

Effect of Different Film Preparation Procedures on the Thermal, Morphological and Mechanical Properties of Pure and Calcite-Filled HDPE Films

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ABSTRACT: The effect of different film preparation procedures on the thermal, morphological and mechanical properties of high density polyethylene (HDPE) films have been studied using differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and ultimate tensile testing. Film preparation procedures included variation in cooling methods, including quenching, forces (fanning) and natural cooling and techniques such as extrusion followed by melt squeezing and compression molding. The heat of fusion (from DSC), the degree of crystallinity (from WAXRD) and the crystallite size (from WAXRD and AFM) were found to be highest for naturally cooled specimens, followed by fan-cooled and quenched ones. AFM images of surface topology exhibit stacked lamellar morphology for forcefully cooled (fan-cooled and quenched) samples and spherulitic 'lozenges' for naturally cooled ones.

The Young's modulus and yield stress [from the universal testing machine (UTM)] were highest for naturally cooled samples, followed by fan-cooled and quenched ones. Among the calcite-filled composites, the 'base film,' which was prepared by extrusion followed by melt squeezing and natural cooling, exhibited the lowest heat of fusion and degree of crystallinity and a similar crystallite size relative to compression-molded films. Lower yield stress, tensile strength and Young's modulus and higher elongation at break were observed for the base film in comparison to the naturally cooled composite film. The low degree of crystallinity and crystallite size in the 'base film' explain all of its mechanical and morphological properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1427–1434, 2004

Key words: crystallization; spherulites; lamellar; atomic force microscopy (AFM); mechanical properties

INTRODUCTION

Polyolefin films are widely used in food packaging, personal and health care items. The general requirement of these films is that they transmit moist vapor (breathability) through pores to maintain a liquid barrier. This is achieved by the proper formulation of composites with incorporation of spherical fillers (e.g. calcite) followed by stretching to induce micro-pores or air holes. Micro-porosity depends on various factors, such as filler loading, filler particle shape and size,^{1,2} molecular weight, distribution of the matrix polymer and film conditioning before cold drawing.^{3,4} One of the prerequisites for micro-porosity is spherical and less self-interactive filler particles, and fatty acid coated calcite belongs to this category. Calcite can be incorporated in concentrations as high as 30 vol % of the polyolefin composites for their application as micro-porous films in the packaging or sanitary industry. We have also reported^{5–7} that 50 wt % calcite-filled polyethylene (PE), poly(propylene) (PP) and their var-

ious co-polymers can be potential candidates for sanitary applications.

When polyolefin films are crystallized from their melts, the growth of crystals is predominantly spherulitic. Upon stretching, the large spherulitic crystals in polyolefin films prevent high extension, which is required for micro-porosity in polyolefin 'base film.' Industrially, the extruded 'base sheet' is generally prepared by quenching in chilled water to prevent large spherulitic growth.^{4,8}

For the preparation of 'base film,'^{5–7} we adopted a different procedure, the details of which are given in the experimental section. In our previous report,⁹ we observed that, although both the compression molded film and the extruded 'base film' are naturally cooled, the former is inferior in ultimate elongation compared to the latter. This difference in properties necessitates a detailed investigation of mechanical and morphological changes that occur during preparation of the films. Thus, several film preparation procedures, including various cooling methods, such as quenching, forced (fanning) and natural cooling, and variation in preparation techniques such as extrusion followed by melt squeezing and compression molding, were employed to study the effect of cooling rate and melt

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squeezing on the crystallinity, mechanical and morphological properties of pure HDPE and composite films.

EXPERIMENTAL

Materials

The polyolefins used in this study were high-density polyethylene (HDPE) supplied by SK Corporation, Korea. The properties of HDPE (3300), as given by the supplier, are a density of 0.954 g/cm³, a melt flow index (MFI) of 0.8 g/10 min, and a heat deflection temperature of 123°C. The stearic acid coated calcite (SST-40) used was supplied by Dowa Co., Japan. Its properties include a density of 2.9 g/cm³, an average particle size of 1.1 μm and a surface area of 4.8 m²/g.

Mixing and compounding

Premixed pure HDPE and calcite in a 50:50 wt % ratio were fed into a Brabender twin screw extruder (PLE 2000) with a length/diameter (L/D) ratio of 16. The mixed compounds coming from the extruder die were passed through a cold-water bath of 20°C, pelletized and then dried. Antioxidants and UV stabilizer were added to the premixed compounds before their addition to the extruder hopper. A temperature gradient was maintained in the barrel of the extruder, and the screw rotation was maintained at 50 rpm. The temperature sequence was 190°C in the feeding zone, 210°C in the compression zone and 220°C in the metering and die zones.

