

Suppression in Melt Viscosity of the Homogeneously Mixed Blends of Polypropylene (iPP–UHMWiPP) in the Presence of an Oxalamide

Ramiro Marroquin-Garcia, Nils Leone, Laurence G. D. Hawke, Dario Romano, Carolus H. R. M. Wilsens, and Sanjay Rastogi*



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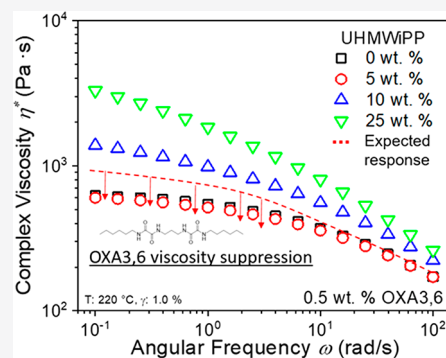


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ABSTRACT: Here we report on the influence of an aliphatic oxalamide-based nucleating agent (OXA3,6) on the viscoelastic and mechanical properties of isotactic polypropylene (iPP) blended with ultrahigh molecular weight iPP (UHMWiPP). The linear viscoelastic properties are investigated by using a plate–plate rheometer; the presence of only 0.5 wt % of OXA3,6 in the iPP–UHMWiPP blends results in a reduction of the complex viscosity in the entire frequency domain examined. This observation holds irrespective of the UHMWiPP weight fraction, up to 25 wt %. The viscosity suppression is attributed to an acceleration of the reorientation times of the chains, especially the longer ones, due to partial alignment of their molecular segments. Furthermore, SAXS measurements on cooled, injection molded samples hint that OXA3,6-containing samples display enhanced alignment under processing conditions (injection molding). Compared to samples without OXA, an increase in the SAXS intensity along the equator is observed in the OXA3,6 samples, implying an enhanced ability of shish-kebab formation. Such a morphological development results in higher yield stress while maintaining the elastic behavior.



INTRODUCTION

Since first reported by Natta and Corradini in 1954, isotactic polypropylene (iPP) has become one of the most important synthetic polymers used for several commodity applications.¹ In 2017, the total European plastic demand represented 51.2 million tons (Mt) per year, where 10 Mt is the consumption of polypropylene alone.² The high commercial relevance of iPP is a result of inherent and very desirable physical properties of the polymer, such as excellent chemical resistance, good mechanical properties (high stiffness), high melting temperature (~160 °C), and low density (~0.90 g/cm³).³ The synergy of these physical properties makes iPP an excellent material for several applications. According to data of 2019, European polypropylene demand can be allocated in three main production sectors: packaging, automotive, and specialty applications (specialized applications such as aerospace, engineering, medical, etc.).⁴ Although more than 50% of those iPP applications is packaging, increasing research attention has been placed in automotive and more specialized products due to the higher added values. However, such high-end applications demand ultimate mechanical properties combined with ease in processing and recyclability.

Several alternatives to achieve high-performance iPP products have been proposed in the past. For example, the mixing and filling of iPP with nonpolymeric fibers (glass fibers) have been extensively reported in the literature, and several products are commercially available.^{5,6} Moreover, the so-called

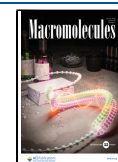
fiber-reinforced polypropylene composites (FRPCs) exhibit 2–3 times higher mechanical properties (tensile strength) without a significant increase in weight when compared to the normal iPP.⁷ Despite their evident advantages, the use of FRPCs presents challenges for recyclability and sustainability, which leads to additional operational costs.⁸ In comparison, the substitution of glass fibers with carbon nanotubes/fibers presents similar challenges as those mentioned above and adds a substantial price increase in the case of carbon fibers.^{9,10} Therefore, new alternatives must be adopted to achieve enhanced mechanical properties without compromising production viability and sustainability.

It is generally accepted that the mechanical properties of a polymer are highly dependent on molecular weight. Thus, ultimate properties can (in theory) be achieved when the sufficiently high molecular weight is obtained during the synthesis and only if the processability of the sample is not compromised. A clear example of molecular-weight-driven ultimate properties is ultrahigh-molecular-weight (UHMW) polymers. A well-documented successful example in such a

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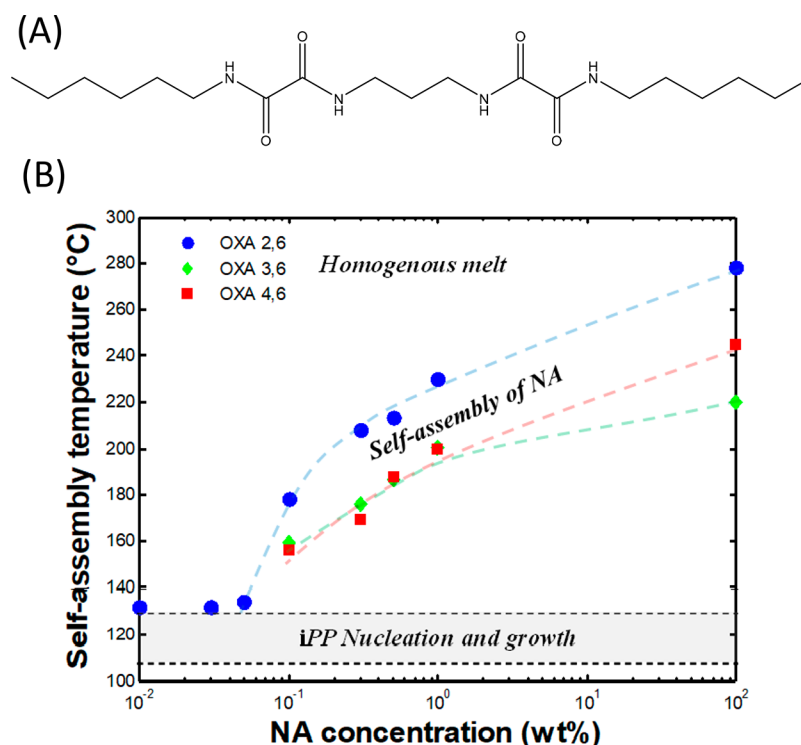


Figure 1. (A) Chemical structure of OXA3,6 nucleating agent. (B) Phase diagram showing the self-assembly of OXA 2,6, OXA 3,6, and OXA 4,6 in commercial iPP grade during cooling (10 °C/min) as a function of nucleating agent concentration. Only OXA3,6 is utilized in this work. Reproduced with permission from ref 21.

class of polymers is ultrahigh-molecular-weight polyethylene (UHMWPE), with the polymer chains having a weight-average molecular weight (M_w) higher than 1 million g/mol. Hence, UHMWPE is often used in several demanding applications including prostheses for hip and knee joint replacement.¹¹ However, it is known that with increasing molecular weight an increase in the viscosity is expected, which follows the relationship $\eta_0 \propto M_w^{3.12}$. The highly nonlinear increase in the zero shear viscosity (η_0) is the result of an increasing number of entanglements per chain. These topological constraints, present in the amorphous region of semicrystalline polymers, distribute homogeneously on melting.¹³ Consequently, because of the high melt viscosity, the processing of UHMW polymers via the common route (melt extrusion) becomes nearly impossible.¹⁴ Notwithstanding the foregoing, UHMW polymers represent an opportunity of achieving ultimate performance without including any filler, making it easier to recycle mechanically. Retrospectively, new methodologies are required to secure ease in processing and product development.

