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Cite as: AIP Conference Proceedings **2289**, 020070 (2020); <https://doi.org/10.1063/5.0029040>  
Published Online: 30 November 2020

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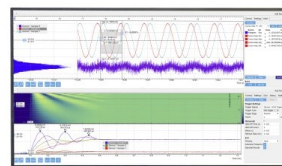
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# Thermal Properties and Nonisothermal Crystallization Behaviour of Polypropylene Nanocomposite

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**Abstract.** Nucleated polypropylene (PP) masterbatch and the nanoclay-containing composite of PP are prepared by reactive processing method to improve the thermo-mechanical properties of virgin PP. PP masterbatch and the nanocomposite exhibits pronounced improvement in crystallization temperature ( $T_c$ ) and the heat distortion temperature (HDT) when compared with neat PP. The melting and nonisothermal crystallization behaviors of the neat PP and the nanocomposite are studied by differential scanning calorimetry. Results indicate that half time of crystallization at a particular cooling rate remains unchanged in neat PP and the nanocomposite. However, super cooling effect is pronounced in the nanocomposite when compared with neat PP. Irrespective of cooling rate there is approximately 14% improvement in  $T_c$  in PP nanocomposite with respect the neat PP. Such an improvement in  $T_c$  with improved thermo-mechanical properties are highly desirable for rigid packaging applications.

## INTRODUCTION

Polypropylene (PP) is widely used commodity polymer due to its excellent cost-performance value. However, improved dimensional stability at high temperature is highly desired to widen the application range of PP. In this context, Polyzimo™ NPP MB JK300 (abbreviated as JK300MB) and Polyzimo™ PNC JK781 (abbreviated as JK781) have been developed in-house by reactive processing. JK300 MB is a PP-based masterbatch (MB) which can be diluted further in PP of different melt flow rates depending on the intended application. Nanoclay is added in Polyzimo™ PNC JK781 in order to improve the thermo-mechanical properties of PP.

It is well-established that thermo-mechanical properties of polymer are influenced by crystallinity and crystal structures of the polymer formed in due course of moulding or shaping it. Since most of the available polymer processing techniques relies on the nonisothermal crystallization process, it is important to study the nonisothermal crystallization behaviour of JK300 MB and JK781 nanocomposites. Interdependence of the crystal growth behavior with the heat distortion temperature is reported here.

## EXPERIMENTAL

### Materials

Polypropylene used in this research is a homopolymer from Sasol, South Africa (grade HHR102). Polyzimo™ NPP MB JK300 (Abbreviated as JK300MB), Polyzimo™ NPP JK 781 (Abbreviated as JK781) are respectively the nucleated PP masterbatch, and the nanoclay containing PP composites developed at CSIR, South Africa. The measured melt flow rate (MFR) of neat PP, JK300MB and JK781 are 3.5, 3.1 and 5.0 g/10 min (ASTM D1238: 230 °C and 2.16 kg), respectively. The nanoclay used is of the layered double hydroxide family and is a product from CSIR, Pretoria.

### Characterization methods

The overall dispersion and distribution of the nanoclay platelets are analyzed by the transmission electron microscopic (TEM) images. Ultramicrotomed section (70 – 80 nm) is prepared with a Leica (Austria) EM FC6 cryo-ultramicrotome using a diamond knife.

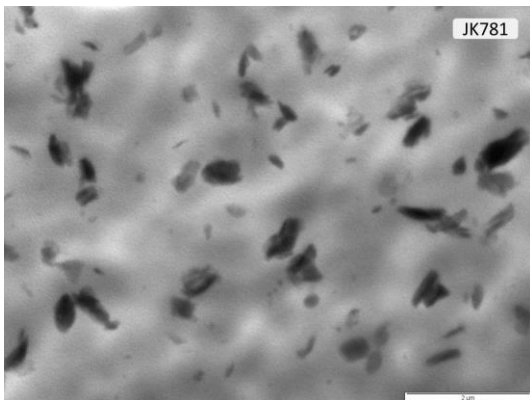
The heat deflection temperature (HDT) and the Vicat softening point were measured using a CEAST HV500 instrument, Italy. The experiments were conducted following ISO75B test standard. The preset deflection and the heating rate used in measurement were 0.34 mm and 120 °C, respectively. The preset penetration depth for Vicat softening point was 1 mm. Injection moulded specimens of dimension 80 x 10 x 4 mm<sup>3</sup> were used to determine the heat distortion temperature.

The nonisothermal crystallization kinetics of neat PP, JK300MB and JK781 was analyzed using differential scanning calorimeter (DSC, model Q2000 TA Instruments) under constant nitrogen flow of 25 mL/min. The sample mass was kept within the range of 5.7 - 5.8 mg for all the measurements. The temperature and the enthalpy of fusion were calibrated with an Indium standard and the baseline was checked following the TA Instruments protocol. The samples were heated from -25 °C to 200 °C at a rate of 20 °C/min, isothermal there for 5 min, then cooled to -25 °C at different cooling rates of 5, 10, 15 and 20 °C/min and heated immediately to 200 °C at a rate of 20 °C/min.