Preparation of 'base film'

Calcite-filled HDPE was extruded into a sheet by using a slit die of 100 × 1.0 mm. In the extruder barrel, the same temperature gradient and screw speed used during mixing were employed. The extruded hot sheet was squeezed between cast rolls, and the thickness of the extruded film was reduced to approximately a half (around 0.5 mm) of its original size by adjusting the nip gap of the front squeezing rolls and the line speed (take-off speed). During the entire take-off process, the 'base film' was cooled at room temperature.

Compression molding

All of the films for tensile tests were compression molded on a Carver laboratory hot press at a pressure of 5 × 10⁴ Pa and a temperature of 180°C. The hot mold was allowed to cool to room temperature (25°C) under pressure (i.e. closed conditions) by circulated chilled water at 5°C (hereafter called quenching), forced air at room temperature (hereafter called fan

cooling) and natural air at room temperature (hereafter called natural cooling). The time needed for cooling by quenching, fan and natural cooling was approximately 5, 120 and 240 min, respectively. Thus, the fastest cooling was observed for quenching, followed by fan and natural cooling. The films were compression molded in the form of sheets, which were cut with a sharp knife into dimensions of 15 × 0.4 × 165 mm³, according to the ASTM D 882-97 guideline for tensile testing.

Thermal properties

The thermal properties were measured using a differential scanning calorimeter (Perkin Elmer, DSC-7). The samples were heated at a rate of 20°C in the temperature range of 50 to 160°C. All results were recorded for the second heating of the samples.

Wide angle X-ray diffraction

An X-ray diffractometer (Philips PW 3719) with a scintillation counter (Philips Corp., USA) was used to obtain scanning curves for the values of 2θ ranging from 10 to 35° for 60 × 40 mm² films. The incident beam (CuK_α, 50 KV, 25 mA) was passed through a Ni-filter, and a pulse height discriminator was used to achieve further monochromatization. All of the X-ray diffraction patterns showed crystalline peaks, which were superimposed on an amorphous halo.¹⁰ The degree of crystallinity (*X_c*) was recorded from the ratios of the areas under the crystalline peaks and the respective halos using the method of Hermans and Weidinger.¹¹

$$X_c = A_c / (A_c + A_a) \quad (1)$$

where *A_c* and *A_a* are the areas of crystalline and amorphous (halo) regions, respectively.

The average size of the crystalline regions (*P*) was determined from the broadening of the peaks by using the Scherrer formula:¹²

$$P = 0.89\lambda / (\beta \cos\theta) \quad (2)$$

where β is the half-width of the peak, θ is the Bragg's angle and λ is the wavelength. The average intercrystallite separation (*R*) in the amorphous region of the sample was evaluated from the position of the maximum of the halo:¹³

$$R = 5\lambda / (8 \sin\theta) \quad (3)$$

Morphology

Atomic force microscopy

Contact modes of a commercial atomic force microscope (AFM) (Topometrix Corporation: Accurex II)

were used for observing surface morphology (topography) of the films at room temperature. A soft cantilever with a sharp tip on its free end was used to probe the interaction between the tip and sample surface. The V-shaped silicon nitride cantilever with a nominal spring constant of 0.03 N/m was 0.6 μm thick, 18 μm wide and 200 μm long with an attached 'super tip' of 20 nm radius. During testing, the tip was in contact with the surface of the sample such that the deflection of the cantilever could be determined by measuring the position of the reflection of a laser light on a four-segment photodetector. The laser light was directed onto the back of the cantilever, and the position of the reflection changed with changes in the cantilever position. The applied repulsive force between the tip and surface was kept constant at 1–5 nN by adjusting the sample height during scanning. In this way, surface topography was imaged.¹⁴ The samples were scanned over a very low area of $3 \times 3 \mu\text{m}^2$ at a rate of 7 $\mu\text{m/s}$.

Tensile properties

The tensile properties of the films (thickness < 1 mm) for $75 \times 15 \text{ mm}^2$ sheets of pure HDPE and $100 \times 15 \text{ mm}^2$ sheets of composite were tested according to ASTM D 882-97, using an Instron 4665 universal testing machine (UTM) (Instron, U.S.A.) at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ humidity. The initial gauge length and the crosshead speed were set at 50 mm and 50 mm/min, respectively, for both pure and calcite-filled films. At least ten specimens were averaged to collect the tensile properties of the samples.

