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เรื่อง

อิทธิพลของตัวเสริมแรงกับสมบัติเชิงกลของพลาสติกโพลีเอทธิลีนและโพรพิลีน

โดย

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Mechanical Properties of Polyethylene Filled with Calcium Carbonate

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The mechanical properties of high density polyethylene (HDPE) filled with calcium carbonate particles were studied. Compounding of polyethylene and filler from 0 to 50 % w/w loading was carried out in a two-roll mill and the test samples were formed by a compression mold. In particular, the effect of filler content and filler size upon tensile strength, elongation, elastic modulus, izod impact strength and hardness were investigated. The results indicate that the tensile strength, modulus and hardness of $CaCO_3$ 1939-filled PE composites increased with an increase of filler content. The elongation at break and impact strength decreased with an increase of filler content. The properties of polyethylene filled with calcium carbonate were found to be similar to carbon-black filled polyethylene.

Key words: Polyethylene, calcium carbonate, mechanical properties.

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ประสิทธิ์ สุมนัสวรพันธุ์ ภัทรพรรณ ประศาสน์สารกิจ กัญจนา ตระกูลคู และ สุดา เกียรติกำจรวงศ์ (2537) สมบัติเชิงกลของโพลิเอทิลีนเติมด้วยแคลเซียมคาร์บอเนต *วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย* 19(2): 235-248

งานวิจัยนี้เป็นการศึกษาสมบัติเชิงกลของโพลิเอทิลีนความหนาแน่นสูงเติมด้วยแคลเซียมคาร์บอเนต การผสมโพลิเอทิลีนกับตัวเติมปริมาณ 0-50 % โดยน้ำหนัก ทำในเครื่องผสมลูกกลิ้งคู่และชิ้นงานทดสอบเตรียมด้วยเครื่องอัดร้อน งานนี้ศึกษาผลของปริมาณและขนาดอนุภาคตัวเติมต่อความต้านแรงดึง ความยืดชาด โมดูลัส ความต้านแรงกระแทกอิซอด และความแข็งของชิ้นงาน จากผลงานวิจัยพบว่าความต้านแรงดึง โมดูลัสและความแข็งแรงของโพลิเอทิลีนผสม $CaCO_3$ 1939 มีค่าเพิ่มขึ้นกับการเพิ่มปริมาณตัวเติม ความยืดชาดและความต้านแรงกระแทกลดลงกับการเพิ่มปริมาณตัวเติม สมบัติของโพลิเอทิลีนเติมด้วยแคลเซียมคาร์บอเนตพบว่าคล้ายคลึงกับโพลิเอทิลีนเติมด้วยคาร์บอนแบล็ก

คำสำคัญ: โพลิเอทิลีน, แคลเซียมคาร์บอเนต และสมบัติเชิงกล

Introduction

The research on the use of relatively cheap filler was stimulated by the price of plastic and a number of publications have recently appeared dealing with mineral fillers(1-5). Adding inorganic fillers to polyolefin is widely recognized as a means of improving some physical properties and elevated-temperature performance. Inorganic particulate fillers, such as talc, silicas and calcium carbonate are inexpensive extenders but lead to increased stiffness and corresponding losses in tensile strength and elongation. Factors including the filler content, particle size, adhesion of filler to the polymer and processing technique affected largely the macroscopic characteristics of filled composites. The mechanical properties were determined from the stress-strain behavior and in some cases supplemented with impact strength. For polypropylene filled with calcium carbonate, the modulus (stiffness) increased with increasing the $CaCO_3$ content, and the changes in the breaking strength were relatively limited whilst the elongation at rupture and the impact strength were reduced(6).

The purpose of the present paper is to report the results of an experimental investigation of the mechanical properties of high density polyethylene (HDPE) when it was modified by the addition of varied amounts of two grades of calcium carbonate and to compare its properties with those of other commercially available fillers.

Experimental

Materials

High-density polyethylene (HDPE) Polene grade R-1760 of density 0.957 g/cm^3 and melt flow index 6.0 g/10 min was supplied by Thai Petrochemical Industry Co., Ltd. Two grades of calcium carbonate, $CaCO_3$ 039 and $CaCO_3$ 1939 were supplied by Surint Omya Chemical Co., Ltd. The characteristics of carbonate fillers are summarized in Table 1.

Preparation of composites

Compounding of polyethylene and filler was carried out in a two-roll mill (model L.R.M 110 from Lab Tech Engineering Co., Ltd). Usually about 20 g of polymer was mixed with $CaCO_3$ filler (10, 20, 30 and 40% by weight of filler) at 150^{o}C for 10-15 min with frequent manual remixing of the mixture for a better dispersion of filler in the polymer. The mixture was then allowed to cool to room temperature.