In the past, melt processing of UHMWPE has been achieved in the presence of a lower molecular weight component such as high-density polyethylene (HDPE).¹⁵ The all-polyethylene composite exhibited good mechanical properties (tension) depending on the amount of UHMWPE used.¹⁶ The latter was attributed to the shear-induced shish-kebab structures induced mainly by the UHMWPE fraction during processing.¹⁷ Nonetheless, challenges during the mixing and extrusion were still observed at UHMWPE contents higher than 5 wt % with respect to the HDPE. Until now, numerous studies have been performed on the UHMWPE melt processability;^{18–20} however, little attention has been placed on other UHMW polymers such as UHMWiPP. The potential of

UHMWiPP lies in its relatively high melting temperature, which is nearly 25 °C higher than UHMWPE. In addition, polypropylene displays higher tensile strength and in specific cases higher impact resistance compared to PE. The direct reinforcement of iPP–UHMWiPP blends can potentially exclude the use of external fillers and additives, which hinder the recyclability and sustainability of the materials.

Recently, our group reported on the viscosity suppression in the presence of oxalamide-based nucleating agent OXA3,6 in commercial, relatively low M_w iPP melts under shear conditions in both the linear and nonlinear flow regime.²¹ Chain alignment in the presence of rhombic-like OXA3,6 structures is hypothesized to cause the viscosity reduction. Although in the linear regime this alignment is presumably partial (i.e., chain sections rather than the entire chain), it can effectively reduce chain friction and, in turn, accelerate the reorientation (reptation) times of the chains, especially of the longer ones.^{22,23} In the nonlinear flow regime, full alignment is possible, leading to flow-induced disentanglement, a process known to induce shear or extensional thinning under constant flow.^{22–24} Concerning the underlying reason allowing OXA3,6 entities to impart chain alignment, a possible mechanism is hypothesized, namely, numerous absorption and desorption (detachment) events of iPP chain segments on OXA3,6 structures.^{21,25} Another possible scenario is that the alignment is induced by a shear amplification mechanism. Such amplification has been reported in composites of nylon-6 and solid nanoplatelets²⁶ as well as composites of iPP and organic, solid nucleating particles²⁷ under processing conditions. It has been attributed to the modification of the shear flow field near the filler particles, that is, the amplification of the local strain or strain (shear) rate in the vicinity of the fillers (nanoplatelets or nucleating particles). Concerning the nano-

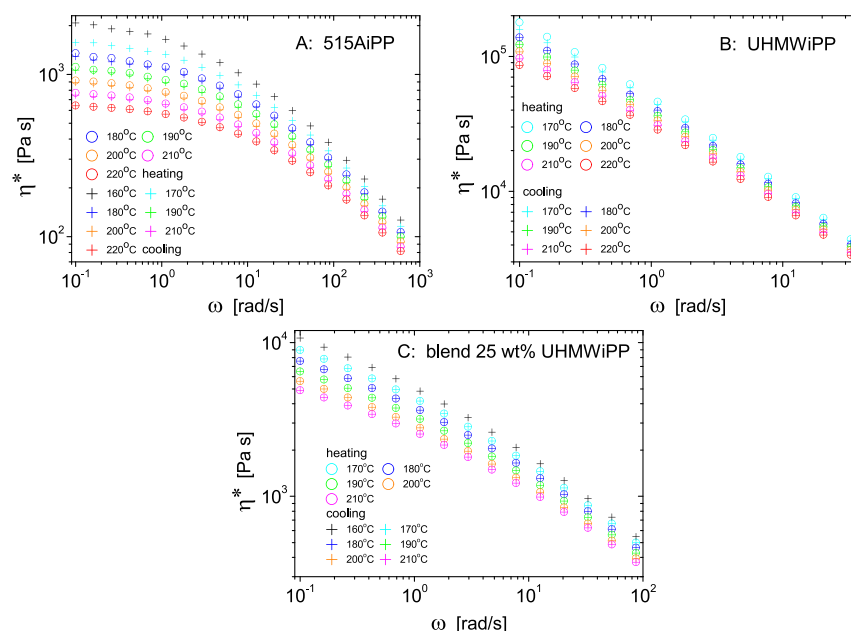


Figure 2. Complex viscosity of the (A) low- M_w iPP grade (515A), of the (B) UHMWiPP grade, and (C) of their blend having 25 wt % UHMWiPP at various temperatures. Open circles (O) refer to frequency sweeps during the heating cycle while plus (+) symbols represent frequency sweeps during the cooling cycle. The color code is the following: black (160 °C), cyan (170 °C), blue (180 °C), green (190 °C), orange (200 °C), magenta (210 °C), and red (220 °C).

platelets, which are of more relevance to the present work as rhombic OXA3,6 entities resemble such structures, the smaller the spacing between them, the larger the shear amplification is. It is important to note that when the applied deformation is already in the nonlinear regime, as in the two aforementioned studies, shear amplification can lead to severe alignment and thus promote the formation of shish-kebab morphologies.

Irrespective of the exact mechanism, whether the interaction between OXA3,6 and iPP will lead to a viscosity decrease or increase strongly depends on the size and morphology of the OXA3,6 particles, which is influenced by the chosen cooling rate of the samples and the OXA3,6 concentration as well.^{21,25} Fast cooling (e.g., 30 °C/min) promotes the formation of OXA3,6 crystallites of nano- and submicrometer size while slow cooling (e.g., 1 °C/min) favors the formation of larger crystallites of micrometer size. The former tends to enhance viscosity suppression while the latter favors viscosity increase.^{21,25} The exact self-assembly (crystallization) temperature of OXA3,6 in iPP melts depends on the OXA concentration as well as the molecular weight of the matrix (see the **Materials and Blending Process** section). It is important to stress, however, that at temperatures moderately higher than the self-assembly temperature, OXA3,6 molecules do not fully dissolve in the polymer matrix but persist as nanoclusters due to weak hydrogen bonding. Such nanoclusters can still confer viscosity suppression.^{21,25}

Having observed viscosity suppression in the presence of OXA in low molar mass polypropylene melts, in this work we mainly focus on UHMWiPP materials as they have a large industrial appeal. In particular, we focus on iPP–UHMWiPP blends aiming to determine whether OXA addition in such blends can also lead to viscosity suppression. Imparting such suppression into iPP–UHMWiPP blends may allow the use of increased UHMWiPP concentrations, effectively increasing mechanical performance without sacrificing the processability via extrusion. We report on a series of iPP–UHMWiPP blends

having different UHMWiPP content in the presence, and absence, of OXA3,6. We evaluate the effect of OXA3,6 on the viscoelastic response of the blends, morphology, and mechanical properties under uniaxial tension.

EXPERIMENTAL SECTION

Materials and Blending Process. The synthesis of N1,N1'-(propane-1,3-diyl)bis(N2-hexyloxalamide), defined as OXA3,6 in the present work, has been performed as reported in the past.²⁵ A schematic illustration of OXA3,6 can be seen in Figure 1A. In iPP melts, OXA3,6 molecules have the ability to self-assemble into rhombic crystallites, the size of which depends on the cooling conditions.^{21,25} As illustrated in Figure 1B, the crystallization or self-assembly temperature of the OXA molecules depends on their concentration in the iPP matrix. At the 0.5 wt % concentration, used in this work, the self-assembly temperature of OXA3,6 is ~190 °C.²¹

A commercially available iPP (515A grade) from Sabic and an ultrahigh molecular weight iPP (UHMWiPP) provided by Reliance Industries Ltd. were used in this study. UHMWiPP samples contained 1 wt % of Irganox 1010 as a thermal stabilizer. All the materials were dried overnight *in vacuo* at 40 °C before their processing. A series of iPP–UHMWiPP and iPP–UHMWiPP–OXA3,6 samples (containing 0.5 wt % OXA3,6) were melt mixed by using a twin-screw extruder (DSM Xplore MC 5.5 mL barrel) for 3 min at 200 °C and 100 rpm. After this, the extrudate was injection molded into (1) dog-bone shape tensile bars (2 mm × 4 mm × 70 mm, with a gauge length of 25 mm) and (2) disk rheometer specimens (2 mm thickness, 25 mm diameter) by using a DSM Xplore, IM 5.5 microinjection molder with a barrel temperature of 200 °C and a mold temperature of 25 °C.

