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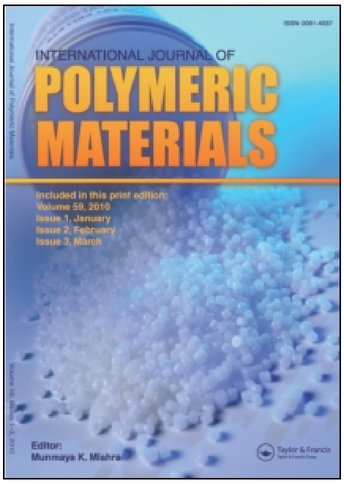

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Crystallization of *i*-PP/CaCO$_3$ Composites and its Correlation with Tensile Properties

S. N. Maiti[a]; P. K. Mahapatro[a]
[a] Centre for Materials Science & Technology, Indian Institute of Technology, Delhi, New Delhi, India

To cite this Article Maiti, S. N. and Mahapatro, P. K.(1990) 'Crystallization of *i*-PP/CaCO$_3$ Composites and its Correlation with Tensile Properties', International Journal of Polymeric Materials, 14: 3, 205 — 222
To link to this Article: DOI: 10.1080/00914039008031514
URL: http://dx.doi.org/10.1080/00914039008031514

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Intern. J. Polymeric Mater., 1990, Vol. 14, pp. 205–222
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Printed in the United Kingdom

Crystallization of *i*-PP/CaCO$_3$ Composites and its Correlation with Tensile Properties

S. N. MAITI and P. K. MAHAPATRO

Centre for Materials Science & Technology, Indian Institute of Technology, Delhi, New Delhi-110016, India.

(Received March 24, 1989)

Investigation of crystallization behaviour of isoatactic polypropylene (*i*-PP) in *i*-PP/CaCO$_3$ composites is carried out through Differential Scanning Calorimetry (DSC) and wide angle X-ray diffraction measurements. The effect of CaCO$_3$ and its surface treatment with titanate coupling agent on nucleation and growth rate of crystallization, crystallite size distribution and crystallinity, is determined from exothermic crystallization peaks of the composites. The filler concentration dependence of crystallinity determined by both the techniques shows good qualitative agreement. Tensile properties viz. tensile modulus, yield stress and elongation were also measured as functions of filler concentration for both untreated and treated CaCO$_3$ filled composites. Crystallinity, tensile strength and elongation decreased with increasing filler content in both the cases whereas tensile modulus increased. Crystallization parameters have been correlated with the tensile properties of *i*-PP/CaCO$_3$ composites.

KEY WORDS Crystallinity parameters, surface treatment, modified interphase, correlation coefficient, tensile modulus, crystallite size distribution.

1. INTRODUCTION

Inorganic particulate fillers are added to commercial thermoplastics to widen their applications[1–4] as well as to reduce the overall cost of the composites. Accompanied modifications in stiffness, heat distortion and mouldability may be sometimes favourable for many applications. However, certain other useful properties such as toughness, elongation-at-break and tensile strength may show declining tendency. Surface treatment of the filler with various coupling agents[4–6] prior to incorporation in the polymer is reported to improve the interaction between the filler and the matrix so that optimum strength properties are achieved.

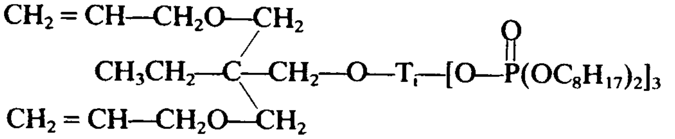
Incorporation of high density polyethylene or short glass fibre as well as other additives[7–9] into *i*-PP has been shown to influence significantly the crystallinity behaviour and morphology of *i*-PP. Therefore, estimation of the crystalline parameters is of direct relevance to explain the mechanical properties of composites where *i*-PP is the matrix polymer.

In the present communication we report the results of crystallization of *i*-PP in *i*-PP/$CaCO_3$ composites in terms of various crystallization parameters from differential scanning calorimetry and X-ray diffraction measurements. These crystallization parameters have been attempted to be correlated with the tensile properties of the composites. The effect of a titanate coupling agent on the above properties and correlations has also been studied.

2. EXPERIMENTAL

2.1. Materials

Isotactic polypropylene (*i*-PP) used was koylene M0030 (MFI 10, density 0.89 g/cm^3) of Indian Petrochemicals Corporation Ltd. Calcium carbonate ($CaCO_3$) used was BDH product (density 2.7 g/cm^3) obtained from Glaxo Laboratories, India. The average particle diameter as determined by hydrometer analysis was 5.5 μm. The coupling agent neopentyl (diallyl) oxy,tri(dioctyl) phosphato) titanate (LICA 12) of following chemical formula:



was obtained from M/s Kenrich Petrochemicals, N.J., USA.

2.2. Surface treatment of $CaCO_3$

LICA 12 (0.5 wt.% on the basis of $CaCO_3$) was dissolved in toluene and the requisite quantity of $CaCO_3$ was added with continuous stirring. The slurry formed was air dried for 24 hrs followed by vacuum drying at 110°C for 4 hrs. The filler developed hydrophobicity on treatment since the particles floated on water while untreated particles sank immediately. Other authors[10,11] also used similar techniques for pretreatment of fillers.

2.3. Preparation of the composites

Vacuum dried *i*-PP and $CaCO_3$ (both untreated and treated) were mixed on a two roll mill at a temperature 160 ± 2°C for ten minutes to prepare thin sheets of the composites containing 0 to 36 volume percent (0 to 60 weight %) filler. Several plies of these sheets were then compressed in a window mold at 200 ± 2°C and at 10.35 MPa pressure to make sheets of 1 mm thickness. Dumb-bell shaped tensile specimens were machined from these molded sheets where DSC and X-ray studies were performed using ground powder of the composites. Unfilled *i*-PP samples were also prepared under identical conditions of mixing and molding.

2.4. Measurements

DSC measurements were performed on a Du Pont thermal analyser (Model 1090) with module 910. In order to eliminate any history of crystallization all the samples were first heated to 200°C and held at this temperature for 10 minutes. Thermograms were recorded during the cooling cycle at constant cooling rate 10°C/min using liquid air. All the data were generated at identical settings of the instrument.