Compression molding of the polymer-filler mixture was done at 150^{o}C in a hydraulic hot press (model LP 20 from Lab Tech Engineering Co., Ltd.) The compound sheet was pressed to a mold plate under a pressure of 2000 psi for 5 minutes after preheating at a temperature of 150^{o}C for 5 minutes. The samples were slowly cooled to room temperature with the pressure maintained during the process. The samples were then conditioned overnight before being testing for mechanical properties.

Mechanical testing

The tensile properties were studied using a Shimadzu tensile tester (model S-100-C) in an extension mode at 10 mm/min extension rate using a 50 kg load cell. The tensile strength, elongation at rupture and the tensile modulus were determined according to ASTM D638. A minimum of six samples were tested in each series. The notch impact resistance (Charpy) was determined according to ASTM D256 at room temperature by using a Toyo Seiki impact tester model 612. The hardness of the composite specimen was measured using a Shore Durometer (model QD from Instrument & Manufacturing Co., Ltd.) according to ASTM D2240.

Results and Discussion

Stress-strain curve

Figure 1 illustrates the stress-strain curves of 10%, 20% and 30% $CaCO_3$ 1939 filled polyethylenes.

Table 1. Properties of calcium carbonate.

	$CaCO_3$ 039	$CaCO_3$ 1939
Physical properties		
Brightness, %	97	97
Moisture content, %	0.2	0.2
Specific gravity	2.7	2.7
DOP absorption, g/100 g	25	25
Oil absorption, g/100 g	20	20
Chemical analysis		
$CaCO_3$	99.0 %	99.0 %
MgO	0.4	0.4
SiO_2	0.2	0.2
Al_2O_3	0.3	0.2
Fe_2O_3	0.1	0.2
Particle size distribution (%)		
Finer than 3 μm	13 %	30 %
Finer than 9 μm	30 %	60 %
Finer than 15 μm	43 %	68 %
Finer than 25 μm	57 %	100 %
Finer than 50 μm	100 %	-

