Highly Filled Polyolefin Plastomer Formulations for Possible PVC Replacement in Flooring

M. BANI-HANI, D. BANU, J. CAMPANELLI, D. FELDMAN

Department of Building Civil and Environmental Engineering, Concordia University, Montreal, Quebec, H3G 1M8, Canada

ABSTRACT: Calcium carbonate highly filled composites of a polyolefin plastomer (POP), and its blends with postconsumer linear low-density or high-density polyethylene (PC-LLDPE or PC-HDPE) were prepared and evaluated. The mechanical properties of compounded POP and its blends were compared with those of a PVC–calcium carbonate formulation used for flooring applications. Tensile and impact properties of calcium carbonate-filled POP composites compare very favorably to the PVC-based formulation at filler loadings as high as 200 phr. Moreover, postconsumer LLDPE or HDPE can replace at least 50% of the POP in these composites without affecting their main properties. DSC analyses indicate that the synergism occurring in mechanical properties for some of the blend compositions, may be related to the ability of the individual polymers to cocrystallize in the respective blends. This article presents the results of a preliminary study. Continued research is expected to contribute toward a complete characterization of the compounded POP/postconsumer PE blends to establish if they can replace plasticized PVC compounds in some or all flooring applications. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1156–1168, 1999

Key words: polyethylene blends; metallocene–polyethylene; postconsumer polyethylene; flooring

INTRODUCTION

A high interest in the synthesis of polyolefins, both homo- and copolymers, has been created in recent years due to the commercialization of a new class of catalyst known as metallocenes. These catalysts consist of a transition metal atom sandwiched between ring structures to form a sterically-hindered site, and a cocatalyst, usually an aluminoxane especially methylaluminoxane. These systems show high activities, good copolymerization behavior, and excellent control of stereoregularity.[1] The most remarkable feature of these catalyst systems is the fact that all metallocene sites produce chains with virtually the same architecture. Due to the uniformity of the active sites, they are sometimes referred to as single-site catalysts.

The polyolefins produced with metallocene catalysts are typically characterized by a narrow molecular weight distribution and uniform incorporation of comonomers, in contrast with the polymers produced by conventional multisite catalysts. The comonomer content, and its chain length strongly influence the crystallization and melting behavior, and also polymer degree of crystallinity.[2] Metallocene-based polymers and copolymers are less crystalline than traditional polyolefins and, by appropriate incorporation of C_4, C_6, and C_8 comonomers along the polymer backbone, it is possible to produce extremely flexible materials.

Because of the wide range in elasticity possible, metallocene-based polyolefin copolymers may be termed either polyolefin plastomers (POP) or polyolefin elastomers (POE), depending on whether the comonomer amount is low or high, respectively. Metallocene-based resins thus have a wider range of physical properties than traditional polyolefins.[3] This versatility makes POP and POE excellent candidates for replacing filled, plasticized PVC in flooring applications.

A major drawback to flexible PVC is the presence of plasticizers. These additives have been traditionally considered inert and nonvolatile, but recent studies show that they may act as human hormone mimics. Plasticizers are also subject to microbial degradation, which leads to the formation of volatile organic compounds (VOC), and to unsightly fungal growth in many flooring products in humid environments.[4]

Polyolefin-based composites can have important advantages over PVC-based ones. The first advantage is that filled POP can be processed without use of plasticizers. The second advantage in using POP or POE is the potential for incorporating postconsumer resins into the composites. More than 75% of recycled plastics is estimated to consist of polyolefins. Incorporation of these materials into PVC flooring tiles would led to large reductions of physical properties because of poor miscibility between PVC and polyolefins. POP, on the other hand, is compatible with postconsumer polyolefins, which could, thus, be used as extenders to lower costs.

This study presents the mechanical and thermal properties of calcium carbonate-filled POP composites. These properties are compared with those of a typical PVC flooring formulation, i.e., filled wear layer for inlaid vinyl flooring and vinyl tile, which comprises cca. 200 phr. fillers, cca. 35 phr plasticisers, and no processing aids.[5] POP used for this research was a metallocene ethylene–octene copolymer produced by Dow Plastics using INSITE technology. It has a linear, short-branched molecular microstructure, in which are also incorporated small amounts of long branches. Due to the quite high percentage of α-olefin (14%), its degree of crystallinity is about 25%. Blends of POP with two postconsumer resins, a high-density polyethylene (PC-HDPE), and a linear low-density polyethylene (PC-LLDPE), were also tested.

HDPE is a homopolymer of ethylene, and has a linear microstructure. Depending on synthesis technology, HDPE molecules either have no branches, or contain a small number of branches, but the polydispersity can be quite high. Most of the commercial products have a melting temperature of about 125–130°C, and a degree of crystallinity of about 60–75%, due to their linear microstructure.[6, 7] LLDPEs are copolymers of ethylene with a small amount of α-olefins ($\sim$2.5–3.5%) produced by conventional multisite catalysts. They have linear microstructures without long-chain branching, but with much short-chain branching. The α-olefins or short-chain branches are distributed nonuniformly at different intervals along a macromolecule, and heterogeneously with different concentrations in different macromolecules.[8] The literature indicates a broad range of melting for LLDPE, with a broad melting peak at aroud 106–110°C, and a sharp one in the range of 120–125°C. The sharp high-temperature peak corresponds to the melting of high molecular weight and low comonomer fractions, while the broad low-temperature peak corresponds to the melting of low molecular weight and high comonomer fractions.[9,10] It degree of crystallinity varies between 45–55%.

EXPERIMENTAL

Materials

The PVC used in all experiments was OXY 1810, a vinyl chloride–vinyl acetate copolymer resin, formulated for high levels of filler. It was supplied by Occidental Chemical Corporation, TX. It had the following characteristics: K value of 57, specific gravity of 1.37, and a vinyl acetate content of 9.7%.

The PVC was formulated with technical grade dioctyl phthalate (DOP) (obtained from Fisher Scientific) as a plasticizer, dibutyltin dilaurate (DBTL) (obtained from American Chemicals) as heat stabilizer, and stearic acid (triple pressed) (obtained from Fisher Scientific) as lubricant.

The calcium carbonate was obtained from Steep Rock Resources Inc., Perth, Ontario. The grade used was Snowhite 12, which has a specific gravity of 2.71, and a mean particle size of 12 microns. It was not surface treated, and it was used in both formulations with PVC and POP.

The POP was a homogenous ethylene–octene copolymer, produced by Dow Plastics using its INSITE technology. It had the following characteristics: octene comonomer content of 14%, a

melt index of 1.6 dg/min, a DSC melting point of 94°C, and a specific gravity of 0.895.