A Phillips Norelco X-ray diffraction equipment with which a Scintillation counter and a recorder are attached, was used for the X-ray diffraction measurements. Radial scans of intensity (I) vs. diffraction angle (2θ) were recorded in the range of 8–40° of 2θ using CuKα radiation.

Tensile properties were measured on a Universal testing machine (Model 1121) according to ASTM D638-82 test procedure at an extension rate of 100% (initial cross head separation 5 cm and cross head speed 5 cm/min). At least five samples were tested for every composite composition and the average value is reported. All tests were carried out at ambient temperature 30 ± 2°C.

3. RESULTS AND DISCUSSION

All the composite samples with untreated CaCO$_3$ showed prominent crystallization exotherm peaks of *i*-PP in the DSC thermograms, Figure 1. While the peak temperature of filled *i*-PP did not show much change upto 35 wt.% CaCO$_3$ in the composites, those with 50 and 60 wt.% filler showed an increase of 3–6 degrees (Table I). With the treated filler in the composites the peak temperatures were

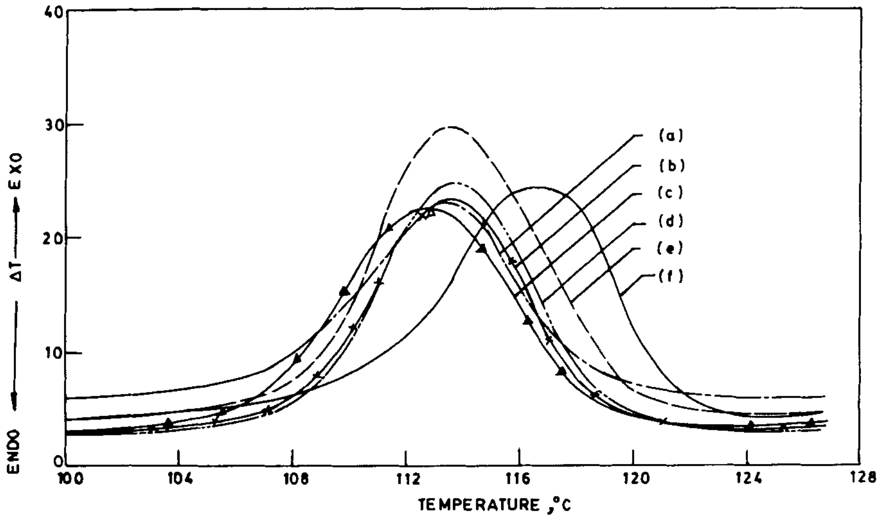


FIGURE 1 DSC thermograms of *i*-PP and *i*-PP/CaCO$_3$ (untreated) composites with varying volume percent of filler: (a) *i*-PP; (b) *i*-PP/CaCO$_3$ 1.9%; (c) *i*-PP/CaCO$_3$ 3.9%; (d) *i*-PP CaCO$_3$ 8.4%; (e) *i*-PP/CaCO$_3$ 16.5%; and (f) *i*-PP/CaCO$_3$ 26.8%.

TABLE I

Values of various crystallization parameters of *i*-PP in *i*-PP/$CaCO_3$ composites from DSC and X-ray diffraction

Sample composition	T_p (°C)	T_{onset} (°C)	T_c-T_p (°C)	S_i (arbitrary units)	ΔW (arbitrary units)	ΔH (J/G)	$(X_c)_{app}$
i-PP	113.6	122.7	4.2	100.0	4.4	62.2	0.67
i-PP/$CaCO_3$ 1.89%	113.9	122.1	4.8	91.5	4.6	78.1	0.68
	(118.6)	(126.4)	(3.8)	(122.7)	(4.5)	(63.6)	(0.55)
i-PP/$CaCO_3$ 3.90%	112.8	121.0	5.5	84.2	4.8	71.8	0.65
	(117.6)	(125.0)	(3.9)	(110.2)	(4.7)	(61.5)	(0.56)
i-PP/$CaCO_3$ 8.37%	113.7	121.8	4.9	91.5	4.4	66.2	0.63
	(118.3)	(125.4)	(3.7)	(100.0)	(4.3)	(53.2)	(0.51)
i-PP/$CaCO_3$ 16.45%	113.7	121.2	4.8	84.29	4.7	54.2	0.59
	(117.6)	(123.9)	(3.4)	(91.5)	(4.2)	(40.7)	(0.44)
i-PP/$CaCO_3$ 26.78%	116.8	123.7	4.6	110.2	4.8	44.8	0.48
	(119.1)	(124.9)	(3.5)	(63.6)	(3.9)	(30.3)	(0.33)
i-PP/$CaCO_3$ 35.42%	119.5	125.3	3.3	158.3	—	40.4	0.43
	(119.2)	(125.4)	(3.8)	(59.8)	(4.3)	(24.7)	(0.26)

Values in parentheses in various columns are for composites with surface treated $CaCo_3$

higher by 4–6°C over unfilled *i*-PP, Figure 2. Various crystallization parameters such as T_p, T_{onset}, T_c-T_p, S_i, ΔH and ΔW (also used by other authors[7,12]) were evaluated from these DSC thermograms and are presented in Table I. For the sake of ready reference the significance of these quantities are summarised below, and illustrated in Figure 3, similar to other reports.[8]

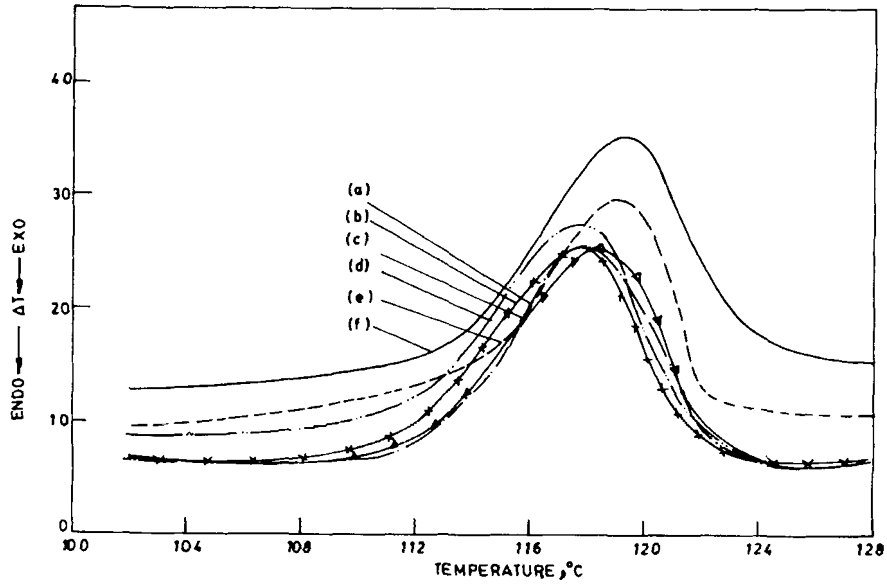


FIGURE 2 DSC thermograms of *i*-PP and *i*-PP/$CaCO_3$ (treated) composites with varying filler content. The symbols are as in Figure 1.