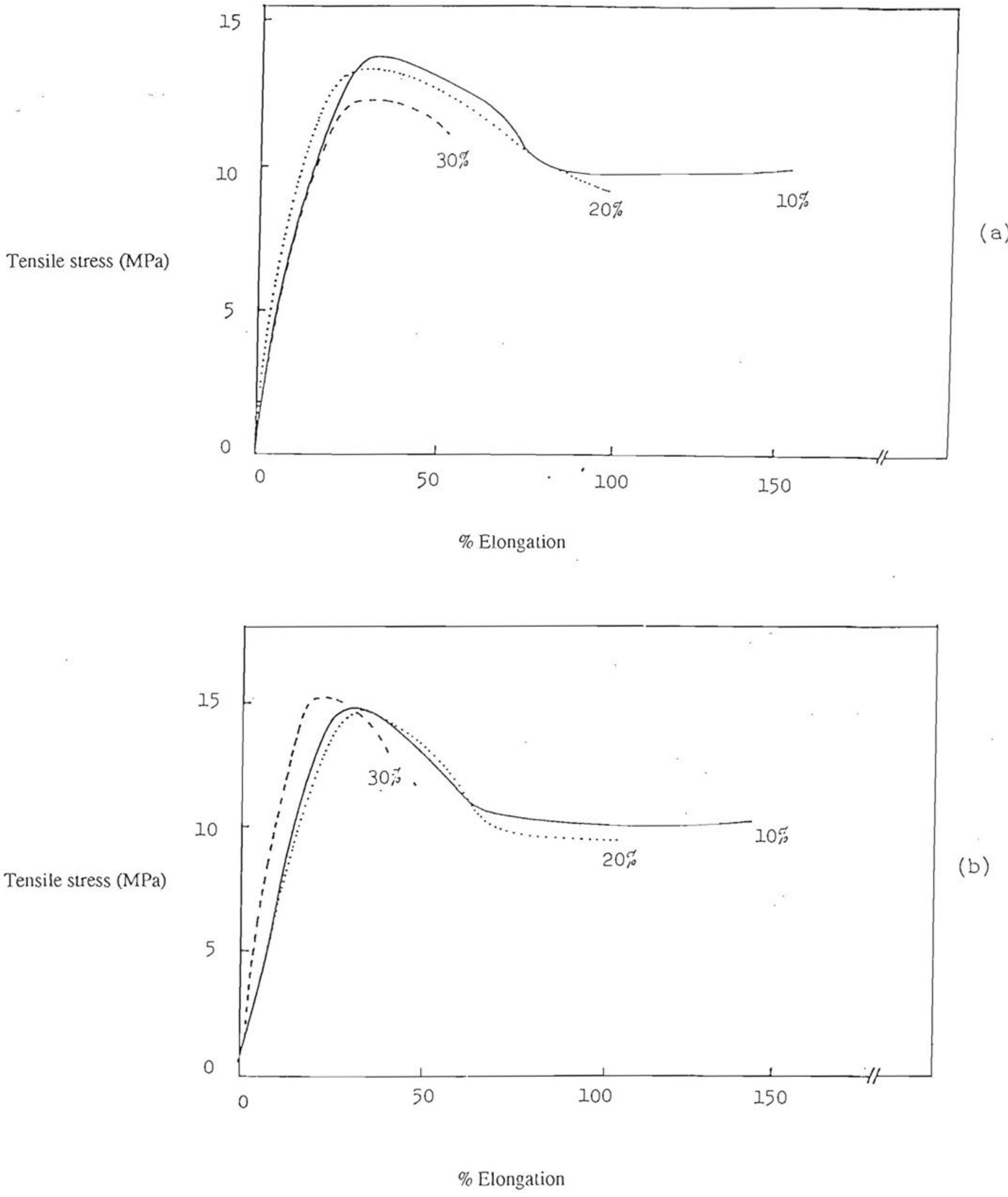

Figure 1. Stress-strain curves for various percentages of filler for (a) $CaCO_3$ 039 (b) $CaCO_3$ 1939: — 10%, ... 20% and ---- 30%.

The larger the amount of filler, the higher the elastic modulus of composites filled with $CaCO_3$ 039. The yield stress and elastic modulus increased while the percent elongation decreased with an increase in $CaCO_3$ 1939 filler content.

Effect of $CaCO_3$ filler content

The mechanical properties of thermoplastic-$CaCO_3$ composites depend upon the properties of the polymer matrix, filler and polymer-filler interface. The $CaCO_3$ used was a fine particle spherical filler of particle size below 50 μm. Figures 2 and 3 show the variation of tensile strength, elongation, tensile modulus and impact strength with filler concentration for $CaCO_3$ 039 and $CaCO_3$ 1939 filled PE, respectively. The results show a steady decrease in tensile strength with the rise in $CaCO_3$039 filler concentration. This may be due to the larger particle size of $CaCO_3$ 039 that causes a poor dispersion of $CaCO_3$ in the matrix. Another reason for the lower tensile strength would be the filler adhesion to the polymer matrix. Due to the smaller particle size of $CaCO_3$ 1939, it does not appreciably influence the tensile strength of high density polyethylene (15-16.5 MPa).

For polyethylene, the main effect of incorporating $CaCO_3$ into the polymer is a reduction in the elongation required at break. The elongation decreased sharply with an increase in the filler content in the polymer. The elongation was not affected much by the $CaCO_3$ grade. The addition of $CaCO_3$ to polyethylene reduces the elongation at break and the impact resistance drastically as shown in Figures 2 and 3.

The most pronounced effect on mechanical properties by adding a rigid filler to a polymer system is upon the tensile modulus. The incorporation of $CaCO_3$ in the polymer matrix increases the tensile modulus. The tensile modulus increased linearly with filler concentration as shown in Figures 2 and 3. The rise in tensile modulus of the composite is due to the higher modulus of $CaCO_3$. As expected, the increase in stiffness is accompanied by a corresponding decrease in ductility. Tables 2 and 3 summarize the mechanical properties of HDPE filled with $CaCO_3$ 039 and $CaCO_3$ 1939, respectively.

Comparison of $CaCO_3$, carbon black and glass fiber fillers

Figure 4 shows the variation of tensile strength, elongation, modulus, impact strength and hardness with carbon black filler concentration. A comparison of the mechanical properties of polyethylene filled with $CaCO_3$, carbon black and fiber glass is provided in Tables 4 and 5. From the Tables, one can see that the $CaCO_3$-filled and carbon black-filled polyethylene have very similar property profiles in the range of loading studied. Table 4 shows that glass fiber filler produced higher tensile strength as the filler concentration increased, followed by carbon black and $CaCO_3$ composites. There is a difference in the elongation values of HDPE-$CaCO_3$ and HDPE-glass fiber filler composites. The carbon black-filled samples produce poor elongation values, while fiber glass-filled HDPE always gives a higher elongation value at 10% and 20% filler content (Table 4). However, the situation is different in the case of the tensile modulus. HDPE-carbon black samples produced the highest modulus (88 MPa) compared to the $CaCO_3$ 1939 composite (63 MPa) at 30% filler content.

Izod impact properties

In polyethylene, calcium carbonate 039 showed a large decrease in impact strength with increasing loading and gave the least decrease in tensile strength (Figure 2). Table 2 shows that the 30% and 40% filled polyethylenes had impact resistances of 39 J/m and 28 J/m, respectively.

