Crystallization of PP in PP/Ni Composites and its Correlation with Tensile Properties

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Synopsis

The effect of nickel (Ni) powder on crystallization of polypropylene (PP) in PP/Ni composites is studied through differential scanning calorimetry (DSC) and wide-angle X-ray diffraction techniques. Interpretation of crystallization exotherm peaks in terms of nucleation and growth rates of crystallization, crystallite size distribution, and crystallinity indicated differences in the morphology of PP in all the composites. Crystallinity and tensile behavior decreased on nickel addition. There is a good qualitative agreement in the crystallinity determined by X-ray diffraction and DSC exotherms, and the variation in both cases, with the volume percent of filler is similar. An attempt has been made to correlate the various tensile properties with the crystallization parameters such as the crystallinity and crystallite size distribution.

INTRODUCTION

Polymer composites made by incorporation of powdery metals into polymer matrices have been of much interest of late as a new group of engineering materials.[1] These materials have higher density, enhanced thermal and electrical conductivity in comparison with plastics, and high corrosion resistance, lower specific weight, ease of processability, and are cheaper in comparison with metals. These materials therefore, are of practical interest to suit specific applications[2] such as discharging static electricity, heat conduction, electrical shielding, electrical heating, converting mechanical to electrical signals, and absorbing electromagnetic waves.

The use of metal fillers in thermoset matrices is well known.[3,4] Extensive research has been carried out with epoxy polymer composites on rheological behavior[5] and mechanical properties.[6-9] On the other hand, reports on the thermoplastic–metal composites are scanty in lieu of their easy processability. Nicodemo and Nicolais,[10] while studying the mechanical properties of styrene-acrylonitrile copolymer filled with iron and aluminium powders, reported enhancement of modulus and reduction in breaking stress and breaking strain. De et al.[11] reported reduction in compressive strength and improvement in microhardness with metal loading in polymethylmethacrylate composites.

In the present article we report the mechanical properties of polypropylene (PP)-nickel composites as functions of metal powder content. An attempt has been made to correlate tensile properties of these composites with various crystallization parameters of PP.

EXPERIMENTAL

Materials

Isotactic polypropylene (PP), Koylene M0030 (melt flow index 10 and density 0.89 g cm^{-3}) of Indian Petrochemicals Corporation Limited, and nickel powder (density 8.9 g cm^{-3}) of Central Drug House were used. Nickel powder was sieved into four particle size ranges and particles of 20–45 μm diameter were used. The average diameter of the particles calculated from the size distribution analysis by Sadiograph method (Model FRITSCH ANALY-SETTE-20) was 40 μm.

Preparation of the Composites

Vacuum-dried PP and nickel powder were mixed on a two-roll mill at 160 $\pm$ 2°C for 10 minutes to prepare thin sheets of the composites with filler content 0.10–3.42 vol%. Several plies of these thin sheets were then moulded on a compression-moulding machine at a temperature 200 $\pm$ 2°C and pressure 1500 psi to make sheets of 1-mm thickness. Dumbbell-shaped specimens were then machined from these sheets. DSC and X-ray diffraction measurements were done on ground powder of the composites. Nonfilled PP samples were also processed through identical conditions of mixing and moulding of the composites.

Measurements

Differential scanning calorimetric measurements of the composites with filler particles of average diameter 40 μm were done on a Du Pont thermal analyzer (Model 1090) with module 910. The samples were heated to 200°C and were kept at that temperature for 5 min to eliminate the effect of any previous history of crystallization. Thermograms were recorded during the cooling cycle at constant cooling rate 10°C/min in liquid air at identical settings of the instrument.

X-ray diffraction measurements of the composites (also with particles of average diameter 40 μm) were done on Phillips Norelco X-ray diffraction equipment provided with a scintillation counter and recorder. Radial scans of intensity (I) versus diffraction angle (2θ) were recorded in the range of 8–35° of 2θ using CuKα radiation.

