

Performance Evaluation of Nucleating Agents in Polypropylene Homopolymer

RAVI KUMAR, VISHWA PRATAP SINGH, MADHUKAR PRAJAPATI, ASHWITH, PRIYANKA SINGH, SATYAJIT SAMANTA AND SAIKAT BANERJEE*

Customer Services & Development Center, HPCL-Mittal Energy Ltd. (HMEL), Gautam Budh Nagar, Sector-65, Noida, Uttar Pradesh, India- 201301

ABSTRACT

Types of nucleating agents and their dosage level play an important role on the crystallinity of the polymer which controls the final properties like optical clarity, stiffness and reduced cycle time during molding. In this study, the efficiency of two different types of commercially available nucleating agents, phosphate ester and dicarboxylic acid based, have been studied. Both the nucleating agents were compounded with molding grade polypropylene homopolymer having melt flow index (MFI) of 12 g/10min at 2.16 Kg and 230°C, in a co-rotating twin screw extruder at two different dosage level, i.e. 300 ppm and 600 ppm. The effectiveness of the nucleating agents was evaluated from several parameters like stiffness, crystallization behavior in terms of crystallization onset, % crystallinity and isotropic shrinkage. A crystallization kinetic study was also carried out at four different cooling rates. Addition of nucleating agent at 300 ppm dosage level showed an increase in flexural modulus of neat polypropylene by around 14%. Dicarboxylic acid based nucleating agent showed better isotropic shrinkage behavior as compared to phosphate ester based nucleating agent at both 300 ppm as well as 600 ppm dosage level. The efficiency of this type of nucleating agent was further supported by comparatively lower activation energy as evaluated from crystallization kinetics study.

KEYWORDS: *Polypropylene homopolymer, Nucleating agent, Stiffness, Shrinkage, Crystallization kinetics*

INTRODUCTION

Polypropylene (PP) and its copolymers are widely used in various applications ranging from

exterior and interior parts of automobiles to disposable packaging such as bags. This is solely due to its stiffness, recyclability and low

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Correspondence author e-mail: saikat.banerjee@hmel.in

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cost as compared to other polymers for engineering application. In spite of having such advantages, polypropylene faces challenges for those applications where outstanding optical property is highly solicited. However, this limitation can be ruled out by incorporating some additives commonly known as nucleating agents. Usually nucleating agents are used in polymers like polypropylene having slow nucleation and crystallization rates as compared to high density polyethylene. It acts as site on which the polymer can crystallize to form spherulites, controls the spherulite growth and rate of crystallization. The main advantage of nucleating agent is that it promotes early onset of crystallization which results in cycle time reduction as well as warpage minimization in injection molding and, by consequence, reducing production costs^[1-3].

Considering all these facts, a large number of nucleating agents have been developed which can be categorized into inorganic, organic and polymeric in nature. However, organic nucleating agents got more preference due to their higher nucleating efficiency and compatibility with polymer matrix. Common organic nucleating agents are substances like sodium and potassium benzoate, phosphate derivative, sorbitol or dicarboxylic acid based derivatives whereas typical inorganic substances are like clay, talc, quartz etc.^[4-6] High-performance organic nucleating agents like dibenzylidenesorbitol derivatives have been widely used in the polyolefin industry^[7-10]. This type of sorbitol based nucleating agent is also known as clarifying agent if it improves the transparency of the polymer matrix. The clarifying agent dissolves in the polymer melt during processing, but solidifies during cooling

providing sites for nucleation. The nucleating efficiency depends on its particle size, morphology, chemical structure and behavior when incorporated into the polymer. The melting point of the nucleating agent should be higher than that of the polymer^[11]. Currently, a few papers are available which describe structure-property correlations of various nucleating agents on morphology and crystallization kinetics of polypropylene^[12-14].