Scanning electron micrographs of the fracture surface

The scanning electron microscope was employed to investigate the fracture surface of the samples from the

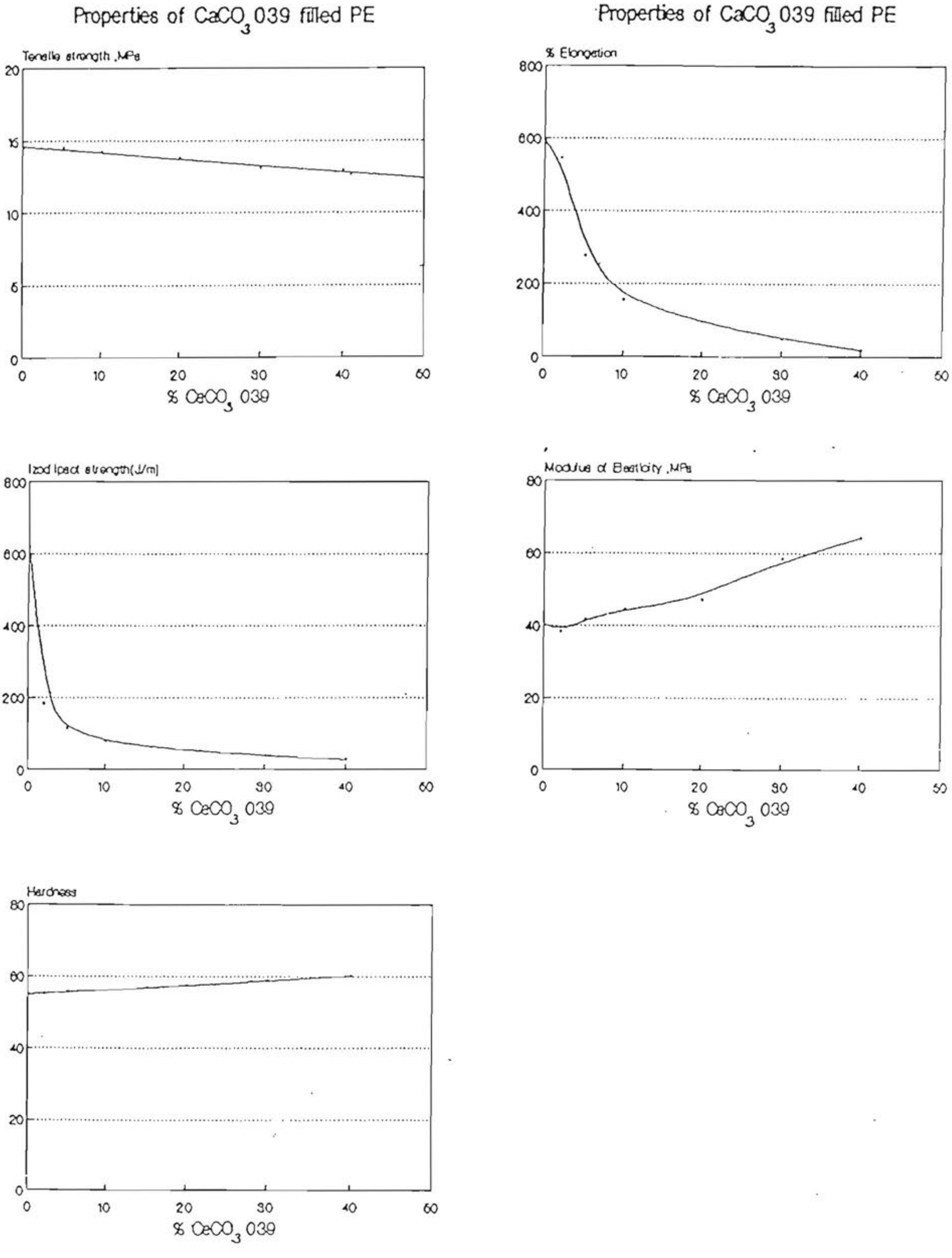

Figure 2. Variation of some properties upon the addition of $CaCO_3$ 039 to polyethylene.