The PC-LLDPE and PC-HDPE were both obtained from Enviroplast, Ville D'Anjou, Quebec. They had the characteristics summarized below.

	PC-LLDPE	PC-HDPE
Melt index dg/min	1	0.5
Specific gravity	0.931	0.949
Crystallinity %	42.7	55.7
DSC melting point °C	112*	129

* There is a second melting point characteristic of LLDPE at 125°C.

Procedures

The formulations of PVC and POP with calcium carbonate are shown in Table I. Resin mixtures over the complete composition range, i.e., 80/20, 50/50, and 20/80 (wt % POP/wt % PC-PE) prepared with POP and PC-LLDPE or PC-HDPE, respectively, were also formulated with the same amount of filler. All the formulations were prepared by melt-mixing in a Haake Rheomix 600 equipped with roller blades. Volume of the mixer was 69 cm³, and a coefficient of filling of 69% was used. Typical operating conditions are summarized in Table II. Several batches were prepared for each formulation. After melt-mixing, the product was ground to a size of 3–5 mm. Subsequently, sheets of 3-mm thickness were molded by compression at 158°C for PVC formulations and 178°C for POP formulations. The molded sheets were cooled from molding temperature to room temperature at a cooling rate of 10°C/min. After cooling, the sheets were cut with a cutting

Table II   Operating Conditions for Melt Mixing

Formulation	T (°C)	Blade Speed (rpm)	Mixing Time (min)
PVC-based	140	40	6
POP-based	175	60	10

die into dog bone specimens (ASTM D638) or notched specimens (ASTM D250) for mechanical testing.

Testing

The tensile strength at yield and tensile strength and elongation at break were measured according to ASTM D638 using an Instron Universal Testing Machine. A crosshead speed that produced rupture of the specimen within 5 min was selected for each type of formulation, and the testing temperature was 23 ± 2°C. The impact strength (Izod) was measured according to ASTM D250 on notched specimens with a model 92T Tinius Olsen Impact Tester.

All the specimens for tensile and impact tests were tested 1 week after their preparation. They were conditioned at 23 ± 2°C and 50 ± 5% RH for 48 h prior to testing. The indicated values are an average of at least five determinations. The coefficients of variance inferior to 10% were taken into account for each set of specimens tested.

The thermal properties of POP, PC-LLDPE, PC-HDPE, and their respective formulations were measured using a 912 DuPont Differential Scanning Calorimeter connected to a DuPont Mechanical Cooling Accessory. At least two specimens of about 10 mg, weighed with an accuracy of ±0.002 mg, were tested for each formulation. To

Table I   PVC and POP-Based Formulations

Component	PVC Composites[a]	POP Composites[b]
	Concentration [phr]	
Resin	100	100
Filler—Calcium Carbonate	200	200
Plasticizer—DOP	35	none
Stabilizer—DBTL	3	none
Lubricant—Stearic Acid	2	2

[a] In PVC formulations. Oxy 1810/PVC.

[b] In POP formulations. Affinity 1140/POP 100 phr, or blends with 20, 50, and 80% PC-LLDPE or PC-HDPE.

Table III   DSC Data for Single and Compounded Polyolefins

Sample Identification	Peak T_m (°C)	Latent Heat of Melting (J/g)	
		Experimental	Calculated
POP	93.6	74.8	—
PC-LLDPE	112.4; 124.8	125.2	—
PC-HDPE	128.7	163.1	—
Compounded POP	94.5	26.6	26.0
Compounded PC-LLDPE	112.8; 124.7	42.9	42.7
Compounded PC-HDPE	128.1	54.8	55.2

obtain a good heat transfer during the DSC scans, films of 0.25-mm thickness were compression molded from each formulation using a Spectra-Tech Universal Film Maker. Subsequently, disks with the same diameter as the specimen pan were punched from films and sealed in aluminum pans.

The DSC thermograms were obtained with a heating-cooling rate of 10°C/min. A first heating was done from 30–180°C. The specimens were held at 180°C for 10 min before cooling to −30°C, and then subjected to a second heating cycle with identical conditions as the first. The latent heats were obtained from the total area of the melting/crystallization peak or peaks including the initial broad region. Crystallinity calculations were based on the latent heat of fusion of 293 J/g for polyethylene perfect crystal.[11] Five different specimens of POP Affinity 1140 were scanned to determine the method's precision. The average results were: heat of fusion 74.8 J/g with a standard deviation of 1.7 J/g, and peak melting temperature 93.6°C with a standard deviation of 0.5°C. The DSC analyses were done on: (1) each of the POP, PC-LLDPE, and PC-HDPE polymers, as well as stearic acid lubricant; (2) the compounded formulations whose compositions are presented in Table I to study the influence of filler and lubricant on the crystallization behavior of the polymers.

RESULTS AND DISCUSSION

Thermal Analysis

Table III presents the DSC results for POP, PC-LLDPE, PC-HDPE alone, or compounded with calcium carbonate and lubricant, as shown in Table I. For compounded resins, the experimental latent heat of melting is compared with the calculated one, which was obtained by an additivity

relationship taking into consideration the weight fraction of resins, and the very small weight fraction of stearic acid lubricant. The latent heat of melting of stearic acid is 189 J/g. Excellent agreement between experimental and calculated data support the conclusion that within the compounds the ability of individual polymers to crystallize is not hindered by the presence of a large proportion of filler.

The DSC thermograms of PC-LLDPE are characterized, as expected, by a broad melting range with two melting peaks at about 112 and 125°C, as can be seen from Table III and Figure 1. The DSC thermograms of PC-HDPE show a single sharp peak and a high latent heat of melting characteristic of highly crystalline polymers. The thermograms for POP reveal a broad melting endotherm with a quite long low temperature tail. In all cases, the presence of 200 phr calcium carbonate has little effect on the shape of thermograms or position of the melting peaks.