In this research article, efficiency of two chemically different nucleating agents have been studied using molding grade polypropylene material as matrix. The nucleating agents were melt mixed in a co-rotating twin-screw extruder at two different dosage level. The changes in mechanical and thermal properties were evaluated based on tensile and flexural performance, heat distortion temperature (HDT) and vicat softening point (VSP). Molecular weight was determined using triple detector gel permeation chromatography (GPC) (i.e. combination of IR, viscometer and light scattering detector). The crystallization behavior and kinetics in terms of activation energy was investigated using differential scanning calorimetry (DSC) at different cooling rates, wide-angle x-ray diffraction (WD-XRD) and mold shrinkage evaluation in both machine & transverse direction. Optical properties like haze & gloss and mold shrinkage were considered as critical parameters to evaluate the overall performance of the nucleating agents. Nucleating agent which results more isotropic shrinkage i.e. the uniform shrinkage both in machine as well as transverse direction is favorable for reducing cycle time without creating any warpage in the final molded product^[15].

EXPERIMENTAL

Materials

Polypropylene homopolymer, Polysure® M12RR (MFI of 12 g/10 min at 2.16 Kg and 230°C) was chosen from HPCL-Mittal Energy Pvt. Ltd., India product portfolio. The molecular weight as determined from triple detector GPC is summarized in Table 1.

Nucleating agents of two different chemical entity,

phosphate ester and potassium salt of 1,2-cyclohexane dicarboxylic acid based was chosen for this study (Figure 1).

Specimen preparation

Each nucleating agent was melt-mixed with the neat PP homopolymer (HPP) in two different concentrations, 300 ppm and 600 ppm. The formulations prepared are summarized in Table 2.

TABLE 1: Molecular weight determination using triple detector GPC.

Parameters	Values
Weight average molecular weight (Mw), g/mol	301600
Polydispersity index (PDI), Mw/Mn	6.8

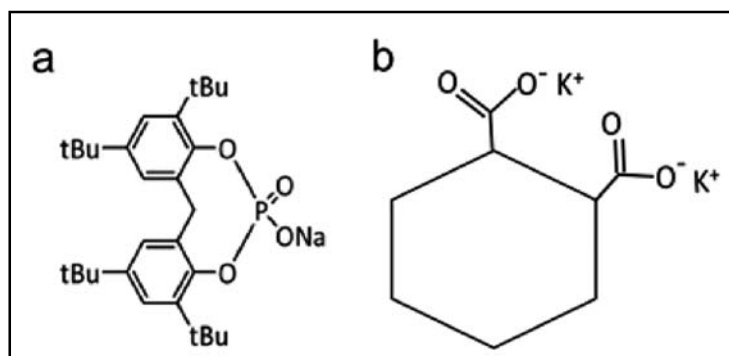


Fig. 1. Chemical structure of: (a) phosphate ester compound and (b) potassium salt of 1,2-cyclohexane dicarboxylic acid, where tBu represents the tertiary butyl group.

TABLE 2: Formulation of neat PP homopolymer with varying nucleating agent concentration.

Sample ID	Nucleating Agent Content (ppm)	
	Phosphate ester compound*	Cyclohexane dicarboxylic acid**
HPP	-	-
HPP-NA-300	300	-
HPP-NB-300	-	300
HPP-NA-600	600	-
HPP-NB-600	-	600

*Phosphate ester type nucleating agent is denoted by NA and **Cyclohexane dicarboxylic acid type nucleating agent is denoted by NB.

The formulations were compounded in a modulated co-rotating twin-screw extruder, Omega-25 from Steer Engineering, India having a screw diameter of 25 mm, L/D ratio of 32, assembled with a gravimetric feeder

and pelletizing unit. A screw speed of 200 rpm was selected for compounding. The temperature profile of the extruder is depicted in Table 3.

TABLE 3: Temperature profile of the twin screw extruder (Zone-1: Near Feeder, DA: Die Adopter, DH: Die Head).

Heating Zone	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9	DA	DH
Temperature (°C)	175	180	185	185	185	190	195	200	205	210	210

After compounding, the test specimens were prepared by using Ferromatik Milacron injection molding machine (Nova Servo 80) of 80-ton capacity. Before molding, the nucleated polypropylene pellets was dried at 80°C in vacuum oven for overnight. Injection molding was performed using parameters as summarized in Table 4.

TABLE 4: Critical parameters for injection molding.

Parameters	Values
Temperature profile	190-210°C
Injection pressure	57 bar
Injection speed	8 mm/s
Injection time	22 s
Total cycle time	47 s
Hold on pressure	56 bar
Hold on time	5 s
Cooling time	27 s
Mold Temperature	60°C

Prior to test, all specimens were conditioned as per ASTM D618 at 23±2°C and 50±10% RH for 48 hrs in a humidity chamber.