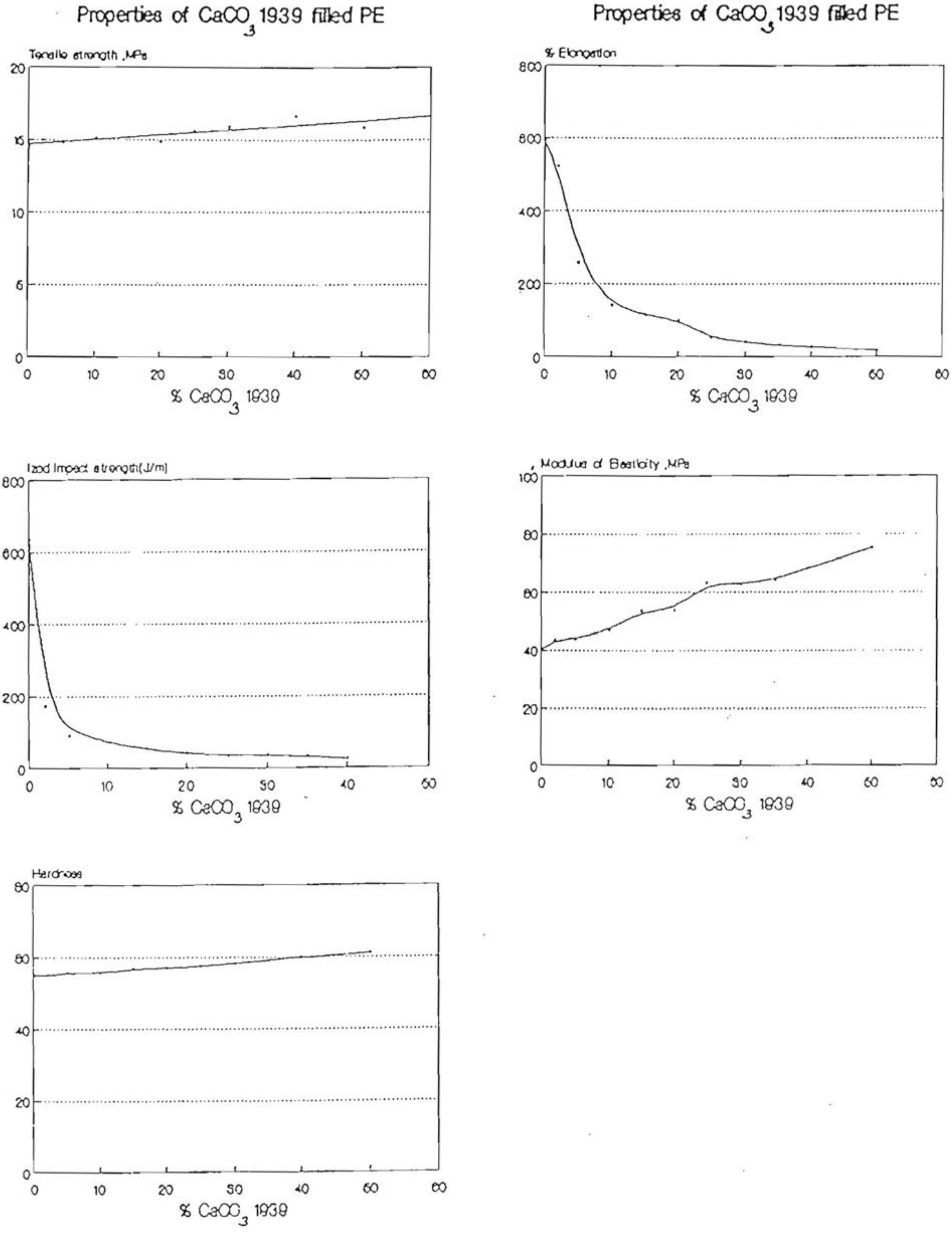

Figure 3. Variation of some properties upon the addition of $CaCO_3$ 1939 to polyethylene.

Table 2. Properties of $CaCO_3$ 039-filled polyethylene.

	% calcium carbonate					
Property	0	5	10	20	30	40
Tensile strength, MPa	14.5	14.5	14.2	13.8	13.1	12.9
Elongation, %	592	276	156	96	48	20
Tensile modulus, MPa	40	42	44	47	58	64
Izod impact, J/m	636	113	78	53	39	28
Hardness	55	55	56	56	59	60

Table 3. Properties of $CaCO_3$ 1939-filled polyethylene.

	% calcium carbonate									
Property	0	5	10	15	20	25	30	35	40	50
Tensile strength, MPa	14.5	15.0	14.8	15.2	14.8	15.6	15.9	15.9	16.6	15.9
Elongation, %	592	256	140	116	100	52	40	32	27	20
Tensile modulus, MPa	40	44	47	54	54	63	63	64	68	75
Izod impact, J/m	636	91	NA	55	42	36	36	33	26	NA
Hardness	55	56	56	57	57	58	58	59	60	61