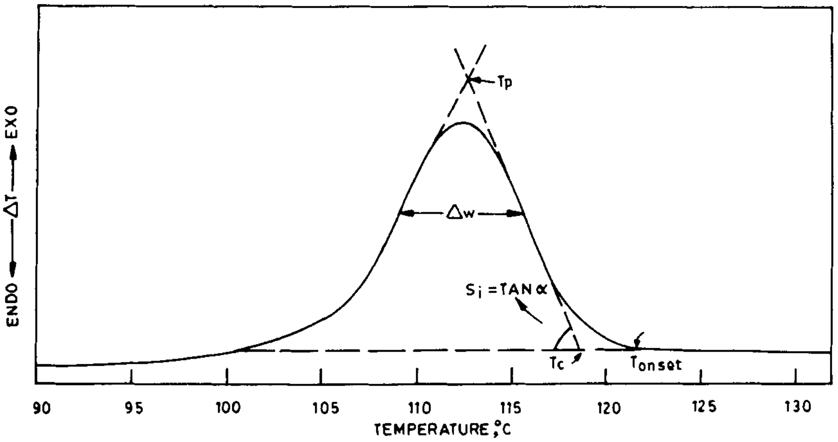


FIGURE 3 Schematic representation of the method of determination of various parameters from DSC crystallization exotherm peak.

i) The peak temperature of the crystallization isotherm, T_p, determined at the point of intersection of the tangents at the two sides of the exotherm.

ii) The temperature of onset of crystallization, T_{onset}, which is the temperature where the thermogram initially departs from the base line on the high temperature side of the exotherm.

iii) Initial slope of the exotherm, S_i, which is the slope of the high temperature side of the exotherm.

iv) The quantity $(T_c - T_p)$, where T_c is the temperature at the intercept of the tangents at the base line and the high temperature side of the exotherm.

v) The quantity ΔH which is recorded by the DSC instrument is a measure of heat of crystallization.

vi) The width at half-height of the exotherm peak Δw, determined after normalization of the peak to constant mass of i-PP component in the sample.

The peak temperature T_p of exothermic peak is a function of cooling rate and is a measure of supercooling. Decrease in T_p implies an increase in supercooling. Increase in rate of nucleation by addition of nucleating agent or by any other means was shown[12,13] to increase T_p (i.e. reduced supercooling) of the crystallization isotherm of i-PP. T_{onset} may have similar significance of T_p except that their interrelationship is inherently dependent through the parameter S_i, which may differ from sample to sample. The quantity S_i, is indicative of the rate of nucleation. Addition of nucleating agents increased[12] the initial slope S_i of the crystallization isotherm of i-PP. The parameter $(T_c - T_p)$ is a measure of the overall rate of crystallization,[12] the smaller the $(T_c - T_p)$, the greater the rate of crystallization. The quantity ΔH is proportional to the heat of crystallization of the given sample and is thus to its degree of crystallinity.[7] The variation in ΔH may be taken to represent the variations in crystallinity in these samples in as much as the measurements on all the samples were done under identical settings of the instrument. The parameter ΔW is a measure of the crystallite size distribution;[7] the smaller the ΔW, the narrower the size distribution of the crystallites.

Variation of the crystalline parameters are presented in Figures 4 and 5 as functions of filler volume percent ϕ_F. For the composites with untreated $CaCO_3$ the parameters T_p, T_{onset} and S_i values are either marginally changed or decreased upto 17 volume percent of filler, and increased beyond this point. ΔH showed an initial increase upto about 2.5 vol.% filler the value decreased beyond this point. (T_c-T_p) and ΔW also increased showing maxima at about 4 vol.% filler. However, at $\phi_F = 36$ (T_c-T_p) value decreased relative to that of unfilled *i*-PP.

From the above results the following observations can be made:

1) In the composite composition range 0–4 vol.% $CaCO_3$ (range 1) the rate of nucleation and growth of crystallization decreases but the overall crystallinity shows a somewhat higher degree of crystallinity of *i*-PP in the composites. Due to slow rate of nucleation larger spherulites will form. However, due to slow rate of growth of crystallization some spherulites will not grow to optimum size and will remain small. Thus, the crystallite size distribution will be broader which is evidenced by slight increase in the crystallite size distribution parameter Δw.

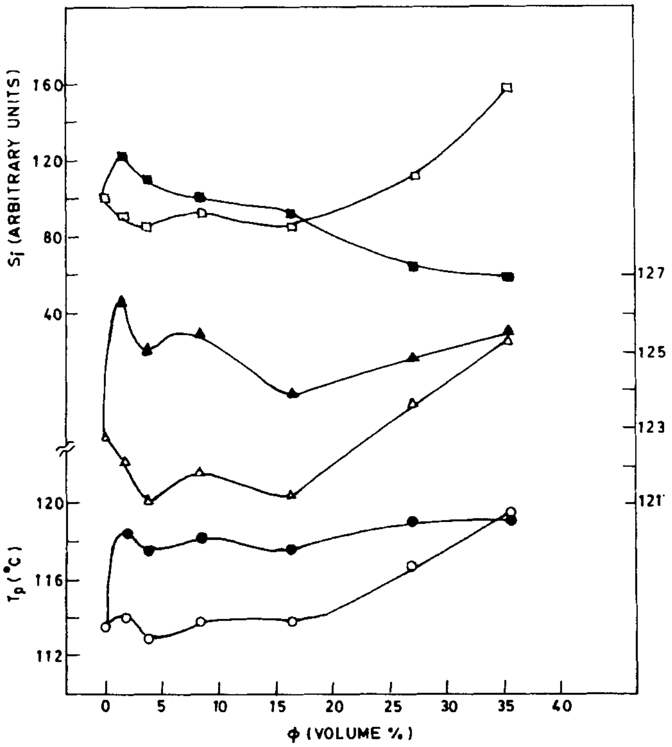


FIGURE 4 Plots of crystallization parameters of *i*-PP/$CaCO_3$ (untreated, open symbols and treated, closed symbols) composites as a function of filler content.