Characterization techniques

Mechanical characterization

The mechanical properties like tensile and flexural of all the non-nucleated as well as nucleated samples were measured using Instron-5966 UTM. The room

temperature tensile properties (e.g. elastic modulus, yielding behavior and failure pattern) was evaluated as per ASTM D638. Injection molded Type-I specimen was pulled unidirectional at a constant speed of 50mm/min. A grip to grip separation of 115mm and gauge length of 50mm was used for this purpose. 'Auto-X' extensometer was used to measure the deformation with more accuracy and precision. The flexural properties like modulus (1% secant) and strength was determined as per ASTM D790 using a 3-point bending fixture. Injection molded rectangular bars was mounted on the cantilever support of span around 50.8 mm and loaded by means of a loading nose midway between the supports. The rate of deflection was maintained at a rate of 1.30 mm/min.

Thermal characterization

Molecular weight plays a critical role in terms of thermal stability. The molecular weight of the polymer was determined using gel permeation chromatography (GPC) from Polymer Char, Spain. The neat PP sample was dissolved in 8 ml of trichloro bezenene (TCB) stabilized with 300ppm butylated hydroxytoluene (BHT) at 160°C. A triple detector (infra-red, viscometer and light scattering detectors) was used for precise measurement.

Melt flow index (MFI) is a measure of the flow properties of polymer melt at low shear rates and is inversely related to the average molecular weight of the resin. The MFI of all the non-nucleated and nucleated compositions were measured as per ASTM D1238 using Gottfert, MI-4 tester at 2.16 Kg load and 230°C temperature.

The % crystallinity, onset of crystallization and melting behavior of the samples were evaluated as per ASTM D3418 using differential scanning calorimeter, TA DSC-250 (Discovery series). Around 8 to 10 mg of sample was heated under nitrogen atmosphere from 23°C to 225°C at a heating rate of 20°C/min and held at that temperature for 5 mins for complete melting of the samples. It was then cooled down to 23°C with a particular cooling rate and then once again heated to 225°C with the same heating rate of 20°C/min. The 1st heating was performed to remove the in-mold residual stress inside the sample if any. The crystallization onset temperature was analyzed from the cooling curve, whereas melting point and % crystallinity was evaluated from the second heating cycle. Enthalpy of fusion for 100% crystalline PP was considered as 209 J/g for the calculation of % crystallinity^[16]. To understanding the crystallization kinetics, DSC was carried out at four different cooling rate 5°C/min, 10°C/min, 15°C/min and 20°C/min.

In combination with DSC, the crystalline structure of the samples was analyzed by wide-angle X-ray diffraction technique (WD-XRD) using Bruker-D8 Advance X-ray diffractometer. Cu-K α was used as X-ray source (wavelength: 1.54 Å) with LYNXEYE detector having energy resolution of 680eV. The % crystallinity was evaluated using DIFFRAC-EVA TOPAS software from area under the Intensity vs 2θ plot, where θ is the Bragg's angle.

Both the heat deflection temperature (HDT) and vicat softening point (VSP) were determined using Instron, HV6M. In case of HDT, the test as per ASTM D648-07 was consisted of supporting a rectangular bar (127 mm in length, 12.7 mm in depth, width of ~3 mm) on two ends in a flat-wise position and applying a flexural stress load to the center of the bar to get maximum stress of $0.455 \pm 2.5\%$ MPa. The specimens were immersed under load in heat transfer medium provided with a means of raising the temperature at $2 \pm 0.2^\circ\text{C} / \text{min}$. The temperature of the medium was measured when the test bar had deflected 0.25 mm. This temperature was recorded as the deflection temperature under flexural load of the test specimen. Similarly, the VSP was measured as per ASTM D1525 as the temperature at which a flat-ended needle of

1mm² circular cross section penetrated the specimen to a depth of 1 mm under a specified load of 10 N using a selected uniform rate of temperature rise, $2 \pm 0.2^\circ\text{C} / \text{min}$.