The thermal characteristics of POP blends with the PC polymers described are discussed in detail below.
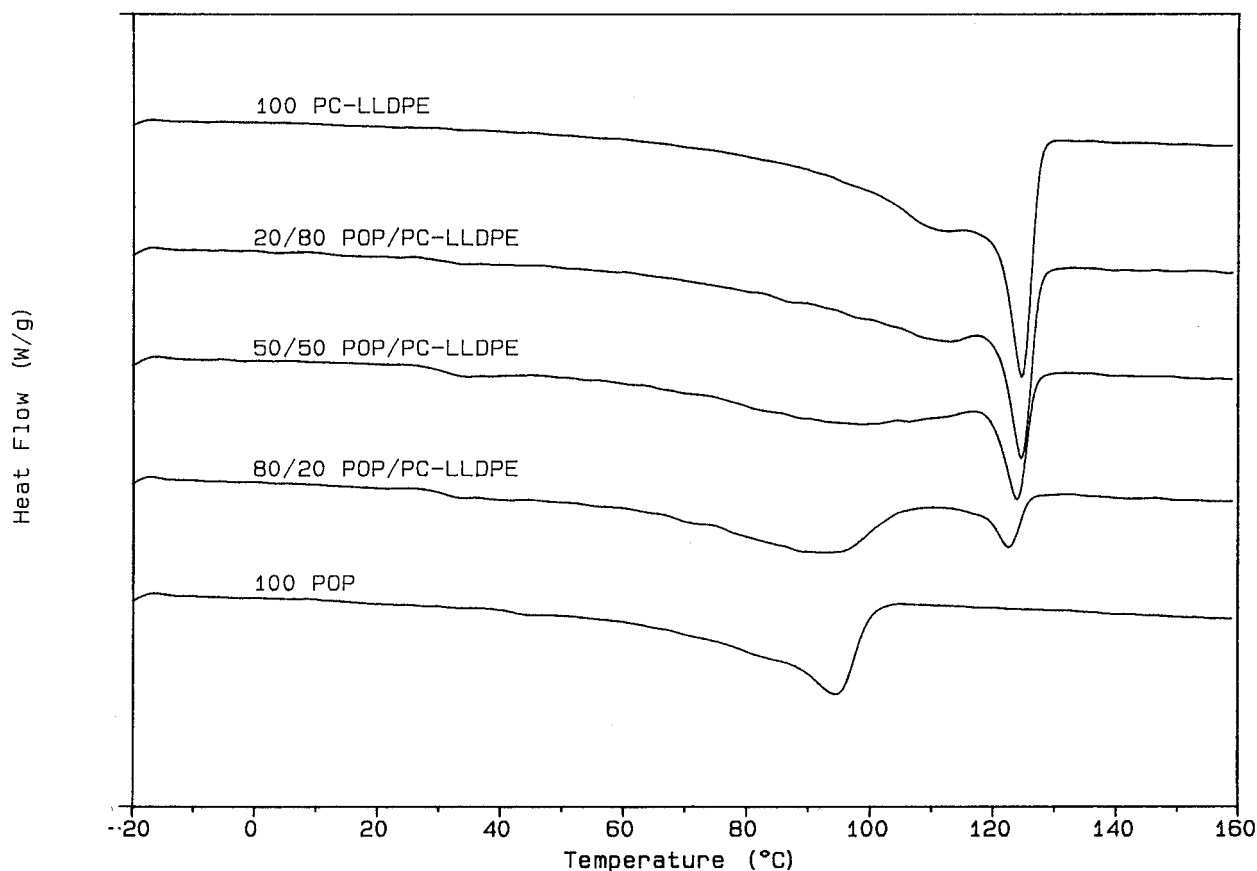
POP/PC-LLDPE Blends

The melting behavior of these blends over the entire composition range is illustrated by the second melting thermogram in Figure 2, and the crystallization behavior is shown in Figure 3. All the blends present two melting peaks: the first broad peak at lower temperature, and the second sharp peak at higher temperature. Their locations are shown in Figure 4(a) and (b), respectively, along with the corresponding crystallization temperatures. 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 12°C between melt-
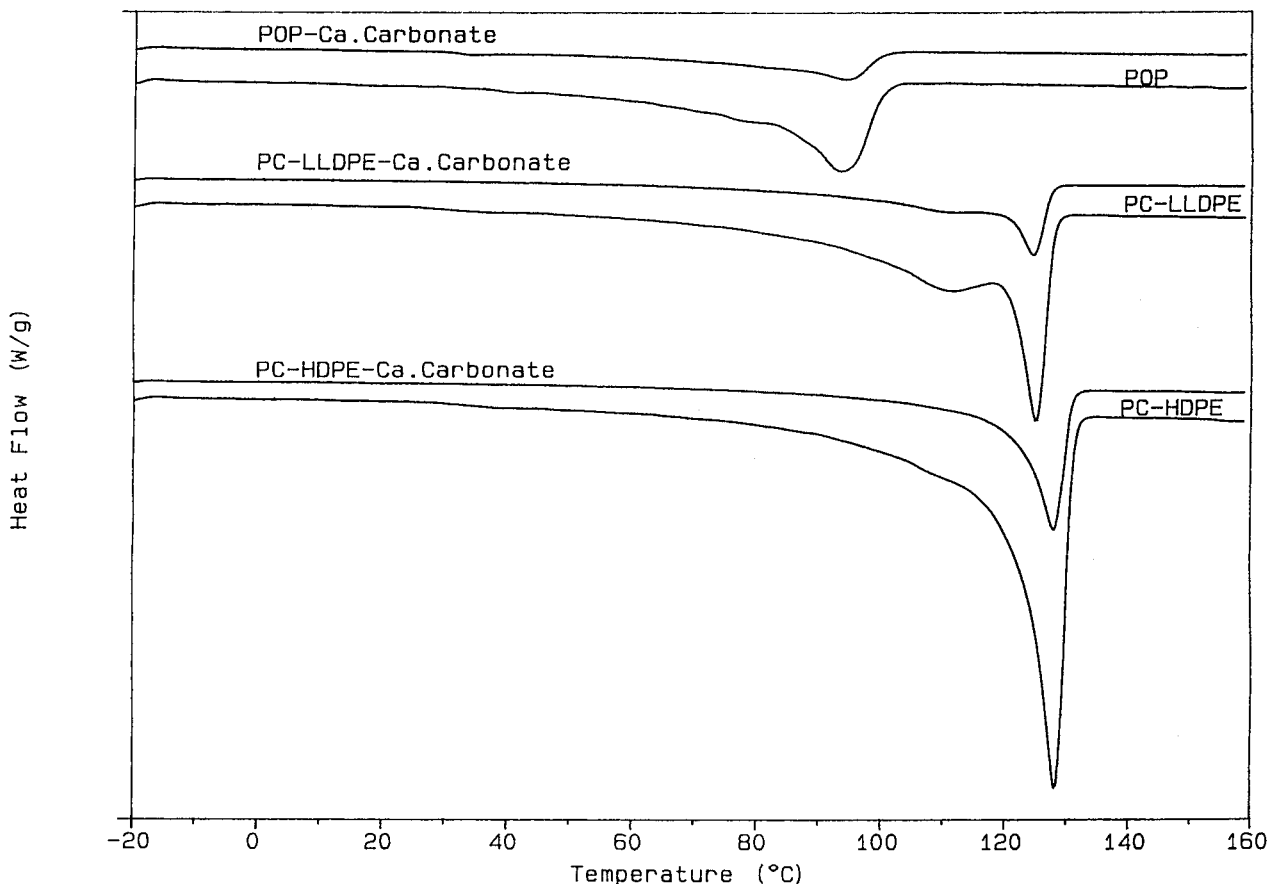
Figure 1 DSC heating thermograms of single and compounded polyolefins.

