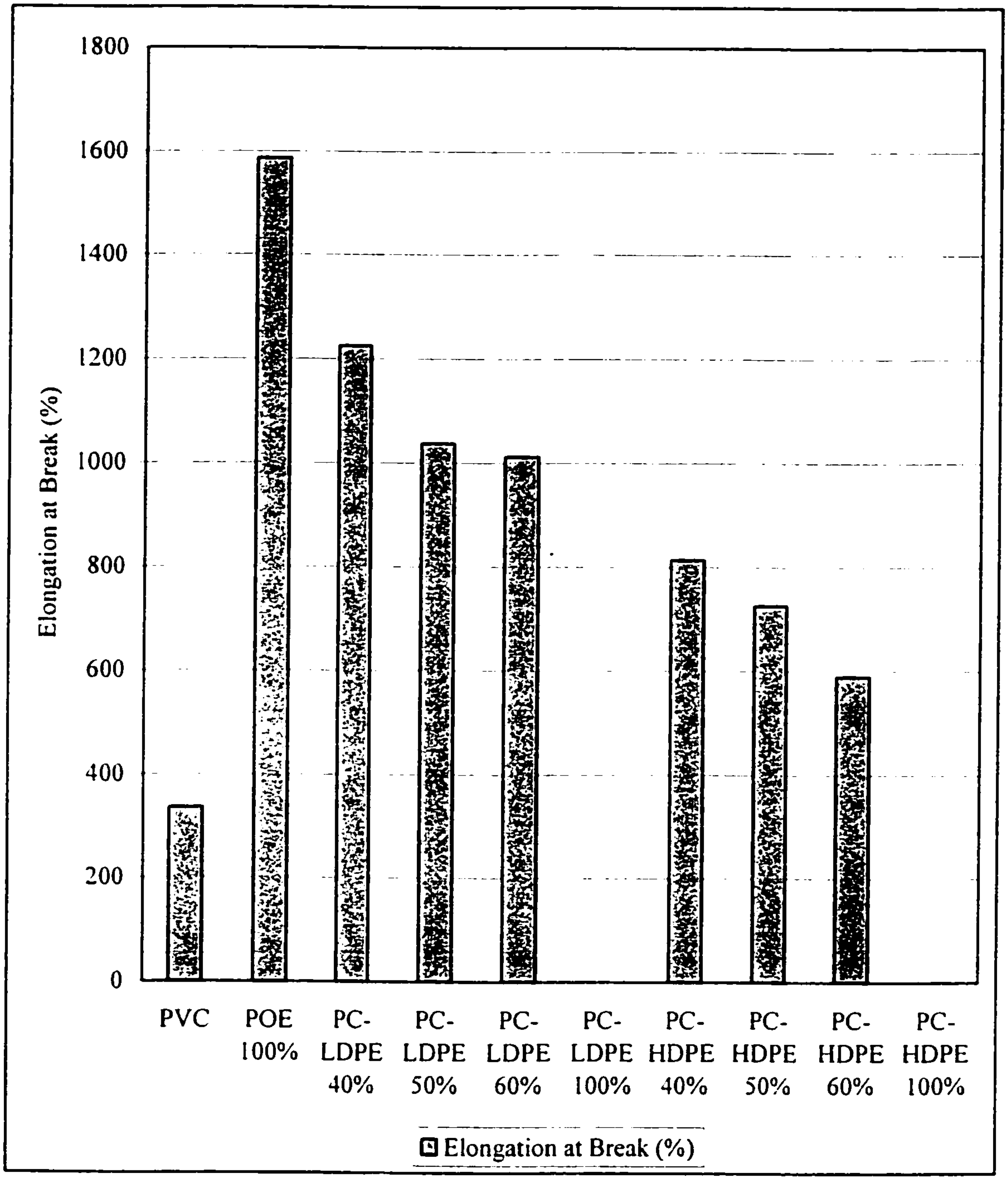

Figure 5.2: Comparison of elongation at break of PVC [70] and POE/PC-PE blend composites