Optical characterization

The gloss (%) was measured using BYK Gardner instrument as per ASTM D2457. A disc of around 85mm diameter and 3 mm thickness was used for this purpose. Gloss angle of 45° was maintained. It was ensured that all the specimen surfaces are free of dust, grease, scratches and blemishes. Before measurement, calibration of the gloss meter was performed against the working reference standard (with a specular gloss of about 100). Similarly, Haze (%) was also measured as per ASTM D1003 on the similar specimen like gloss using Hunterlab-Vista haze meter.

Shrinkage characterization

The shrinkage measurement was carried out as per ASTM D955. Injection molded Type B disc samples of diameter ~85 mm and thickness of ~3mm was used for this purpose. Samples were prepared using Axxicon mold. The mold shrinkage was measured after 24 hrs of molding in both the machine direction (MD) and transverse direction (TD). A ratio of MD/TD provided the isotropic shrinkage of the molded material i.e. more the ratio closer to unity, more is the isotropic shrinkage.

RESULTS AND DISCUSSION

Thermal characterization

The effect of nucleating agent on melt flow behaviour is depicted in Table 5. Addition of nucleating agents to PP homopolymer is found not to affect the MFI significantly. The same behaviour was also observed with different types of nucleating agents at two different dosage levels, 300 ppm and 600 ppm.

The addition of nucleating agents up to 300 ppm was found to enhance HDT of neat PP homopolymer by around 19°C (Table 5)^[17]. This may be due to improvement in stiffness of the material as a consequence of increase in %

crystallinity which was observed during mechanical and thermal property evaluation as described in later section of this study. However, at a dosage of 300 ppm, both types of nucleated PP showed similar performance. Even no

significant improvement was found with further increase in nucleating agent concentration from 300 ppm to 600 ppm. There was no significant change in VSP as well with addition of nucleating agents.

TABLE 5: Evaluated properties of non-nucleated and nucleated polypropylene homopolymer.

Property	Unit	Experimental Value				
		HPP	HPP-NA-300	HPP-NB-300	HPP-NA-600	HPP-NB-600
MFI at 230°C, 2.16 kg	g/10 min	12.7±0.2	12.6±0.1	12.2±0.4	13.3±0.1	13.1±0.5
HDT	°C	99.3±1.1	118.4±0.9	116.3±1.1	119.5±1.2	118.3±1.1
VSP	°C	152.9±0.1	152.8±0.2	153±0.5	152.3±0.2	152.8±0.1
Flexural Modulus	MPa	1557±8.5	1773±28.1	1765±24.1	1778±30.6	1754±25.4
Tensile Yield Strength	MPa	34.9±0.6	37.6±0.4	37.7±0.2	37.4±0.5	36.8±0.3
Gloss	%	48.4±0.2	50.7±0.2	48.5±0.4	50.7±0.2	49.6±0.4
Haze	%	95.3±0.4	92.9±0.5	89.6±0.1	87.6±0.6	94.8±0.3
Shrinkage, MD	%	1.36±0.04	1.14±0.01	1.12±0.03	1.13±0.01	1.05±0.03
Shrinkage, TD	%	1.39±0.02	1.29±0.02	1.13±0.06	1.25±0.04	1.12±0.01
Shrinkage Ratio (MD/TD)	-	0.98	0.884	0.991	0.904	0.938

Mechanical characterization

As shown in Table 5, addition of nucleating agents increased the flexural modulus or stiffness of the neat PP by ~14% which is quite significant^[18]. However, 300 ppm dosage depicted almost equivalent modulus as compared to 600 ppm dosage. Tensile yield strength was also found to increase by ~8% on addition of 300 ppm of both types of nucleating agents.

Optical characterization

Both the nucleating agents showed similar optical performance as shown in Table 5. No

significant change in surface gloss was observed. Addition of nucleating agent improved the transparency by reducing the % Haze to some extent. While adding 300 ppm and 600 ppm of NA type nucleating agent to the PP matrix, the haze property decreased by a value of 3% and 8%, respectively. However, NB type nucleating agent showed better efficiency as compared to NA at 300 ppm dosage level showing a decrease in haze value by ~5%. This may be attributed to the formation of smaller size crystallites, which reduced the light scattering significantly resulting improvement in optical clarity