ing and crystallization temperatures. For polymers in the molten state, a significant degree of supercooling, usually about 10°C below the melting temperature, is required before crystallization commences.[12] As can be seen from Figure 4(a), the location of the low temperature peak increases from about 92°C in the 80/20 POP/LLDPE blend to about 112.8°C in the 20/80 blend, a difference of approximately 20°C. The location of the high temperature peak changes within only 2°C, from 122.6 to 124.6°C, depicting that the melting of low comonomer fractions are not too sensitive to blend composition. In contrast with 80/20 and 50/50 blends where the low temperature peak is well defined, in the 20/80 blend it becomes more diffuse and appear like a shoulder. The shape and the position of the low-temperature melting peaks, and the slightly higher than expected degree of crystallinity (Figs. 2 and 5) in 80/20 and 50/50 blends can be taken as an evidence of a partial cocrystallization between the two polymers. This cocrystallization would occur between the low molecular weight, high comono-

mer fractions of LLDPE, which melt at lower temperature, and molecules of POP of adequate length. The literature shows that the occurrence of a single intermediate melting peak, and sometimes a difference in crystallinity, would be observed when polyethylene blend components can cococrystallize.[2,12–16] In conventional LLDPE, the low molecular weight, high comonomer fractions have a heterogeneous distribution, and consequently, the folding of these polymer chains during crystallization is not uniform, resulting thicker lamellae with a relatively low number of tie molecules. These tie molecules pass through crystalline lamellae into amorphous regions producing interphase bonding. In the blends, more nucleating agents will be present for cocrystallization due to the narrow comonomer distribution along the chains of POP. Consequently, thinner lamellae will result having more tie molecules. In this way, the spherulite size will be reduced because the spherulite growth is limited by contact with other similarly developing centres.[12,17] According to the literature, a decrease in melting

Figure 2 DSC heating thermograms of POP/ PC-LLDPE blends.

temperature of semicrystalline polymers can be taken as evidence of decreasing spherulite size.[17,18] Indeed, the decreasing melting temperature of the low-temperature peak can be seen clearly in Figures 2 and 4(a). In the 80/20 composition, this decrease is even lower than the melting temperature of POP, whereas in the 20/80 composition, it is slightly higher than the melting temperature of the PC-LLDPE.

From the DSC data of POP/ PC-LLDPE blends it may be concluded that in the 80/20 and 50/50 blends the two polymers partially cocrystallize. The location of the common melting point suggests that cocrystallization occurs between the high comonomer fractions of PC-LLDPE and POP, and that the size of the spherulites thus formed is probably smaller than in either individual polymer. DSC data show an increase in blend crystallinity as progressively more PC-LLDPE is present in the blend.