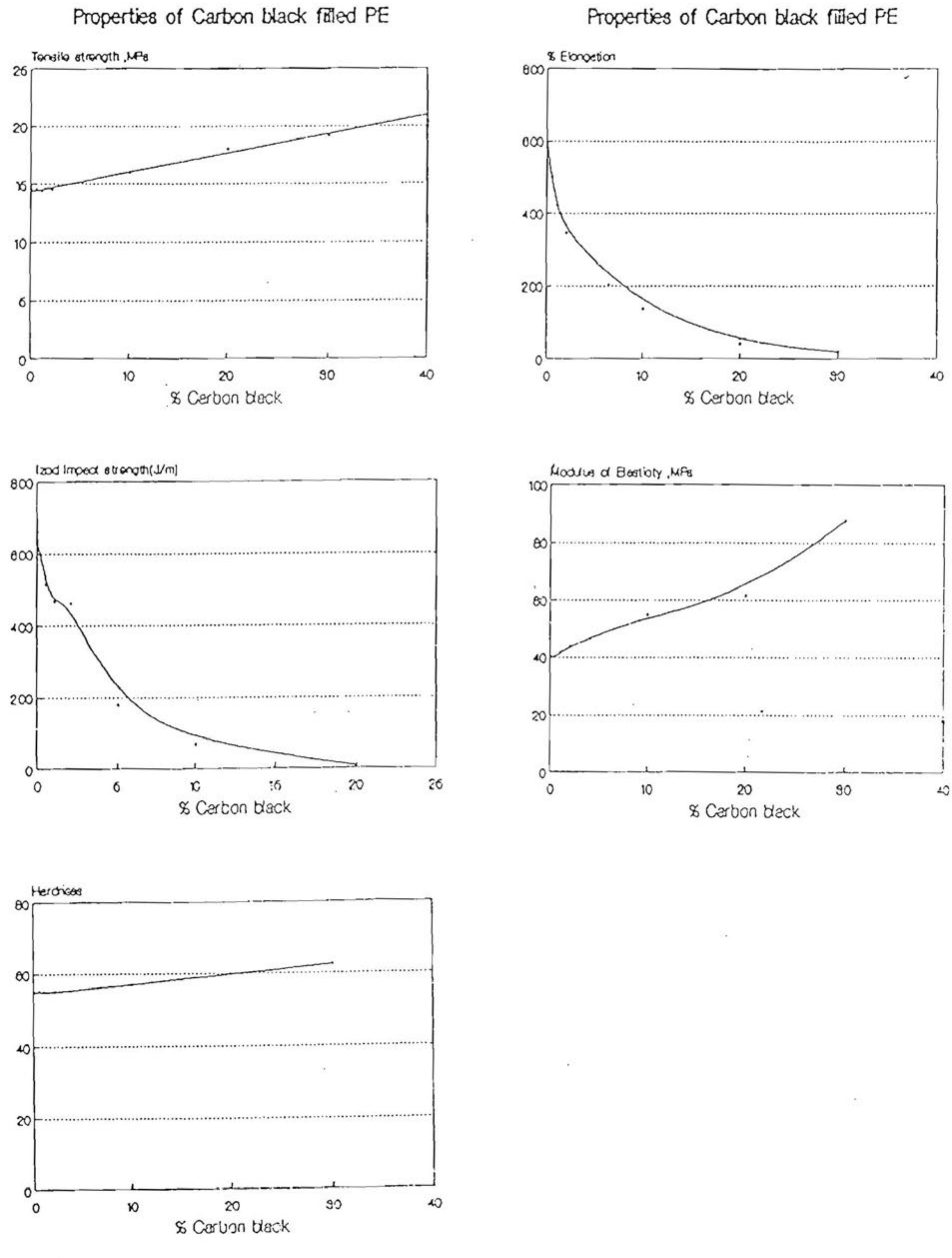

Figure 4. Variation of some properties upon the addition of carbon black to polyethylene.

Table 4. Properties of glass-reinforced, calcium carbonate-filled and carbon black-filled polyethylene at 10% and 20% filler concentrations.

Property	Unfilled	Fiber glass		Carbon black		$CaCO_3$ 039		$CaCO_3$ 1939	
		10%	20%	10%	20%	10%	20%	10%	20%
Tensile strength, MPa	14.5	18.8	24.0	16.0	18.0	14.2	13.8	15.2	14.8
Elongation, %	592	240	148	136	40	156	96	140	100
Tensile modulus, MPa	40	52	63	55	62	44	47	47	54
Izod impact, J/m	636	43	39	67	9	78	53	68	42
Hardness	55	60	65	57	60	56	56	56	57

Table 5. Properties of calcium carbonate-filled and carbon black-filled polyethylene at 30% filler concentration.

Property	Unfilled	Carbon black	$CaCO_3$ 039	$CaCO_3$ 1939
Tensile strength, MPa	14.5	19.2	13.1	15.9
Elongation, %	592	20	48	40
Tensile modulus, MPa	40	88	58	63
Izod impact, J/m	636	NA	39	36
Hardness	55	62	59	58

uniaxial tensile tests. The electron micrographs (Figures 5-8) show the fracture surface of HDPE filled with calcium carbonate at various percentages. These figures show the thorough dispersion of the filler achieved in the polymer and the difference in filler particle size. The particles, especially the large sized ones in $CaCO_3$ 039, have no "wetting" with the polymer matrix. At higher magnification, Figures 7 and 8 show holes which were occupied by the filler and indicate the relative ease in loosening the larger particles out of the polymer matrix compared with the smaller ones. Therefore, the $CaCO_3$ 039-filled HDPE exhibited a lower tensile strength than $CaCO_3$ 1939-filled HDPE. Both types of calcium carbonate do not seem to have any polymer-filler-interface bonding. Hence the calcium carbonate appears to act as an inert filler which does not reinforce the polymer phase.