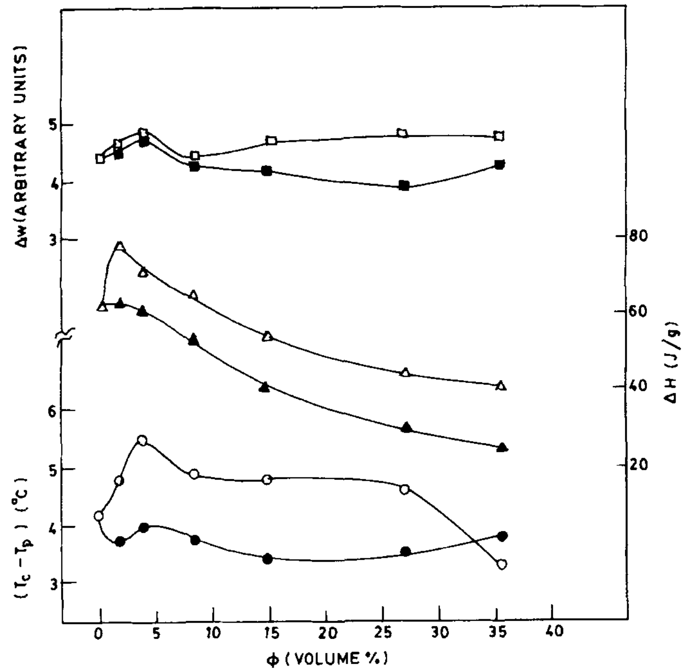


FIGURE 5 Plots of various crystallization parameters of *i*-PP/CaCO$_3$ (untreated, open symbols and treated, closed symbols) composites versus CaCO$_3$ concentration.

2) In the composite composition range $\phi_F = 4\text{–}16.5$ (range 2) rate of nucleation at first showed a small increase upto 8.5% filler and then decreased marginally while crystal growth rate showed a slow increase and the crystallinity registered a steady decrease. Due to increased nucleation rate larger number spherulite would form which would remain similar in size and will not have sufficient time to grow larger due to increased crystal growth rate. This means a narrow distribution of spherulites which is evidenced by a slight lowering in the value of Δw upto about $\phi_F = 8.5$. However, beyond this point and upto $\phi_F = 16.5$ nucleation again decreased giving broader distribution of crystals (increase in Δw).

3) Finally, in the composite composition range 16.5–36 vol.% CaCO$_3$ (range 3) nucleation rate and crystal growth rate showed an increase while over all crystallinity registered a decrease. In this region also crystals of small and large will coexist giving a broader crystal size distribution. This is manifested by an increase in the parameter Δw.

For the composites with surface treated CaCO$_3$, the variation in the above crystalline parameters (also shown in Figures 4 and 5) are somewhat different.

Here in range 1 of composite composition nucleation rate and crystal growth rate increases while overall crystallinity shows an initial marginal increase at $\phi_F = 1.5$, the value decreases upto $\phi_F = 4$. The nucleation rate also shows a maximum at $\phi_F = 1.5$. However, some crystals will still remain small so that crystallite size distribution showed a broad distribution i.e. Δw showed an increase.

In the range 2, nucleation rate decreased, the crystal growth rate showed a slow increase and crystallinity decreased. The size distribution parameter shows a decrease meaning narrower spherulite size distribution in the morphology of *i*-PP in the composites.

In the range 3, nucleation rate decreases, growth rate also decreases (after an initial increase) and crystallinity decrease, Δw shows a narrow distribution upto $\phi_F = 27$ and beyond this point the distribution again becomes somewhat broader.

3.1. X-ray diffraction studies

X-ray diffractograms (plots of intensity (I) against diffraction range (2θ)) of the composites are shown in Figures 6 and 7. In the diffraction pattern *i*-PP shows several diffraction maxima and those at 2θ values 14, 17, 18.5 and 21.7° are very intense; the peak at 21.7° is a doublet. These characteristic peaks of crystalline *i*-PP were similar to earlier reports.[8,9] The *i*-PP/$CaCO_3$ (untreated) composites show all the characteristic peaks of *i*-PP with no other additional peaks. This means that *i*-PP is the only crystallizable component in this two component composite. However, all the peaks reduce in height, indicating decrease in crystallinity of *i*-PP, with increase in $CaCO_3$ concentration.

From these diffractograms the degree of crystallinity (X_c) was estimated using

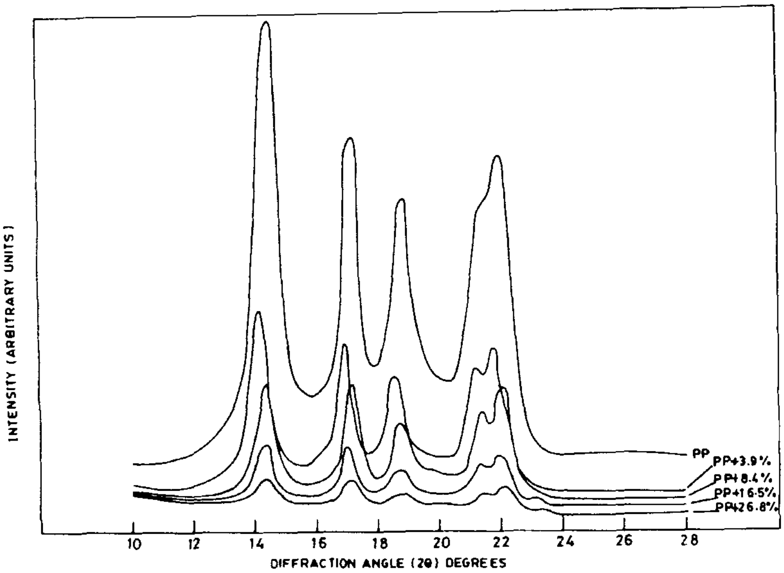


FIGURE 6 X-ray diffractograms of *i*-PP and *i*-PP/$CaCO_3$ (untreated) composites of varying filler concentration.