POP/PC-HDPE Blends

The melting behavior of these blends, over the complete composition range, is illustrated by the second melting thermogram in Figure 6. As with the PC-LLDPE blends, there is a similarity between the melting and crystallization thermograms. A difference of about 12°C between melting and crystallization temperatures can be seen in Figure 7. Figure 6 shows that the 80/20 blend presents two clearly defined melting peaks. The first one is at around 92°C, and can be attributed to POP. The second is at around 124°C, and can be attributed to HDPE. However, the low-temperature melting peak is shifted from around 95°C, as it is in compounded POP to 92°C. The second peak is shifted from around 128°C, as it is in compounded PC-HDPE, to around 124°C. From Figure 8 it can be seen that for the 80/20 blends there is a small difference between the experimental and the calculated crystallinities. For the other compositions, the values of calculated and experimental crystallinity are the same. The changes in the position of the melting peaks, and differences in the crystallinity, observed in the 80/20 blends could result from a partial cocrystallization. The literature reported on the basis of detailed X-ray analysis of conventional LLDPE,
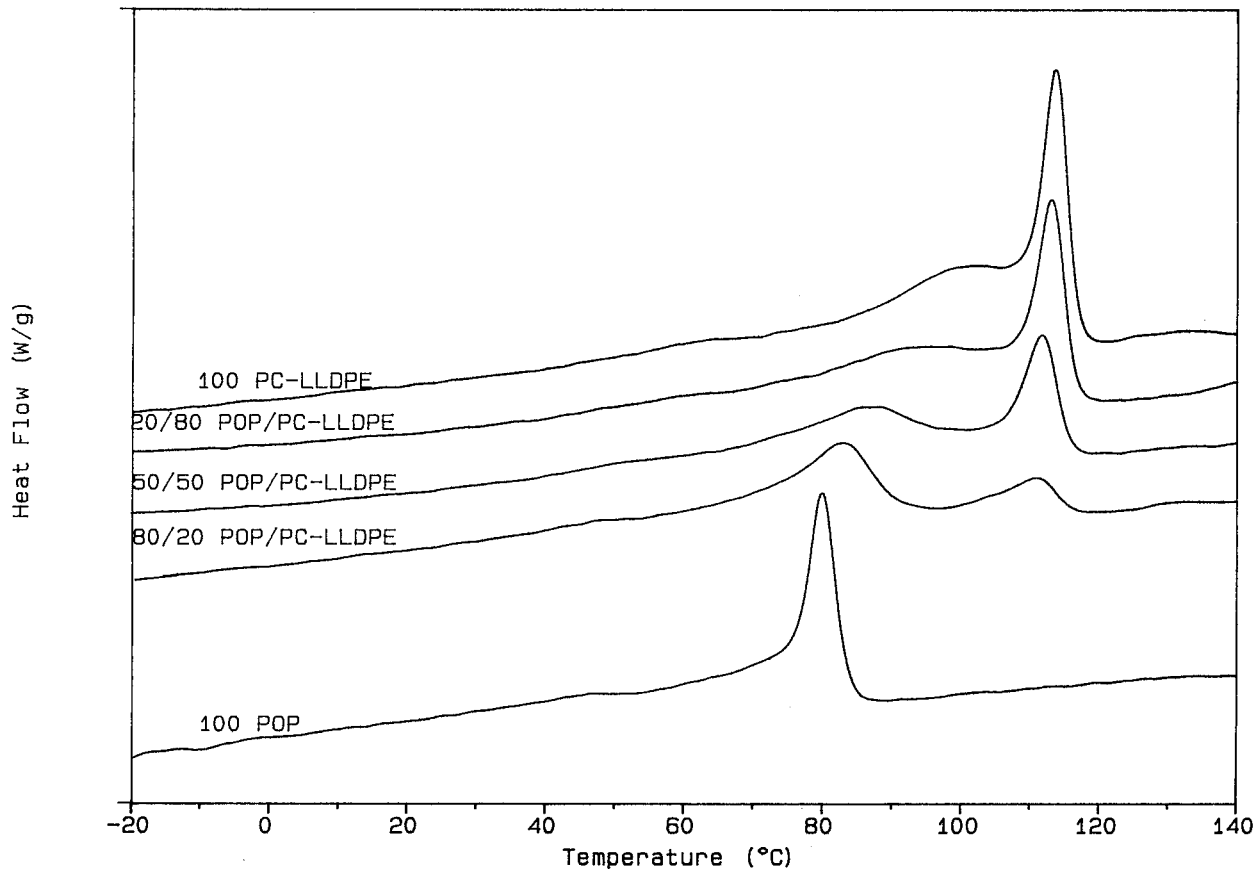
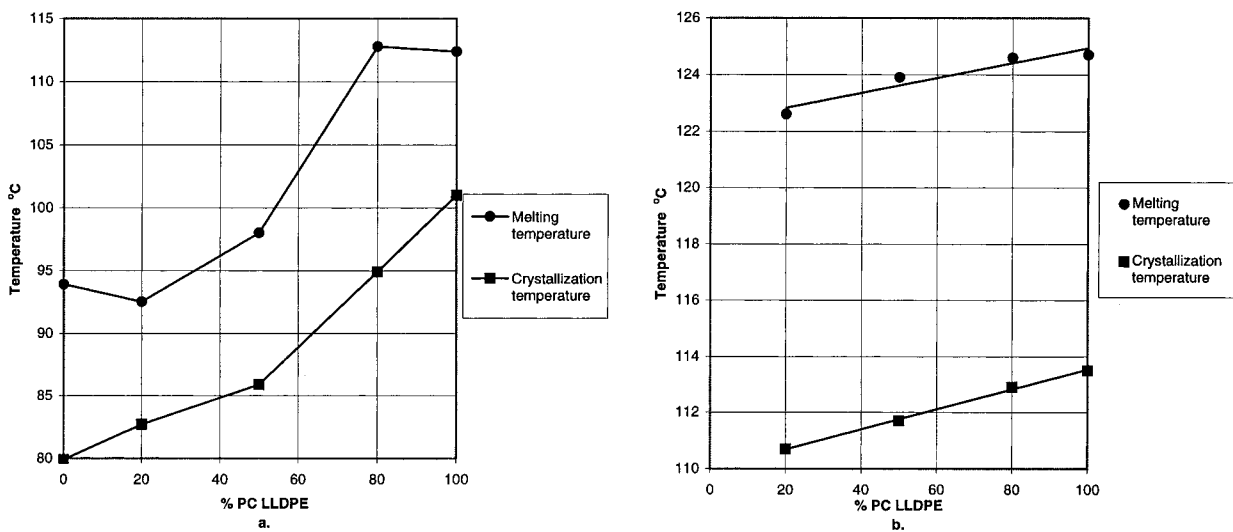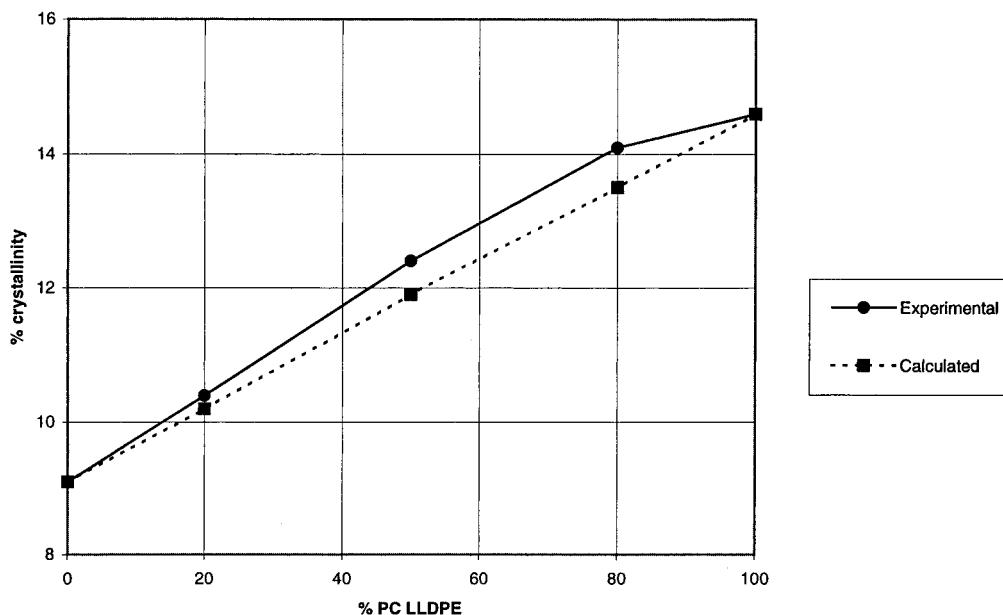**Figure 3**   DSC cooling thermograms of POP/PC-LLDPE blends.

Figure 4   Melting and crystallization temperatures as functions of blend composition: POP/PC-LLDPE blends. (a) first peak, (b) second peak.

Figure 5 Percent cystallinity as a function of blend composition: POP/PC-LLDPE blends.

show that the unit cell of linear PE could accommodate some limited amounts of HDPE, resulting in a limited range of cocrystallization.[13] It should be noted that for the other compositions, the first melting peak is not clearly defined. It appears like a shoulder in 50/50 blends, and is practically not discernable in 20/80 blends, as can be seen from Figure 6. From the DSC data of POP/ PC-HDPE blends, it may thus be concluded that only in the 80/20 blends can some partial cocrystallization occur.