RESULTS AND DISCUSSION

Thermal properties

The DSC second-heating thermograms are shown as heat flow (mW) versus temperature ($^\circ\text{C}$) in Figure 1(a) for pure HDPE and Figure 1(b) for filled HDPE. The melting temperatures and heats of fusion of all samples are recorded in Table I. The melting temperature was calculated from the intersection of the maximum slope between the peak and the baseline. Irrespective of the cooling method (quenching, fanning, natural cooling) and the formation procedure (compression molding, extrusion) procedures, the melting temperature of both pure and calcite-filled HDPE films remains almost unchanged at 119°C . The heat of fusion (J/g), which is directly proportional to the degree of crystallinity (the heat of fusion of HDPE samples divided by the heat of fusion of a perfect crystal or a single crystal of PE), is found to be dependent on cooling rates. The higher the cooling rate, the lower the heat of fusion, and therefore the lower the crystallinity observed. Since all of the specimens were pre-

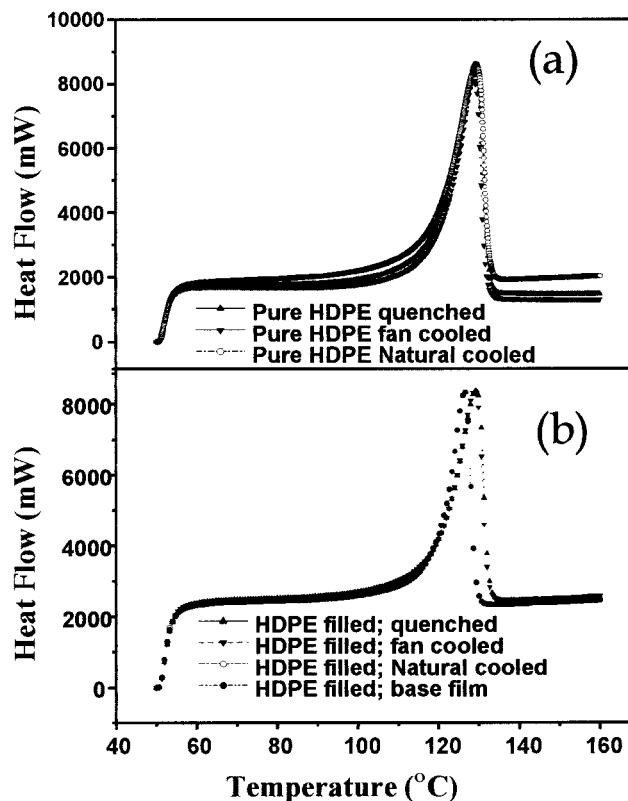


Figure 1 DSC thermograms of HDPE film specimens: (a) quenched, fanned and naturally cooled (compression molded) pure HDPE films; (b) quenched, fanned and naturally cooled films (compression molded) and extruded 'base film' of calcite/HDPE composites.

pared by cooling in various ways from the HDPE melt, it is expected that the crystalline growth will be mainly spherulitic, consisting of a well-organized lamellar structure.⁸ For quenched (fast cooled) specimens, the presence of a more folded chain lamellar structure in the HDPE spherulites may induce a lowering of crystallinity. For slow natural cooling, a well-organized lamellar ridge-like structure may develop, leading to an increase in crystallinity. From Table I, the calcite-filled composites show lower heats of fusion compared to the pure HDPE films. It is expected that the presence of 50% filler in HDPE should reduce the heat of fusion for the filled composite to half of that for pure HDPE. But, as observed from Table I, the reduction is less than half. A possible explanation is the calcite-hindered crystallization of HDPE, leading to a decrease in the crystalline phase. Although both the 'base film' and the naturally cooled film were prepared at room temperature, the heat of fusion of the former is lower than that of the later. This may be due to the hindrance of crystallization induced by the squeezing and subsequent pulling of the extruded 'base film.'

TABLE I
Thermal, Morphological, Tensile and Impact Properties of Pure and Calcite-Filled HDPE Films Prepared by Quenching in Chilled Water at 5°C, Force Cooling by Fan and Natural Cooling at Room Temperature

Properties		Compression Molded						Extruded Base Film
		Pure HDPE Films			Calcite-Filled HDPE Films			
		Quenched	Fan-Cooled	Naturally Cooled	Quenched	Fan-Cooled	Naturally Cooled	
Thermal	Melting temperature (°C)	119.3	119.4	119.4	119.8	119.9	119.6	118.1
	Heat of fusion (J/g)	128.1	130.6	137.9	74.0	76.9	78.2	67.9
X-ray diffraction	Crystallinity (%)	64.7	66.0	69.6	37.4	38.8	39.5	34.2
	Crystallinity (%)	64	69	71	58	63	65	56
	Average crystallite size (nm)	51.32	58.06	59.6	45.98	52.32	52.56	40.86
Morphology	Inter crystallite separation (nm)	0.517	0.517	0.517	0.521	0.517	0.516	0.520
	AFM height profiles (nm)	82	213	241	121	123	161	476
Tensile	Young's modulus (MPa)	735.0	864.2	872.9	1362.4	1486.7	1734.6	976.1
	Yield stress (MPa)	18.7	20.7	21.6	12.7	13.4	15.4	13.3
	Elongation at break (%)	982.4	794.4	296.0	42.4	10.4	7.9	982.0
	Tensile strength (MPa)	25.4	25.3	21.2	10.9	12.5	14.9	13.3