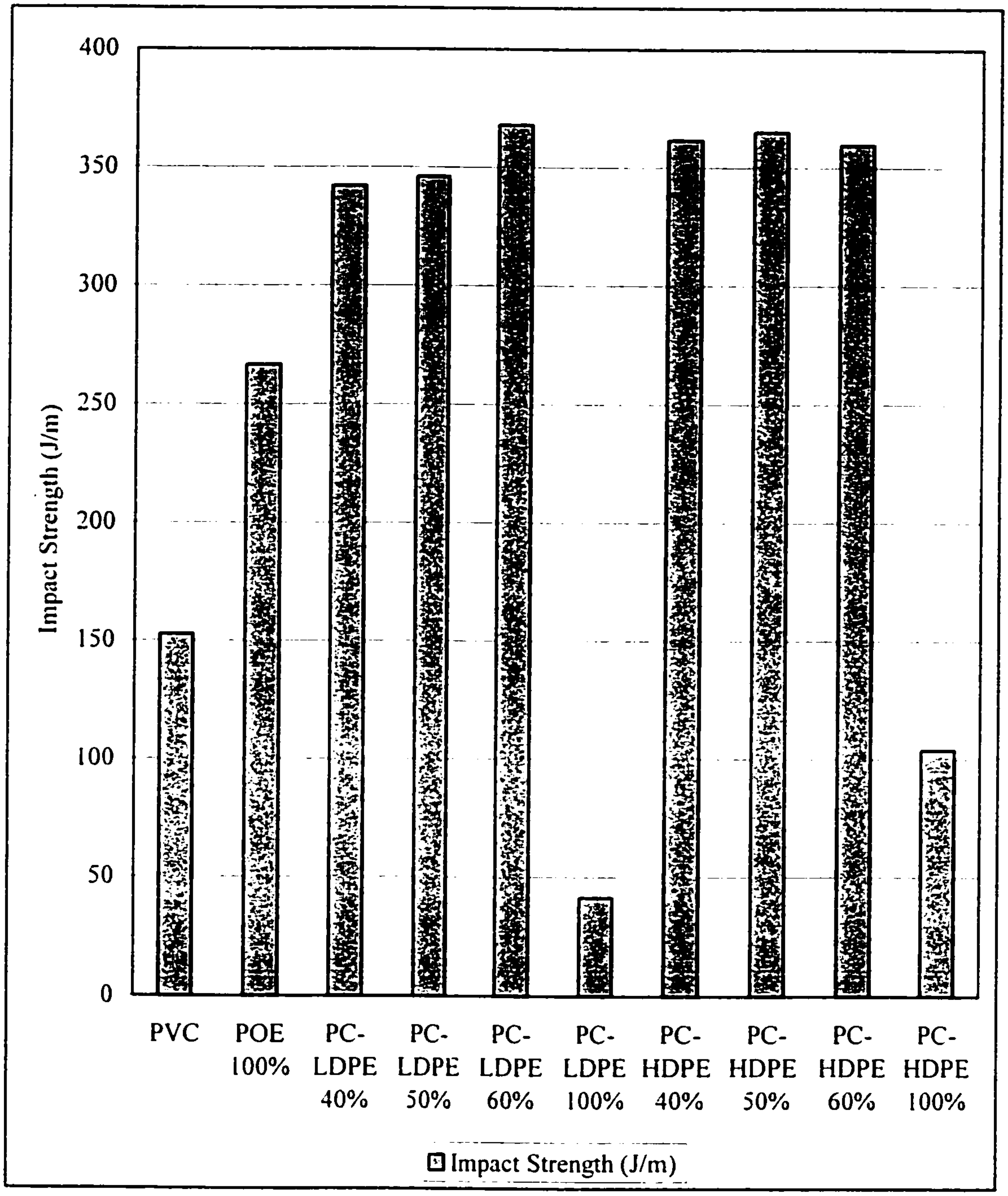

Figure 5.3: Comparison of impact strength of PVC [70] and POE/PC-PE blend composites