Tensile properties were measured on an Instron Universal testing machine (Model 1121) at an extension rate 100% (initial crosshead separation 5 cm and crosshead speed 5 cm/min) according to ASTM D638 test procedure. At least five samples were tested in each case and the average value reported. All tests were performed at ambient temperature of 30 $\pm$ 1°C.

RESULTS AND DISCUSSION

Prominent crystallization exotherm peak of PP was observed in all the composite samples and also in nonfilled PP in the DSC thermograms. Figure 1 shows the exotherms for the samples at the same temperature scale. The exotherm peaks are observed at 112.5 $\pm$ 1°C. Various crystallization parameters such as T_p, T_{onset}, $T_c - T_p$, S_i, ΔH, and ΔW (also used by other
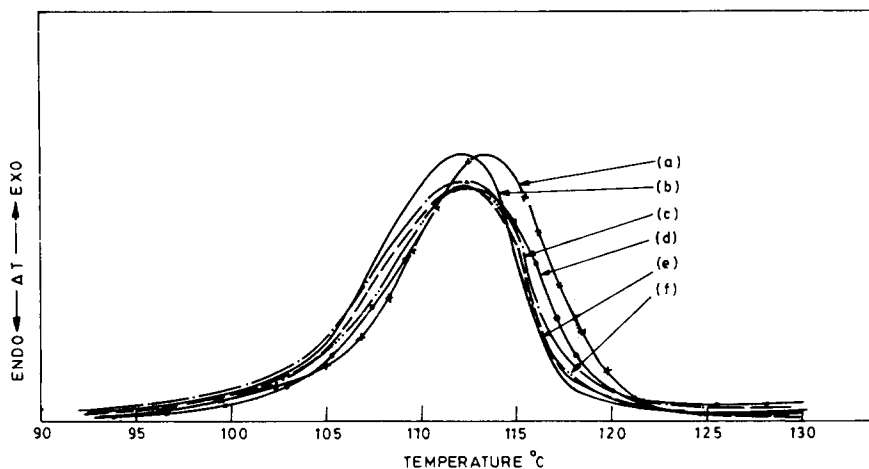
Fig. 1. DSC thermograms of PP and PP/Ni composites of varying volume percent of filler: (a) PP (b) 0.1% Ni (c) 0.5% Ni (d) 1% Ni (e) 2% Ni (f) 3.42% Ni.

authors[12, 13]) were evaluated from these exotherms and are shown in Table I. The significance and method of estimation of the above parameters are well described by Gupta and Purwar.[14]

Variation of these crystalline parameters as functions of filler contents is shown in Figure 2. T_p and S_i decreases with increasing filler content, showing minimum in the range of 0.1–0.5 vol% of filler (ϕ_F), while T_{onset} and ΔH showed a decreasing trend without showing any prominent minimum. On the other hand, ΔW showed an initial decrease showing a minimum at 0.1% filler vol%, the value increases beyond this point showing inappreciable increase beyond $\phi_F = 0.5\%$. The parameter ($T_c - T_p$) initially decreases at $\phi_F = 0.1$,

TABLE I
Values of Various Crystallization Parameters of PP Components
in PP/Ni Composites from DSC Thermograms and X-ray Diffraction