Characterization Methods. Differential scanning calorimetry (DSC) was performed on the samples by using a TA Instruments Q2000 DSC. All measurements were conducted at 10 °C/min and up to a maximum temperature of 220 °C, unless indicated otherwise. The exothermic crystallization observed during the cooling of the samples was used to define peak crystallization temperature (T_c) and the onset of crystallization temperature ($T_{c,onset}$). The peak crystallization temperature is considered as the maximum value in the exotherm curve, whereas the intersection of the tangents of the baseline and the

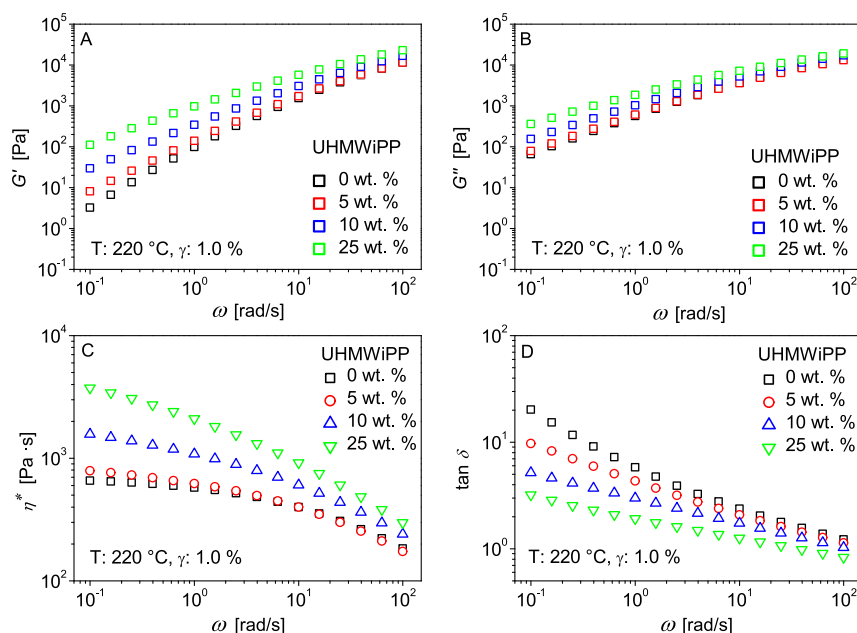


Figure 3. Viscoelastic properties of iPP–UHMWiPP at 220 °C. (A) Storage modulus, G' , as a function of frequency. (B) Loss modulus, G'' , as a function of frequency. (C) Frequency-dependent complex viscosity, η^* . (D) Frequency-dependent loss tangent. All measurements were performed by using a strain of 1.0% in the viscoelastic regime.

crystallization curve is considered to be the onset temperature for crystallization.

Polarization optical micrographs were taken between cross-polarizers (using a 530 nm λ -wave plate) on an Olympus BX53 microscope mounted with an Olympus DP26 camera and a Linkam hot stage. The samples were heated to 220 °C at a rate of 30 °C/min. Samples were kept under isothermal conditions for 3 min, followed by a cooling step at 10 °C/min until crystallization was observed. Optical micrographs depicting the morphological changes at different times/temperatures were recorded during the cooling step.

The viscoelastic properties of the blends were characterized by using an Anton Paar 702 twin-drive rheometer. A parallel plate geometry having a diameter of 25 mm and a gap of 1 mm was used and a fixed strain of 1%. The temperature-dependent complex viscosity of the iPP–UHMWiPP and iPP–UHMWiPP–OXA3,6 materials was evaluated at 220 and 160 °C. For all samples, a first frequency sweep was performed in the viscoelastic regime at 220 °C between 628 and 0.1 rad/s. After this, the temperature was decreased to 160 °C, and a second frequency sweep was conducted under similar angular frequency conditions. The cooling rate was 10 °C/min. With regard to the individual components, i.e., the S15A and the UHMWiPP grades as well as the 75 wt % S15A–25 wt % UHMWiPP blend, frequency sweeps were performed between 160 and 220 °C to construct the master curves. These sweeps were performed at intervals of 10 °C. To assess the possibility of degradation, the sweeps were performed both during heating (to 220 °C) and cooling (back to 160 °C).

Wide-angle X-ray diffraction (WAXD) and two-dimensional (2D) small-angle X-ray scattering (SAXS) were performed on the injection-molded bars by using a SAXSLAB Ganesha diffractometer. The sample-to-detector distance was 80 mm for the WAXD and 1076.3 mm for the SAXS. Both measurements used Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) and silver behenate ($d_{001} = 58.380$ Å) as calibrant.

Tensile testing of the injection-molded tensile bars was conducted by using a Zwick 100 tensile tester machine equipped with a 1 kN load cell. Samples were measured at room temperature, and the deformation rate was varied from 0.5 to 50 mm/min after the 2% strain point.

Molecular weight and the polydispersity were determined by using size exclusion chromatography (SEC). The measurements were performed at 150 °C on a Polymer Char GPC-IR built around an

Agilent GC oven model 7890, equipped with an autosampler and the Integrated Detector IR4. The polymer concentration was 1 mg/mL by using 1,2-dichlorobenzene as solvent and eluent with a flow rate of 1 mL min⁻¹. The SEC-data were processed by using Calculations Software GPC One.

RESULTS AND DISCUSSION

Thermal Degradation of the Samples. This section discusses the possibility of thermal degradation during the rheological measurements performed in this work, as we wish to circumvent any doubts on the observed changes in melt viscosity. Although the experimental results shown in this section refer to samples without the nucleating agent, the conclusions drawn here are expected to hold for the samples with OXA3,6, too. This is because the latter is anticipated to not influence the thermal degradation behavior of the iPP materials. Figure 2 presents frequency sweep data for the low- M_w iPP grade (S15A), the UHMWiPP grade, and a blend having 25 wt % of UHMWiPP and 75 wt % of the iPP (S15A). In the figure, open circles (O) represent small-amplitude oscillatory shear (SAOS) data obtained during the heating cycle (from 160 to 220 °C) while plus (+) symbols refer to SAOS measurements recorded during the cooling cycle (from 220 to 160 °C). Different colors in the figure refer to different temperatures. Independent of the heating and the cooling runs, no difference in the storage and the loss moduli is obtained at the recorded temperatures. However, data collected at 160 or/and 170 °C during the heating cycle show considerable deviation from that recorded during the cooling run (see for example Figure SI-1). For the temperatures higher than 170 °C, all three samples exhibit remarkably good overlay in the recorded storage and loss moduli during the heating and the cooling runs. This fact strongly suggests that all rheological measurements, recorded in the defined thermal cycles presented in this work, are not influenced by thermal degradation.