Conclusion

An experimental study was carried out to investigate the effects of filler content and filler size on the elastic modulus, tensile strength and elongation of $CaCO_3$-filled HDPE. The results are as follows :

1. The elastic modulus and tensile strength of $CaCO_3$ 1939-filled HDPE increased with an increase of filler content.

2. The break elongation and impact strength decreased with an increase of filler content. The interesting finding is that the HDPE can accomodate $CaCO_3$ fillers as high as 30% by weight. The most important effect of mineral filler is therefore to improve the room temperature tensile modulus.

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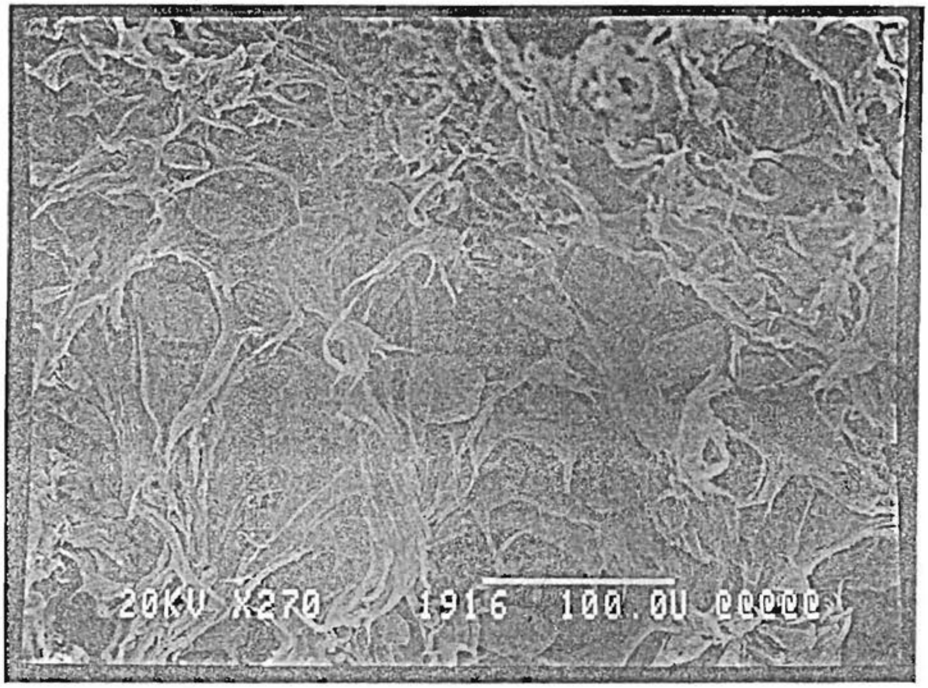

Figure 5. Electron micrograph of fracture surface of HDPE filled with 30% $CaCO_3$ 039. Magnification x 270.

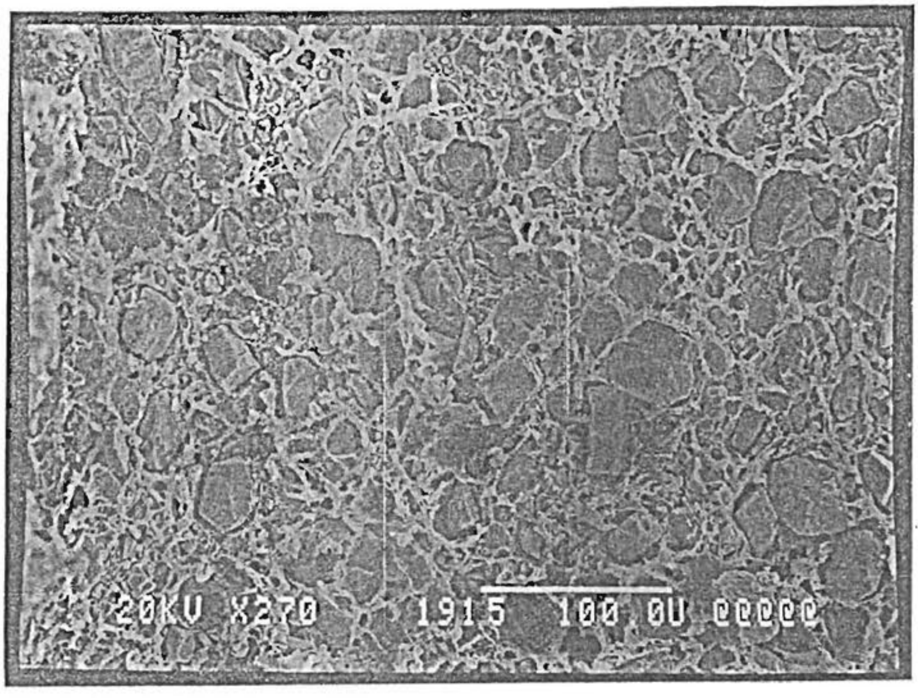

Figure 6. Electron micrograph of fracture surface of HDPE filled with 40% $CaCO_3$ 039. Magnification x 270.