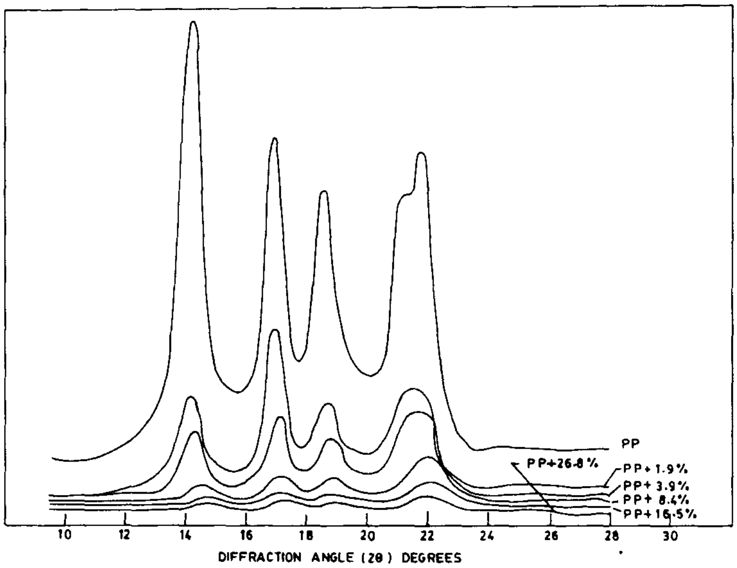


FIGURE 7 X-ray diffractograms of *i*-PP and *i*-PP/CaCO$_3$ (treated) composites with varying CaCO$_3$ contents.

the following expression, also used by other authors.[14,15]

$$X_c = \frac{\int_0^\infty S^2 I_{cr}(S)\, ds}{\int_0^\infty S^2 I(S)\, ds} \cdot K \qquad (1)$$

Here, $I_{cr}(S)$ is the coherent intensity concentrated in the crystalline peaks and $I(S)$ is total coherent intensity scattered; S is the total scattering vector and is equal to $(2/\lambda)\,\mathrm{Sin}\,\theta$. K is the correction factor which is governed[14,15] by atomic scattering factors as well as the disorder function. Due to the uncertainty about the value of this disorder function, the factor is ignored by assuming $K = 1$. Thus, the degree of crystallinity determined in these calculations are denoted as apparent degree of crystallinity $(X_c)_{\mathrm{app}}$ which should be used for comparison of the parameter within similar classes of materials[8,9] only.

I_S^2 vs. S curves were drawn from the experimental I vs. 2θ curves. Amorphous scattering curve and the base line were drawn according to the method suggested by Sotton *et al.*[15] The crystallinity values for various samples are shown in Table I and the variation of crystallinity with CaCO$_3$ concentration is shown in Figure 8. With the untreated CaCO$_3$ in the samples the crystallinity shows a slow decrease from that of unfilled *i*-PP. When CaCO$_3$ was treated the $(X_c)_{\mathrm{app}}$ first decreases rapidly upto $\phi_F = 2$, the value increases slightly upto $\phi_F = 4$ and beyond this point crystallinity decreases with increasing CaCO$_3$ content.

Thus the variation of X-ray crystallinity with increasing CaCO$_3$ content shows a qualitative resemblence with the variation of DSC crystallinity parameter ΔH,

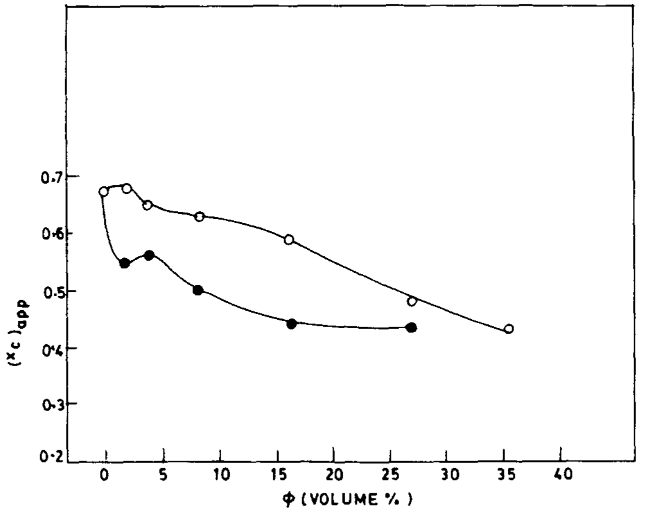


FIGURE 8 Variation of X-ray crystallinity with filler concentrations for i-PP/$CaCO_3$ (untreated, open symbols and treated, closed symbols) composites.

particularly at higher ϕ_F values. At lower filler content the ΔH values show an increase where $(X_c)_{app}$ values register decrease. However, the interesting point to note is that the crystallinity of i-PP decreases with increase in filler content and the values of the samples with surface treated $CaCO_3$ remains always lower than the crystallinity with untreated $CaCO_3$ at corresponding volume percent of $CaCO_3$. This may imply that surface modification with the titanate coupling agent introduced some kind of interaction with i-PP so that the crystallinity of the latter is interfered to a significant extent in comparison to the cases when untreated $CaCO_3$ is used as a filler.

3.2. Tensile properties

Variations of tensile properties such as tensile yield strength, yield elongation and tensile modulus are shown in Figure 9 as functions of $CaCO_3$ volume percent.

Following observations were made for the composites with untreated $CaCO_3$ as the filler:

In region 1 of composite composition (0–4 vol.% $CaCO_3$), tensile strength and elongation decreases (tensile strength shows a small minimum at $\phi_F = 2$) while modulus increases. In this region DSC crystallinity shows a small increase and larger spherulites form (or increase in spherulite size distribution ΔW) of i-PP.

In region 2 of composite composition (i.e., 4–16.5 vol.% $CaCO_3$) tensile strength and elongation decreases while modulus increases after a small initial decrease. This region corresponds to the decrease in crystallinity and formation of small spherulites (i.e., narrower distribution of crystallites) of i-PP.