## RESULTS AND DISCUSSION

### Dispersion characteristics

The TEM image showing the distribution of nanoclay in JK781 is presented in **Figure 1**. The nanoclay platelets are depicted by the black entities. It is evident from the figure that nanoclays are well-dispersed and distributed in the polymer matrix.



**FIGURE 1.** The transmission electron microscopic image showing the distribution of nanoclays in JK781.

## Heat deflection temperature (HDT) and Vicat softening point

HDT of a polymeric material is the temperature at which material deforms to a certain extent under a specified load. It indicates whether a material can withstand a wide span of temperature under certain stress. On the other hand, the Vicat softening point determines the hardness of the material. HDT of neat PP, JK300MB and JK781 are tabulated in **Table 1**. It is evident that in compared to neat PP, there are approximately 10% and 24% improvements in HDT in JK300MB and JK781, respectively. The key factor affecting the HDT can be the restricted relaxation of macromolecules either by altering the crystal growth behavior or by incorporation of stiff filler particles. [1]. Such improvement in HDT can reduce the injection moulding cycle time for big part significantly and increase the productivity. The subsequent section correlates the nonisothermal crystallization and crystal growth with the observed improvement in HDT. The Vicat softening point remains unaltered in neat PP and JK300MB; a marginal increment noticed in JK781 can be attributed to the stiffness introduced by the dispersed nanoclay particles.

**Table 1.** Heat deflection temperature and the Vicat softening point for different samples.

Sample	HDT	Vicat softening point
PP	62.6±0.9	155.7±0.6
JK300MB	69.2±0.1	155.5±0.2
JK781	77.9±0.5	156.3±0.6

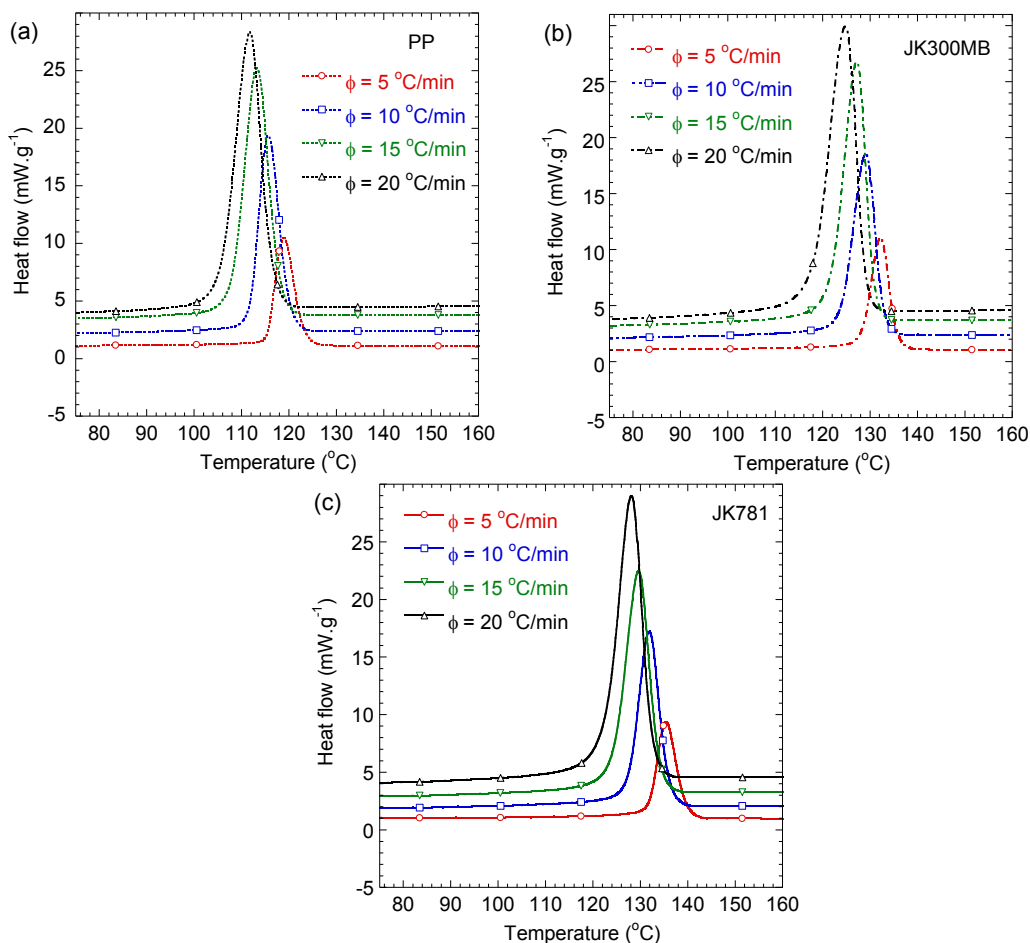
## Nonisothermal crystallization behavior

