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Development of a highly nucleated and dimensionally stable isotactic polypropylene/nanoclay composite using reactive blending

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A B S T R A C T

Polypropylene (PP) is one of the most widely used commodity polymer. However, it has a low upper service temperature. Addressing this challenge, we introduced reactive blending of PP, maleic anhydride-grafted PP (PP-g-MA) and (3-aminopropyl)triethoxysilane (3APTES) in the presence of nanoclay, which results in a highly nucleated PP composite with improved dimensional stability. At the processing temperature, the reaction between maleic anhydride, which is already grafted on the PP chain, and 3APTES forms N-substituted maleimide-grafted PP. The results indicated that the introduction of branched structures on PP chains increased the chain bulkiness and led to the formation of stable nuclei that initiate crystallization at high temperatures. By offering nucleating sites, the dispersed nanoclay particles facilitated the nucleation process to a greater extent. Compared with the neat polymer matrix, the crystallization temperature of the composite was 15.5 °C higher with moderate improvements in the heat distortion and Vicat softening temperatures. This is most likely the first report where such an improvement in crystallization temperature has been achieved for isotactic PP homopolymers. In summary, reactive processing of the PP/nanoclay composite in the presence of PP-g-MA and 3APTES has potential for the development of high-performance PP-based advanced materials.

1. Introduction

Because of its excellent cost-performance value, polypropylene (PP) is one of the most widely used commodity polymers. However, PP has a low upper service temperature [1], which can be correlated with the heat distortion temperature (HDT) and Vicat softening point. One way to address this drawback is to introduce cross-linking between polymer chains because cross-linking leads to a polymer matrix with higher thermal and thermo-mechanical stabilities [1]. In the case of PP, the chemical inertness makes functionalization and cross-linking very difficult. One way to cross-link PP chains is via peroxide reactions followed by silane-water cross-linking. Free radicals are usually generated during peroxide reactions in the first step. In the second step, the silane-grafted polymer is cross-linked via exposure to a humid environment [2]. However, both steps are tedious and not commercially viable.

Another potential approach is the incorporation of additives, such as inorganic fillers [3–6], cellulose [7], natural fibers [8], etc. Several studies have been conducted on the effect of additives on the thermo-mechanical properties of PP. In most cases, surface treated fillers were used to improve the phase interaction between the polymer matrix and filler surface. For example, to improve the dispersion of glass fibers in the PP-matrix, it was necessary to modify the glass fiber surface with γ-aminopropyltriethoxysilane [3]. So far, the greatest improvement in HDT of PP was achieved with 50% cellulose in the presence of maleic anhydride-grafted PP (PP-g-MA), and it is approximately 66 °C higher than that of neat PP (MFI = 75 g/10 min, measured at 230 °C and 2.16 kg) [7]. Therefore, by adding fillers, the HDT of PP can be improved to a certain extent.

Cross-linking or the introduction of a network structure in a polymer matrix usually imposes restriction on the macromolecular chain mobility. Hence, the cross-linked material can stay rigid and exhibit dimensional stability [9]. In this direction, the restriction on the polymer chain mobility can be obtained by incorporation of filler which in turn also enhances the HDT of the neat polymer matrix [8]. The improvement in the HDT of the PP matrix also depends on other factors, such as crystallinity, crystal size [10], β-crystal formation [11], orientation of crystals in the presence of a

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nucleating agent [12], and relaxation and recrystallization during thermal annealing [13].

Sirisinha et al. [14] used the silane grafting and water crosslinking method to prepare a PP-based composite with stearic acid-coated calcium carbonate. They found that, besides silane grafting, the addition of stearic acid coated calcium carbonate on top of silane grafting can improve the HDT of PP (MFI = 3.64 g/10 min) by 80 °C. For this reason, they prepared a master-batch of PP and stearic acid-coated calcium carbonate. Then, the masterbatch was tumble-mixed with vinyltrimethoxysilane and dicumyl peroxide solution and kept in a nitrogen environment overnight. Subsequently, the mixture went under further extrusion and molding processes prior to the water crosslinking step. However, this process is tedious and not energy efficient; therefore, it is not commercially viable.

U.S. Patent No. 4,146,529 to Yamamoto et al. [15] discloses reaction of an endo-bicyclo[2.2.1]-5 heptine-2,3dicarboxilic anhydride-modified PP with an amino or epoxy silane. The purpose of this reaction was to use the alkoxy groups to bind the fillers and to react with the non-grafted carboxylic anhydride to form low odor and non-volatile products [15]. A very fast reaction between aminosilane and the grafted acid anhydride was also reported in the European patent EP 1 021 486 B1 on silane vulcanized thermoplastic elastomers [9]. In this case, the carboxylic anhydride was grafted on the rubber phase polymer (elastomer). The authors used SILQUEST A-186 [γ-(3,4-epoxycyclohexyl) ethyltrimethoxy-silane], SILQUEST A-187 (γ-glycidoxypropyl-trimethoxysilane) and SILQUEST A-189 (γ-mercaptopropyltrimethoxysilane), and studied the effect of mixing sequence on the crosslinking and mechanical properties; however, there were no improvement in the HDT. To overcome this challenge, the authors first blended all of the ingredients for 5 min and then added the thermoplastic polymer and silane. In another process, all of the ingredients were mixed at the same time. However, the end product originating from their reaction mechanism was not a stable one.