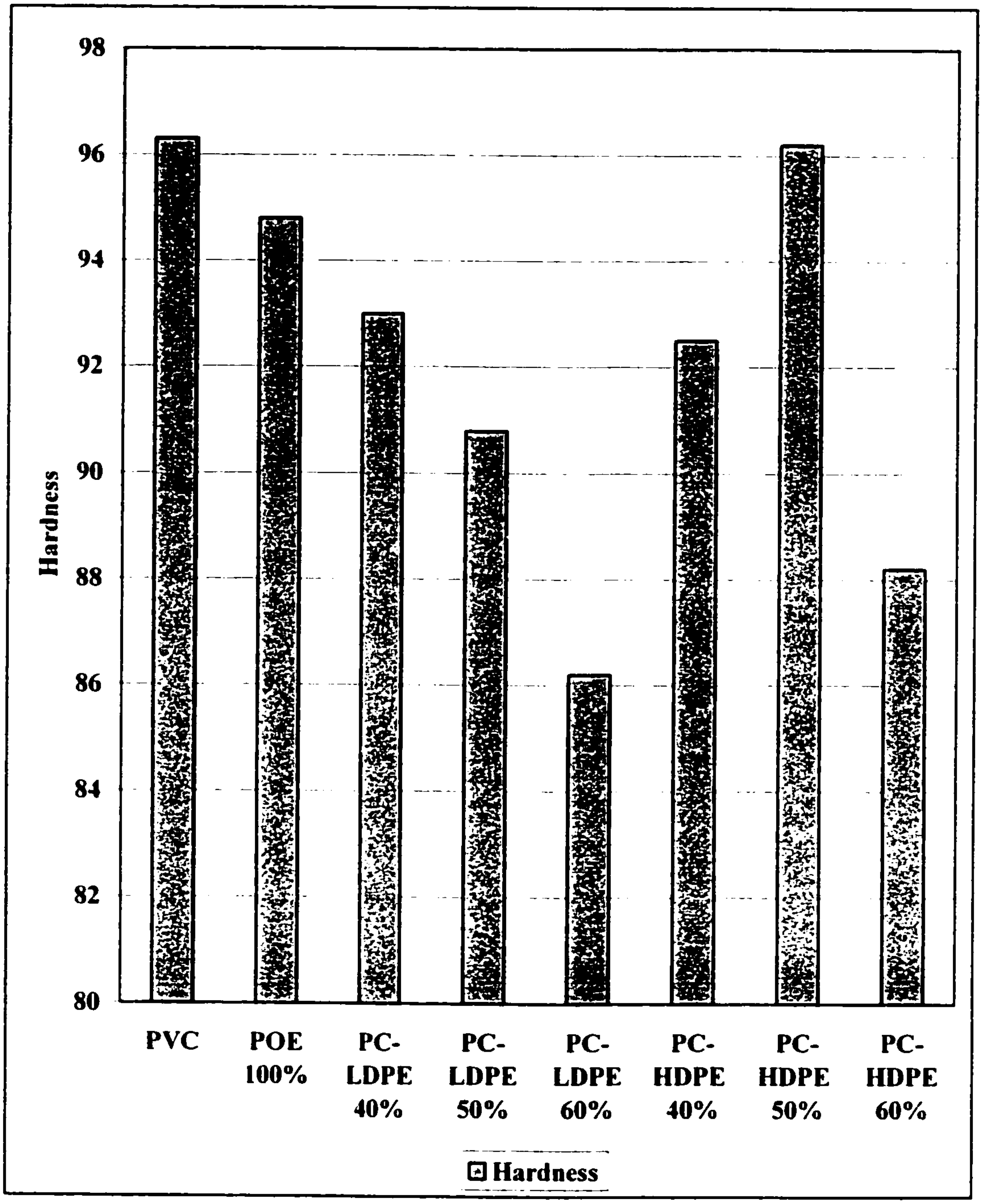

Figure 5.4: Comparison of hardness of PVC [70] and POE/PC-PE blend composites

Table 5.2: Comparison of tensile properties of unweathered PVC and weathered POE/PC-PE blend composites

Sample Identification	Young's Modulus (MPa)	Yield Strength (MPa)	Break Strength (MPa)	Elongation at Break (%)
PVC [70]	22.7	3.51	6.01	336
POE	683	2.65	6.64	1567
POE/PC-LDPE (%)				
60-40	1180	4.19	6.76	1278
50-50	1206	4.29	6.56	1205
40-60	1295	4.68	6.1	970
0-100	1940	6.52	5.41	-
POE/PC-HDPE (%)				
60-40	1405	5.39	6.14	894
50-50	1602	6.16	5.95	767
40-60	1753	6.8	5.53	514
0-100	2299	-	8.47	-