In region 3 of the composite composition (i.e. 16.5–36 vol.% $CaCO_3$) tensile strength decreases, elongation registers a marginal decrease while modulus shows

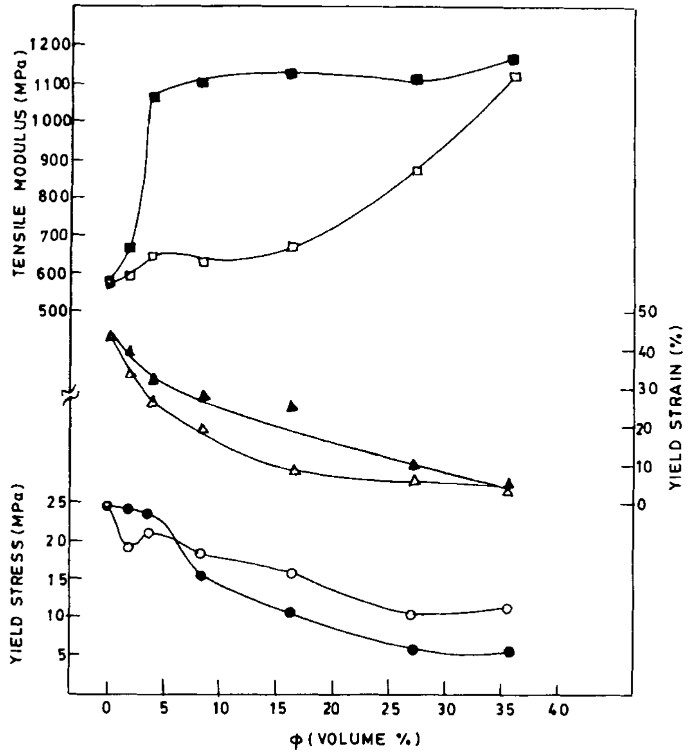


FIGURE 9 Plots of tensile properties of *i*-PP/CaCO$_3$ (untreated, open symbols and treated, closed symbols) composites as functions of composite composition.

a sharp increase. This region is consistent with the formation of large spherulites (increase in the parameter ΔW) and decrease in the crystallinity of *i*-PP.

In the composites with surface treated CaCO$_3$ the variation in tensile properties were somewhat different from the former.

In the region 1 (0–4 vol.% CaCO$_3$) tensile strength and elongation decreases while modulus shows a significant increase. However, the decrease in tensile strength is only marginal. This region is consistent with increase in DSC crystallinity and formation of broad crystal size distribution.

In the region 2 (4–16.5 vol.% CaCO$_3$) tensile strength and elongation continue to decrease while modulus shows a marginal increase. This region is consistent with decrease in crystallinity and narrow spherulite size distribution in the morphology of *i*-PP.

Finally, in the region 3 (16.5–36 vol.% CaCO$_3$) tensile strength and elongation decrease, modulus increases inappreciably. This region corresponds to decrease in crystallinity and coexistence of small and large spherulites in *i*-PP.

It may be noted that in the range 1 yield strength decreased only marginally but beyond this point the value decreases remaining always lower than the values with untreated CaCO$_3$ at corresponding filler levels. Elongation decreases at all filler levels, the values, however, remain higher than the composites with untreated $CaCO_3$. The modulus at first showed a fast increase upto $\phi_F = 4\%$ and beyond this point the increase is only marginal. The modulus values are always higher than the values with untreated $CaCO_3$ in the composites. Decrease in yield stress, modulus and elongation was observed by the present authors[9] in *i*-PP/Ni composites while decrease in tensile strength, modulus, yield stress, and increase in elongation was reported[16] for blends based on *i*-PP.

3.3. Correlation of tensile properties with crystallization parameters

Increase in the nucleation rate, degree of supercooling and overall crystallinity of *i*-PP was shown by Beck and Ledbetter[12] on addition of nucleating agents into the polymer. They also reported a consequential systematic effect on the tensile properties of *i*-PP so that tensile strength, modulus, yield stress, and breaking elongation exhibited linear variations with T_p. Recently Gupta and Purwar[8] reported similar correlations of tensile properties with various crystalline parameters such as T_p and ΔW in their study of blends based on *i*-PP. The present authors[9] also have found linear correlations of tensile properties with crystalline parameters such as ΔW, ΔH, and X_c in their study of nickel powder filled *i*-PP composites. In this study similar correlations of tensile properties of *i*-PP

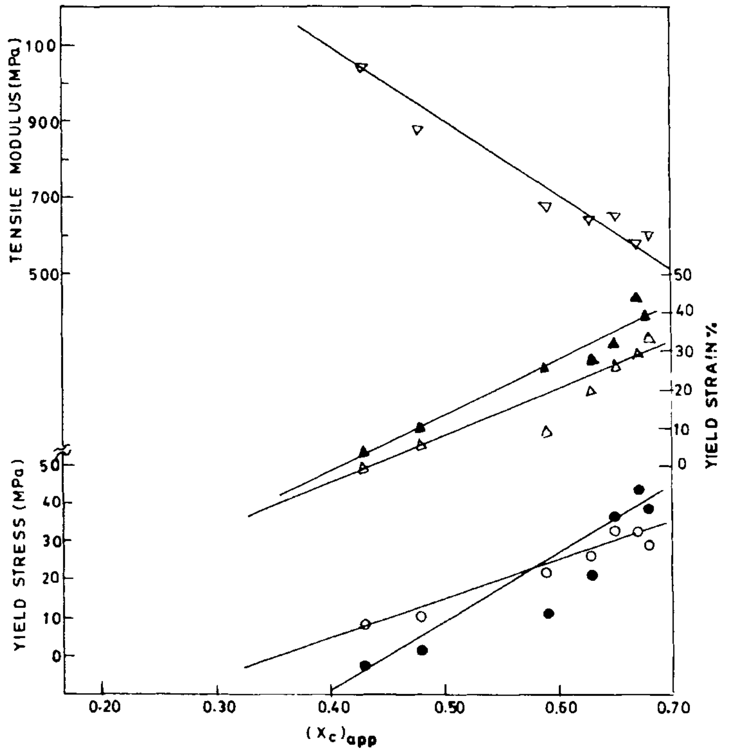


FIGURE 10 Correlation of the tensile properties with $(X_c)_{app}$ in *i*-PP/$CaCO_3$ (untreated, open symbols and treated, closed symbols) composites.

