INFLUENCE OF TALC PARTICLE SIZE ON NUCLEATING EFFICIENCY OF COMMERCIAL ISOTACTIC POLYPROPYLENE (IPP)

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Abstract

The commercial Isotactic Polypropylene (iPP/PP) is a semi-crystalline polymer with three different crystal forms α, β and γ. Nucleating agents, especially α-type, are added to iPP to increase the rate of crystallization, improvement in stiffness, strength and clarity. Modification of iPP with α-nucleator talc leads to significant changes in the structural, morphological and thermal properties due to the accelerated rate of nucleation. In present investigation; the influence of 5 wt. % talc with different particle sizes on the nucleating efficiency of iPP has been investigated by differential scanning calorimetry. The α-nucleator talc favored formation of α phase along with γ phase in trace, as evidenced by XRD. From this study it can be concluded that, talc has a strong heterogeneous nucleating effect and the particle size of the talc is decisive for haze and the nucleating efficiency. Similarly, the interfacial bonding between talc and iPP as shown by FTIR analysis is appreciable and also justified through scanning electron micrographs.

Key Words: Isotactic Polypropylene; Talc; Nucleating Efficiency; Crystallinity.

Graphical Abstract

1. Introduction

Polypropylene is a thermoplastic polymer with innumerable applications. Beside, isotactic polypropylene (iPP) is an important commercial polymer because of its versatility which stems in recyclability, cost effectiveness and good mechanical performance [1–4]. Despite widespread applications iPP suffers from major drawbacks like flammability, high thermal expansion, low stiffness, etc. Hence to improve its properties, talc incorporation as filler is advocated by many researchers, as the combination of iPP with inorganic fillers like talc offers the synergistic combination of properties [5]. M. Gahleitner et al. reviewed that 5 wt % of talc addition leads to increase in the nucleating efficiency by 40%, as the talc has low free energy [6]. Recent research has generated advances in iPP-talc composites that are sufficient to motivate new technological applications viz. exterior automotive components, under bonnet components etc. [7]. Practically the addition of talc as a nucleating agent increases the nucleation efficiency and degree of crystallinity. The iPP mainly crystallize in several forms denoted as α, β, γ and septic [8,9], but the most stable form among all crystal structures is α form. Commercial iPP grades predominantly crystallize into α form whereas; β form is observed occasionally and is less stable phase [10].

The comparative study from the commercial view point elucidates the effects of talc on crystallization is of more technological significance. The crystallization process depends on the nucleation efficiency of the nucleator. In addition, there are numerous parameters including concentration, surface area, distribution, particle size etc. in order to decide the efficiency. Hence, the present contribution aims to explore the effects of different talc size on the nucleating efficiency of iPP as very less literature has been documented till date regarding the particle size effect on nucleation efficiency of iPP. T. C. Chung et al. demonstrated that, to enhance polymers with nanofillers and produce nanocomposites, the solution method [11] is employed in which the fillers are added to a polymer solution using solvents such as toluene, xylene, chloroform and acetonitrile to integrate the polymer and filler molecules. Hence against this background, in the present investigation the iPP is reinforced with talc filler via solution method and the characterization was done in order to ascertain the effect of talc size on nucleation efficiency.
2. Experimental Details

2.1 Materials and Sample Preparation

The commercial grade Isotactic Polypropylene (iPP) granules were procured from S.W.D. Plastic Industries, Nagpur. Three grades of talc were supplied by Imerys Talc, Italy viz. Luzenac HAR® T84, Steamic®005 F and Jetfine®3CA. The particle size, surface area, percent talc addition and the respective codes assigned to the samples are listed in Table 1.

