Different β Nucleants and the Resultant Microstructural, Fracture, and Tensile Properties for Filled and Unfilled iso Polypropylene

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ABSTRACT: This article explores the use of two β nucleants to improve the fracture behavior of filled and unfilled homo-polypropylene (PP). The first was based upon an organic quinacridone, whereas the second was based upon the inorganic calcium pimelate. Formulations containing various concentrations of nucleant were prepared using single screw extrusion and then characterized by X-ray diffraction, differential scanning calorimetry (DSC), Izod impact strength, and tensile testing. The quinacridone nucleating agent produced higher levels of β crystallinity and better improvement in strain to failure, whereas the calcium pimelate imparted greater improvement in impact strength regardless of whether the PP was filled or unfilled. No direct relationship between β crystallinity and fracture properties was observed though synergistic enhancement in impact strength was evident. By varying the concentration of calcium carbonate in the calcium pimelate from 10 : 1, 5 : 1, 2 : 1, and 1 : 1 weight composition of calcium carbonate to pimelic acid, similar property enhancements were achieved regardless of composition although the 10 : 1 sample did produce superior elongation to break. The importance of cooling rate on microstructure within each sample was explored via a through the thickness study using DSC and nano-indenting methods. Variations in the β content through the thickness were related to cooling and found to be independent of sample composition and processing. Elastic properties varied inversely with β content. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Isotactic polypropylene (PP) is a global commodity polymer widely used due to its combination of superior mechanical and thermal properties, chemical resistance, processability, recyclability, and price-to-performance ratio. However, a lack of impact resistance has limited its even wider usage prompting research into adding rubbers,[1–4] rigid thermoplastics,[5–7] block copolymers,[8–10] and nanocomposite methods[11–13] to overcome this deficiency. Another strategy, which avoids many inherent disadvantages of these additive approaches, is to nucleate formation of the β crystalline phase of PP, an inherently tougher structure, in preference to the more thermodynamically favorable α crystalline phase.

The α crystalline phase of PP consists of aggregates of large spherical lamellae radiating out from a central point with sharp clearly defined boundaries.[14] Within these crystallites, however, tangential lamellae can also grow forming a "cross-hatched" microstructure thus reducing molecular mobility.[15] These structural features all contribute to the formation of a brittle material with low impact performance. In contrast, the β crystalline phase consists of sheaf like aggregates of lamellar which grow unidirectionally, attaining a spherical structure only after continued branching of the sheaves at completion of crystallization.[16–18] Other factors which contribute to the improved toughness is the absence of any cross-hatched structure that reduces mobility, smaller spherulites with more diffuse boundaries, and higher density of tie layers linking the amorphous regions to the crystallites.[15,19] Furthermore, the β crystalline structure also has a lower packing density which imparts lower cohesive forces that allow greater plastic flow and hence improved toughness.[20] During failure, the bundles separate, producing voiding and crazing, and unfolding lamellae while initiating the polymorphic β to α transition.[21] These processes and structural features are not available or present in the α structure and all contribute toward enhancing fracture resistance.

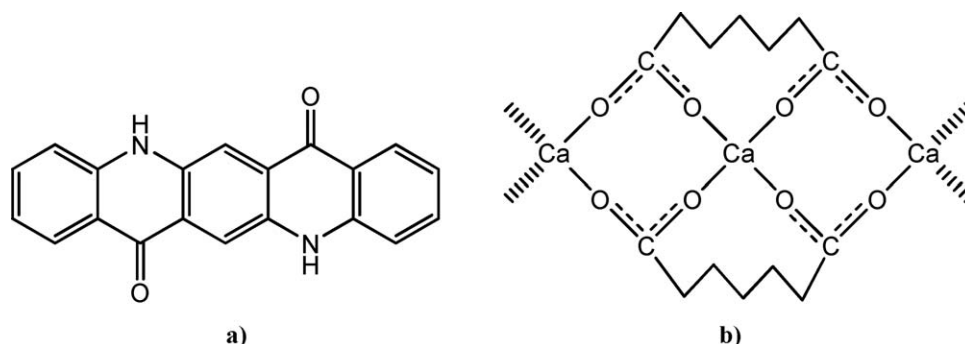Recent research has focused upon studying the impact of β nucleation on mechanical properties,[22,23] searching for

Figure 1. Generalized chemical structures of the active constituents in the β nucleating agent master batches studied. The commercial MPM-1113 is based upon (a) quinacridone and (b) is made from calcium pimelate.

synergistic behavior with already filled polymers[24–26] and investigating highly active or selective nucleants.[27] Despite the differences between the α and β crystal phases, a direct relationship between increasing β crystallinity and impact strength is not yet clear because of the difficulty in controlling overall crystallinity, spherulitic size, and distribution. Typically, there is a critical concentration of β nucleant above which impact properties diminish.[28–32] Tordjeman et al.,[33] however, established a relationship between β crystallinity and tensile properties by strictly controlling overall crystallinity and spherulitic size. Young's modulus and yield stress were found to decrease, whereas the yield strain and elongation to break increased with increasing β crystallinity. Although synergistic toughening with multiple modifiers would seem achievable because of the different mechanisms involved, the results so far have been mixed and inconclusive.[26,34,35] Grein and Gahleitner[24] suggested a synergy between small ligament length for a rubber modified PP blend, whereas Bai et al.[36] reported synergistic behavior when β nucleation changed failure from a crazing mechanism to a shear yielding and cavitation mechanism. Calcium pimelate, used in this work, is an effective,[28] selective, and thermally stable[37] nucleating agent primarily because of the similarity of its (001) crystallographic spacing (11–13 Å) with that of the same handed helices of PP (11 Å). It has also been shown that the increased cost associated with this nucleant can be offset by using pimelic acid supported on a nano-$CaCO_3$,[38] producing similar levels of toughness enhancement at lower nucleant concentration.[39]