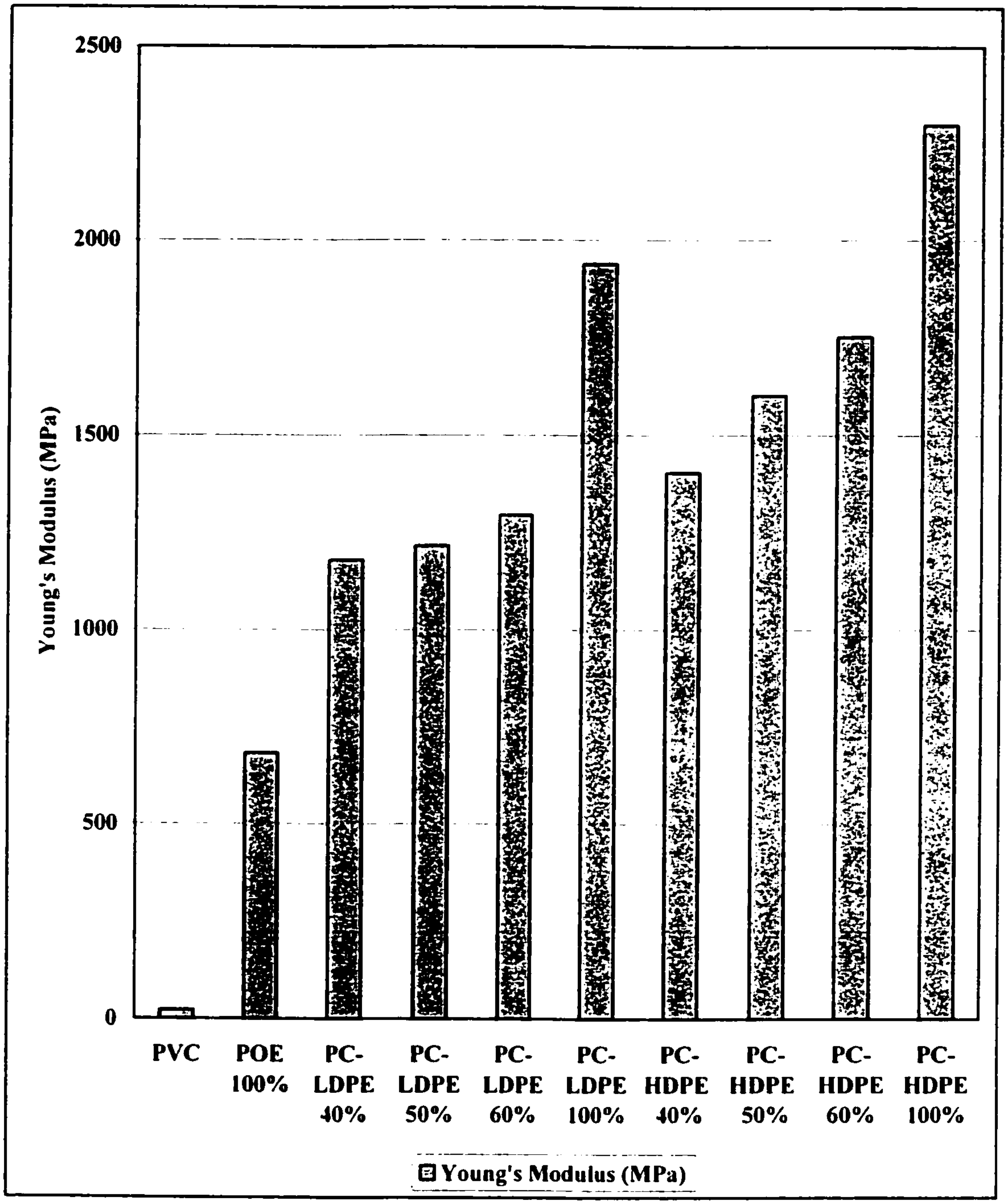

Figure 5.5: Comparison of Young's modulus of unweathered PVC [70] with weathered POE and POE/PC-PE based composites

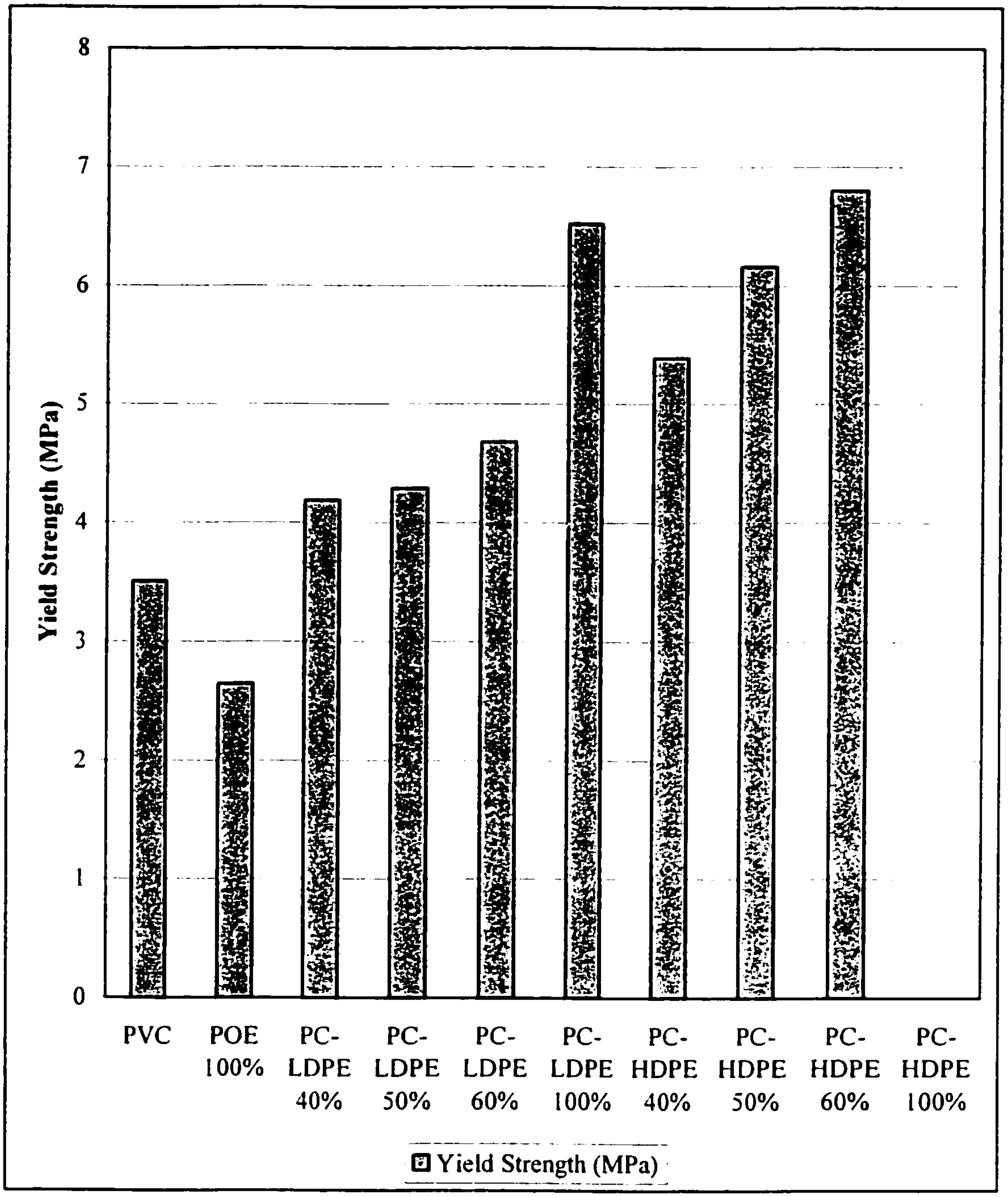

Figure 5.6: **Comparison of yield strength of unweathered PVC [70] with weathered POE and POE/PC-PE based composites**