Shrinkage property evaluation

PP due to its semicrystalline nature shows mold shrinkage behavior while being cooled which may lead to dimensional instability of the molded part. Table 5 depicts mold shrinkage and shrinkage ratio of all the compositions in machine and transverse direction. The shrinkage ratio close to unity signifies isotropic shrinkage. In spite of showing higher shrinkage among all the formulations, the neat PP homopolymer (HPP) showed a uniform shrinkage in both machine direction (MD) and transverse direction (TD) making the shrinkage isotropic in nature. Although as depicted, the addition of nucleating agent found to improve the shrinkage behavior, but it is desirable that the shrinkage should also be isotropic in nature to avoid distortion in shape of the final product. In all the cases, shrinkage found to be more in transverse direction compared to machine direction. Among all formulations phosphate based nucleating agent (NA) at 300 ppm i.e. HPP-NA-300 showed inferior isotropic shrinkage performance, whereas dicarboxylic acid based nucleating agent HPP-NB-300 seemed to be the superior formulation.

Crystallization behavior

Any crystallization process consists of two stages, nucleation and crystal growth which is a thermodynamically controlled phenomenon [19-20]. The nucleation may happen by the polymer chain itself or in-presence of external additives like nucleating or clarifying agents. The first phenomena is known as homogeneous nucleation whereas the latter is called heterogeneous nucleation. In case of nucleation, the solute or macro-molecules

make a stable cluster of critical size which is known as nuclei. Once nuclei is formed, the crystal grows on that nuclei [21-22]. Crystal growths are also of two types: primary and secondary. The primary growth is fast outward growth of lamellae known as spherulites whereas secondary growth is a slow process filling the lamellar interstices [23-25]. The addition of external nucleating agents promotes the formation of nucleation providing sites to grow and the growth of the crystals depends on rate of cooling [26]. Also, depending upon the types

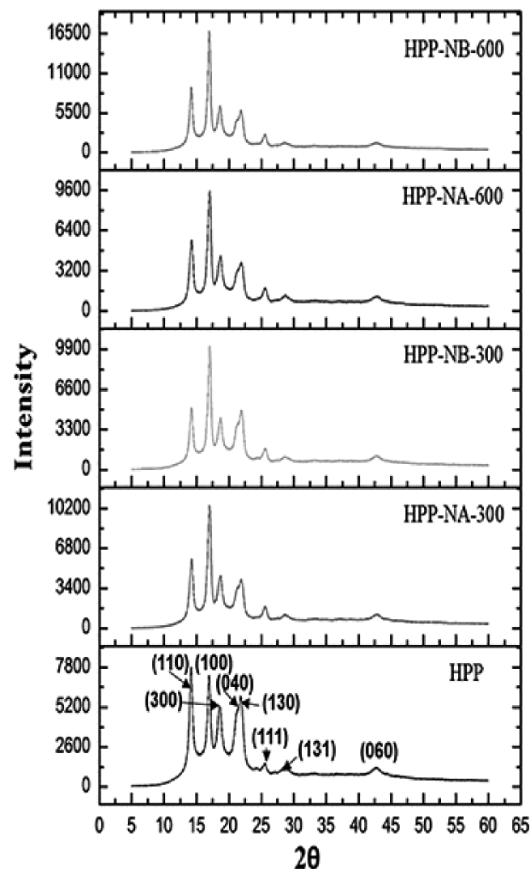


Fig. 2. WD-XRD patterns of non-nucleated & nucleated PP, where θ is the Bragg's angle.

of nucleating agents, different types of crystals are formed among which monoclinic α and trigonal β forms play critical role. The stable α form mainly contributes towards stiffness of the material, whereas β form is responsible to improve toughness of the material.

Figure 2 depicts the WD-XRD patterns of non-nucleated and nucleated PP homopolymer. The crystal planes (110), (100), (040), (130), (111), (131) and (060) correspond to α crystal, the

plane (300) relates to existence of β crystal. The fraction of β crystal, $\sigma(\beta)$, can be estimated using Equation 1 [27-28].

$$\sigma(\beta) = I(\beta) / \{ I(\beta) + I(\alpha_1) + I(\alpha_2) + I(\alpha_3) + \dots \} \quad (1)$$

where, $I(\beta)$ is the intensity of the β peak and $I(\alpha)$ is the intensities of corresponding α peaks. The estimated % crystallinity and crystal fractions are summarized in Table 6.

TABLE 6: Crystallinity (%) and crystal fraction obtained from WD-XRD.