This article explores the effect of β nucleation upon mechanical properties and the search for synergistic behavior in a filled homo-PP. A modified PP containing titanium dioxide and an elastomer (PP-m) and an unmodified homo-polypropylene (PP-um) have been nucleated with two different β nucleation agents; an organic nucleating agent based upon quinacridone and the inorganic nucleating agent calcium pimelate. The resulting mechanical properties are presented and related to the β crystallinity content. The effect of reducing the concentration of pimelic acid in the calcium pimelate nucleating agent was also investigated. The heterogeneity of crystallinity (and elastic properties) through the thickness of a sample and the importance of cooling rate on crystallinity was also studied. Crystallinity was determined using X-ray diffraction (XRD) and differential scanning calorimetry methods (DSC), whereas optical microscopy was used to inspect the crystal structure. Mechanical properties were evaluated using notched Izod impact and tensile testing methods.

EXPERIMENTAL

Materials

Two commercially available homo-PP formulations were investigated in this research. They were PP-um, an unmodified PP resin which only contains an anti-oxidant and calcium stearate, and PP-m, the modified variant, which contains 5 wt % and 3 wt % of an elastomeric impact modifier and titanium dioxide, respectively. The quinacridone based β nucleant, MPM-1113, was supplied by Mayzo in masterbatch form (homo-PP). Pimelic acid was purchased from Sigma-Aldrich and calcium carbonate was supplied by Solvay Chemicals. The chemical structure of the quinacridone, and the calcium pimelate are shown in Figure 1(a,b), respectively. All chemicals were used as received.

Sample Preparation

Each PP, PP-um and PP-m, was modified separately with the two β nucleants at different concentrations. The quinacridone-based nucleant, MPM-1113 masterbatch, was added to the PP at concentrations of 0.10, 0.25, 0.40, and 0.55 wt %, whereas the calcium pimelate masterbatch was added at concentrations of 0.1, 0.2, 0.4, and 1.0 wt %. Preparation of these formulations was performed using an Axon ab Plastmaskiner single screw compounder equipped with an 18-mm screw and a $L : D$ ratio of 38 : 1. Along the length of the screw barrel, the temperature was gradually increased from 190 to 215°C, whereas the screw speed used was 125 rpm. As the polymer exited the barrel, it was quenched using a water bath at ambient temperature. Injection molding was performed using a Battenfeld BA 800 CDC injection molder at 210°C to produce the tensile and notched Izod impact test specimens.

The minimum amount of pimelic acid required to nucleate the β phase was investigated by preparing a range of calcium pimelate nucleant with the composition of calcium carbonate : pimelic acid varied from 10 : 1, 5 : 1, 2 : 1, and 1 : 1. This was done by blending up to 3 g of the calcium carbonate and pimelic acid together in different weight ratios and mixing

vigorously in a ring mill for 1.5 min at room temperature. The powder was then placed in an oven for 2 h at 160°C.

Characterization

Notched Izod impact testing was carried out according to ASTM-256 using a Radmana ITR 2000 instrumented impact tester. Samples were impacted at a rate of 3.7 ± 0.2 ms^{-1}, and the impact strength was determined from an average of 10 different specimens.

Tensile properties were determined according to ASTM D-638-03 using an Instron 5565 universal testing machine fitted with a 30 kN load cell. Type I dogbone samples were placed in the instrument grips and subjected to tensile loading at a rate of 0.5 mm min^{-1} until the specimen had deviated 1.1% from linear viscoelastic behavior. Measurements were then stopped, the extensometer removed, and testing recommenced at a rate of 250 mm min^{-1} until ultimate failure. Each measurement is an average of five different specimens.

DSC was used to quantify β crystallinity using a TA Instruments DSC-2920 (DE). A sample of about 5 mg was placed in an aluminum crucible and heated from 30°C to 220°C at a rate of 10°C/min in nitrogen. The areas attributed to the α and β phase peaks were used to determine the total β crystallinity according to Grein.[20] Through the thickness, β crystallinity measurements were made with the same methodology using a Mettler Toledo 821e DSC on microtomed samples about 0.1-mm thick. The change in elastic properties through the thickness of the polymer was also determined, but only for the quinacridone nucleated PP-m sample using a Tribo Indenter nano-indenting device (Hysitron Incorporated, Minneapolis, USA) fitted with a Diamond pyramid tip and the distance between each point was about 100 μm.