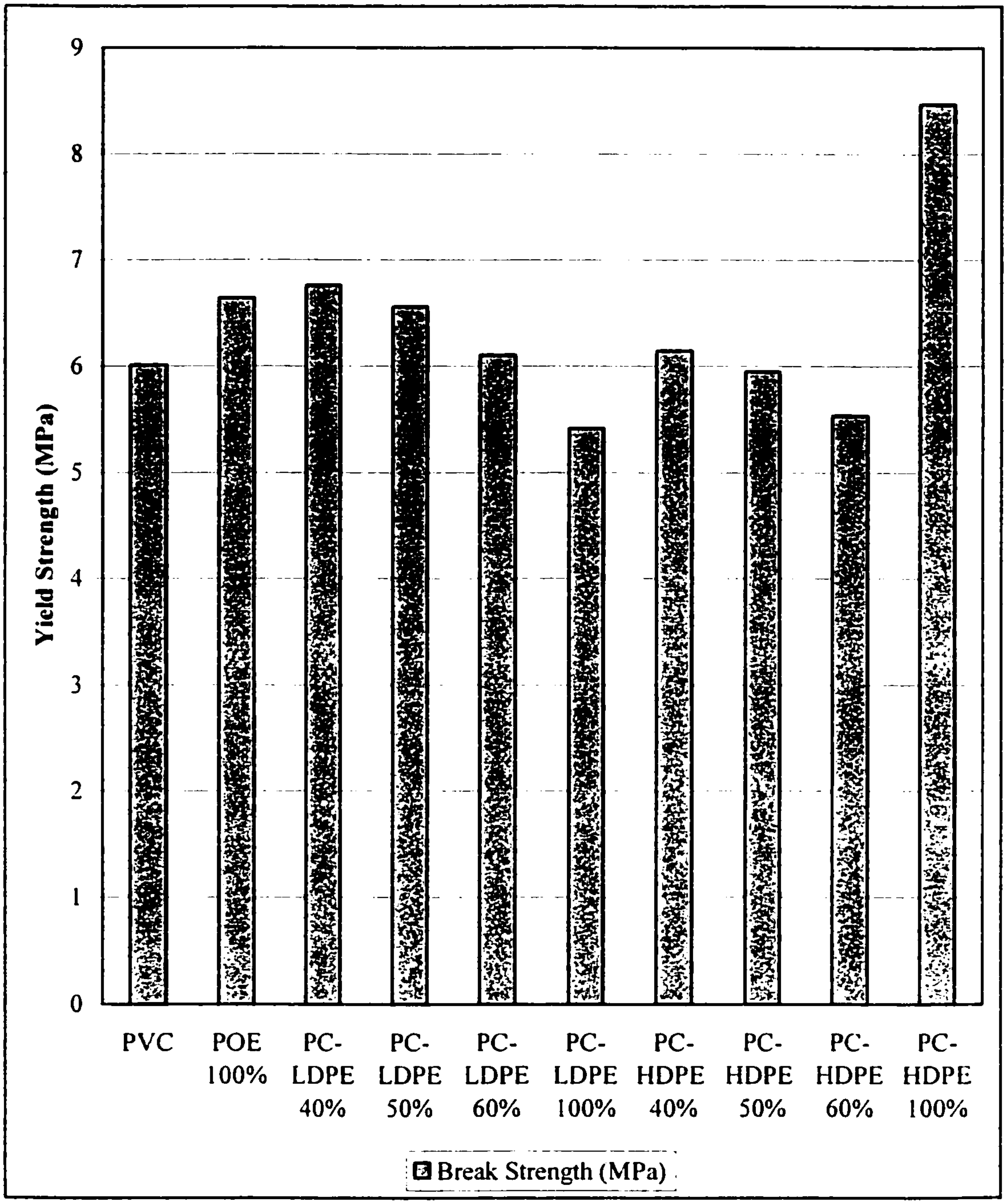

Figure 5.7: Comparison of break strength of unweathered PVC [70] with weathered POE and POE/PC-PE based composites