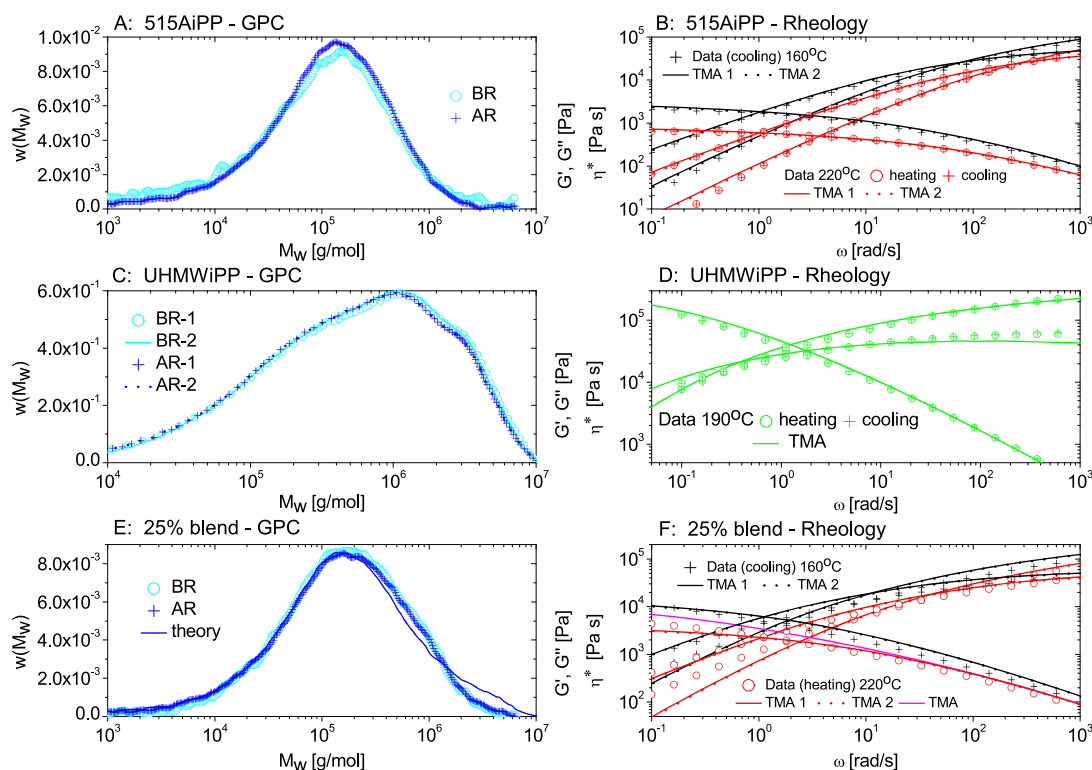


Figure 4. Upper: 515A iPP grade. Middle: UHMWiPP grade. Bottom: blend of 75 wt % 515A and 25 wt % UHMWiPP. Left panels show experimental GPC traces obtained before and after the rheology measurements (BA and AR, respectively). BA signals are shown by cyan symbols while AR signals are shown by blue symbols. The right panels depict the corresponding SAOS data as well as tube model predictions using the AR GPC traces. Solid lines labeled as TMA 1 do not consider short chains ($Z \leq 2$) as solvent whereas dashed lines (TMA 2) do. Black, green, and green curves refer to 160, 190, and 220 °C, respectively. The magenta line in the lower panel refers to 220 °C. It is obtained by using the light blue GPC trace shown in the left panel.

This conclusion is further strengthened by GPC measurements performed on the samples obtained before and after the rheology measurements. As readily seen in the left panels of Figure 4, presented later in the paper, the GPC signals of the three aforementioned iPP samples are very similar before (BR) and after rheology (AR). The absence of degradation is further supported by the reasonable match of the experimental frequency sweep data with the theoretical estimates using the well-established tube model (right panels of Figure 4).

Melt Miscibility of iPP–UHMWiPP Blends. Commercial entangled iPP grade (Sabic 515A) with a M_w of 230 kg/mol and a polydispersity ($\bar{D} = M_w/M_n$) of 7.3 was blended with an entangled UHMWiPP (Reliance) ($M_w = 1.2 \times 10^6$ g/mol and a $\bar{D}$ of 16.8). A series of iPP–UHMWiPP blends were prepared by varying the UHMWiPP content by 0, 5, 10, and 25 wt %. In the past, several groups have studied the effect of the molecular weight on the melt mixing ability of several olefin-based blends.^{28–30} In the case of UHMW polymers, Chen et al. evaluated the miscibility of UHMWPE with low-density PE (LDPE), high-density PE (HDPE), and linear low-density PE (LLDPE). Their study suggested complete melt miscibility of the UHMWPE–LDPE pair, whereas phase separation was observed in the latter two cases.³¹ Recently, a melt processing study of UHMWPE–HDPE blends revealed that good indicators of homogeneous mixing with an increasing amount of UHMW content are (i) a gradual increase of the storage $G'(\omega)$, the loss moduli $G''(\omega)$, and the complex viscosity $\eta^*(\omega)$ and (ii) a gradual decrease of the phase angle δ .³² These effects became more pronounced at the lower frequencies. A subsequent study by the same group

characterized the extent of UHMWPE dissolution during melt compounding through theoretical and experimental rheology; a higher content of UHMWPE led to a multicrossover point behavior in the melt miscible blends.³³ In our study, the miscibility of the iPP–UHMWiPP blends was evaluated by utilizing oscillatory shear rheometry, and results are presented in Figure 3.

The frequency-dependent storage and loss moduli of the four blends at 220 °C are illustrated in Figures 3A and 3B, respectively. Clearly, the sample with no UHMWiPP content (0 wt %) displayed the lowest G' and G'' values over the entire frequency range, which is attributed to the relatively low M_w . A gradual increase in G' and G'' values is observed as the UHMWiPP content increases. In more detail, at low frequencies (e.g., 10^{-1} rad/s) the values of G' and G'' for the 25 wt % sample are 2 and 1 decade, respectively, higher in comparison to the 0 wt % sample; the corresponding values for the 5 and 10 wt % samples lie in between the two extremes. A similar effect is observed in the case of complex viscosity (η^*) and is illustrated in Figure 3C. Samples containing 0 and 5 wt % UHMWiPP display a zero-shear viscosity (η_0) plateau at low frequencies (e.g., 10^{-2} – 10^{-1} rad/s). Such a plateau is not apparent in the blends having 10 and 25 wt % of UHMWiPP. In these two blends, an increase in complex viscosity is observed with an increasing amount of UHMWiPP. Contrary to the other graphs, $\tan \delta$ values display a gradual decrease with increasing UHMWiPP content over the whole range of frequencies. The increasing amount of UHMWiPP in blends shows a systematic deviation in the curves when compared to the 0 wt % sample. In the high-frequency region, the

viscoelastic properties are dominated by fast relaxation provided by the short chains; partial substitution of these short chains by the long UHMWiPP leads to a small decrease in the $\tan \delta$ value (5, 10, and 25 wt %). On the other hand, the low-frequency region is mainly characterized by high relaxation times associated with the long chains. Consequently, the absence of such long-time relaxing chains in the case of sample 0 wt % leads to a considerable increase of the $\tan \delta$ in comparison to the other blends. All the aforementioned findings are in accordance with the studies reported in HDPE–UHMWPE blends.³² These findings suggest that the investigated materials are homogeneously blended. This is also supported by the adequate reproduction of the SAOS data by using the tube model (Figure 4), which is developed considering the blended polymer melt as homogeneous.

To further evaluate the mixing state of the samples, a second frequency sweep was performed at 160 °C, and the results are illustrated in Figure SI-2. As is evident from Figure SI-2, the crossover point ($G' - G''$) shifts to lower frequencies as the content of UHMWiPP increases, indicating that the UHMWiPP is being “dissolved” in the iPP matrix. Therefore, it can be concluded that the presented iPP–UHMWiPP materials behave as a homogeneous mix rather than phase-separated blends.