A Bruker D8 Advance X-ray Diffractometer with CuKa radiation (40 kV, 40 mA) with a LynxEye detector was used to determine the XRD pattern. The samples, as received, were scanned over the 2-theta range 2°–82° with a step size of 0.02° and a count time equivalent of 74 s per step. Analyses were performed on the collected XRD data for the samples using the Bruker XRD search match program EVA™. Crystalline phases were identified using the ICDD-JCPDS powder diffraction database, and the α/β ratio was determined according to Jones et al.[40]

Optical microscopy was performed using an Olympus BH-2 light microscope at a lens magnification of 10×. To prepare the samples for investigation, a film of polymer heated to 200°C using a Mettler FP82 HT hot stage followed by rapid cooling to 125°C and holding for 5 min until crystal growth was complete.

RESULTS AND DISCUSSION

Comparison of Nucleating Agents

A key advantage over traditional toughening methods of the β nucleation approach is that only very low concentrations of nucleant are required to produce large improvements in mechanical properties. As a consequence, there is negligible impact upon processability. However, the choice of nucleating agent can be important in terms of cost as well as crystal structure selectivity, thermal stability, and thus ultimately, performance. For
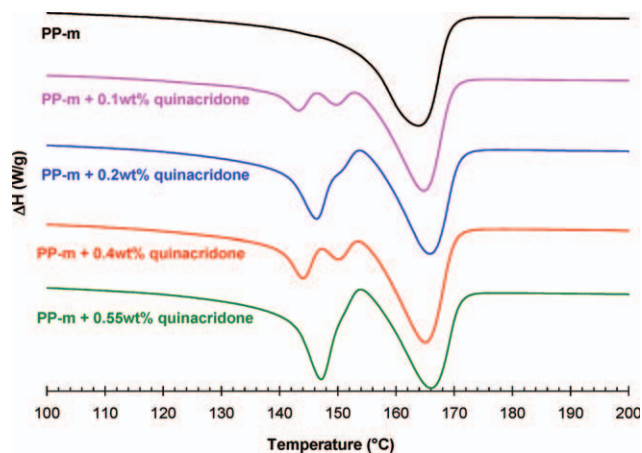

Figure 2. Effect of increasing β nucleant concentration on PP-m as measured according to DSC for the quinacridone-based nucleant. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

this reason, two different types of β nucleating agents were compared with respect to their effectiveness in promoting β crystal content and hence improvement in mechanical properties. DSC is a convenient technique to determine the extent of β phase formation because it has a lower melting point than the α phase producing a second distinct peak that can be quantified. DSC traces in Figure 2 show the effect of β nucleation where the newly formed β phase has a peak at about 147°C, quite distinct from the α phase peak at 165°C. This example illustrates nucleation of the modified PP at varying concentrations of the quinacridone as well as the variability that can occur. Two of the traces exhibit a doublet peak, previously attributed to variations in the ordering of the β structure.[16]

The absolute and relative β crystallinities of all the formulations prepared, as calculated according to Grein,[20] are shown in Table I. The results show that increasing β nucleant concentration did not produce any systematic increase in total β crystallinity and relative β within the crystalline phase, highlighting the catalytic nature of the nucleation process. Despite the scatter in the results, the presence of an elastomer appeared to have negligible impact on the total β crystal content, regardless of which nucleant was used. Figure 3 compares the nucleation with each of the formulations at a concentration of 0.2 wt % nucleant and illustrates the superior selectivity of the calcium pimelate. The quinacridone nucleant tends to produce two β peaks of varying size and breadth, whereas the calcium pimelate exhibits a single peak. The quinacridone nucleant, however, despite the large variations observed in Table I (due to the inherent difficulties in quantifying β crystallization using DSC and XRD analysis) produces higher absolute and relative β crystallinity compared with the calcium pimelate.

The optical micrographs in Figure 4 illustrate the effect of nucleation on the PP-um microstructure by comparing the non-nucleated PP-um with its quinacridone and calcium pimelate nucleated counterparts. As described previously, the virgin PP-um displays large spherulites typical of the α phase, varying in size from about 20 to 80 μm in diameter. Although clearly growing radially from a central nucleating core, their close

Table I. Summary of the α and β Crystal Structures Showing the Overall and Relative Crystallinities, as Measured Using DSC and XRD. Calcium Pimelate was synthesized from 2:1 CaCO₃:pimelic acid

Sample	Total crystallinity in polymer (%)		Relative crystalline phase within crystalline region	
	α	β	β-DSC	β-XRD
PP-um	48.4	0	0	8
PP-um + 0.1 wt % quinacridone	24.9	17.4	41.2	64
PP-um + 0.2 wt % quinacridone	24.9	18.1	34.2	69
PP-um + 0.4 wt % quinacridone	23.7	24.5	50.1	56
PP-um + 0.55 wt % quinacridone	25.0	22.6	47.4	51
PP-m	43.4	0	0	11
PP-m + 0.1 wt % quinacridone	23.6	8.2	25.9	14
PP-m + 0.2 wt % quinacridone	24.2	22.1	25.9	44
PP-m + 0.4 wt % quinacridone	28.3	17.1	47.7	14
PP-m + 0.55 wt % quinacridone	24.1	12.7	37.6	47
PP-um + 0.1 wt % calcium pimelate	31.5	14.8	31.9	26
PP-um + 0.2 wt % calcium pimelate	32.9	14.55	30.7	59
PP-um + 0.4 wt % calcium pimelate	31.8	15.4	32.7	26
PP-um + 1.0 wt % calcium pimelate	33.8	14.2	29.6	21
PP-m + 0.1 wt % calcium pimelate	26.3	19.4	42.4	15
PP-m + 0.2 wt % calcium pimelate	26.9	13.6	33.6	29
PP-m + 0.4 wt % calcium pimelate	29.1	16.1	35.7	22
PP-m + 1.0 wt % calcium pimelate	28.5	17.7	38.3	32