Wide angle X-ray diffraction

The wide-angle X-ray diffraction (WAXRD) curves are shown in Figure 2(a) for pure HDPE and 2(b) for calcite-filled composites. Irrespective of the cooling procedure, a major primary and a minor secondary

crystalline peak are observed, respectively, between 2θ values of $20.5\sim 22.5^\circ$ and $23.3\sim 24.5^\circ$ for both the pure HDPE and its composites. The primary peak is probably due to the crystallinity of the straight chain PE segment, whereas the secondary peak is assigned to the crystallinity of the branched chain segment of HDPE. It is interesting to note that both the primary and secondary peaks are affected by the addition of calcite and various cooling patterns. The peak intensity for pure HDPE is much higher than that for the similarly cooled calcite composite. In addition, regardless of pure polymer or filled composite, the peak intensity increased inversely with cooling rate.

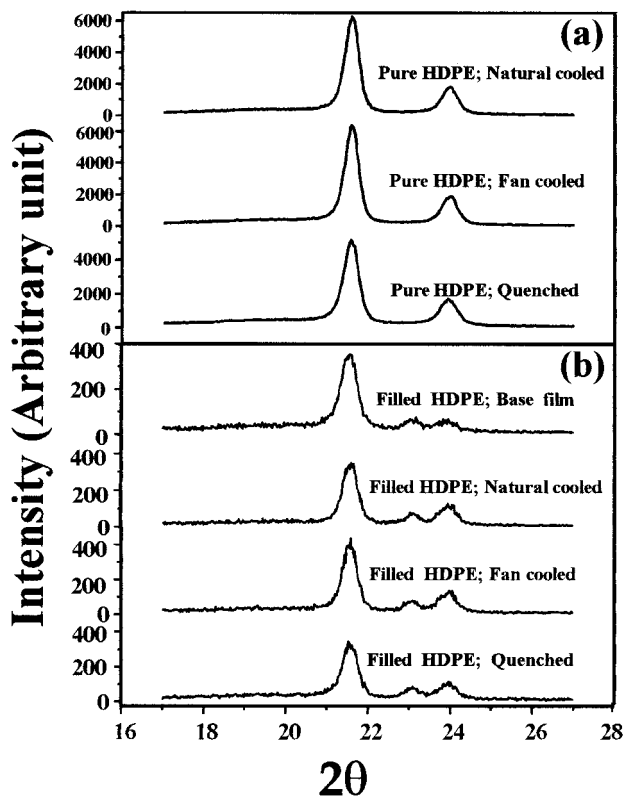


Figure 2 Wide angle X-ray diffraction patterns of calcite-filled HDPE film specimens: (a) quenched, fanned and naturally cooled (compression molded) pure HDPE films; (b) quenched, fanned and naturally cooled films (compression molded) and extruded 'base film.'

The degree of crystallinity,¹¹ average crystallite size (P)¹² and intercrystallite separation (R)¹³ perpendicular to the (110) plane of the present system, calculated from eqs. (1) and (2), are listed in Table I. Irrespective of pure HDPE or filled composite, the degree of crystallinity and the average crystallite size are minimized for the fastest cooling method (quenching), followed by fan cooling and natural cooling. The calcite composites show lower degrees of crystallinity and crystallite size compared to the respectively cooled pure polymers. The decrease in crystallite size upon addition of calcite is believed to be caused by the hindering of lamellar structure formed from the polymeric phase by the calcite particles. In addition, the intercrystallite separation is observed to be of almost the same order regardless of sample. Although both the extruded 'base film' and compression-molded, naturally cooled films are calcite-filled and prepared by natural cooling, the 'base film' exhibits a lower degree of crystallinity, a lower average crystallite size and intercrystallite separation than the naturally cooled film. The lower degree of crystallinity of the 'base film' is believed to be due to the destruction and the reformation of crystallites during pulling and squeezing opera-

tions. During this process, more lamellar chain folding was allowed, leading to the lowering of the degree of crystallinity.