Property	Unit	Result Obtained				
		HPP	HPP-NA-300	HPP-NB-300	HPP-NA-600	HPP-NB-600
Crystallinity	%	51.3	63.3	57.8	69.6	52.8
β -Crystal Fraction	-	0.195	0.137	0.134	0.141	0.134

Addition of nucleating agent to PP homopolymer matrix (HPP) found to increase the crystallinity which resulted in improvement in stiffness as shown in Table 5. Not only crystallinity, addition of nucleating agents also found to influence the crystal form. The amount of β crystal found to decrease with addition of nucleating agent which may have contributed towards the enhancement of stiffness.

Heterogeneous nucleation behavior

The addition of nucleating agent in PP was found to increase the crystallization onset temperature by 10°C to 13°C. To understand the crystallization behavior of neat PP and nucleated PP at different dosage, all the parameters obtained from DSC analysis are summarized in Table 7.

For all compositions, with an increase in rate of cooling from 5°C/min to 20°C/min, the

crystallization onset temperature (T_{onset}), end temperature (T_{end}) and crystallization peak temperature (T_p) found to shift towards lower temperature side (Figure 3a). This may be because, at higher cooling rate the polymer chains do not get enough time to initiate crystal formation resulting in a delay in crystallization onset. The early onset of crystallization was also evident with addition of nucleating agent to neat polymer matrix which provides nucleation sites to the polymer chain to grow crystal structures (Figure 3b). The addition of NA type nucleating agent at 300 ppm level to PP matrix promotes early onset of crystallization by around 8°C at 10°C/min cooling rate, where as in case of NB nucleating agent the early onset was found to be by around 10°C. However, at 600 ppm dosage level no significant improvement in crystallization onset was observed.

TABLE 7: Non-isothermal crystallization and melting parameters.

Sample ID	Cooling Rate (k)(°C/min)	T _{onset} (°C)	T _p (°C)	T _{onset} -T _p (°C)	T _{end} (°C)	T _m (°C)	Crystallinity (%)
HPP	5	123.3	120.9	2.4	116.7	164.3	52.6
	10	121.0	118.5	2.5	112.2	163.8	51.5
	15	119.1	116.2	2.9	108.0	164.0	56.2
	20	118.1	114.4	3.7	105.5	164.4	54.1
HPP-NA-300	5	132.4	129.3	3.1	124.7	166.5	51.5
	10	129.4	126.3	3.1	119.0	165.0	54.5
	15	127.2	123.4	3.8	112.8	166.1	52.1
	20	126.2	122.9	3.3	114.1	164.5	54.8
HPP-NB-300	5	134.0	130.7	3.3	125.8	166.1	62.0
	10	130.6	127.1	3.5	119.3	165.7	59.4
	15	128.6	125.1	3.5	115.7	164.8	55.2
	20	127.2	122.9	4.3	111.4	164.0	53.5
HPP-NA-600	5	134.4	131.3	3.1	126.1	168.5	54.6
	10	132.0	129.0	3.0	121.6	165.6	53.3
	15	129.7	125.9	3.8	116.2	166.1	52.7
	20	128.3	123.7	4.6	111.2	166.1	52.1
HPP-NB-600	5	132.4	128.9	3.5	124.8	165.4	53.9
	10	129.1	125.5	3.6	119.6	163.9	50.3
	15	127.0	123.2	3.8	115.3	164.0	51.5
	20	125.6	121.1	4.5	111.4	164.4	48.8