Modeling of the Samples without OXA3,6 Using the Tube Model. To examine further the possibility of thermal degradation and/or phase separation, the SAOS responses of the two individual components, as well as their blends, have been modeled by using the time marching algorithm (TMA), a tube model approach for the linear flow regime.³⁴ Prior to considering the iPP materials of this study, the model was applied to various iPP grades found in the literature, i.e., the so-called iPPM9 grade of Eckstein et al.³⁵ and the CiPP grades of Hamad et al.,³⁶ as to determine the TMA material parameters. These parameters are namely the entanglement molecular weight, M_e , the entanglement relaxation time, τ_e , and the entanglement plateau modulus, G_N^0 .³⁷ As detailed in the Supporting Information (section SI-3), at the reference temperature of 190 °C, the parametrization for all iPP materials is $G_N^0 = 0.427$ MPa, $\tau_e = 7.5 \times 10^{-8}$ s, and $M_e = 5.5266$ kg/mol. For model predictions at temperatures other than 190 °C, G_N^0 and τ_e values are adjusted according to the horizontal and vertical shift factors described in the text.

Focusing on the present materials, Figure 4B shows the comparison of the tube model predictions and the S15A SAOS data. Black curves refer to 160 °C while red curves to 220 °C. The symbols represent the corresponding data from Figure 2. The lines refer to TMA outcomes, which are obtained by using the after rheology (AR) GPC trace of Figure 4A. Notice that in Figures 4B and 4F there are two sets of lines, solid and dashed. The barely visible dashed lines (labeled as TMA 2) overlap in practice with the solid ones (labeled as TMA 1). They have been obtained assuming that short chains up to two entanglements long behave as solvent. The volume fraction of the $Z \leq 2$ chains is 0.065, which turns out to be very low as for the fast relaxing chains ($Z \leq 2$) to have a noticeable effect on the overall response. The comparison between experimental findings and model predictions reveals a good model performance at both 160 and 220 °C. This finding strongly supports our notion of the S15A melt consisting of linear chains solely. Concerning the vertical shift factors, $b_T = 1.0302$ from 190 to 160 °C and $b_T = 0.9762$ from 190 to 220 °C. With regard to the horizontal shift factors, an activation energy of

36.9 kJ/mol is used. This E_a value gives the best superposition of the various frequency sweeps when a master curve is constructed at $T_0 = 190$ °C. The master curve can be seen in Figure SI-4a.

Figure 4D presents the comparison of the TMA outcomes (green lines) and the UHMWiPP rheology data (green symbols) at 190 °C. The complex viscosity data are the same as those in Figure 2B. In obtaining the tube model predictions, neither vertical nor horizontal shift was applied to G_N^0 and τ_e . Concerning the GPC trace, the average response of the two after rheology (AR) signals was used. (The two GPC signals measured after rheology are shown in Figure 4C by blue curves.) This average GPC response is shown in Figure SI-5b (AR-av). Within the frequency window 10^{-1} – 10^3 rad/s, the model describes the experimental findings with sufficient accuracy. Arguably, GPC resolution is reduced for molecular weights exceeding (approximately) 2×10^6 g/mol due to the inhomogeneous dissolution of long chains in common GPC solvents.³⁸ Hence, a separate frequency sweep covering frequencies lower than 10^{-1} rad/s was also performed at 190 °C. The G' , G'' , and η^* outcomes of this sweep can be seen in the lower panels of Figure SI-5. Because its ω range extends to 10^{-3} rad/s, this sweep contains contributions from the reorientation of chains that are longer than 2×10^6 g/mol. As explained in section SI-3, chains in the 2×10^6 g/mol $\leq M_w \leq 7 \times 10^6$ g/mol range dominate the viscoelastic response up to $\omega = 10^{-1}$ rad/s (approximately) while longer chains have significant influence at lower frequencies. Therefore, a high- M_w tail should be added to the (after rheology) GPC response to reproduce the G' , G'' , and η^* outcomes in the entire frequency domain. This high- M_w tail (shoulder) comprises chains that have a molecular weight exceeding 7×10^6 g/mol. It is important to mention, however, that small to moderate deviations between SAOS data and TMA predictions are anticipated when the considered molecular weight distribution comprises chains longer than 2×10^6 g/mol. For example, in Figure 4D, we would notice small to moderate differences between various TMA predictions even in the $\omega = 10^{-1}$ rad/s region depending on the exact shape the molecular weight distribution would have in the 2×10^6 g/mol $\leq M_w \leq 7 \times 10^6$ g/mol regime. Nevertheless, such variations would not have been dramatic.

The lower panel of Figure 4 refers to the iPP blend having 25 wt % UHMWiPP. The left panel shows the GPC results. Cyan symbols refer to the trace obtained before rheological measurements (BR) while blue symbols correspond to the trace obtained after rheology (AR). The blue line (labeled as “theory”) is obtained by mixing the following two curves: (1) the AR GPC trace of the S15A component, i.e., the blue curve shown in Figure 4A, and (2) the constructed trace that approximately incorporates the M_w tail of the UHMW component; the latter trace can be seen in Figure SI-5b (labeled as AR-av-1). This “theory” curve does not fully overlap with the experimental AR distribution. It exhibits a more pronounced and broader high M_w tail as it is supposed to account for the GPC limitations above the $M_w \geq 2 \times 10^6$ g/mol limit. Nevertheless, the comparison of the two distributions is reasonable. The right panel presents the rheology data (symbols) together with the TMA predictions (lines). Black and red curves refer to 160 and 220 °C, respectively. These predictions are obtained by using the AR measured trace. At 160 °C, the experimental response is slightly overpredicted at early and intermediate frequencies.

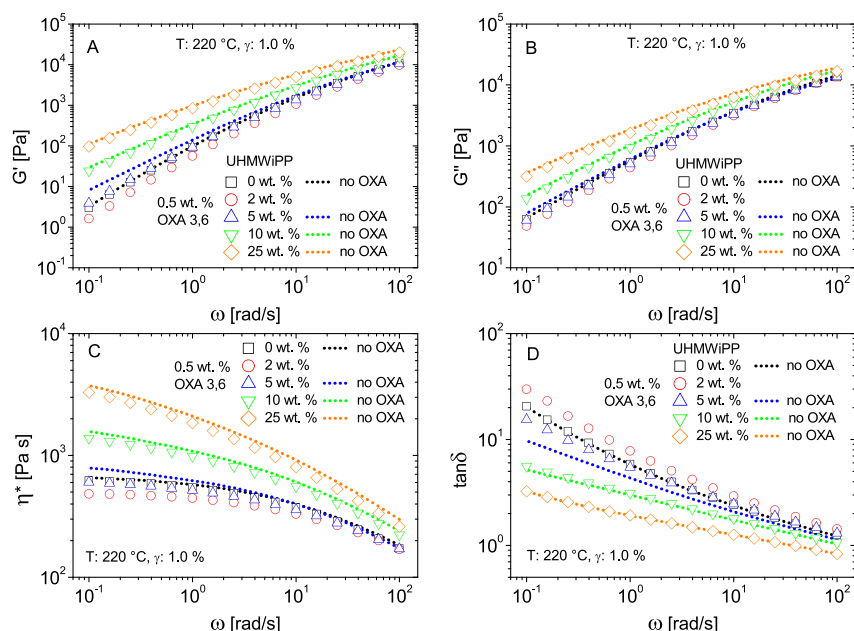


Figure 5. Effect of OXA3,6 in the viscoelastic properties of iPP-UHMWIPP at 220 °C. (A) Storage modulus, G' , as a function of frequency. (B) Loss modulus, G'' , as a function of frequency. (C) Frequency-dependent complex viscosity (η^*). (D) Frequency-dependent loss tangent. Dashed lines correspond to the iPP-UHMWIPP data without OXA3,6. All measurements were performed by using a strain of 1.0% in the viscoelastic regime.