From Table I, it is interesting to note that the degree of crystallinity of pure HDPE measured by WAXRD is similar to that measured by DSC, whereas the degree of crystallinity of filled HDPE measured by WAXRD is higher than that measured by DSC. To calculate the extent of crystallinity from DSC measurements, all heat of fusion values were divided by the heat of fusion values of perfect crystals or single crystals of PE. (The reported heat of fusion value for a single PE crystal is 198 ± 10 J/g.¹⁵) The reported percent crystallinity from WAXRD listed in Table I was measured for (110) planes. Both the HDPE and the calcite phases can contribute to diffraction at (100) planes. By assuming the (110) plane to be a major crystalline plane, all the crystalline parameters from WAXRD are calculated. Thus, the difference originates from the method of measurements.

According to Table I, the degree of crystallinity from X-ray diffraction and DSC of the calcite composites were found to be lower than the values for corresponding pure HDPE samples; in fact, the degree of crystallinity values from DSC are almost half those of pure HDPE. For the DSC measurement, a known amount of sample was used, and the heat of fusion values reported in Table I are per gram of sample weight. The degree of crystallinity from DSC is the ratio of the heat of fusion of HDPE to that of a single polyethylene crystal. As DSC shows an initial response to the polymeric phase, the presence of 50% calcite in the composite films induces a reduction of the heat of fusion, and hence the degree of crystallinity, to almost half the values for pure HDPE samples.

Morphology

The AFM (contact mode) images are presented in Figures 3(a,b) for pure HDPE and calcite-filled composites, respectively. In these images, brighter regions represent the hard, crystalline phase and the darker regions usually represent the soft, amorphous phase.⁴ Quenched, pure HDPE and all calcite-filled samples (quenched, fanned and naturally cooled) show an ordered ridge pattern in both dark and bright regions. These patterns indicate a stacked lamellar morphology originating from the fast cooling of the melt. A smaller degree of lamellar folding is observed in pure HDPE quenched samples, leading to a large but irregular lamellar structure. For fanned and naturally cooled pure HDPE, irregularly sized 'lozenges' are embedded in the lamellae. The stacked lamellar morphology is clearly evident in calcite-filled quenched and fan cooled HDPE samples, and the stacked lamellar thickness can be approximately measured by counting the number of stacks throughout the entire

probed area in both lateral and longitudinal directions. The stacked lamellar thickness was 39–47 and 41–55 nm during quenching and fan cooling, respectively, whereas 'lozenges' of spherulitic structure were observed during natural, room temperature cooling of the calcite-filled HDPE composites. The lozenges are irregularly sized and embedded in lamellae. The base film, which was also prepared by natural cooling, displays the same lozenge-like, spherulitic structures as those observed in natural cooling. Moreover, irregular, small-sized lozenges grew into a big hexagonal spherulitic structure (500–700 nm). The crystallite size of all samples observed by AFM was much larger than that exhibited in X-ray diffraction. During cooling of the sample from its melt, since cooling starts from the surface of the film, the surface acts as a nucleating site for the crystals. This induces lowering of the crystallite size at the surface compared to the bulk. As AFM is used for probing the surface and X-rays are diffracted throughout the bulk, it is expected that AFM should show lower crystallite size. But the observed values indicate just the opposite. The probable reason is the method of calculation of particle size from WAXRD, as all the crystalline parameters are calculated by assuming major diffraction from (110) planes.

The height profiles for all samples whose contact topology is presented in Figures 3(a,b) are listed in Table I. The height profile is indicative of the nature of the surface roughness. All of the calcite-filled composites showed lower height profiles than the pure HDPE except for the quenched and base film, which exhibited higher values than the respectively cooled samples. For both films, pure HDPE and its composite, the height profile was higher for naturally cooled samples, followed by fan cooled and quenched ones. This indicates that the naturally cooled specimen, which grew into a big spherulitic structure, exhibited a rougher surface than the fan cooled and quenched specimens, which grew into stacked lamella. Among the calcite-filled systems, the base film shows the highest height profile, indicating the roughest surface.

Tensile properties

Stress–strain properties are exhibited in Figure 4(a) for pure HDPE and Figure 4(b) for calcite-filled composites. The mechanical properties, such as Young's modulus, elongation at break, ultimate tensile strength (UTS) and yield stress are listed in Table I.