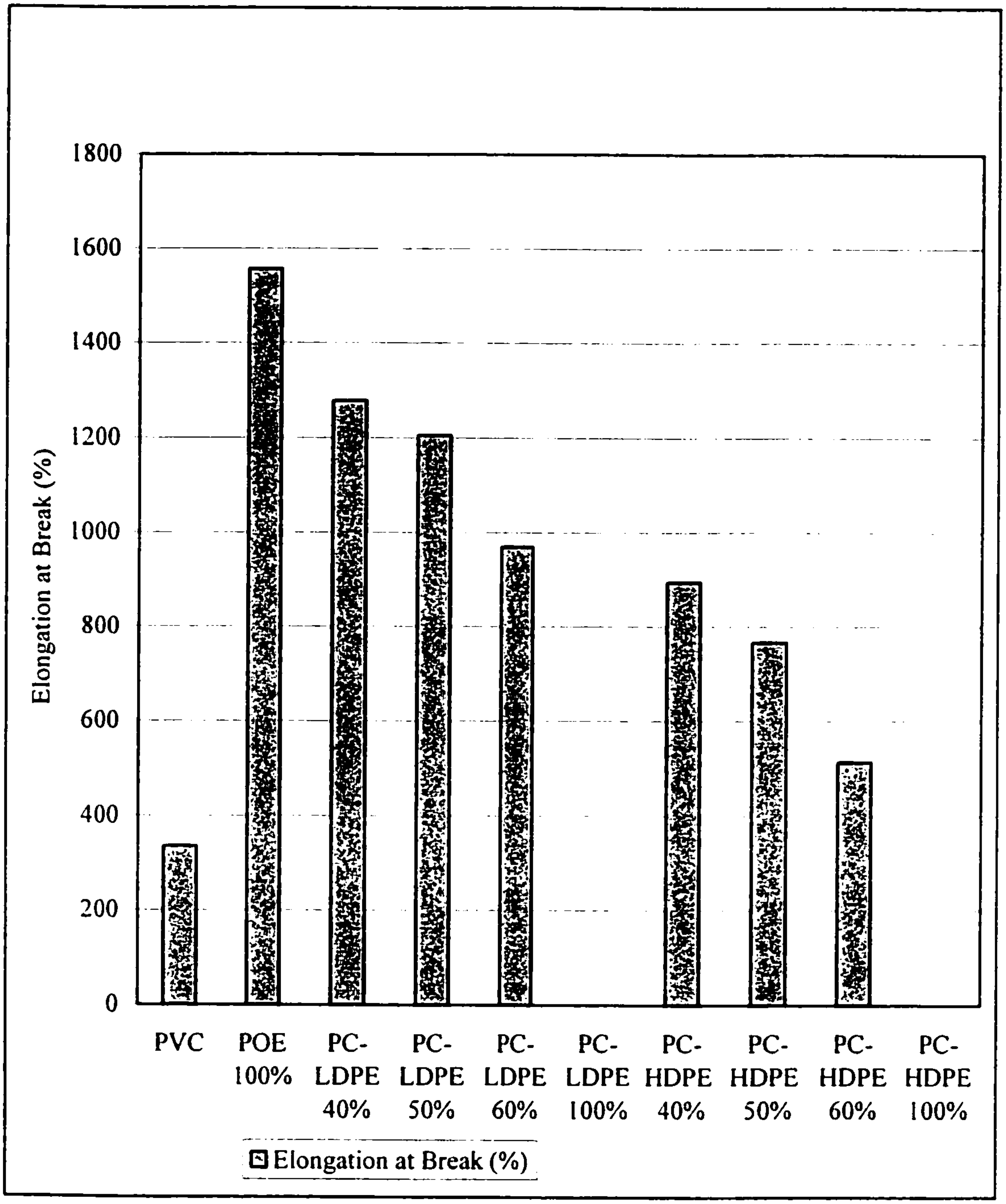

Figure 5.8: Comparison of elongation at break of unweathered PVC [70] with weathered POE and POE/PC-PE based composites

Based on the present study, it may be concluded that:

1. Polyolefin elastomers can incorporate relatively higher amounts (upto 40% to 60%) of post-consumer resin into the formulation, which is very important from the point of view of the cost.
2. No plasticizers are required in the production of POE/PC-PE production, thereby eliminating potentially hazardous class of materials.
3. The blend of polyolefin elastomer with post-consumer polyethylene does not follow additivity rule and the property values are much less than expected on the basis of linear rule due to changes in the molecular structure of recycled resins.

5.2 RECOMMENDATIONS FOR FUTURE WORK

Future studies should focus on :

1. To explore the possibilities to bring the properties of POE/PC-PE composites closer to those of PVC composites and also the cost comparison between the two.
2. Testing of VOC emission.
3. Stability to fungus and microorganisms.
4. Testing for toxicity of smoke.
5. Adhesion of the composites to a polyurethane wear layer commonly used in flooring applications.
6. Dynamic contact angles between the wear layer and the composites for coatability of the composites.