Mechanical Tests

Table IV summarizes the results obtained in the tensile and impact tests for the formulations described in Table I. The tabulated data show that the tensile and impact properties of POP-based formulations compare very favorably to the PVC based ones. In particular, the higher values in elongation and impact strength point to superior toughness in POP samples. This point is significant because high filler loadings typically have large adverse effects on the toughness of mixtures made with conventional polyolefin resins. The results also show that POP resins can easily accommodate calcium carbonate loadings of 200 phr while maintaining adequate mechanical properties. On the other hand, Table IV shows that formulations of single PC-polyolefins have very poor mechanical properties. In contrast with POP

formulations that undergo ductile deformation under the experimental conditions, both PC–polyolefin compounds are brittle. The calcium carbonate loading is clearly much too high for the PC–polyolefins to function as effective binders. Compounded blends of POP with 20, 50, and 80% PC-LLDPE or HDPE were, therefore, prepared and tested. The results of the mechanical tests performed on these blends are discussed below.They are presented in Table V.
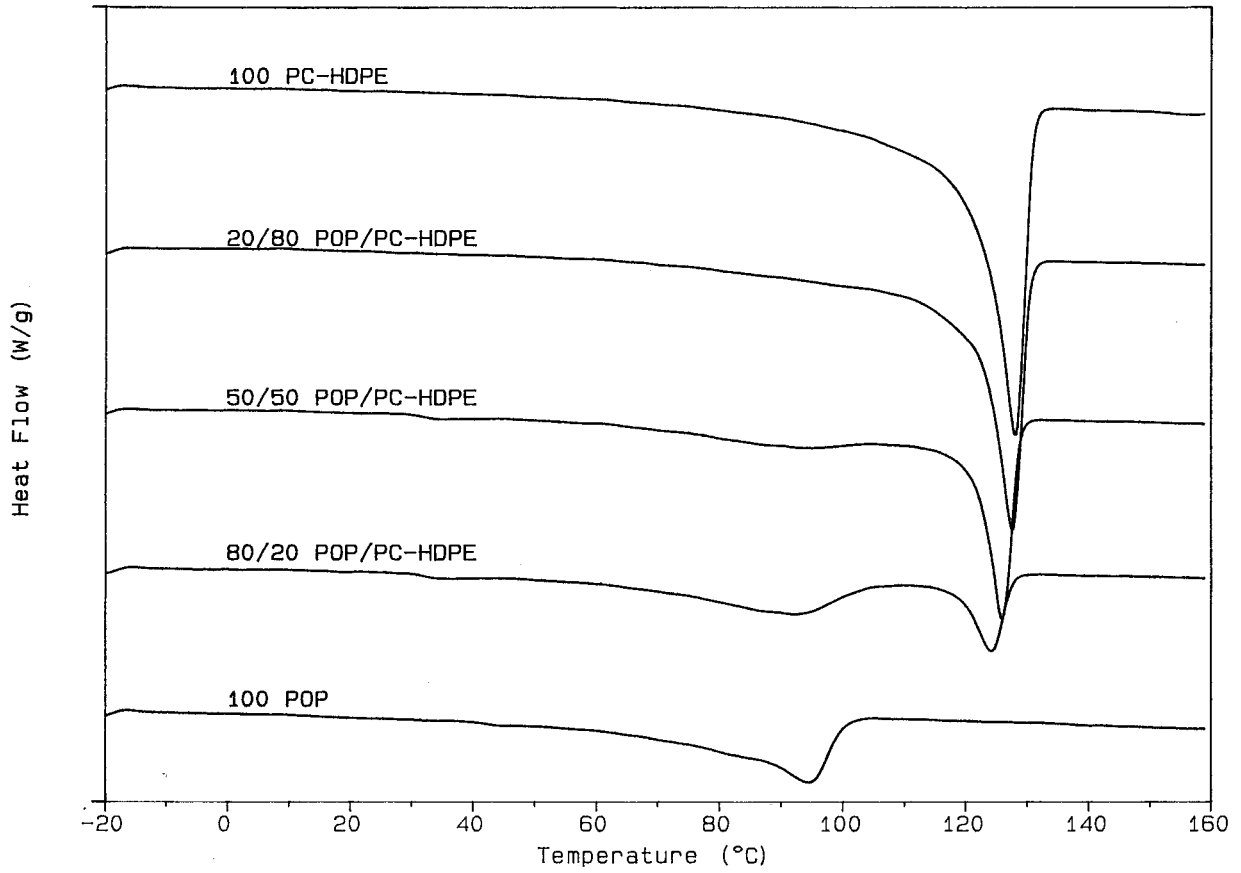
POP/PC-LLDPE Blends

Figure 9 outlines the results obtained in the tensile and impact tests for these blends, over the entire composition range. It shows the normalized tensile and impact data, so that the data for unblended POP represent 100%. In the same figure, calculated tensile and impact data, assuming additivity of each blend's components, are represented by dashed lines.

The variation of the yield strength with composition shows a general trend to increase, which is expected, taking into account the yield strength difference between POP and PC-LLDPE (Table IV). However, the experimental data are lower than the calculated ones, especially for the 50/50 blend.

When compared with POP alone, the ultimate properties of POP/PC-LLDPE decrease moderately in the 80/20 and 50/50 blends. Tensile
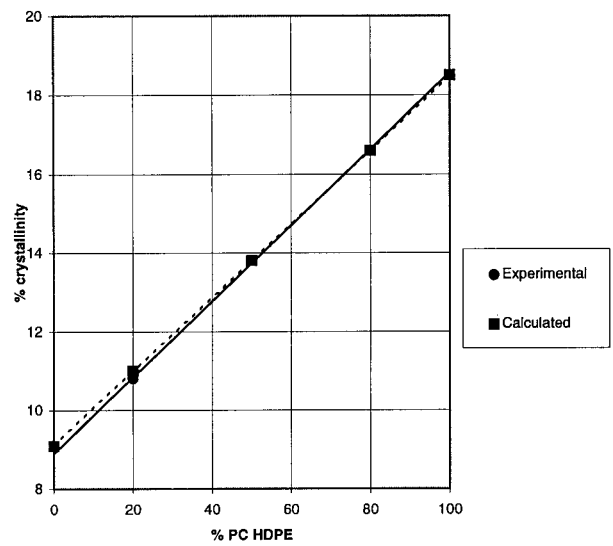
Figure 6 DSC heating thermograms of POP/PC-HDPE blends.
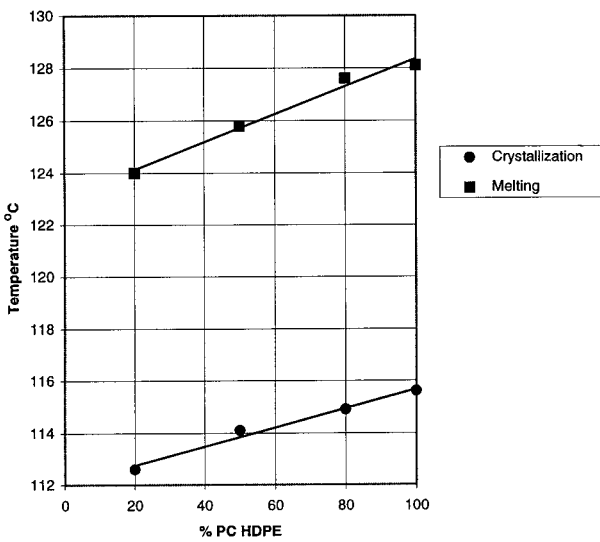
Figure 7 Meting and crystallization temperatures as functions of blend composition: POP/PC-HDPE blends.