Therefore, there is still a need to study and fundamentally understand the reaction between the carboxylic anhydride and the aminosilane. Usually, carboxylic anhydride, e.g., the maleic anhydride (MA) portion in PP-g-MA, is used as a compatibilizer to enhance the interactions between immiscible polymers or the polymer and the filler material. Although the main role of PP-g-MA is the compatibilization of PP, either with other polymers or the filler, it is sometimes difficult to achieve high-level improvements in properties in such a blend or composite. The main reason for this is the shorter chain length of PP-g-MA; however, the chain length can be increased via network formation. It is expected that, in the presence of aminosilane, the MA portion of PP-g-MA will react with the amine functional group of the silane. This might introduce chain bulkiness or the formation of a network structure of PP-g-MA. As a result, the mobility of the polymer chains will be hindered. Such restriction on the polymer chain mobility can improve the upper service temperature or HDT of the resulting blend and composite.

Another challenge with the PP matrix is its lower crystallization temperature. The crystallization of a polymeric material at a high temperature will improve the productivity by reducing the cycle time of the molding processes. This will make the process more energy efficient and economically viable. Over the last few years, several nucleating agents including nanoclay have been used to improve the crystallization temperature (T_c) of PP. Liu et al. [16] reported that, in the presence of co-intercalated organoclay (hexadecyltrimethyl-ammonium and epoxypropyl methacrylate-modified montmorillonite, MMT), the crystallization temperature of PP can be improved by 12 °C. In presence of PP-g-MA and C15A (commercially available organoclay, Cloisite®15A), an improvement of 7 °C in T_c can be achieved [17]. The same level of improvement can also be achieved with C20A (commercially available organoclay, Cloisite®20A) [18]. In the presence of the nucleating agents, such as *cis*-calcium hexahydrophthalate and disodium bicyclo[2.2.1]heptane-3-dicarboxylate, the T_c of syndiotactic PP improved by 17 °C and 11 °C, respectively [19]. However, such nucleating agents might not reduce the odor of MA in PP-g-MA.

Hence, our primary objective is to understand how the carboxylic anhydride (e.g., MA) that is grafted on PP will react with silane. The question that arises now is how such reaction will affect the properties of the final blend. On the one hand, the reaction may reduce the odor of MA, and on the other hand, it will enhance the PP-g-MA chain bulkiness. Improvement in chain bulkiness may affect the crystallization and the melting behavior of neat PP. Therefore, it is necessary to understand how this reaction affects the flow properties, chain bulkiness and, thus, the thermo-mechanical properties of the PP matrix. The next question is how the addition of organoclay will affect the reaction and hence the thermo-mechanical properties of the final composite.

In this study, we used the organically modified South African bentonite (commercial product from our team, Betsopa OM™) as a filler and 3APTES as a chain extender for the network formation. In the first step, the mechanism of reaction between MA of PP-g-MA and 3APTES has been investigated by blending PP, PP-g-MA and 3APTES. Thereafter, the role of this reaction in the nanoclay-based PP composite was investigated using various techniques, such as Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), melt-state rheology, polarized optical microscopy (POM) and heat distortion temperature (HDT) and Vicat softening point measurements.

2. Experimental methods

2.1. Materials

The PP homopolymer (trade name HHR102) was a commercial product from Sasol, South Africa. The measured melt flow rate (MFR) of PP was 3.56 ± 0.32 g/10 min (ISO 1133, 230 °C/2.16 kg). The PP-g-MA supplied by VinPoly Additives, Delhi, India. According to the supplier, the grafting level of MA was 1 wt% and the measured MFR was 58.50 ± 1.55 g/10 min (ISO 1133, 190 °C/2.16 kg). The organoclay used was Betsopa OM™ (Betsopa), a commercially available organically modified bentonite from our laboratory. Betsopa is a South African calcium bentonite modified with dimethyl dihydrogenated tallow quaternary ammonium surfactant. 3APTES was purchased from Sigma Aldrich, South Africa. The chemical structure of PP-g-MA, 3APTES and the surfactant used to modify Betsopa are presented in different parts of Scheme 1.

2.2. Pre-processing characterization and processing of blend and composites

The melting temperatures (T_m) of the as-received PP and PP-g-MA were determined using differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. The results are presented in Fig. S1, Supporting Information. PP showed a single melting endotherm with a melting peak at 164 °C. On the other hand, PP-g-MA exhibited melting peaks at 157.4 °C and 164.4 °C. Therefore, based on the DSC results, the selected processing temperature was 190 °C.

To determine the thermal stability of various starting materials at the processing temperature, thermogravimetric analyses were conducted at 190 °C. The TGA results (Fig. S2, Supporting Information) showed that the neat polymers and Betsopa are quite stable at the selected processing temperature. Although 3APTES