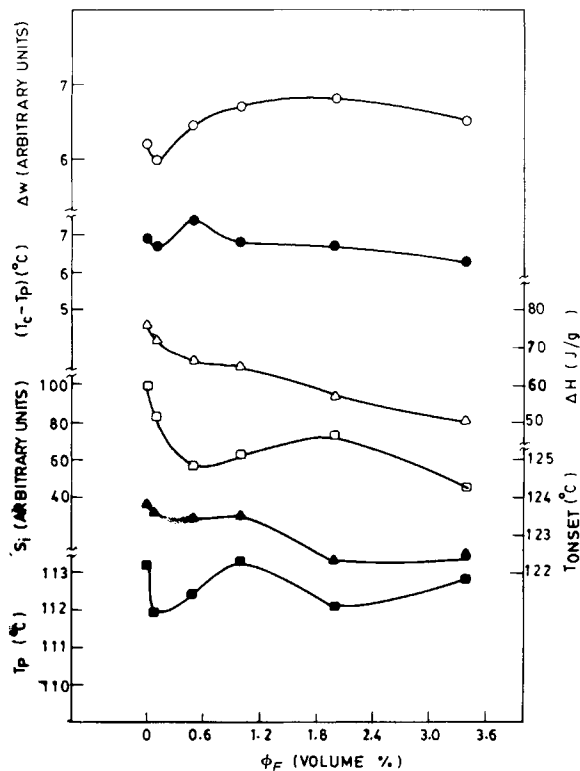| Sample (vol% filler)	T_p (°C)	T_{onset} (°C)	$T_c - T_p$ (°C)	S_i (arbitrary units)	ΔW (arbitrary units)	ΔH (J/g)	$(X_c)_{app}$
PP	113	123.8	6.9	100	6.2	75.6	0.66
PP/Ni (0.1%)	111.9	123.5	6.7	83.3	6.0	71.6	0.63
PP/Ni (0.5%)	112.4	123.4	7.4	56	6.4	66.4	0.64
PP/Ni (1%)	113.3	123.5	6.8	63	6.7	64.5	0.61
PP/Ni (2%)	112.1	122.3	6.7	73.5	6.8	57.2	0.58
PP/Ni (3.42%)	112.7	122.5	6.3	45.4	6.5	50.0	0.57

Fig. 2.   Plots of various crystallization parameters as functions of filler concentration.

then increases, showing a maximum at $\phi_F = 0.5$ and then shows a slow decrease beyond this point.

In the composite composition range $\phi_F = 0$–0.5 vol% (range 1), addition of nickel powder decreases the rate of nucleation and growth of crystallizate, thus reducing the degree of crystallinity of PP. Spherulites resulting were small in number due to low nucleation rate and small in size due to slow crystallization growth rate. The crystallization size distribution parameter ΔW decreases upto $\phi_F = 0.1\%$, partially supporting this morphological description of PP.

In the region of composite composition $\phi_F = 0.5$–2 vol% (range 2), the nucleation rate and crystallization growth rate increases; crystallinity, however, decreases inappreciably. Thus, the spherulites formed will be small in size and large in number. However, due to an increase in the crystallization growth rate some larger spherulites may also result. The crystallite size distribution parameter ΔW registers an increase in this range, supporting this morphology of PP.