Young's modulus is the manifestation of the stiffness of a compound. It is calculated from the initial slope of the stress–strain plot [Fig. 4(a,b)] within the range of the elastic limit of stretching. The yield point is defined as either a distinct maximum or a region of strong curvature approaching zero-slope on the stress–strain curve.¹⁶ From Figure 4(a,b), the Young's modulus and the yield stress of the naturally cooled

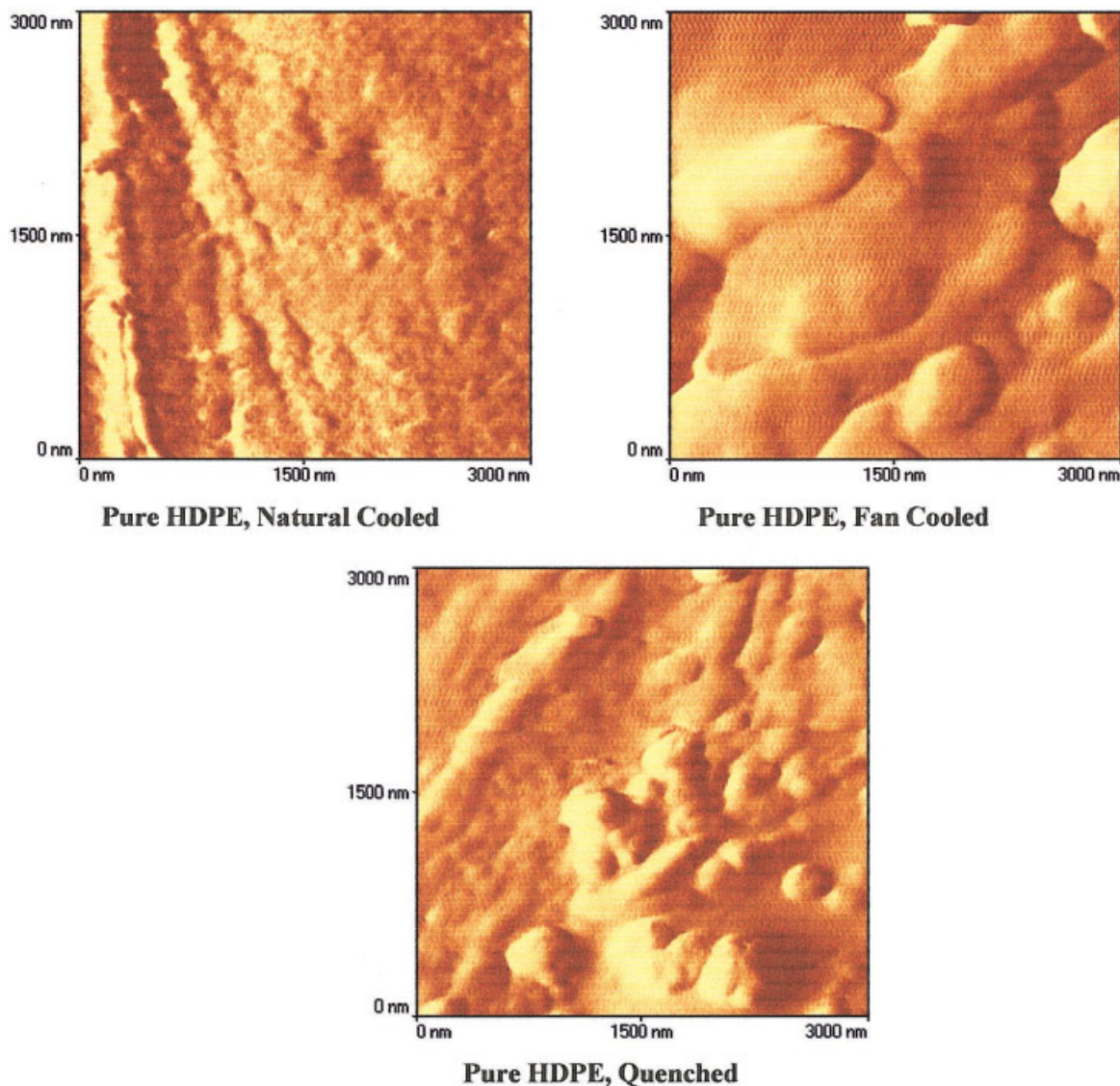


Figure 3 AFM morphology of: (a) quenched, fanned and naturally cooled (compression molded) pure HDPE films and (b) quenched, fanned and naturally cooled (compression molded) films and extruded 'base film' of HDPE/calcite composites.

films are observed to be the highest, followed by fan cooled and quenched films. Quenching of films reduced the degree of crystallinity, whereas room temperature forced (fan) or natural cooling allowed the crystals to grow into larger spherulites embedded in a lamellar structure, and hence increasing crystallinity. The increase in crystallinity induced the increase in Young's modulus and yield stress for films cooled at room temperature. According to Figure 4(a), strain hardening or strain-induced crystallization was observed after the yield point.¹⁷ The strain hardening is at a maximum for the quenched film, followed by fanned and naturally cooled samples. This is predictable from the highest elongation and hence the highest tensile strength of the quenched pure HDPE films, followed by fanned and naturally cooled ones. For calcite-filled composite films, the elongation at break

follows the same trend as that for pure HDPE films against different cooling patterns, whereas the tensile strength exhibits the opposite trend.