For the same temperature, the low ω regime is reproduced satisfactorily. Concerning the comparison at 220 °C, the G' terminal response is underestimated evidently (about a factor of 5). Nevertheless, the G'' terminal response is captured much better, and thus the η^* low ω regime is only moderately underestimated. As mentioned above, discrepancies of this order can be attributed to the fact that precise determination of the GPC trace in the $M_w \geq 2 \times 10^6$ g/mol range is troublesome. To realize this, consider that at 220 °C the terminal relaxation of the high- M_w tail of the UHMW component is shifted to higher frequencies as compared to 160 °C. Therefore, by use of the same molecular weight distribution, the model performs better at 160 °C as the contribution of the high- M_w tail of the UHMW component to the SAOS data is not significantly reflected in the examined ω range. Moreover, consider the magenta TMA line. This line corresponds to η^* predictions at 220 °C obtained by using the “theory” distribution curve. In contrast to the TMA outcome using the AR trace, it moderately overpredicts the terminal response of the blend. For completeness, we note that in obtaining TMA predictions the reference τ_e value at 190 °C has been shifted to 160 and 220 °C by using an activation energy of 38.05 kJ/mol, obtained according to $E_a = 0.25 \times 41.5$ kJ/mol + 0.75×36.9 kJ/mol; 41.5 kJ/mol is the activation energy for the UHMW grade. It has been extracted by time-temperature superposition of the frequency sweeps at various temperatures (see Figure SI-4b). The master curve of the 25 wt % UHMWIPP can be seen in Figure SI-4c. It has been obtained by using $E_a = 38.05$ kJ/mol.

In conclusion, the quality of the above comparison is decent, implying that to a good approximation the dynamic response of the blends complies with the standard tube model predictions. Recall that the tube model describes chain reorientation of a homogeneous entangled melt.³⁹ In this respect, the reasonable match between model outcomes and SAOS data supports the notion of homogeneous blending of

the two iPP components (515A and UHMW). Nevertheless, it does not constitute a direct proof of homogeneity; rheology and tube modeling should be complemented by classical techniques like SAXS to provide independent evidence of homogeneity. The indications from rheology and tube modeling allows us to believe that blend miscibility is not a concern for this study. Finally, our earlier conclusion of no thermal degradation is reinforced since the GPC traces prior and after rheology are practically the same, and moreover, the SAOS data are reproduced adequately by using the experimental D 's.

Effect of Molten OXA3,6 on the Melt Properties of iPP-UHMWIPP Blends. A series of iPP-UHMWIPP-OXA3,6 blends were prepared by using the previously mentioned iPP grades (515A) and UHMWIPP. The content of UHMWIPP was varied (0, 5, 10, and 25 wt %), and a fixed OXA3,6 content of 0.5 wt % was added in all samples. Recall that, independent of UHMWIPP content (see Figures 1 and 8), OXA3,6 molecules persist as nanoclustered surfaces at the temperature of the measurement. The linear viscoelastic properties of the blends with and without OXA3,6 were measured by placing the samples in the rheometer at 220 °C. Dynamic oscillatory frequency sweeps were performed after 3 min at an isothermal temperature of 220 °C. Figure 5 presents the obtained data. There, symbols refer to samples with OXA3,6 while dashed lines to samples without OXA3,6.

Strikingly, in the presence of 0.5 wt % OXA3,6, the 5 wt % UHMWIPP blend displays very similar viscoelastic behavior in comparison to the pure iPP (0 wt %) (compare squares and upper triangles). These findings are striking because with the addition of UHMWIPP the complex viscosity and the $\tan \delta$ are expected to show pronounced deviation from the pure iPP. However, the presence of OXA3,6 appears to mitigate the anticipated pronounced deviation in 5 wt % UHMWIPP-iPP blend. This observation becomes more remarkable once the experiments are performed in the samples ranging between 0

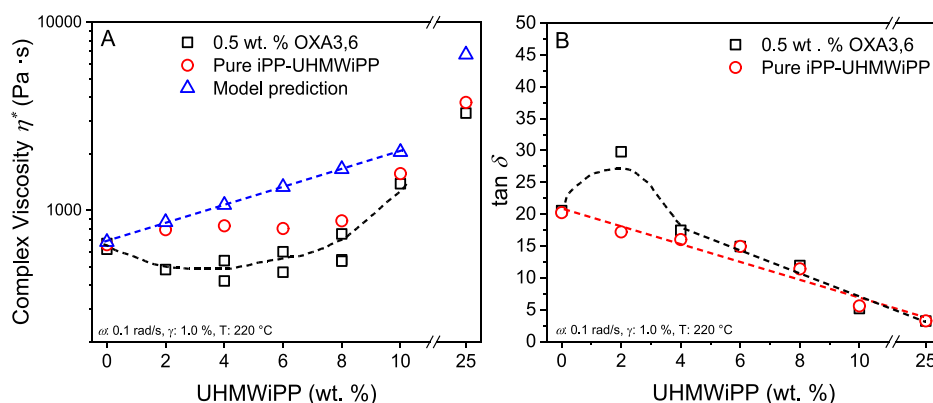


Figure 6. Effect of OXA3,6 in the viscoelastic response at various UHMWiPP content. (A) Complex viscosity at 0.1 rad/s for pure iPP-UHMWiPP blends (red), the blends having OXA3,6 (black), and model prediction for the pure blends (blue). (B) Loss tangent at 0.1 rad/s for pure blends (red) and OXA3,6 containing blends (black). For data clarity, trend lines are provided in the same color.

and 5 wt % of UHMWiPP blends (see Figure 6), the observations that we will discuss later. For the 0 and 5 wt % UHMWiPP samples, the values of G' and G'' tend to merge over almost the whole frequency range (Figure 5A,B). Additionally, if we analyze the frequency-dependent complex viscosity (Figure 5C), instead of an increase in viscosity, we observe a slight decrease (in the logarithmic scale) in the complex viscosity for the 5 wt % sample in comparison to the 0 wt %. This behavior is in complete agreement with previous observations, where the addition of 0.5 wt % of OXA3,6 led to a decrease in viscosity in an iPP melt.⁴⁰ Finally, when analyzing the loss factor (Figure 5D) of the 5 wt % UHMWiPP blend, we can observe a pronounced increase in $\tan \delta$ with decreasing frequency. This observation is similar to the blend having 0 wt % UHMWiPP and deviates from the samples having 10 and 25 wt % of UHMWiPP. To recall, the contributions of long chains are likely to be more pronounced at the low frequencies and are characterized by an increase in the elasticity of the blend, i.e., decrease in $\tan \delta$. These results strongly suggest that in the 5 wt % sample OXA3,6 can selectively speed up the reorientation process of the long chains, i.e., the high- M_w tail of the 515A chains and the UHMWiPP chains; thus, the contribution of the long chains is not as pronounced as anticipated.