proximity to other spherulites has produced highly randomized shapes as they butt up against each other during growth. The boundaries between them, whilst distinct, exhibit both linear and highly irregular contours that vary greatly in their clarity. This is indicative of differences in interfacial strengths and would be expected to contribute to the poor impact of the α form of PP-um. In contrast to this slow crystallite growth and low nuclei concentration, the higher concentration of nuclei and faster crystal growth resulting from β nucleation produces a very different microstructure. This is evident in Figure 4(b, c) for the quinacridone and calcium pimelate based β nucleants, respectively, which exhibit much smaller and irregularly shaped spherulites (of the order of a few microns in size) similar to the sheaf life bundles described elsewhere.[28,32] The heterogeneous microstructure and diffuse boundaries between crystals would also be expected to contribute to improved impact performance. When comparing the effectiveness of the different β nucleating agents shows that calcium pimelate produces smaller spherulites than the quinacridone nucleant. This greater efficiency and the subsequent increased rate of crystal growth no doubt relates to the surface stabilized crystallization mechanism discussed.

The combined effect of β nucleant and elastomer addition on impact strength is shown in Figure 5. The impact strength of PP-m formulations increase enormously with only 0.1 wt % of nucleant added, increasing from about 19.2 J/m to a maximum of between from 40 to over 80 J/m depending on the formulation. Synergistic improvement in impact strength is evident

because each nucleated modified PP-m formulation displays a significantly higher impact strength compared with the corresponding nucleated unmodified PP-um formulation. The quinacridone nucleated system, regardless of concentration, improves
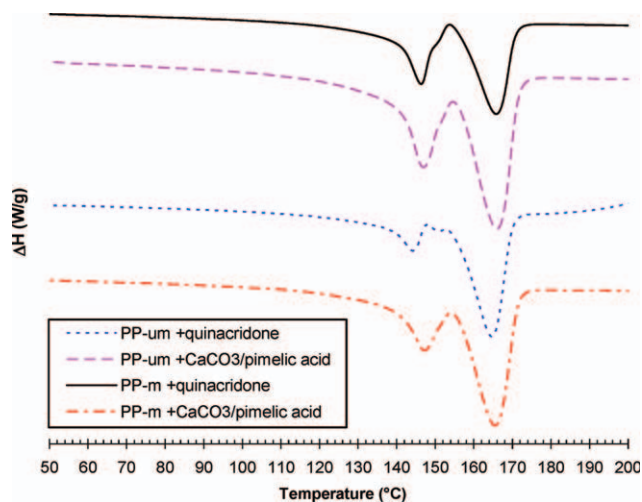

Figure 3. Comparison of the effect of the quinacridone- and CaCO₃-pimelate-based nucleants on the crystallization of the β phase as measured via DSC, for both PP-m and PP-um at 0.2 wt % additive concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
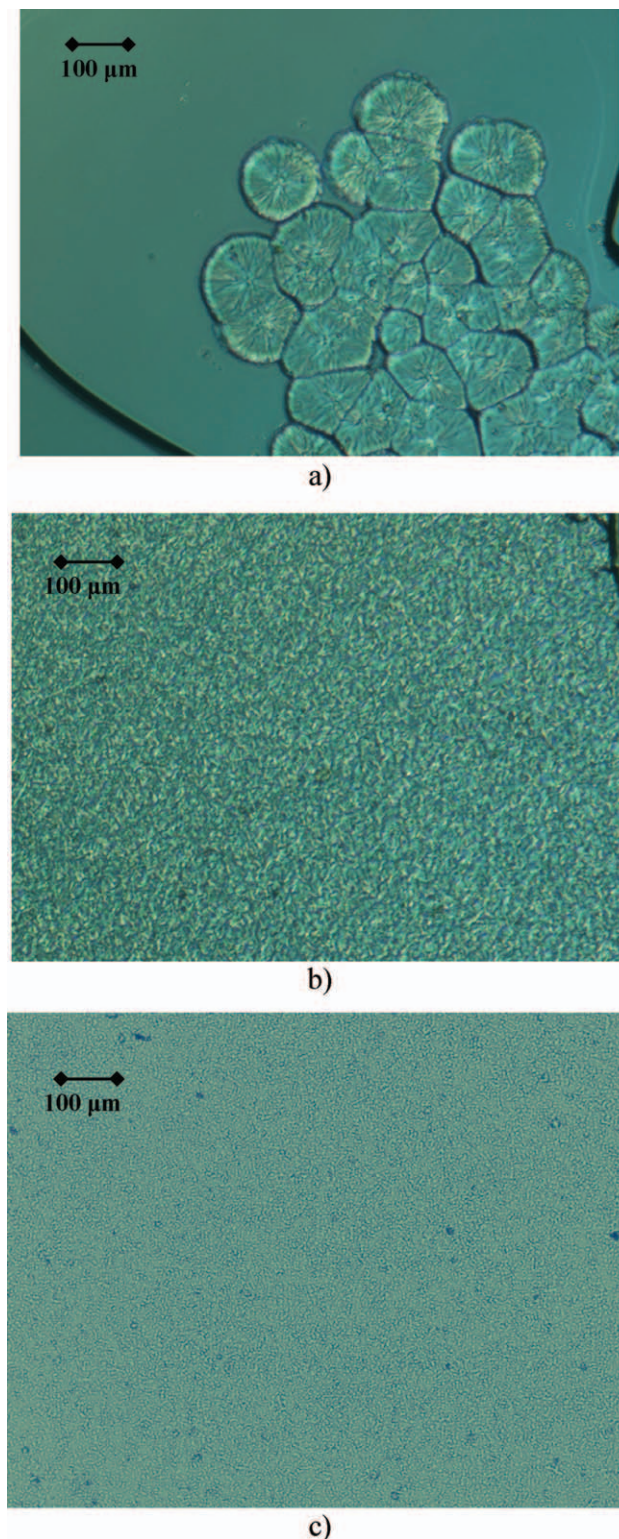
Figure 4. Optical micrographs revealing the difference in α and β crystallinity before and after βnucleation for PP-um. (a) PP-um, (b) PP-um, nucleated with 0.2 wt % quinacridone, and (c) PP-um, nucleated with 0.2 wt % CaCO$_3$/pimelic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the impact strength about sixfold, whereas the calcium pimelate nucleated system, on average, is more than doubled (excluding the 1 wt % nucleant formulation). In contrast, the impact strength of the non-nucleated formulation only increase by 60% as a result of elastomer/TiO$_2$ modification as the impact strength of the PP-um is 12.2 J/m, whereas PP-m was 19.2 J/m.