Figure 8 Percent crystallinity as a function of blend composition: POP/PC-HDPE blends.

Table IV   Results of Tensile and Impact Testing for Formulations with PVC, POP, PC-LLDPE, and PC-HDPE Compounded with Calcium Carbonate

Matrix Resin	Yield Strength (MPa)	Break Strength (MPa)	Elongation (%)	Impact Strength (J/m)
PVC	2.77	5.55	336	154.0
POP	2.80	7.82	1600	278.3
PC-LLDPE	7.42	6.04	8	40.0
PC-HDPE	6.84	6.64	3	110.0

strength at break is close to the calculated values. Elongation is 10 and 40% higher, respectively, than the calculated values. In the 20/80 blend, however, both ultimate properties decrease dramatically, becoming even lower than the calculated values. In contrast with 80/20 and 50/50 blends, which undergo ductile deformation under the experimental conditions, this blend is brittle.

As can be seen from Figure 9, the results of the impact strength tests essentially follow the same trends as the other results. When compared with unblended POP, the normalized impact strength increases gradually to a level of 108 and 127 in the 80/20 and 50/50 blends, respectively. It then decreases to a level of 32, in the 20/80 blends, which is lower than the calculated one. The initial increase in impact strength may be due to differences in melt rheology during the compounding of the various calcium carbonate-filled blends. The final blend viscosity will depend on the ratio of higher viscosity PC-LLDPE to lower viscosity POP present in the mixer. Melt viscosity affects the dispersion of filler particles, which in turn, affects the impact strength.

The variation in the mechanical properties as function of blend composition shows significant differences among the blends. It is interesting to note that these differences seem to be correlated with the ability of the individual polymers to cocrystallize. In the 80/20 and 50/50 blends the me-

chanical property levels are at least equal to or slightly higher than those expected on the basis of an additivity rule for the blend components. In the 20/80 blends the mechanical properties are very poor, and lower than those expected on the basis of an additivity rule.

Thermal analysis has shown that the individual polymers can cocrystallize for the 80/20 and 50/50 blends. The corresponding decrease in spherulite size and increase in number of tie molecules provide strength to the spherulites and the amorphous phase, thus resulting in a stronger and tougher material. The same concept of tie molecules is suggested by the literature for explaining several improved mechanical properties of LLDPE or metallocene-PE blends with other polyolefins.[19,20]

The actual values of the properties of these blends are summarized in Table V. From the data presented in Table V it can be clearly seen that the tensile and impact properties of the 80/20 and 50/50 blends compare very favorably to the PVC formulations. Again, higher values in elongation and impact strength point to superior toughness in these blends and to possibilities of using at least 50% PC- LLDPE for their production.

POP/PC-HDPE Blends

Figure 10 summarizes the results obtained in the tensile and impact tests for POP/PC-HDPE

Table V   Results of Tensile and Impact Tests for POP/PC Resins Blend Formulations

POP-PC Resin Blend	Yield Strength (MPa)	Break Strength (MPa)	Elongation (%)	Impact Strength (J/m)
80/20 LLDPE	3.44	7.31	1396	299.4
50/50 LLDPE	4.45	6.78	1143	353.6
20/80 LLDPE	6.30	5.04	9	77.0
80/20 HDPE	4.15	7.14	1272	334.4
50/50 HDPE	5.44	5.58	467	359.7
20/80 HDPE	6.87	6.29	24	218.8
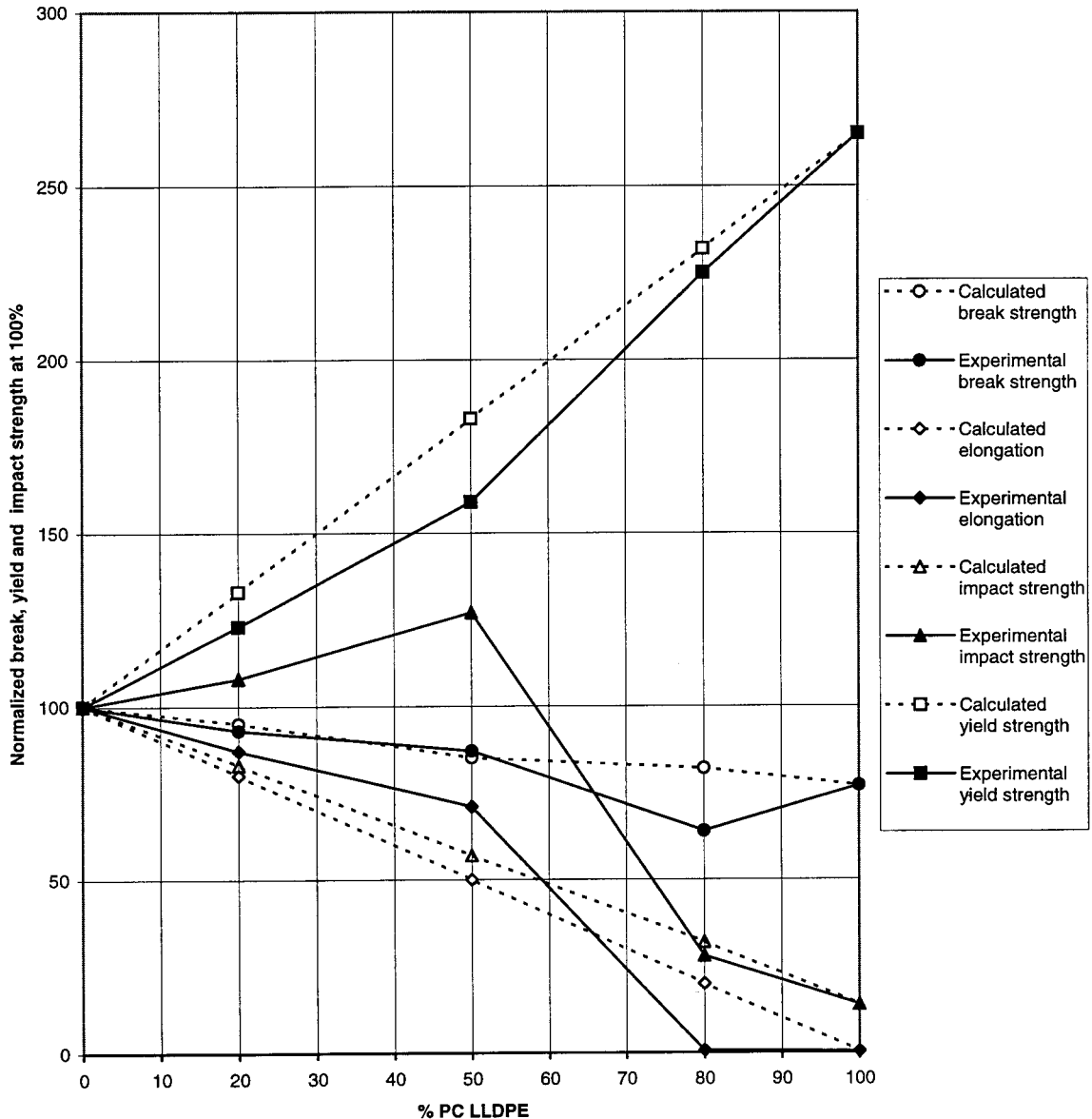
Figure 9 Normalized tensile and impact test data for POP/PC-LLDPE blends.