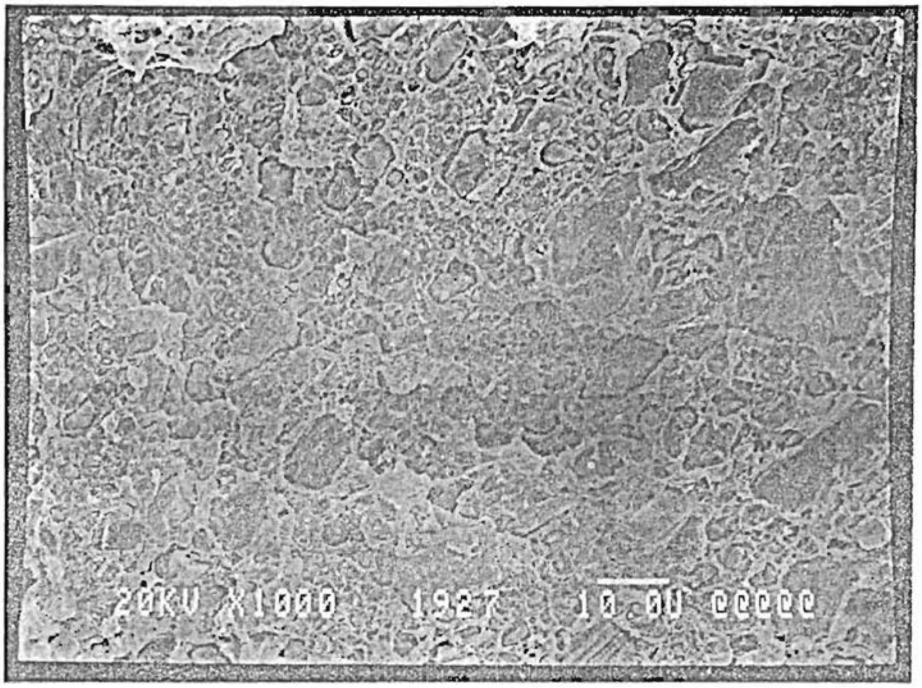

Figure 7. Electron micrograph of fracture surface of HDPE filled with 40% $CaCO_3$ 1939. Magnification x 1000.

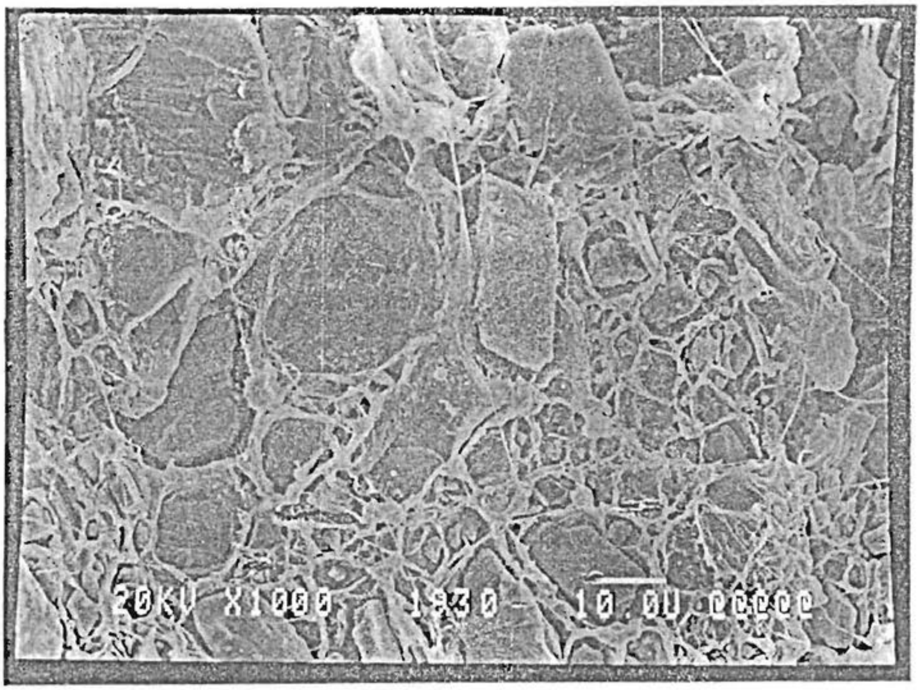

Figure 8. Electron micrograph of fracture surface of HDPE filled with 40% $CaCO_3$ 039. Magnification x 1000.

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