When comparing the effectiveness of the two nucleants, it is clear that calcium pimelate produces superior impact strength regardless of whether the PP was modified or not. Although the quinacridone nucleant promotes a higher level of β crystallinity, the smaller particle sizes produced by the calcium pimelate revealed in Figure 4 clearly have a significant impact upon impact strength. Another point of difference is that the quinacridone formulation seems unaffected by increasing nucleant, whereas the calcium pimelate formulations display a maximum impact strength at 0.2 wt % nucleant concentration followed by a decrease in performance. This may reflect a better dispersion of the organic nucleant rather than the inorganic one based upon polarity considerations. Moreover, when the impact results are plotted as a function of β crystallinity in Figure 6, the lack of any dependency upon β crystallinity content is apparent. However, it does show that the calcium pimelate imparts higher impact strength at comparatively lower β content regardless of the formulation, PP-um or PP-m. This can be attributed at least in part to the smaller particle sizes produced by the calcium pimelate nucleant. Therefore, within the relatively narrow range of β crystallinity studied here, it is suggested that no direct relationship with impact strength is apparent. The key point of difference between the work of Tordjeman et al.[33] presented here is that β content varies over a much smaller range and high velocity impacts are measured rather than static tensile properties.

With respect to the strain to failure as a measure of toughness, the effectiveness of the different nucleants is reversed. Figure 7 shows that the organic quinacridone nucleant produces the
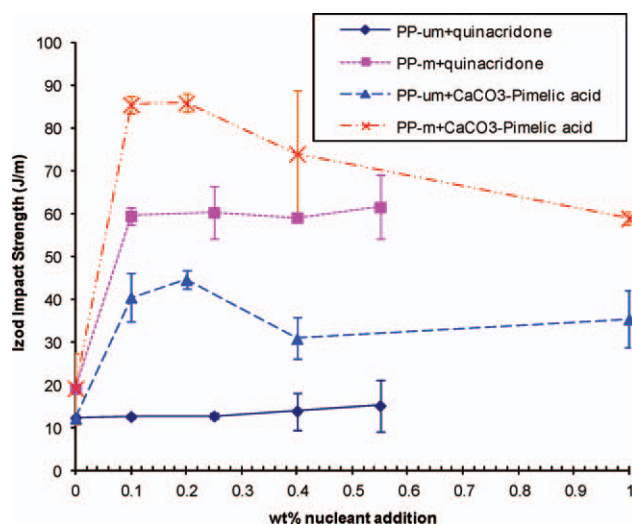

Figure 5. Plot of Izod impact strength as a function of nucleant addition for PP-um and PP-m using the quinacridone- and CaCO$_3$/pimelic acid-based β nucleants. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
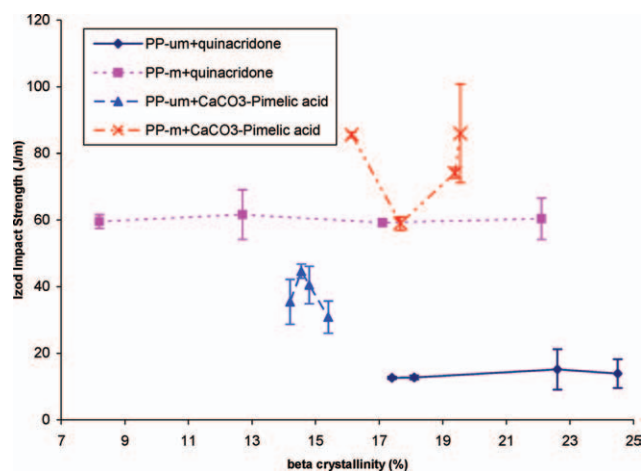
Figure 6. Plot of Izod impact strength as a function of β crystallinity for PP-um and PP-m using the quinacridone- and CaCO$_3$/pimelic acid-based β nucleants. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