**Table 2.** Thermal parameters associated with the crystallization and the successive melting.

Sample	$\phi$	$T_{on}$	$T_c$	% $T_c$ improvement	$\Delta H_c$	$t_{1/2}$	$T_m$	$\Delta H_f$	Super cooling
PP	5	130.6	118.9		102.0	2.33	164.3	101.6	45.4
	10	125.6	115.6		102.9	1	163.3	102.7	47.7
	15	124.4	113.2		101.2	0.74	164.1	100.5	50.9
	20	123.8	111.7		97.6	0.61	163.8	97.6	52.1
JK300MB	5	142.3	132.2	11.2	106.8	2.01	166.2	107.2	33.9
	10	140.1	129.1	11.6	105.0	1.10	165.8	105.1	36.8
	15	137.1	127.1	12.2	105.5	0.7	165.6	105.9	38.5
	20	138.3	124.7	11.7	105.2	0.7	165.7	105.2	41.0
JK781	5	147.5	135.5	13.9	97.6	2.4	166.5	97.8	31.1
	10	143.4	131.9	14.1	96.7	1.2	166.0	96.6	34.1
	15	142.2	129.6	14.5	93.8	0.8	165.9	93.8	36.3
	20	140.0	128.1	14.7	95.0	0.6	165.7	95.0	37.6

The difference in crystallization behaviors in neat PP, JK300MB and JK781 at various cooling rates are illustrated in **Figure 2**. The thermal parameters associated with crystallization and successive melting are tabulated in **Table 2**. It is apparent that at any particular cooling rate the onset ( $T_{on}$ ) and the crystallization peak ( $T_c$ ) temperatures shift towards the higher temperatures in JK300MB when compared with the neat PP. A further improvement in crystallization temperatures can be achieved in JK781 in the presence of nanoclay. At any given cooling rate, approximately 11% and 14% improvement in  $T_c$  with respect to the neat PP is observed in JK300MB and JK781, respectively. To the best of our knowledge such improvement in  $T_c$  is quite unique. An et al. has recently studied the effect of sorbitol, rosin, carboxylate and phosphate types nucleating agents on the crystallization kinetics of PP [2]. The highest improvement in  $T_c$  has been observed in PP/sorbitol nucleating agent system. During cooling from melt at a rate of 10°C/min, PP/sorbitol crystallizes at 129.8 °C while JK300MB and JK781 crystallize at 129.1 and 131.9 °C. Depending on the dispersion and distribution of nanoclay (including LDH) in the polymer nanocomposites,

nanoclay sometimes facilitates the crystallization by offering nucleating sites [3] but sometimes it inhibits the crystallization [4]. Branched macromolecular structure formation during reactive processing facilitates the crystallization process in JK300MB. Uniformly distributed nanoclay in JK781 allows further improvement in  $T_{on}$  and  $T_c$  by offering more nucleating sites.  $T_{on}$  and hence  $T_c$  show inverse proportion relationship with the cooling rate. During rapid cooling, polymer chains cannot release their kinetic energy fast enough and hence takes longer time to overcome the nucleation energy barrier [5].



**FIGURE 2.** DSC thermograms of nonisothermal crystallization at various cooling rates (a) neat PP, (b) JK300MB and (c) JK781.

It is evident from the **Table 2** that the overall crystallinity (presented by  $\Delta H_c$ ) slightly decreases in JK781 when compared with neat PP and JK300MB. Despite of the fact that the cooling rate does not have significant influence on the extent of crystallization (presented by  $\Delta H_c$ ), it influences the half time of the crystallization ( $t_{1/2}$ ). A notable reduction in  $t_{1/2}$  is observed with increase in cooling rate from 5 to 15 °C/min. Further increase in cooling rate does not have significant effect on  $t_{1/2}$ . Reduction in  $t_{1/2}$  with increase in cooling rate is indicative to the faster nucleation at the high cooling rates.

During subsequent melting, JK300MB and JK781 melt at higher temperature ( $T_m$ ) than the neat PP. the enthalpy of fusion ( $\Delta H_f$ ) follows the similar trend as  $\Delta H_c$ . The degree of supercooling observed in JK300MB is lower than that of neat PP and it reduces further in the presence of nanoclay in JK781. Moreover, in all the samples examined, profound supercooling is observed with increase in cooling rate. As the samples cooled rapidly, polymer chains cannot release their kinetic energy fast enough and as a result formation of stable nuclei occurs at lower temperature. Thus the  $T_c$  shifts towards the lower temperature and the degree of

supercooling becomes more pronounced [5]. Nucleation and the crystal growth mechanism eventually enhances the HDT of the nanocomposite JK781 by 24% with respect to the neat PP.

## CONCLUSION

In conclusion, the intended improvement in the thermomechanical properties, in particular, the HDT of the nucleated polypropylene masterbatch and the nanoclay-containing composite of PP are explained by the rate dependent crystallization process. Reactive processing enhances the  $T_c$  of neat PP by 11 %. Further improvement in  $T_c$  (14%) can be achieved by incorporation of nanoclay during the reactive processing. Nucleation and the crystal growth mechanism eventually enhances the HDT of the nanocomposite JK781 by 24% with respect to the neat PP. Such an improvement in  $T_c$  and HDT are highly desired for the injection moulding applications.

## ACKNOWLEDGMENTS

The authors would like to thank DSI, CSIR and Centre for Nanostructures and Advanced Materials for financial support.

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