Finally, in the region $\phi_F = 2$–3.4 vol% (range 3), the crystallization nucleation rate, growth rate, and overall crystallization decreases, the rates of decrease being somewhat slower than those in range 1 of composite composition. The crystallite size distribution parameter shows only an inappreciable decrease in this range of filler concentration. Thus the morphology of PP appears to be similar to that in range 1 of the composite composition.
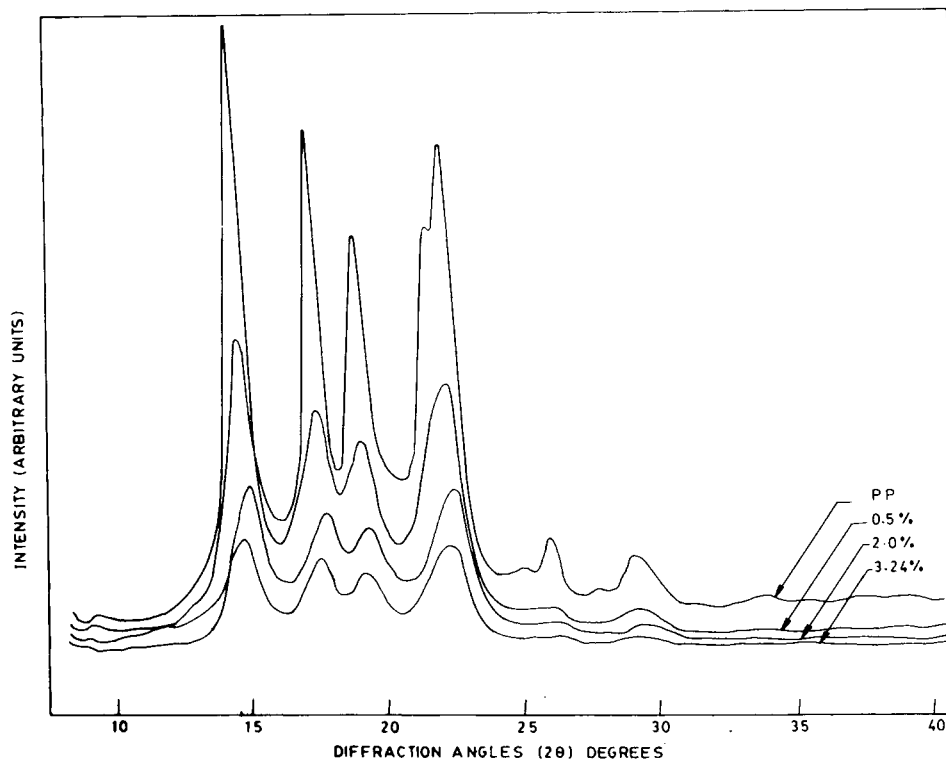
Fig. 3.   X-ray diffractograms of PP and PP/Ni composites of varying filler concentration.

X-Ray Diffraction

X-ray diffractograms of the composites are shown in Figure 3 as the intensity (I) versus diffraction angle (2θ) plots. Polypropylene shows several intense diffraction maxima at 2θ values 14°, 17°, 18.5°, and 21.7°, similar to earlier reports.[14,15] The last of the peaks appear to be a doublet. Diffraction patterns of the PP/Ni composites show all the characteristic peaks of PP. However, with the addition of filler the doublet changes into a singlet and the peak intensities show a corresponding decrease with increase in filler concentration.

The degree of crystallinity (X_c) was calculated from the diffractograms using the following expression:[14,16]

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

where $I_{cr}(s)$ is the coherent intensity concentrated in the crystalline peaks and $I(s)$ is the total coherent intensity scattered; S is the scattering vector expressed as $S = (2/\lambda)\, \mathrm{Sin}\,\theta \cdot K$ is the correction factor which in these calculations is taken to be unity.[16,17] The degree of crystallinity calculated is denoted as apparent crystallinity $(X_c)_{app}$, which may be used for comparison.[14]

From the experimental I versus 2θ curves IS^2 versus S curves were drawn. Amorphous scattering curve and the base line were drawn according to the procedure suggested by Sotton et al.[17] Apparent crystallinity values are shown
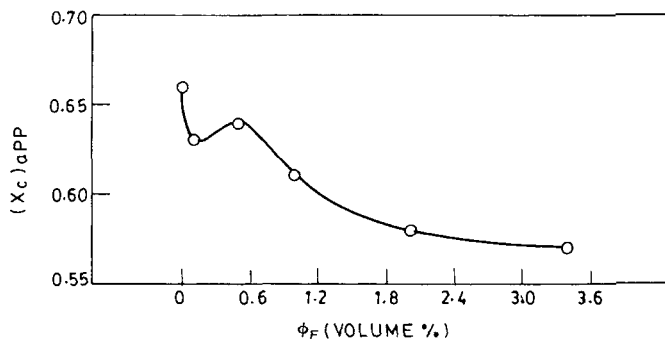
Fig. 4.   Variation of X-ray crystallinity with filler concentrations for PP/Ni composites.

in Table I and the variation in crystallinity with filler content is shown in Figure 4. With increase in nickel powder content in the composites, the crystallinity decreases from that of nonfilled PP showing a minimum at $\phi_F = 0.1$ vol%, then the value increases slightly upto $\phi_F = 0.5$ and beyond this point the crystallinity registers a slow decrease upto $\phi_F = 3.4$ studied. It may be noted that the variation of $(X_c)_{app}$ with filler concentration agrees qualitatively with the variation of crystallinity parameter ΔH in DSC measurements, although the latter does not show any sharp minimum. Thus the $(X_c)_{app}$ data provides a supporting evidence that the overall crystallinity decreases with increasing nickel powder concentration in PP/Ni composites.