It is noteworthy that for all the samples containing OXA3,6 values of η^* are lower in comparison to the samples without OXA3,6 (compare symbols and dashed lines in Figure 5C). Furthermore, we observe that the suppression effect is less evident for the pure 515A grade. Recall that the 515A grade has a relatively low average M_w ($= 230$ kg/mol) and a very broad dispersity ($\bar{D} = 7.3$). In our two previous studies the iPP average molecular weights were larger (310 and 430 kg/mol) and the distributions were narrower (3.4 and 4.3, respectively). There, for the same OXA3,6 concentration (0.5 wt %) and temperature (220 °C), the viscosity suppression was considerably larger than the one observed here for the 515A grade (see Figure 3 of ref 21, for example). Therefore, even for the non-UHMW materials, it appears that systems with longer chains experience more profound viscosity suppression. Thus, it could be concluded that the presence of an UHMWiPP component in the current blends triggers the ability of the OXA3,6 nanoclusters to reduce the melt viscosity, presumably via accelerating the reptation process of the high molecular weight component. Notice that a similar decrease in viscosity has been reported for UHMWPE in the presence of solid fillers

such as graphene oxide nanosheets (GON) and single-wall carbon nanotubes (SCNTs).^{41,42}

To further investigate the OXA3,6 influence on the relaxation of the high molecular weight chains, an additional set of blends, having 2–8 wt % UHMWiPP with and without 0.5 wt % OXA3,6, was prepared. The concentration of UHMWiPP was varied from 2 to 8 wt % by using the same blending conditions as described earlier. The effect of OXA3,6 on the viscoelastic response of the material was evaluated at 220 °C and compared to samples without the nucleating agent. Anticipating the reorientation acceleration of the high- M_w chains to be more evident at low frequencies, we first focus on the lowest measured frequency, namely $\omega = 0.1$ rad/s. Figure 6A presents the complex viscosity values at this frequency as a function of UHMWiPP content. Figure 6B shows the corresponding $\tan \delta$ data. In both figures red circles refer to the blends without nucleating agent while black squares correspond to blends with OXA3,6. In Figure 6A, blue triangles represent TMA predictions for the OXA exclusive blends.

Excluding the 6 wt % data point, the measured η^* response of the pure blends exhibits a smooth increase up to 8 wt %. At higher UHMWiPP content the viscosity increases rapidly. The tube model predictions also exhibit two distinct regions of viscosity increase. Nevertheless, unlike the data, the first region extends up to 10 wt %; moreover, the η^* increase is steeper than that observed experimentally. We believe the reason for this deviation is twofold. First, the experimental 6 and 8 wt % data points likely underestimate the actual response of the blends; a sum of experimental errors (i.e., weighing, extrusion, and rheology) could have caused the content mismatch between the desired and the actual value (e.g., 5 wt % instead of 6 wt %) which might have contributed to this underestimation. Second, as the UHMWiPP content increases, the sensitivity of the model predictions on the ambiguously determined high- M_w tail of the UHMW component increases as well. Thus, with increasing UHMWiPP content, the tendency of the model to overpredict the experimental response increases (see section SI-4 for more details). In conclusion, we anticipate the onset of the second regime of viscosity increase to occur in the 8–10 wt % range, with the exact UHMWiPP wt % not being unambiguously determined.

In vast contrast with pure blends and model predictions, samples having OXA3,6 (black squares) appear to go through a minimum, the average value of which is 430 Pa·s at 6 wt %

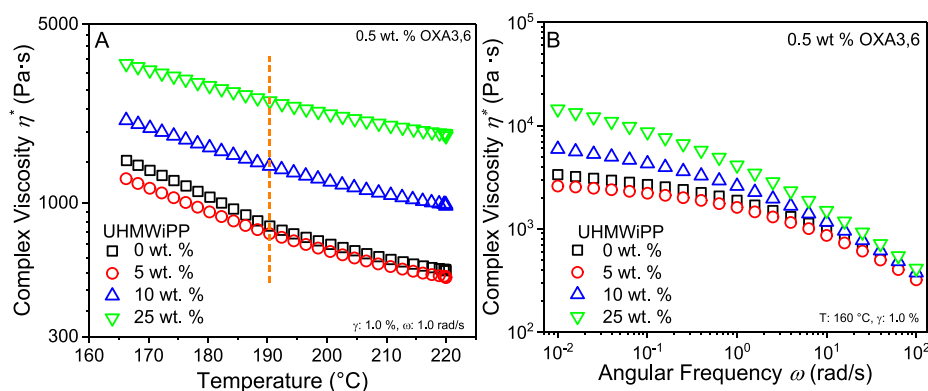


Figure 7. (A) Temperature-dependent complex viscosity of iPP–UHMWiPP–OXA3,6 blends upon cooling; the dotted line indicates the change in the slope. (B) Frequency-dependent complex viscosity of same materials at 160 °C after cooling.

and represents a decrease of nearly 40% in comparison to the blend without OXA3,6. Evidently, up to 6 wt % of UHMWiPP, the viscosity values of the samples having OXA 3,6 remain below the sample without OXA3,6 (621 Pa·s). After 6 wt % the viscosity values gradually approach those without the nucleating agent. Nevertheless, it is worth noticing that the samples having OXA3,6 displayed lower viscosity values over the whole range of UHMWiPP content hinting at the ability of OXA3,6 in enhancing chain reptation of the long chains in the blend. For fixed nucleating agent concentration, this ability tends to decrease with increasing UHMWiPP content. We will comment on this feature below.

Figure 6B illustrates the elastic effect of the UHMWiPP in the blends at the low-frequency (0.1 rad/s) region. Overall, a linear decrease in the $\tan \delta$ values is observed for the pure samples without OXA3,6 as a function of UHMWiPP content (red dotted line). As mentioned earlier, this is a strong indication that the UHMWiPP chains are “dissolved” in the iPP component during the blending process.³² In the case of OXA3,6 samples (dotted black curve), the elastic contribution is somehow lost as the UHMWiPP content decreases, with the $\tan \delta$ response being characterized by a sudden increase at 2 wt %. As the UHMWiPP content increases, the loss tangent values become similar to the samples without OXA3,6.

An explanation for the (apparent) diminishing ability of OXA3,6 to suppress viscosity, as UHMWiPP content increases, can be given as follows. When the UHMWiPP content exceeds 8–10 wt %, the UHMW chains self-entangle. This hypothesis agrees well with the observations for the pure blends and the corresponding model predictions. At low content, the UHMW chains form entanglements only with the (relatively) low- M_w chains of the 515A component. When UHMWiPP self-entanglements are formed, the mobility of the UHMW component significantly decreases. Such self-entanglements would counteract the ability of the OXA3,6 nanoclustered surfaces to align the chains and accelerate their relaxation. To confirm this explanation, longer measurements on the high wt % blends are required to rule out the possibility of sizable viscosity suppression in the plateau zone of η^* (recall that this ω regime has not been accessed; see Figure 5C). Even if this hypothesis is valid, considerable viscosity decrease in the terminal regime might be possible by increasing the OXA3,6 concentration (recall the OXA3,6 concentration is 0.5 wt % in all experiments).