REFERENCES

[1] http://www.americanplasticscouncil.org/benefits/economic/economic.html

[2] Michelsen, T., 1999. Building Materials (Plastics), in: Kirk Othmer Encyclopedia of Chemical Technology, 4th Edition, Volume 4, pp 628-663. John Wiley & Sons

[3] Elvers, B., Rounsavill, J.F and Schulz, G (eds.) 1988. Floor Coverings, in: Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition Vol A11: 269-277, Wiley-VCH

[4] Elvers, B., Rounsavill, J.F and Schulz, G (eds.) 1988. Plastics, Additives, in: Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition Vol A20: 474-507, Wiley-VCH

[5] Godish, T., 1995. Sick Building Syndrome: Definition, Diagnosis and Mitigation, pp. 115-129, Lewis Publishers, Boca Raton

[6] http://www.rppi.org/peg2.html

[7] Portnoy, R & Domine, J., 1999. Medical Applications of Metallocene-catalyzed Polyolefins, in: Metallocene-based Polyolefins, Volume 2 edited by John Scheirs, W. Kaminsky, John Wiley & Sons

[8] Jester, Thomas. C (ed.), 1995. Twentieth-Century Building Materials: History and Conservation, McGraw Hill, New York

[9] Betso, S et al., 1999. Constrained Geometry-catalyzed Polyolefins in Durable and Wire and Cable Applications, in: Metallocene-based Polyolefins, Volume 2 edited by John Scheirs, W. Kaminsky, John Wiley & Sons

[10] http:// cciw.ca/glimr/data/chlor-alkali/chap10.htm

[11] Bani-Hani, M.; Banu D; Feldman, D, 1999. "Highly Filled Polyolefin Plastomer Formulations for Possible Replacement in Flooring", Journal of Applied Polymer Science, Vol. 74, pp 1156-1168

[12] Wilson A. S., 1995. Plasticisers: Principles and Practice, pp 24-25, Institute of Materials, London.

[13] Chanda, M. and Roy, S. K., 1993. Plastics Technology Handbook, 2nd ed., pp 381-392. Marcel Dekker, Inc.

[14] Colletti. J. T., Renshaw J. T & Schaefer R. E, 1998. Stain Resistance in Resilient Sheet Flooring Applications; The Role of Plasticizer, Journal of Vinyl and Additive Technology, Vol. 4, N 4, pp 233-239

[15] Wilson A. S., 1995. Plasticisers: Principles and Practice, pp 187-189, Institute of Materials, London.

[16] Buszard, D. L., 1984. Theroritical Aspects of Plasticization, in Titow, W. W., (ed.) PVC Technology, pp 120-138. Elsevier Applied Science, London

[17] Axtell, F. H. and Ratanapaka, J., (ed.) Polyvinyl chloride, Soft calcium carbonate filled, in: Salamone, J. C.,(ed.) Polymeric Materials Encylepaedia, Vol. 9:7079-7085. CRC Press, Boca Raton.

[18] Wilson A. S., 1995. Plasticisers: Principles and Practice, pp 30-36, Institute of Materials, London.

[19] Titow W. V., 1984. PVC Technology, 4th Edition, pp 10-11

[20] Gustafsson, H , 1992. Building Materials Identified as Major Sources for Indoor Air Pollution. A Critical Review of Cases, Swedish Council for Building Research, D10.

[21] Wilson A. S., 1995. Plasticisers: Principles and Practice, pp 75-109, Institute of Materials, London.

[22] Webb, J. S. et al., 1999. Plasticizers Increase Adhesion of the Deteriogenic Fungus Aureobasidium pullulans to Polyvinyl Chloride, Journal of Applied and Environmental Microbiology, Vol. 65, N8, pp 3575-3581.American Socienty of Microbiology.

[23] Brown, A. E., 1945. Problems of Fungal Growth on Resins, Plastics and Plasticizers, Report No. 6067, US Office of Scientific Research and Development, Washington DC.

[24] Tinius, K. M., 1964. Plasticizers. Khemia, Moscow-Leningrad

[25] Bezveliev AG., 1983. Plastmassy, 2:8-9

[26] Gumargalieva, K. Z. et al., 1999. The Influence of Biodegradation on the Loss of a Plasticizer from Poly(vinyl chloride), Journal of Polymer Degradation and Stability, Vol. 63, pp 111-112, Elsevier Sciences Ltd.

[27] Jaakola, J. K. et al. 1999. Interior Surface Materials in the home and the Development of Bronchial Obstruction in Young Children in Oslo, Norway, American Journal of Public Health, Vol. 89, N2, 187-192

[28] Oie L., et al., 1997. Residential Exposure to Plasticizers and its Possible Role in Pathogenesis of Asthma, Environmental Health Perspectives, 105: 972-978

[29] Toxicological Profile for DEHP, 1993, US Department of Health and Human Services, Washington DC.

[30] Rittfeldt, L et al. 1984. Indoor air Pollutants Due to Vinyl Floor Tiles, Proc. 3rd International Conference on Indoor Air Quality and Climate Vol. 3, Stockholm.

[31] Hirvoen, A. et al., 1990. Thermal Desorption of Settled Household Dust, 5th I International Conference on Indoor Air Quality and Climate, Vol., 3, pp 743-746

[32] Rosell L , 1990. High Levels of Semi-VOC in Indoor Air Due to Emission from Vinyl Floorings, in: Proceedings of 5th International Conference on Indoor Air Quality & Climate, Vol. 3, Toronto, 707-711,.