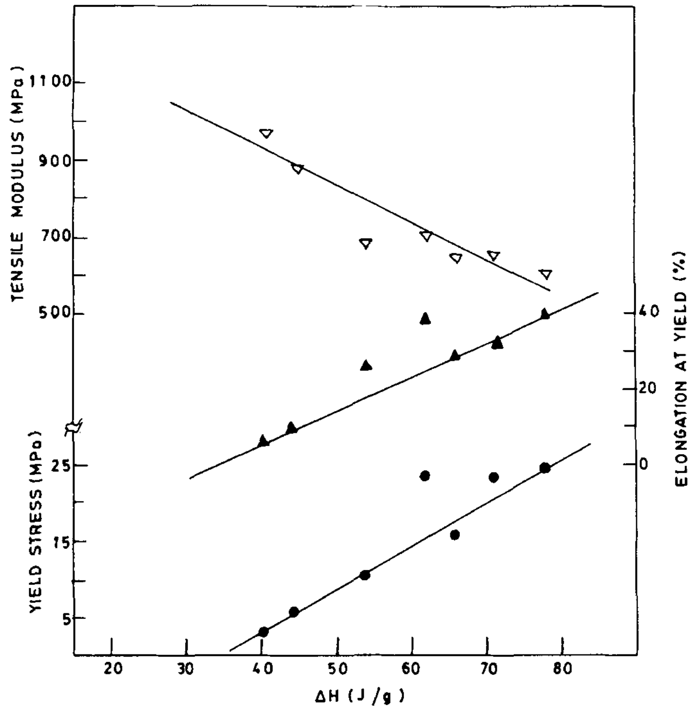


FIGURE 11 Correlation of the tensile properties with ΔH for i-PP/CaCO$_3$ (untreated, open symbols and treated, closed symbols) composites.

composites filled with untreated and surface treated CaCO$_3$ with crystallization parameters such as X_c, T_p, ΔH and ΔW as shown in Figures 10–15, are reported. Linearity of the correlations were estimated by regression analysis on the data and coefficient of correlation was calculated for each case. Considering some scatter of the data points in such experimental work we accepted correlations with coefficient of correlations greater than 0.70 to represent a moderate linearity of the correlation. For the composites with untreated CaCO$_3$ we obtained the following expressions of linear correlations:

$$\sigma_y = 49.47X_c - 11.96 \tag{2}$$

$$\sigma_y = 222.56 - 1.79T_p \tag{3}$$

$$E = 1446.16 - 12.02\Delta H \tag{4}$$

$$E = 1878.61 - 1947.74X_c \tag{5}$$

$$E = 79.59T_p - 8412.50 \tag{6}$$

$$\varepsilon_y = 127.34X_c - 55.69 \tag{7}$$

where σ_y, E and ε denote tensile yield stress (MPa), tensile elastic modulus (MPa) and yield strain, respectively.

Correlation of X-ray and DSC crystallinity parameter $(X_c)_{\text{app}}$ and ΔH and T_p are presented in Figures 14 and 15, and the expressions for the linear correlations

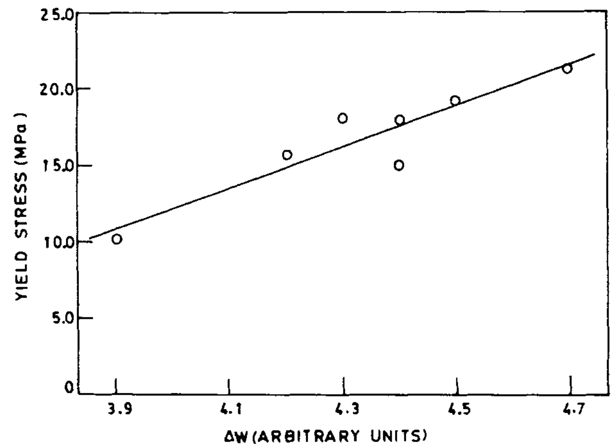


FIGURE 12 Plots of correlation of yield stress of *i*-PP/$CaCO_3$ (treated) composites with ΔW.

are shown below:

$$X_c = 4.93 - 0.038T_p \tag{8}$$

$$X_c = 0.007\Delta H - 0.20 \tag{9}$$

$$\Delta H = 603.57 - 4.74T_p \tag{10}$$

These correlations are significantly linear with coefficient of correlations 0.86,

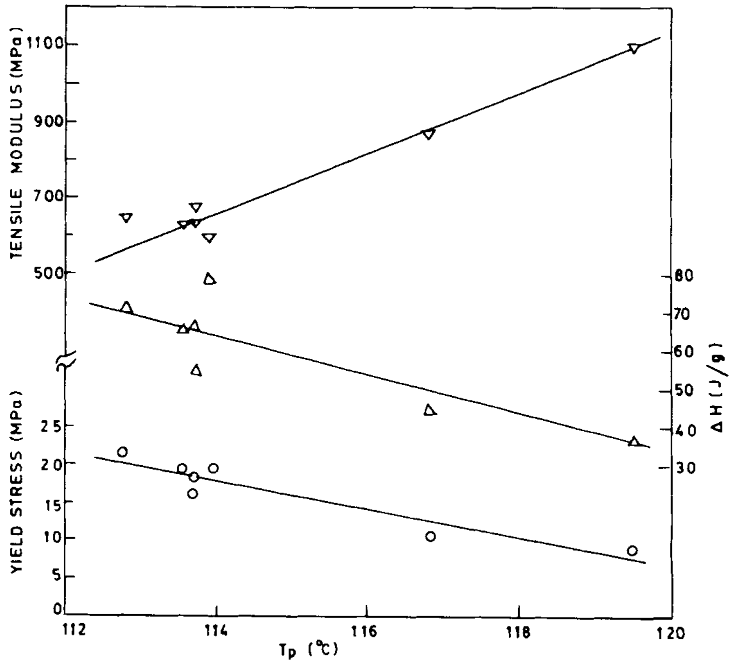


FIGURE 13 Correlation of (○) yield stress, (▽) tensile modulus and (△) ΔH of *i*-PP/$CaCO_3$ (untreated) composite with T_p.