Tensile Properties

Tensile properties: tensile modulus, yield stress, and yield strain of PP/Ni composites, are plotted as functions of filler volume percent in Figure 5.
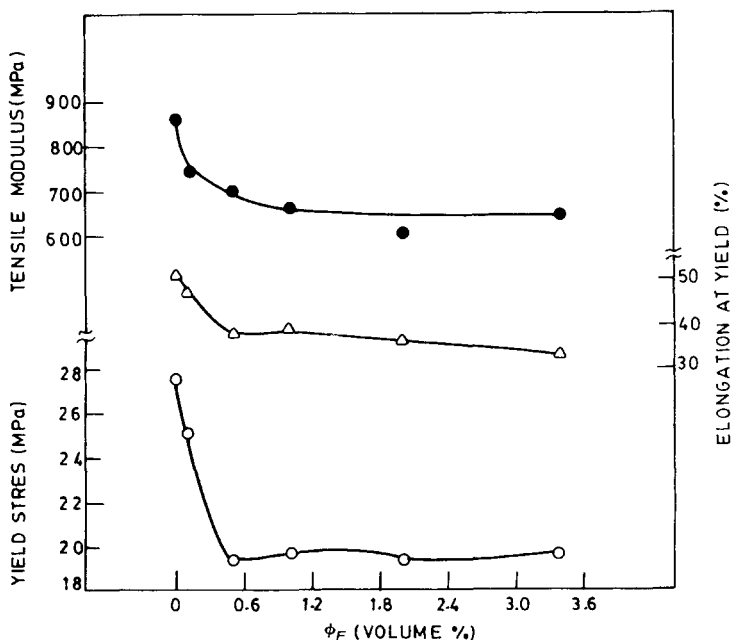

Fig. 5.   Plots of tensile properties of PP/Ni composites as functions of composite composition.

In the range 1 of composite composition ($\phi_F = 0$–0.5%), yield stress and yield strain decreases showing a non-sharp minimum at 0.5 vol% filler. Tensile modulus also shows a decrease upto $\phi_F = 0.5$. This region corresponds with the decrease in crystallinity and the formation of smaller spherulites (or decrease in spherulite size distribution of PP).

In the range of composite composition ($\phi_F = 0.5$–2%), yield stress and yield strain show an inappreciable increase, whereas modulus registers a slow decrease. This region corresponds to slow decrease of crystallinity and the formation of smaller spherulites of PP. In the region $\phi_F = 2$–3.4% of the filler concentration yield strength, yield strain and modulus show a very slow decrease. This region is consistent with the formation of large spherulites and overall decrease of crystallinity of PP.

Values of yield strength, modulus, and yield strain are lower for the composites than those of nonfilled PP in all the regions of the composite composition.

Correlation of Mechanical Properties and Crystallization Parameters

It was reported by Beck and Ledbetter[13] that the addition of nucleating agents increased the nucleation rate, degree of supercooling and the crystallinity of PP which in turn registered a systematic effect on the tensile properties of the polymer. Tensile strength, modulus, yield stress, and elongation at break showed linear variations with T_p. Similar correlations of tensile properties with crystalline parameters such as T_p and the spherulite size distribution parameter ΔW were also reported in the study of blends based on PP by Gupta and Purwar.[14] In the present study we report similar correlations of tensile properties of filled PP composites with X_c, ΔH and ΔW, as shown in Figures 6–8. Regression analysis was performed on the data to determine the linearity of the correlations. Coefficient of correlation was calculated in each individual case. The closer the value of the coefficient of correlation to unity, the better the linearity of the fit. Values of coefficient of correlations are presented in Table II for various pairs of these parameters. Due to the extremely low values of the coefficient of correlations, linear relationships of some of these pairs of parameters were rejected straightaway. Correlations with coefficient of correlation greater than 0.55 were taken to represent a moderate linearity of the correlation. We obtained the following expressions of linear correlations:

$$\sigma_y = 80.97 - 9.24\,\Delta W$$

$$\sigma_y = 0.47\,\Delta H - 8.59$$

$$\sigma_y = 1.41 X_c - 0.65$$

$$E = 2170.62 - 227.72\,\Delta W$$

$$E = 11.53\,\Delta H - 34.82$$

$$E = 2873.58 X_c - 1080.48$$

$$\epsilon = 150.41 - 17.05\,\Delta W$$

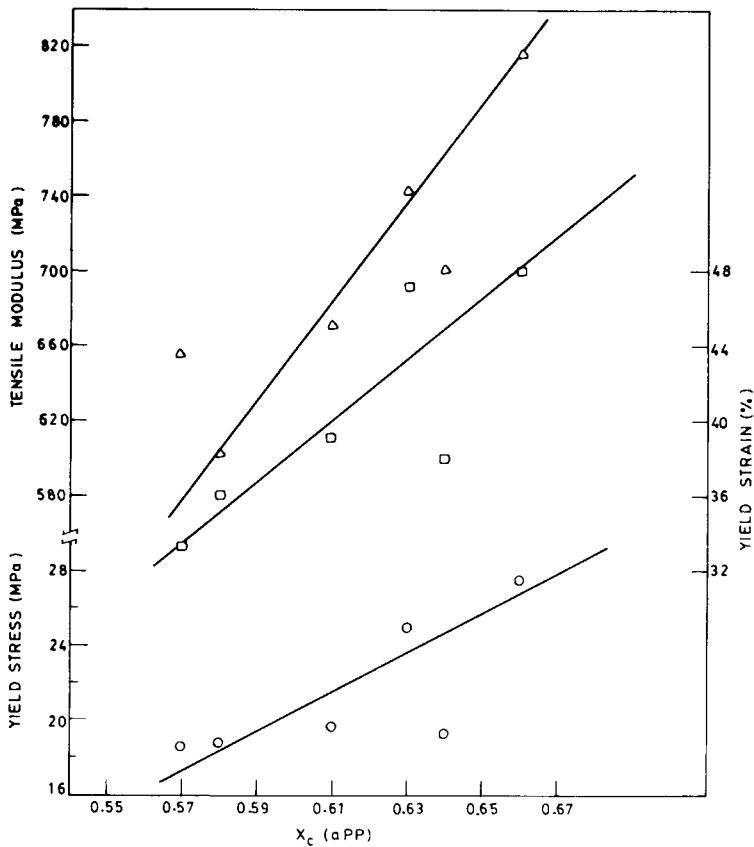$$\epsilon = 0.68\,\Delta H - 3.060$$

$$\epsilon = 164.28 X_c - 60.34$$

Fig. 6.　Correlation of the tensile properties with X_c.

where σ_y, E, and ϵ represent tensile yield stress, tensile elastic modulus, and yield strain, respectively.

Correlation between X-ray and DSC crystallinity parameters $(X_c)_{app}$ and ΔH is presented in Figure 9. The correlation is sufficiently linear with a coefficient of correlation 0.9 indicating the consistency of the DSC and X-ray crystallinities.

From the above correlations (shown in Figures 6–9 and Table II), it is suggested that tensile yield strength and tensile modulus are distinctly related to the crystallinity of the polypropylene in the composite as well as the crystal size distribution parameter ΔW. These correlations once again appear to confirm the effect of crystallization of PP component on the tensile properties of the composite.