The Young's modulus of the calcite-filled composites was found to be higher, whereas the yield stress was lower than the values for corresponding pure films, regardless of the film cooling processes (Table I). The incorporation of fillers generally induced an increase in the stiffness and the Young's modulus of the composites.¹⁸ The added calcite in the pure HDPE increased the stiffness and modulus but decreased the degree of crystallinity of the polymeric phase (from DSC and WXR studies) and reduced the yield stress and tensile strength. It is interesting to note that, although the 'base film' was also prepared by cooling naturally, it showed a lower Young's modulus, yield stress and tensile strength compared to the naturally

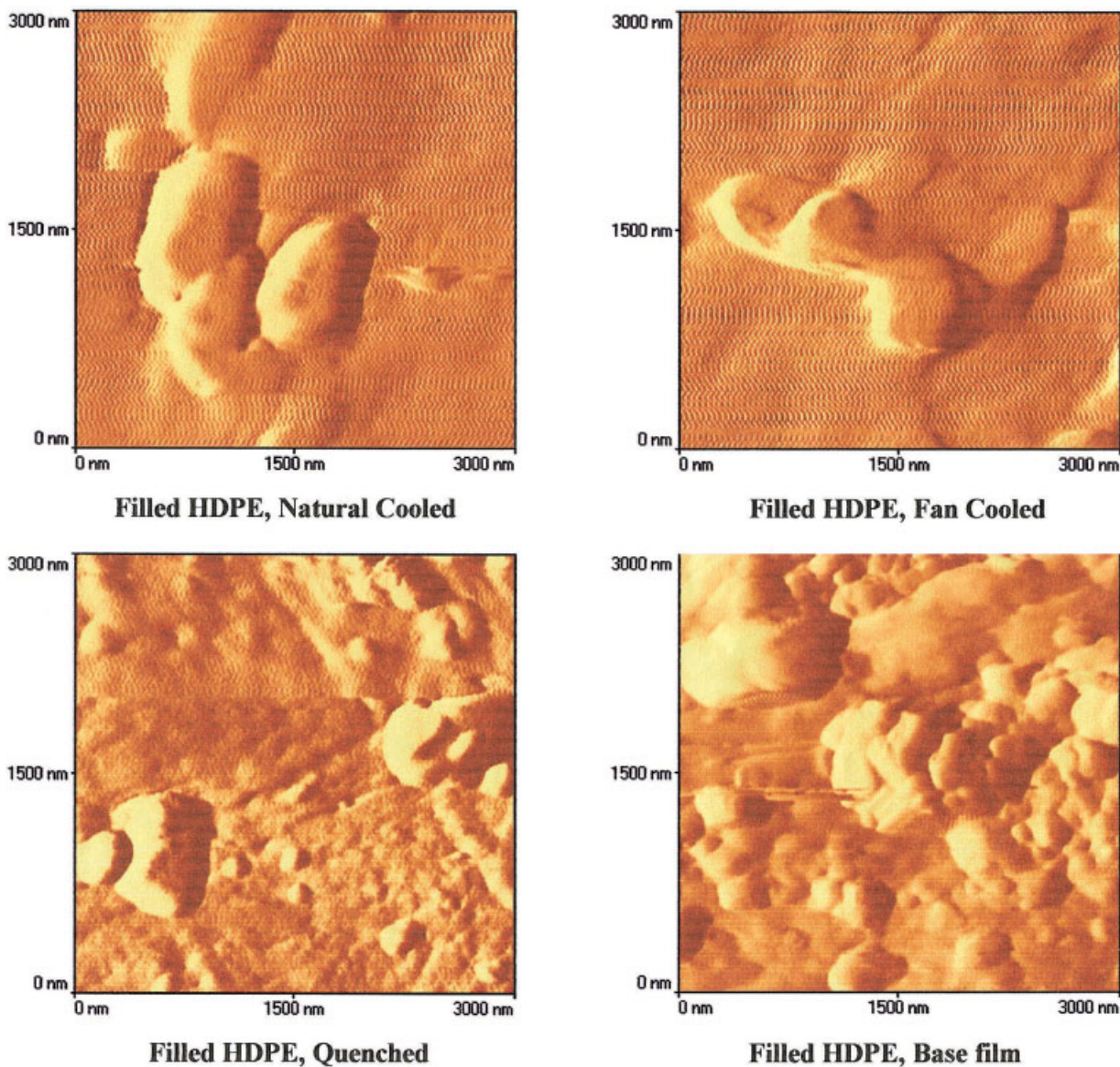


Figure 3 (Continued)