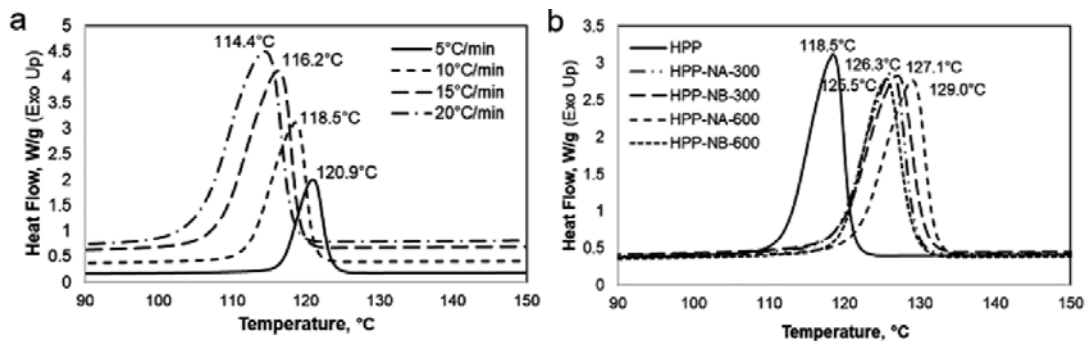


Fig. 3. Cooling curves of: (a) non-nucleated PP (HPP) at different cooling rates, and (b) non-nucleated & nucleated PP (HPP) at 10°C/min. The Temperatures denote crystallization peaks.

The difference between onset of crystallization and peak temperature, $T_{\text{onset}} - T_p$, is inversely related to rate of crystallization, i.e. lower the value, higher the crystallization rate. As shown in Table 7, in both non-nucleated and nucleated PP, the crystallization rate decreases with increase in cooling rate. Addition of nucleating agent also found to decrease the crystallization rate. The % crystallinity was measured by taking account of 209 J/g, the theoretical enthalpy value for 100% crystalline polypropylene [29]. However, in case of HPP-NB-300, the % crystallinity was found to be at little bit higher side. There was no significant change in melting point (T_m).

To understand the effect of both types of nucleating agent and rate of cooling, overall crystallization time (t_c) was calculated using Equation 2.

$$t_c = (T_{\text{onset}} - T_p)/k \quad (2)$$

where, T_{onset} is the crystallization onset temperature, T_p is the crystallization peak temperature and k is the rate of cooling. As shown in Figure 4, an increase in cooling rate reduces the overall crystallization time, which implies that faster is the cooling, faster is the crystallization.

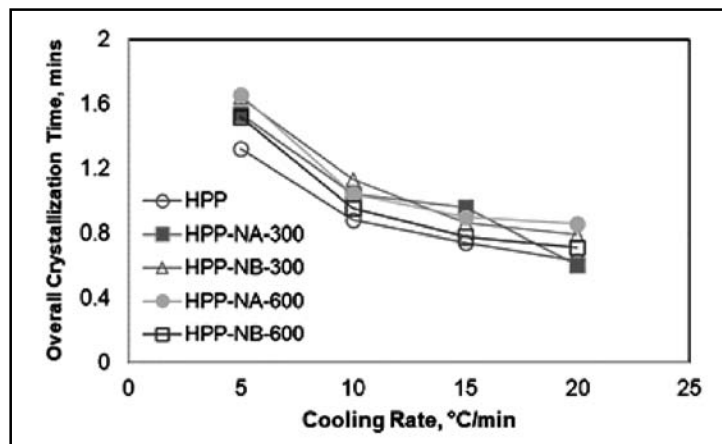


Fig. 4. Effect of cooling rate and nucleating agents on overall crystallization time.

The nucleation efficiency (ϕ) of a nucleating agent for a given matrix can be estimated using Equation 3 as proposed by Fillon et al. [30-31]

$$\phi = (T_p - T_p(PP)) / [T_p(\text{opt}) - T_p(PP)] \quad (3)$$

where, T_p is the crystallization maxima of nucleated PP, $T_p(PP)$ is the crystallization maxima of non-nucleated PP and $T_p(\text{opt})$ is

the optimum self-nucleation temperature of PP reported as 164.5°C. The comparative study of nucleation efficiency at different cooling rate is summarized in Figure 5. At 300 ppm dosage, NB type nucleating agent shows better efficiency at all four different cooling rates as compared to NA type nucleating agent. Nucleating efficiency was found to deteriorate

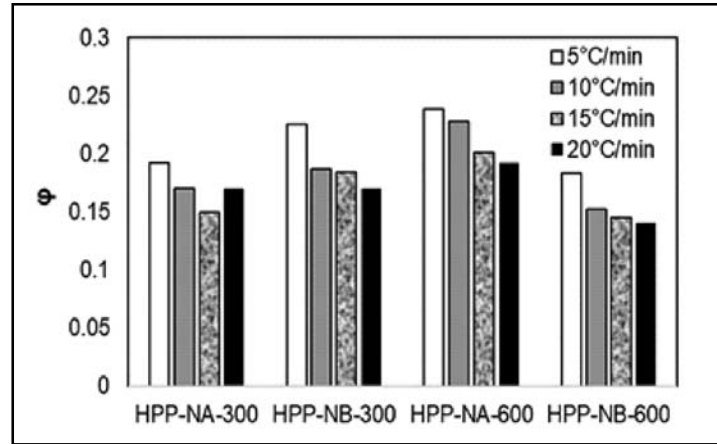


Fig. 5. Effect of cooling rate and nucleating agent concentration on nucleation efficiency.

with increase in cooling rate as the polymer chains do not get enough time to form crystals at higher cooling rate.