largest improvement in strain to failure for both the PP-um and PP-m formulations, whereas the calcium pimelate displays only modest improvements regardless of nucleant concentration. This most likely reflects the role of the inorganic nucleating agent in preventing ductile flow of the polymer during deformation. Inorganic modifiers are well-known to reduce the tensile strain to failure of polymers in this case appear to have a large effect upon this property. The modulus and strength values in Table II follow a typical behavior with the PP-m sample having reduced strength and modulus, whereas the PP-um systems are relatively unaffected.

Varying the Calcium Carbonate/Pimelic Acid Composition
The nucleating action of calcium pimelate originates from the pimelic acid being supported on the calcium carbonate surface in such a way that the PP is fixed in a specific configuration. The β crystallization is then facilitated through the similar
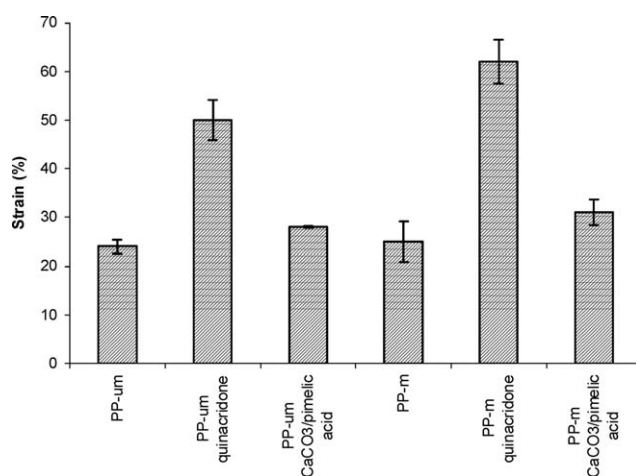
Table II. Tensile Modulus (1% Sec) and Strength for PP-m and PP-um Samples Modified with 0.2 wt % Nucleant Addition

Sample ID	Modulus (MPa)	Strength (MPa)
PP-um	1158.2 (92.7)	34.6 (1.57)
PP-um + calcium pimelate	1141.0 (32.6)	35.5 (0.1)
PP-um + quinacridone	1055.7 (10.5)	31.8 (0.1)
PP-m	1211.6 (54.5)	33.4 (0.3)
PP-m + calcium pimelate	938.0 (15.2)	29.8 (0.1)
PP-m + quinacridone	1030.3 (21.4)	29.6 (0.11)

length scales of the pimelic acid chain length and the PP. From a commercial perspective, β nucleation adds significant cost to the process (despite the low levels of addition) because of the pimelic acid. It is interesting to explore, therefore, whether reducing pimelic acid content in the calcium pimelate can still achieve similar enhancements in impact strength. To clarify the role of the calcium pimelate, pimelic acid and calcium carbonate only formulations were also evaluated and compared against calcium pimelate of varying compositions. Figure 8 shows that the β nucleant continues to produce large increases in impact strength, going from 19 J/m to about 45 J/m regardless of the composition of the β nucleant. In addition, the strain to failure produces similar results to those reported earlier, increasing only modestly with β nucleation. The importance of the pimelic acid being supported on the calcium carbonate is evidenced by the lack of improvement in properties of the pimelic acid and calcium carbonate only formulations. Table III shows that the modulus and yield strength are also unaffected by the compositional changes even though the absolute and relative β crystallinity increased modestly from 18 to 21% (absolute) and 35 to 44% (relative), respectively, as the pimelic acid concentration increased. These results again highlight the independence of mechanical properties from modest variations in β crystallinity and the very low levels of pimelic acid needed to produce the β

Figure 7. Strain to failure of the PP-um and PP-m using the quinacridone- and CaCO$_3$/pimelic acid-based β nucleants.
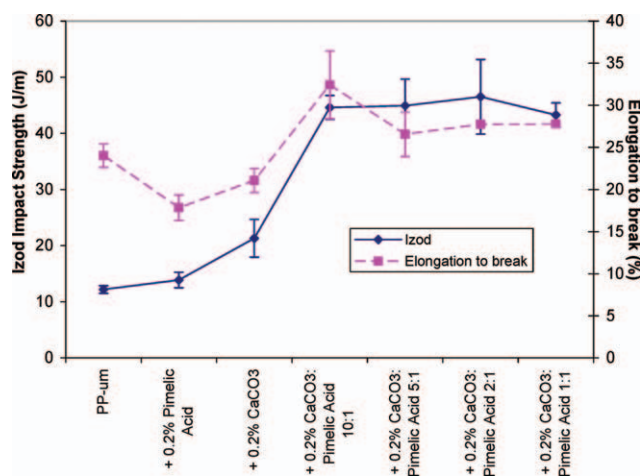