It has been pointed out that the lower values of ΔW imply smaller spherulites in the morphology. Therefore from the above results it may be stated that the modulus and yield stress decrease with increasing size of the spherulites as well as with decrease in the crystallinity of PP in the composites. Yield stress and tensile strength of PP on addition of nucleating agents was reported[18,19] to increase with decreasing spherulite size. Kuhre et al.[20] showed that increase in crystallinity through the addition of nucleating
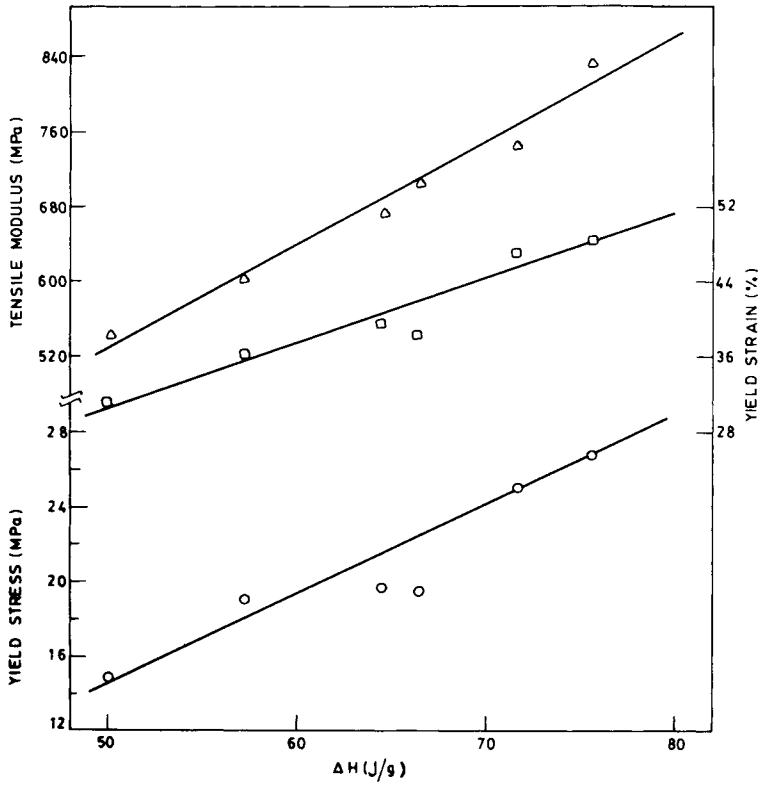
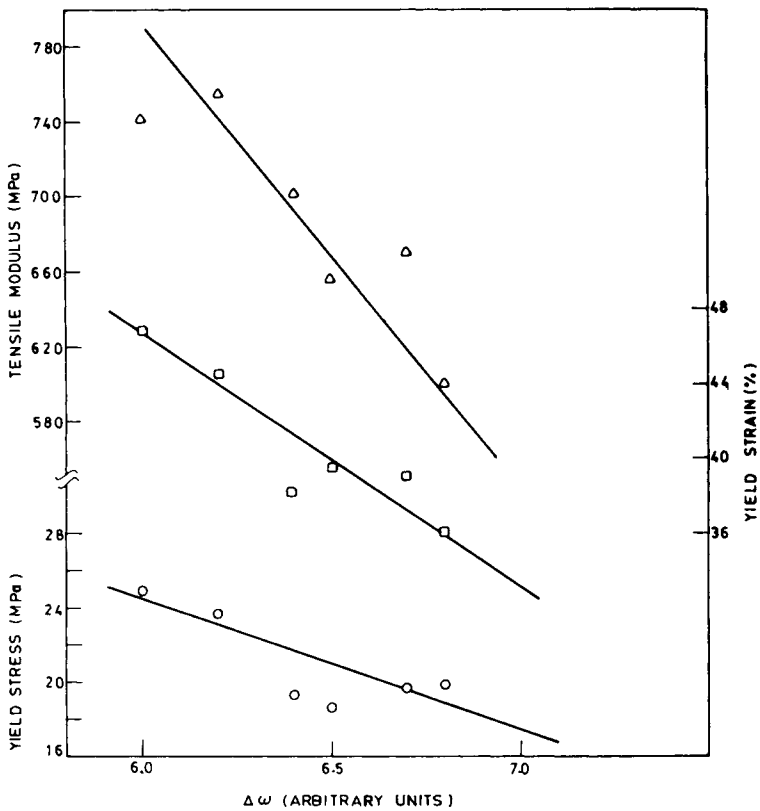Fig. 7.   Correlation of the tensile properties with ΔH.