In solution method, 25ml of Xylene and 3.00g of iPP was taken in a beaker and were thoroughly mixed, and then the beaker was transferred to a hot plate. The mixture was continuously heated with constant stirring until the iPP granules started dissolving. Once the granules dissolved completely the contents of beaker was immediately poured into a petri dish. It was then kept in the oven (preheated at 80°C) for 12 hours. A film of iPP was formed which was then analyzed further. Beside, 2.85g of iPP and 0.15g of T1 (i.e. ~5% by weight of the mixture) was thoroughly mixed in a beaker with 25ml of Xylene and continuous film of PP+T1 was obtained by solution method as mentioned. The same procedure is repeated for T2 and T3 to obtain PP+T2 and PP+T3 respectively.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Talc Grade</th>
<th>Codes</th>
<th>Particle Size (µm)</th>
<th>BET surface area (m²/g)</th>
<th>% Talc Addition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polypropylene</td>
<td>PP</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Luzenac HAR® T84</td>
<td>T1</td>
<td>11.7</td>
<td>19.5</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Steamic®005 F</td>
<td>T2</td>
<td>5.7</td>
<td>8.0</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>Jetfine®3CA</td>
<td>T3</td>
<td>3.5</td>
<td>14.5</td>
<td>5</td>
</tr>
</tbody>
</table>

2.2 Characterization

XRD analysis of iPP and its talc reinforced composites was performed on Panalytical X’Pert Pro (model-PW 3040/60) diffractometer with Cu Kα radiation (λ = 1.54Å) generated at voltage of 45 kV and current of 40 mA. Scanning was done in the 2θ angle of 10 to 80° with a scan step size and time per step of 0.01° and 15 sec., respectively. The morphological changes due to talc addition and subsequent effect on nucleation were investigated using Scanning Electron microscope (SEM-JEOL 6830A). Prior to the study of iPP surface morphology; the material is coated with thin platinum coat using auto sputter to make the material conducting for obtaining images.

Fourier Transform Infrared spectra of iPP and talc filled PP were recorded using a Perkin Elmer Spectrum One FTIR. Potassium Bromide (KBr) was used for collecting the background and a total of 20 scans were taken. Thermal behavior of iPP and iPP-talc composites was analyzed using Mettler Toledo differential scanning calorimeter (DSC 821) equipped with an intracooler. The instrument was calibrated with high purity indium and zinc standards. All the experiments were carried out in sealed Aluminum pans in nitrogen environment. For recording self nucleation, crystallization and melting exotherms; samples weighing around 10 mg were heated at a heating rate of 10°C/min.

3. Results & Discussion

3.1 X-Ray Diffraction Studies

As mentioned, the iPP exists in three crystalline forms majorly α, β and γ form. Out of which α is monoclinic and γ is triclinic phase whereas, β is in hexagonal form as reported by M. Gahleitner et al. [5]. In order to study the effect of different sized talc fillers on the crystal structure of iPP, XRD analysis has been carried out. The diffractograms of iPP and its composites (PP + T1, PP + T2 and PP + T3) are presented in Fig. 1.

The diffractogram for iPP clearly reflects the five characteristic peaks at 14.03°, 15.05°, 16.91°, 18.63° and 21.60° at position 2θ. In this, the peaks at 14.03°, 16.91°, 18.63° and 21.60° correspond to α-phase whereas, peak at 15.05° corresponds to γ-phase [4]. The characteristic peaks of polypropylene are observed in PP + T1, PP + T2 and PP + T3 ascertain the presence of polypropylene. In addition to these peaks, two prominent peaks at 28° and 29° position are observed. This justifies the presence of talc particles in polypropylene matrix. In addition, it was observed that the d-spacing for PP, PP + T1, PP + T2 and PP + T3 is found to be ~5 Å ascertaining the α-nucleation, matching the (010) face of PP [6], whereas, no β-phase peak was observed in any of the samples.
This variation in the size of spherulites in PP+T1, PP+T2 and PP+T3 when compared to PP is specifically due to difference in size of the talc particle added to PP. Smaller the talc particle size, more is the surface area available for nucleation. As the particle size is small in T3, the number of particles available in 5% weight is more. Therefore, more nucleates are formed and the nucleation efficiency is highest in T3 added talc as compared to T1 and T2. This also supports the result obtained through XRD for increase in the crystallinity in case of T3.
3.3 FTIR Analysis

The chemistry plays an important role in order to determine the structure, hence the FTIR spectra were generated in order to determine types of bonds present in the samples especially between the talc and the PP. Fig. 4 gives the spectrograph of percent Transmittance (%T) against wave number (cm⁻¹) in a comparative mode for PP, PP+T1, PP+T2 and PP+T3.