Figure 8. Plot of the Izod impact strength and strain to failure for 0.2 wt % CaCO$_3$/pimelic acid modified PP-um showing the effect of varying the CaCO$_3$/pimelic acid ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Tensile Modulus, Strength, and Strain to Failure for 0.2 wt % CaCO3/Pimelic Acid Nucleated PP-um Illustrating the Effect of Varying CaCO3/Pimelic Acid Weight Ratios on Mechanical Properties and Crystallinity

PP-um nucleated with:	Modulus (1% sec) (MPa)	UTS (MPa)	Total crystallinity in polymer (%)		Relative crystalline phase within crystalline region	
			α	β	α	β
–	1168.5 (29.0)	25.6 (4.2)	43.4	0	100	0
0.2 wt % CaCO$_3$	1274.8 (23.1)	31.9 (1.6)	–	–	–	–
0.2 wt % pimelic acid	1354.9 (91.6)	35.2 (.7)	–	–	–	
0.2 wt % CaCO$_3$/pimelic acid (10 : 1)	1172.6 (34.4)	27.3 (2.8)	32.4	17.7	64.6	35.4
0.2 wt % CaCO$_3$/pimelic acid (5 : 1)	1194.5 (13.3)	29.8 (1.1)	30.7	18.9	61.9	38.0
0.2 wt % CaCO$_3$/pimelic acid (2 : 1)	1141.0 (32.6)	29.3 (0.8)	30.1	19.6	60.5	39.4
0.2 wt % CaCO$_3$/pimelic acid (1 : 1)	1163.2 (6.8)	29.1 (0.7)	27.2	21.4	55.9	44.1

crystalline phase. The strategy of reducing pimelic acid composition is, therefore, one that has the potential to significantly reduce the overall cost of the formulation without affecting property enhancement.

Exploring Through the Thickness Properties

Crystallization of the β phase is highly dependent upon rates of cooling above the melt. Given that cooling rates vary through the thickness of a material, it follows that the β crystal content would also vary throughout the thickness of any given sample. The variation in β crystal content was, therefore, determined for a variety of samples and processing conditions as shown in Table IV. These conditions included varying the β nucleant (organic or inorganic), the cooling rate, and elastomer content. Figure 9 shows examples of DSC traces taken from the core to the surface of a quinacridone nucleated sample. In this example, the β phase clearly increases closer to the core, illustrating the promotion of β crystal growth at slower rates of cooling. Furthermore, the higher rates of cooling closer to the surface also appear to be less selective, producing the dual β crystal peaks closer to the surface.

The overall crystallinity is plotted in Figure 10 as a function of distance from the core for all samples and invariably the results all display a parabolic profile, starting with a low β crystallinity at the surface increasing to a maximum at the sample core. Despite the difficulty in accurately calculating the β crystal content using DSC, the results show remarkable consistency. The same information is then plotted as a function of cooling time from 210°C to below 105°C obtained from finite element analysis simulations as shown in Figure 11. A temperature of 105°C was chosen, as it is well below the crystallization temperature of the β phase and should inhibit any further crystallization from occurring. The plot clearly shows β phase formation behaves as might be expected. The longer it takes to cool to 105°C, the higher is the absolute β crystal content. Overlaying the data on the same scale also shows that despite the scatter, a master-curve is produced thus suggesting that regardless of the presence of elastomer/TiO$_2$, nucleant, or processing conditions, the nucleation mechanism remains broadly unaffected.

Given that the β crystal content has been shown to vary throughout the thickness of the PP blends and that β crystal content has been shown to affect elastic properties, it would

Table IV. Formulations Used to Investigate the Through the Thickness Crystallinity, Including the Processing Variable and the Calculated Crystallinity

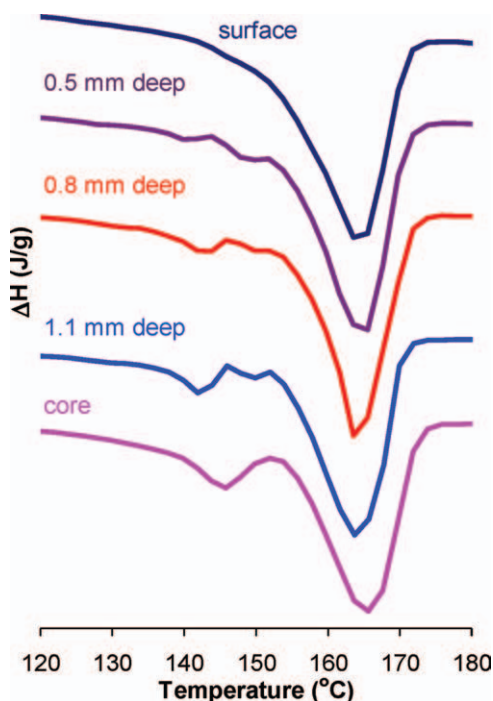| Polypropylene	β nucleant	Mold temperature (°C)	Hold time (s)	β Crystalline phase	
				Average (%)	Maximum (%)
Unmodified	Quinacridone	50	30	6.1	10.3
Modified	Quinacridone	50	30	9.1	15.2
Modified	CaCO$_3$/pimelic acid (2 : 1)	90	60	9.6	15.1
Modified	Quinacridone	105	60	9.9	13.2
Modified	Quinacridone	105	30	12.0	17.1