Fig. 8.   Correlation of the tensile properties with ΔW.

TABLE II
Values of the Coefficient of Correlation for the
Linear Correlation of Various Parameters

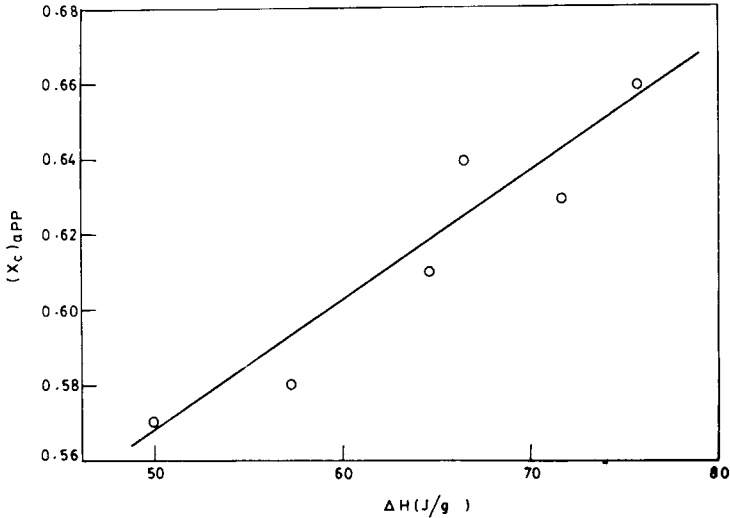| Tensile property	Crystallization parameter	Coefficient of correlation
Yield strength	T_p	0.02
	ΔW	0.57
	ΔH	0.70
	X_c	0.56
Elastic modulus	T_p	0.12
	ΔW	0.59
	ΔH	0.68
	X_c	0.74
Yield strain	T_p	0.04
	ΔW	0.56
	ΔH	0.86
	X_c	0.69

Fig. 9. Correlation of DSC and X-ray crystallinity parameters.

agents enhanced the tensile strength. Remaly and Schultz[21] reported similar correlations of spherulite size of PP with varying proportion of nucleating agents with tensile strength and yield stress.

CONCLUSIONS

The information about crystallization of PP in PP/Ni powder composites can be obtained from the crystallization exotherms of PP in DSC thermograms of the composites. The crystallinity calculated from these thermograms is in good agreement with those determined from X-ray crystallinity.

At low volume percent of filler (0–0.5), crystallinity decreases with a reduction in spherulite size giving somewhat rapid reduction in tensile strength, modulus, and elongation at break. Beyond this point, up to $\phi_F = 2\%$,

crystallinity shows a slow decrease and spherulite size increases somewhat. Tensile strength and elongation show marginal increase while modulus shows a slower decrease at these filler concentrations. In the region of filler content 2–3.4 vol% both crystallinity and spherulite size showed slow decrease. This is accompanied by corresponding slow decrease in modulus, tensile strength, and elongation.

Roles of crystallinity and crystal size distribution parameters are also evident from these results. Tensile modulus, tensile strength, and elongation are dependent on crystallinity and crystallite size distribution parameters.

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