[33] Andersson, B. et al., 1984. Mass Spectrophotometric Identification of 2-ethylhexanol in Indoor Air: Recovery Studies by Charcoal Sampling and Gas Chromatographic Analysis at the Micrograms Per Cubic Meter Level, Journal of Chromatography, 291, 257-163.

[34] Saarela, K& Sundell, L., 1991. Comparative Emission Studies of Flooring Materials with Reference to Nordic Guidelines. Proceedings of IAQ 91: Healthy Buildings, ASHRAE, Atlanta.

[35] http:// www.greenpeace.org

[36] Ghosh M. K., and Maiti S.K, 1999. Polyolefins Technology – A Comprehensive Review, Journal of Polymer Materials, June' 99, pp113-134

[37] Gunther A and Langowski H, 1997. Life Cycle Assessment Study on Resilient Floor Coverings, International Journal of LCA, V2, N2, pp 73-80

[38] Olefin Polymers, in: Kirk Othmer Encyclopedia of Chemical Technology, 4th Edition, Volume 17, pp 703-784. John Wiley & Sons

[39] Johnson J, " Halogen Free Resilient Flooring" US Patent 5391612

[40] Thoen Johan A et al. " Filled Polymer Composites" US Patent 5973049

[41] Viet Dao "Sheets or film Products Obtained from Plastic Compounds" Patent No. WP 99/07784

[42] Simpson Brian et al. " Floor Covering" Patent No. WO/96/04419.

[43] Naoyuki N et al. "Polyolefin Resin Composition And Building Material Containing The Same" Patent No. WO 0119912

[44] Thoen Johan et al. " PVC-free Foamed Flooring and Wall Coverings" US Patent 5910358

[45] Boldizar Antal et al, 19 , Simulated Recycling of Post consumer High Density Polyethylene Material in: Journal of Polymer Degradation & Stability, Elsevier Publication.

[46] Oblisis O., 1997. Conventional Polyolefins, in: Handbook of Thermoplastics, pp 1-18, Marcel Dekker Inc.,

[47] Kim Y. S. et. Al, 1986. Melt Rheological and Thermodynamic Properties of Polyethylene Homopolymers and Polyethylene/α-olefin Copolymer with Respect to Molecular Composition and Structure, Journal of Applied Polymer Science, Vol 59, pp 125-137

[48] Kamisky, W and Scheirs, J, 1999. Metallocene-based Polyolefins, Volume 1 John Wiley and Sons.

[49] Feldman D. and Barbalata A., 1996. Synthetic Polymers: Technology, Properties, Applications. Chapman and Hall

[50] Zamora, M, Miller, T. and Brennan, A., 1997. Plastics Engineering, Vol. 53 No. 5, pp 75-79.

[51] Macadams John, Markets Expanding Very Rapidly and Technology Growing at Unequalled Rate, Modern Plastic Encyclopedia, 1995, pp B3-B5

[52] Reisch Marc S, Thermoplastic Elastomers Target Rubber and Plastic Markets. C & EN, August 1996, pp 10-14

[53] www.stratica.com

[54] www.dupont.com

[55] www.tarkett.com

[56] Technical Literature of Engage-8440, DuPont Dow Elastomers.

[57] Steep Rock Resources Inc. Technical Information Sheet, Snowhite 12, 1997

[58] ASTM D792-98, 1998. Test Method for Density and Specific Gravity (Relative Density) of Plastics by Displacement, American Society for Testing and Materials

[59] Technical Literature of Hostavin ARO8, 2001. Clariant Canada (Inc.)

[60] Technical Literature of Hostavin N 30, 2001. Clariant Canada (Inc.)

[61] ASTM D638-99, 1999. Test Method for Tensile Properties of Plastics, American Society for Testing and Materials

[62] ASTM D256-97, 1997. Test Method for Determining the Izod Pendulum Impact Resistance of Notched Specimens of Plastic, American Society for Testing and Materials

[63] ASTM D 2240-97,1997. Test Method for Hardness Properties of Plastics, American Society for Testing and Materials

[64] Shah, Visu, 1984. Handbook of Plastics Testing Technology, pp 129-140, John Wiley & Sons.

[65] ASTM F970-99, 1999. Test Method for Static Load Test, American Society for Testing and Materials

[66] ASTM 5208-91, 1991. Standard Practice for Operating fluorescent (UV) Condensation Apparatus for Exposure of Photodegradable Plastics, American Society for Testing and Materials

[67] ASTM 3417-99, 1999. Test Method for Determining Enthalpies of fusion and Crystallization of Polymers by Differential Scanning Calorimetry, American Society for Testing and Materials

[68] ASTM 3418-99, 1999. Test Method for Determining Transition Temperatures of Polymers by Thermal analysis, American Society for Testing and Materials

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

[70] Zhu, Hui, 2000, Plasticized lignin-PVC blends for flooring, Thesis (M.A.Sc.)-- Dept. of Building, Civil & Environmental Engineering, Concordia University, Montreal, Quebec, Canada