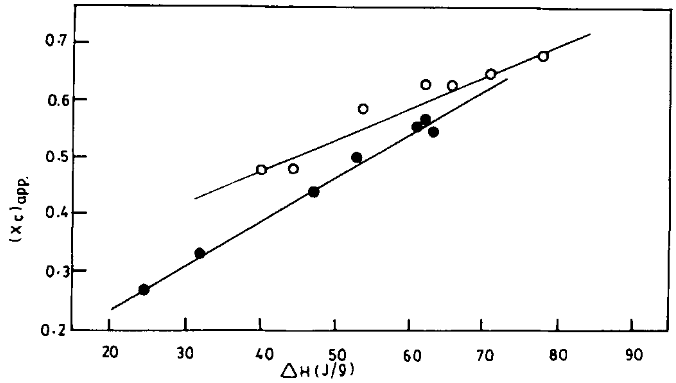


FIGURE 14 Plots of correlation of $(X_c)_{app}$ with ΔH in *i*-PP/$CaCO_3$ (untreated, open symbols and treated, closed symbols) composites.

0.86 and 0.70, respectively, indicating good consistency between X-ray and DSC crystallinity as well as nucleation of crystallization versus X-ray and DSC crystallinity.

Proceeding in the similar way as above the following expressions for the linear correlations between tensile properties and crystalline parameters were obtained for the composites with surface treated $CaCO_3$.

$$\sigma_y = 0.54\Delta H - 9.94 \tag{11}$$

$$\sigma_y = 58.45X_c - 11.76 \tag{12}$$

$$\sigma_y = 29.75\Delta W - 112.89 \tag{13}$$

$$\varepsilon_y = 0.86\Delta H - 15.58 \tag{14}$$

$$\varepsilon_y = 97.20X_c - 20.36 \tag{15}$$

$$X_c = 0.008\Delta H + 0.07 \tag{16}$$

$$X_c = 7.05 - 0.056T_p \tag{17}$$

The correlations in Eqs. (16) and (17) represent linear correlations between X-ray

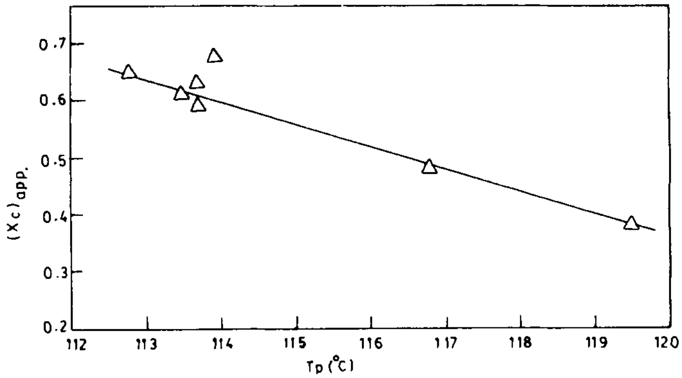


FIGURE 15 Correlation of $(X_c)_{app}$ with T_p in *i*-PP/$CaCO_3$ (untreated) composites.

TABLE II

Coefficient of correlation for the linear correlation of various parameters

Tensile property	Crystallization parameter	Coefficient of correlation
Tensile strength (r_y)	T_p	0.70 (0.32)
	ΔW	0.30 (0.70)
	ΔH	0.61 (0.93)
	X_c	0.83 (0.84)
Tensile modulus (E)	T_p	0.94 (0.08)
	ΔW	0.30 (0.70)
	ΔH	0.71 (0.41)
	X_c	0.93 (0.33)
Elongation-at-yield (ε_y)	T_p	0.45 (0.37)
	ΔW	0.31 (0.39)
	ΔH	0.63 (0.93)
	X_c	0.76 (0.92)

Values of coefficient of correlations at parentheses denote values for composites with treated $CaCo_3$.

crystallinity vs. DSC crystallinity and nucleation for the composites with treated $CaCO_3$.

From the above correlations shown in Figures 9–14 and Table II, several observations can be made. For the composites with untreated $CaCO_3$, the tensile strength, tensile modulus and tensile elongation are distinctly related to the crystallinity of the *i*-PP in the composites. These correlations thus indicate the importance of crystallization of *i*-PP component on the tensile properties of the composites. Treatment of the surface of $CaCO_3$ with the coupling agent modifies its interaction with *i*-PP matrix which is manifested in the correlations which were at variance with those exhibited by untreated $CaCO_3$ filled composites. Thus, crystallite size distribution parameter ΔW assumed importance along with crystallinity and exhibited distinct linear correlations with tensile strength. Furthermore, while elongation also showed linear correlation with crystallinity parameter, tensile modulus did not show any linear correlations. However, it may be pointed out that those pairs of parameters which exhibited too low values of coefficient of correlation, the correlations may be more complex in nature than the simple linear correlations.

Lower values of ΔW indicate smaller spherulites in the *i*-PP morphology. Thus the above results indicate that modulus increases while tensile yield strength and elongation decreases with increase in spherulite size as well as decrease in crystallinity of *i*-PP in the composites. Yield stress and tensile stress of *i*-PP was shown[17,18] to increase with decreasing spherulite size. Increase in crystallinity through incorporation of nucleating agents was reported by Kuhre *et al.*[19] to increase the tensile strength. Similar correlations of spherulite size of *i*-PP with tensile strength and yield stress were reported by Remaly and Schultz[20] in the presence of varying proportions of nucleating agents.

CONCLUSIONS

Crystallization of *i*-PP in *i*-PP/$CaCO_3$ composites was studied from exothermic crystallization peaks of *i*-PP by DSC. The degree of crystallinity is in good agreement with that estimated from X-ray studies.

In the region of very low filler concentration the crystallinity of *i*-PP seems to be increasing in the composites. This induces a slight increase in tensile strength and modulus which is manifested by an increase in the crystallite size distribution parameter. In the moderate range of filler content the crystallinity registered a steady decrease and tensile strength, elongation also decreases while modulus increased after a small initial decrease. In the higher range of filler loading, the overall crystallinity decreases with coexistence of small and large crystals. This crystallinity results reflect in the decrease in tensile strength, elongation and a sharp increase in the tensile modulus of the composites. Similar type of correlation also exists between crystallization behaviour and tensile properties of the composites with surface treated filler.

This study indicates that the crystallinity has an important role on the tensile properties of composites based on crystalline polymers. Comparison of the results of crystallization and tensile properties between untreated *i*-PP/$CaCO_3$ and treated *i*-PP/$CaCO_3$ composites shows some interaction between the polymer and the filler after the treatment with the titanate coupling agent.

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