blends over the complete composition range. The calculated values assuming the additivity of the blend components are also shown by dashed lines. As with POP/PC-LLDPE blends, the results are presented in normalized form, and the actual values are shown in Table V.

If compared with the calculated values, the ultimate tensile properties of the 80/20 blend are very close, whereas the yield and impact properties are higher. Under the experimental conditions, the blend undergoes ductile deformation. In 50/50 and 20/80 blends the ultimate properties are lower than the calculated ones,

with the 50/50 blend exhibiting the greatest deviation. The unexpected increase in the impact strength may be due, as in the case of PC-LLDPE blends, to the improved dispersion of the filler during the compounding step resulting from favorable blend rheology. Cocrystallization in the 80/20 blend may also contribute to improved tensile and impact properties of this particular composition. Here, the concept of tie molecules can be used as with POP/PC-LLDPE blends. The results presented in Table V, show that the 80/20 and 50/50 blends exhibit higher tensile and impact properties than PVC formu-
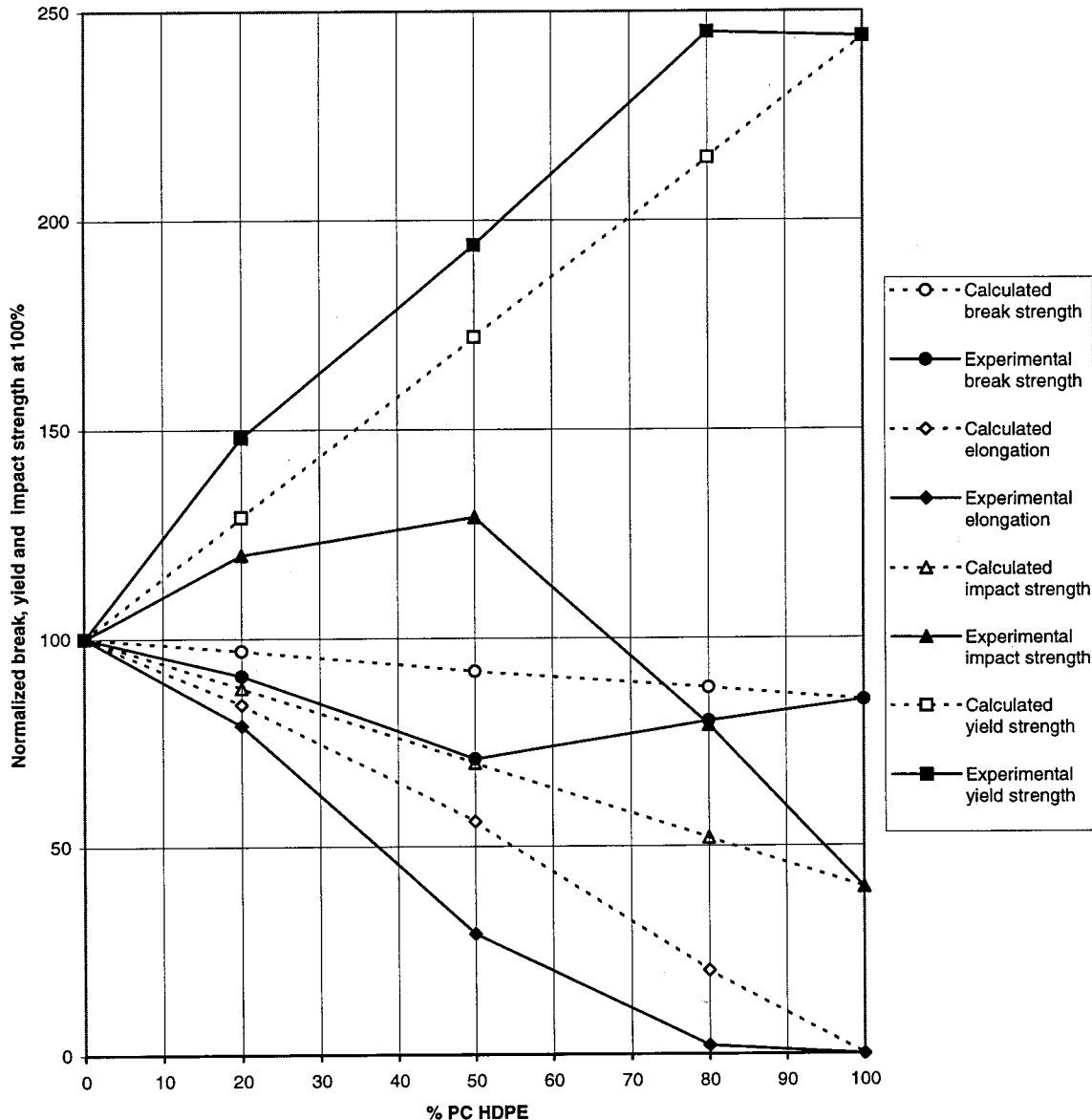
Figure 10   Normalized tensile and impact test data for POP/PC-HDPE blends.

lations. Higher values in elongation and impact strength point to possibilities of using at least 50% PC-HDPE for their production.

CONCLUSIONS

Tensile and impact proerties of calcium carbonate-filled POP composites compare very favorably to PVC-based formulations at filler loading as high as 200 phr. Moreover, postconsumer polyolefins can replace a significant percentage of POP in these formulations. For both PC-LLDPE and PC-HDPE, 50/50 blends with POP are found to retain satisfactory elongation and impact properties when compared to PVC formulations.

A synergism in mechanical properties occurs for some of the blend compositions. Results of DSC analyses indicate that this synergism may be related to the ability of the individual polymers to cocrystallize in the respective blends.

Further studies should be done for complete characterization of POP/ postconsumer polyolefins blends for establishing if they can replace plasticized PVC in some or all flooring formulations.

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