cooled composite film (Table I). From Figure 4(b), the nature of the stress–strain plot for the ‘base film’ is similar to that of pure HDPE. The slow cooling (natural cooling) could result in big spherulitic structures, but the consequent melt squeezing and pulling process obstructs the free formation of lamellae embedded into spherulites, causing more chain folding. This leads to the lowering of the degree of crystallinity and the crystallite size of the base film compared to the naturally cooled sample (from WAXRD and AFM studies). The small crystallite size of the ‘base film’ explains its low yield stress, whereas the reduction of the degree of crystallinity in the ‘base film’ (DSC and WAXRD) induced a reduction in stiffness, leading to the lowering of Young’s modulus and tensile strength compared to the naturally cooled composites. Among the calcite-filled HDPE films, the ‘base film’ exhibited

the highest elongation at break. The low crystallinity and particle size induced the extension of the inelastic region in the stress–strain plot and the melting and recrystallization of crystals at high strain, inducing strain hardening. All of the factors resulted in higher elongation and lower tensile strength and yield stress in the ‘base film’ compared to the naturally cooled calcite-filled sample.

CONCLUSIONS

The various filmmaking procedures have some effect on thermal, morphological and mechanical properties. DSC studies indicate that the incorporation of calcite in HDPE reduces the degree of crystallinity of the polymeric phase. Regardless of whether HDPE was filled or pure, the heat of fusion and hence the degree

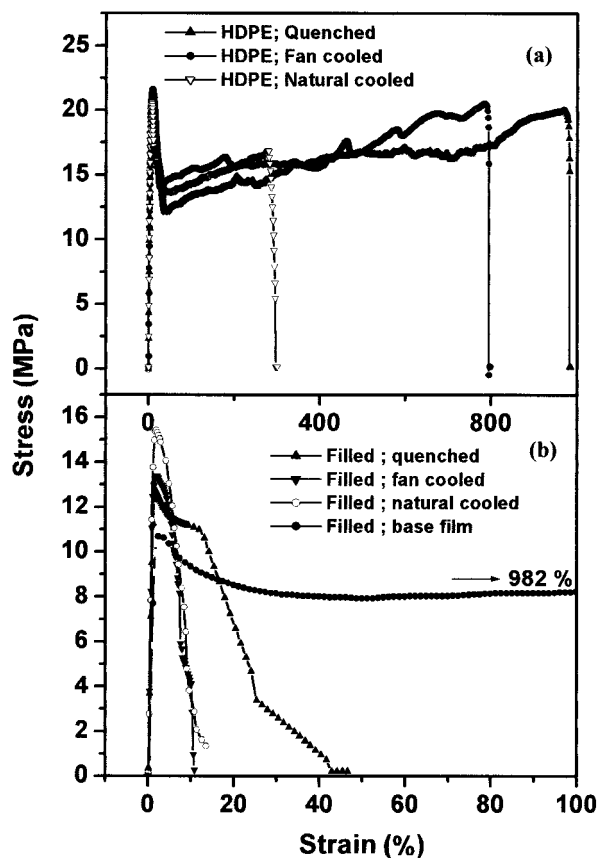


Figure 4 Tensile properties of calcite-filled HDPE film specimens: (a) quenched, fanned and naturally cooled (compression molded) pure HDPE films and (b) quenched, fanned and naturally cooled (compression molded) films and extruded 'base film.'

of crystallinity was highest for naturally cooled samples, followed by fan cooled and quenched ones. Among the calcite-filled composites, the 'base film' exhibited the lowest heat of fusion (DSC) and degree of crystallinity and crystallite size (WAXRD). The AFM morphological studies indicate a correlation of crystallinity to surface roughness of the films. The higher the crystallinity, the higher the roughness. AFM images of surface topology exhibit stacked lamellar morphology for forcefully cooled (fan cooled and quenched) samples and spherulitic 'lozenges' for naturally cooled ones. On incorporation of calcite, Young's modulus increases due to an increase in overall stiffness, but yield stress decreases from the lowering of the crystallinity of the polymeric phase. Irre-

spective whether HDPE was calcite-filled or pure, Young's modulus and yield stress was highest for naturally cooled samples, followed by fan cooled and quenched ones. For all types of cooling, strain hardening was observed in pure HDPE films. The base film exhibits lower yield stress, Young's modulus and tensile strength due to its low degree of crystallinity and small particle size compared to the naturally cooled composite film. The strain hardening observed in the 'base film' induces its highest elongation among the calcite-filled composites.

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