In case of PP, the peaks obtained at 2949 cm⁻¹ and 2837 cm⁻¹ represents symmetrical and asymmetrical C-H stretching vibrations of CH₂ and CH₃ in polyolefin chain [15]. A peak at 1456 cm⁻¹ corresponds to asymmetric in plane CH₃ bending, whereas a peak at 1375 cm⁻¹ ascertains the presence of C-H rocking vibration. The peak at 1261 cm⁻¹ indicates the CH₂ wagging and bands from 719 cm⁻¹ to 670 cm⁻¹ are owing to C=C stretching vibrations [16].

In PP +T1, peaks at 2907 cm⁻¹ and 2838 cm⁻¹ corresponds to C-H bond stretch from PP, whereas in case of PP+T2 and PP+T3 the peak representing the C-H bond stretch found to be shifted at 2950 cm⁻¹ & 2839 cm⁻¹ and 2959 cm⁻¹ & 2839 cm⁻¹ respectively. Similarly the peaks representing asymmetric in plane CH₃ bending, C-H bond rocking vibrations and C=C bond stretching vibrations as in case of PP are also found to be shifted in case of talc added PP. Thus it can be stated that all the peaks which are the characteristic features of PP are invariably observed on talc addition also, with slight shifting in the peak position. Beside the characteristic peaks, two more prominent peaks are found in talc added PP, one is in the range between 1015 cm⁻¹ to 1050 cm⁻¹ which corresponds to Si-O stretching from talc. This Si-O bond stretch ascertains the presence of talc; whereas second broad peak between 3550 cm⁻¹ to 3650 cm⁻¹ representing the hydroxyl bonding O-H bond is also observed [17,18]. This bond indicates that the free O-H group of talc forms hydrogen bonds with PP which is observed in PP/talc composite at ~ 3550 cm⁻¹ in the form of a broad hump. The emergence of this new broad band indicates that hydrogen bonding is taking place between the talc and the iPP. Similar type of bonding was reported in case of talc and PBT [19].

3.4 DSC Analysis

The self nucleation was carried out in order to calculate the nucleation efficiency in synthesized samples. The polymer when partially melted before cooling and recrystallizing, leads to the self nucleation [20]. Here the residual crystallites formed in the melt acts as a nucleation centre, responsible for the formation of smaller spherulites.

In this the DSC measurements were performed applying the same method as documented by A. Romankiewicz et al. [10]. The nucleation efficiency is calculated by using equation (1) given as:

\[
E = \frac{\frac{T_c \text{ nuc} - T_c \text{ pure}}{T_c \text{ max} - T_c \text{ pure}} \times 100}
\]

where, \( T_c \text{ nuc} \) is the crystallization temperature of pure PP with 5wt% of the nucleating agent (for PP+T1=165.2°C, PP+T2=166.7°C and PP+T3 = 167.9°C), \( T_c \text{ pure} \) is the crystallization temperature of pure PP (=164°C) and \( T_c \text{ max} \) is the crystallization temperature established in the self-nucleation test (=169 °C). The efficiencies thus calculated are PP+T1=24%, PP+T2=54% and PP+T3=78%. The microstructures obtained are thus in accordance with the calculated efficiency data, as T1 has the largest particle size; its nucleation efficiency is also found to be less as compared to T3. Thus it can be said that with reduction in talc particle size, there is improvement in the nucleation efficiency. On physical observation of the samples it can be marked that the smaller particle size reduces the haze in PP, whereas, the presence of large size particle are responsible for increase in the haze.

4. Conclusion

The nucleation efficiency of iPP on addition of 5 wt. % talc with different particle sizes by solution method has been investigated in this study. The chemical bonding between talc and iPP ascertains the talc as an active nucleation centre there by accelerating the nucleation of the iPP. Thus, the particle size ratio plays the decisive role in determination of the nucleation efficiency. Thus as per the processing perspective, this study demonstrates that addition of smaller sized (≤ 3.5µm) talc in iPP can improve its processing by increasing the rate of production.

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