Figure 9. Raw DSC thermograms illustrating the increasing presence of β crystalline phases from the surface to the core of the sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

also be expected that these properties would also vary through the thickness of the sample. To verify this, nano-indentation studies were carried out on a single quinacridone nucleated PP-m formulation and the resultant behavior is shown in Figure 12. In contrast to the DSC studies, the elastic properties decrease when approaching the core of the sample. This is to be expected as the results already reported in Table II show that increased β content reduces modulus (elastic properties), whereas increasing impact strength (toughness).
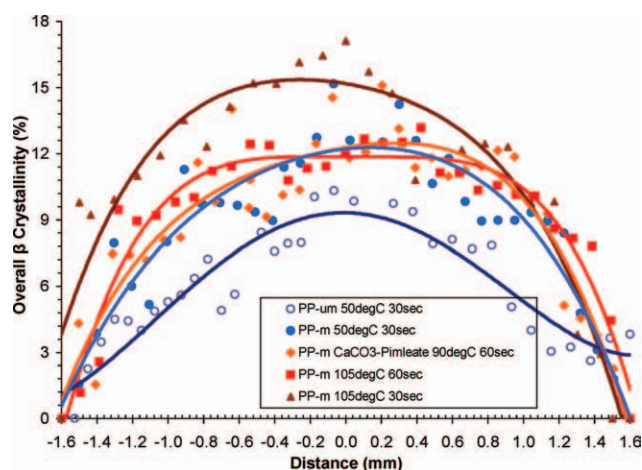

Figure 10. Overall β crystallinity of nucleated PPs subjected to varying injection molding conditions showing the variation in β crystallinity through the thickness of the sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
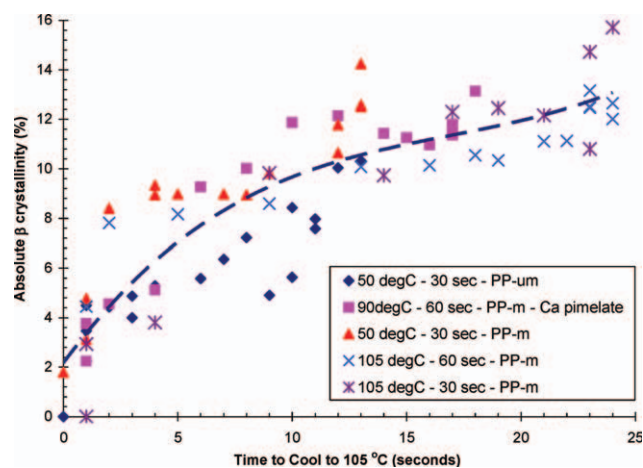

Figure 11. Overall β crystallinity of nucleated PPs subjected to varying injection molding conditions plotted as a function of simulated cooling rates at varying locations within the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

Improving the toughness of a homopolymer PP via β nucleation is a very effective strategy particularly when constrained by the amount of additive that can be added. This work has compared the effectiveness of two different nucleating agents, the organic-based quinacridone and the inorganic-based calcium pimelate. Toughness was investigated as a function of strain to failure and impact strength and they both displayed excellent, though contrasting improvements. Although the quinacridone nucleant produces higher corresponding β crystal content and higher strain to failure, the calcium pimelate gave significantly better impact strength regardless of elastomer content and appeared to have greater selectivity. Synergistic improvements in the strain to failure and impact strength were evident for both nucleants. No relationship between the impact strength and β crystal content was observed though the varying particle sizes produced by the different nucleants appeared to play an
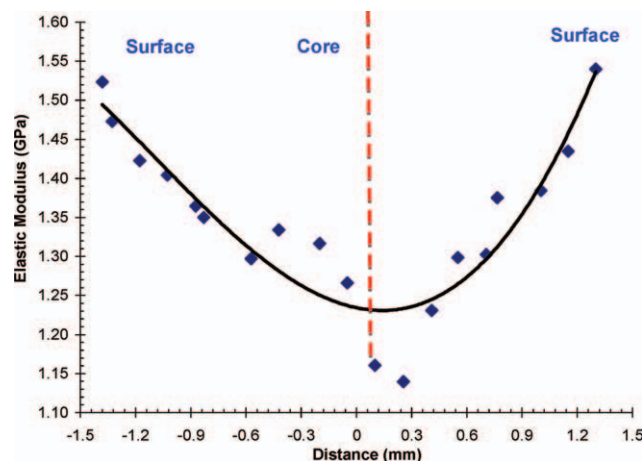

Figure 12. Illustration of the effect of varying β crystalline phases through the thickness of a sample on the elastic modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

important role in determining impact strength. Varying the calcium carbonate : pimelic acid composition from 10 : 1 to 1 : 1 highlighted the robustness of the nucleation process in that similar improvement in impact strength and β crystal phase could be achieved by varying the pimelic acid content. Through the thickness, thermal analysis and tensile properties analysis illustrated the dependency of properties upon cooling rates and crystallization. However, the independence of the β crystal content across a range of samples further highlighted the robustness of the nucleation mechanism occurring throughout the bulk of the sample.

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