Crystallization activation energy

By considering the influence of various cooling rates, Kissinger [32] proposed that the activation energy could be determined by calculating the variation of the crystallization peak temperature with the cooling rate. Equation 4 can be used to estimate the activation energy.

$$d[\ln(k/Tp^2)]/d(1/Tp) = - Ea/R \quad (4)$$

where, *k* is the rate of cooling, *T_p* is the crystallization maxima, *E_a* is the activation energy and *R* is the universal gas constant. Activation energy was evaluated from the slop of $\ln(a/Tp^2)$ vs $1/Tp$ plot as shown in Figure 6.

The activation energy values as obtained for all the compositions are summarized in Table 8. It is found that non-nucleated PP requires

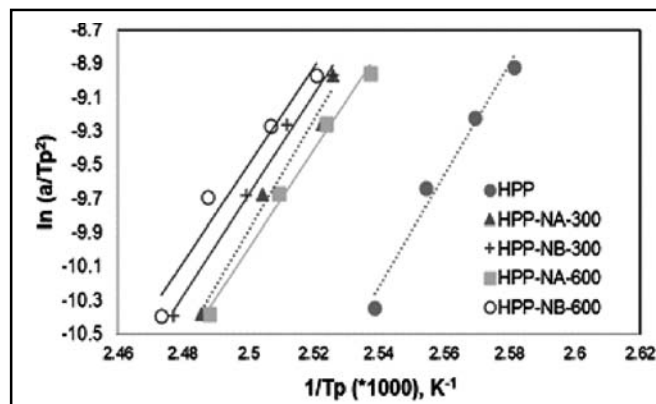


Fig. 6. Activation energy estimation of non-nucleated and nucleated PP using non-isothermal Kissinger plot.

higher activation energy 'Ea' (HPP) that restricts the movement of polymer chains towards growing crystal surface^[33]. Addition of nucleating agents facilitated the crystallization process by reducing the activation energy. At lower nucleating agent concentration (300 ppm) NB type nucleating

agent found to be more effective as compared to NA type nucleating agent as it required 10% less energy for crystal growth. However, no significant reduction in activation energy was found by increasing the nucleating agent content from 300 ppm to 600 ppm.

TABLE 8. Activation energy for neat and nucleated PP.

Sample ID	Ea/R	Ea, kJ/mol	R-squared from curve fitting
HPP	32949	273.9	0.979
HPP-NA-300	32810	272.8	0.979
HPP-NB-300	29717	247.1	0.993
HPP-NA-600	28894	240.2	0.992
HPP-NA-600	29193	242.7	0.956

CONCLUSIONS

The addition of nucleating agents to PP homopolymer showed enhancement in properties like crystallization onset, stiffness without sacrificing isotropic shrinkage behavior. However, nucleation efficiency clearly found to depend on chemical nature of the nucleating agent. Addition of both phosphate ester and 1,2-cyclohexane dicarboxylic acid salt based nucleating agents improved early onset of crystallization of neat PP by 10°C to 13°C without any significant change in significant isotropic shrinkage behavior. The stiffness and strength of the neat PP was found to be enhanced by ~14% and ~8%, respectively on addition of nucleating agents. However, there was no major improvement in property while increasing the nucleating agent dosage from 300 ppm to 600 ppm. The crystallization kinetic study was carried out in order to understand the efficiency of two different nucleating agents.

An increase in cooling rate was found to delay the crystallization onset temperature and reduced the overall crystallization time (t_c). Also, the estimation of nucleation efficiency (ϕ) and crystal form (β fraction) showed that, dicarboxylic acid salt type nucleating agent performed better at all different cooling rates compared to phosphate ester type nucleating agent.

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