The observed viscosity reduction at $\omega = 0.1$ rad/s does not necessarily mean that OXA3,6 facilitates processability of the

blends. This is because the applied strain is in the linear flow regime, and moreover industrial processing takes place at much larger rates (100–1000 s^{-1}). A direct way to assess the OXA effect under processing conditions would have been capillary measurements, though such experiments are often disputed because of the wall effect. (It is suggested that high molar mass chains form a layer near the wall facilitating flow of the low molar mass chains in the bulk.⁴³) An alternative way to assess the nucleating agent influence at fast deformation rates is to utilize the Cox–Merz rule.^{44,45} This rule is empirical, and it states that at $\omega = \dot{\gamma}$ the complex and steady shear viscosities are equal. Although we have not experimentally verified the applicability of the Cox–Merz rule to the current blends, we anticipate the rule to hold, at least for the low wt % UHMWiPP samples, as this is the case for polydisperse linear chains.⁴⁵ In this respect, we have plotted the complex viscosity as a function of UHMWiPP content, at $\omega = 100$ rad/s. This figure can be seen in section SI-4 (Figure SI-6A). The curves of Figure 6A are replotted as well to facilitate comparison. In addition, for both $\omega = 0.1$ rad/s and $\omega = 100$ rad/s, Figure SI-6B presents the viscosity ratio $\eta^*(\text{OXA})/\eta^*(\text{pure})$ as a function of UHMW concentration, where $\eta^*(\text{OXA})$ and $\eta^*(\text{pure})$ denote the complex viscosity values of the blends with and without OXA3,6, respectively. As evident from Figure SI-6, though moderately reduced, the ability of the nucleating agent to suppress viscosity is preserved even at fast rates. In particular, the $\eta^*(\text{OXA})/\eta^*(\text{pure})$ ratio at $\omega = 100$ rad/s exhibits the same qualitative behavior as the respective ratio at $\omega = 0.1$ rad/s, but in the 2–8 wt % regime the high-frequency ratio values are moderately larger than the low-frequency ratio values. These findings suggest that OXA3,6 has the ability to suppress viscosity even under processing conditions. This is also suggested by the SAXS measurements to be presented later in the paper.

Effect of Crystalline OXA3,6 on the Viscoelastic Properties of iPP–UHMWiPP Blends. To exclude the presence of large OXA3,6 aggregates (crystals) in the iPP–UHMWiPP melt, we evaluate the crystallization behavior of OXA3,6 under oscillatory dynamic conditions. We analyzed samples containing 0.5 wt % OXA3,6 with 0, 5, 10, and 25 wt % UHMWiPP. In the rheometer the blends were kept under isothermal conditions at 220 °C and subsequently cooled to 160 °C. Cooling of the samples was performed at 10 °C/min while applying a fixed strain and angular frequency of 1.0% and 10 rad/s, respectively. Figure 7 shows the temperature-dependent complex viscosity (A) and the frequency sweep

performed under isothermal conditions at 160 °C after the cooling process (B). From Figure 7A it is evident that the viscosity suppression effect, observed at 220 °C for sample 5 wt % (Figure 5C), persists upon cooling to 160 °C. This finding suggests that the OXA3,6 nanoclusters do not assemble to large structures (aggregates) under the applied cooling conditions and/or within the time scale of the temperature sweep. If this was not the case, several iPP segments of the same chains would have been absorbed on the same OXA3,6 particles leading to a viscosity increase as reported in our earlier studies.²¹ This finding is further supported by the measurements shown in Figure SI-7 where the viscoelastic response of the blend with OXA3,6 is below the comparative example blends without the nucleating agent. With the increasing UHMWIPP content, the decrease in viscosity appears to be less pronounced. This result is in line with our hypothesis that the OXA3,6 effect gradually diminishes with the increasing content of UHMWIPP in the blend due to the restricted mobility of the long chains. Measurements at very low frequencies that demand longer experimental time are desired to measure the terminal relaxation of the UHMWIPP chains. However, experimental challenges arising due to crystallization of the UHMWIPP at the relatively low experimental temperature (160 °C) cannot be ignored.⁴⁶

The crystallization onset of the OXA3,6 for blends having 0 and 5 wt % of UHMWIPP occurs at approximately 190 and 204 °C, respectively (Figure 8). This clearly illustrates that the increase in melt viscosity promotes the self-assembling process of the OXA3,6 molecules, retrospectively influencing the crystallization kinetics of the nucleating agent. Combined with the reduced chain mobility due to the temperature decrease, the reduced chain mobility at those temperatures manifests itself as a change in the curve slope (see dotted line in Figure 7A). As expected, at higher UHMWIPP content (10 and 25 wt %) the viscosity increases linearly upon cooling, and the effect of OXA3,6 crystallites is slightly less visible. Furthermore, analyzing samples 10 and 25 wt % of the pure materials (Figure SI-8), it is evident to notice the similarity in the curve shape. Nonetheless, viscosity values for the OXA3,6 containing samples remained slightly lower when compared to the iPP-UHMWIPP blend without OXA3,6 (Figure SI-7).

To gain insight into the crystallization of OXA3,6 in the blend, we evaluate the crystallization under quiescent conditions using an optical microscope equipped with polarizers in combination with a hot stage. The blends were analyzed following the same thermal protocol as in the rheometer (see above). OXA3,6 crystallization was analyzed visually, and the crystallization onset was determined by the starting change in birefringence using a 530 nm λ -wave plate. From Figure 8 it is evident that the OXA3,6 crystallization onset shifts to a higher temperature as the content of UHMWIPP is increased. This can be related to the relatively low mobility of OXA3,6 molecules at high UHMWIPP concentration. Low mobility is normally associated with poor dispersion and diffusion, which results in localized areas with concentrated OXA3,6. Upon cooling, the relatively high concentrated areas will promote the crystallization to larger OXA3,6 nanostructures. The previous result agrees with the experimental change of complex viscosity upon cooling (Figure 7A).

Crystallization Morphology and Mechanical Properties of the Blends in the Presence of OXA3,6. The nucleation efficiency of OXA3,6 for the polymer was evaluated

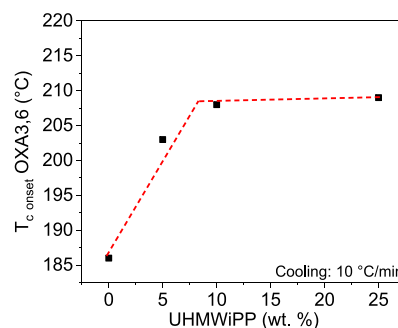


Figure 8. Crystallization onset of OXA3,6 as a function of UHMWIPP content in the four iPP–UHMWIPP blends; the $T_{c \text{ onset}}$ trend is indicated by the dotted line. The crystallization of OXA3,6 in the blend is followed by using optical microscopy.

by means of DSC, and the resulting cooling thermograms are presented in Figure 9. As expected, DSC results reveal an

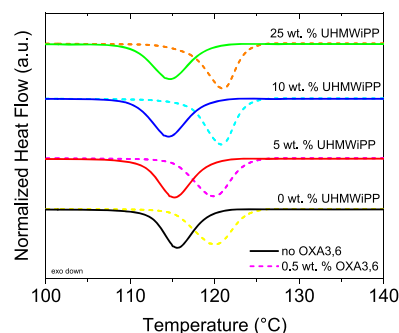


Figure 9. DSC first cooling thermograms of iPP–UHMWIPP and iPP–UHMWIPP–OXA3,6; the cooling rate was 10 °C/min.

increase in the crystallization temperature of roughly 5 °C in the presence of OXA3,6. Such an effect was independent of the UHMWIPP content, and the analyzed samples displayed the same crystallization onset ($T_c = 124$ °C). Nevertheless, a clear sharpening in the crystallization peak at high UHMWIPP concentration (10 and 25 wt %) is visible, which indicates the presence of an increased number of nuclei formed upon cooling. The latter was attributed to a larger number of OXA3,6 nanoparticles; this increases the surface area per volume ratio, thus enhancing its crystallization efficiency in the presence of UHMWIPP.

To note, the measured exothermic process by DSC, which demands the evolution of 3D structure, is less sensitive than the aggregation process prior to crystallization as assessed by rheology. Thus, in this case, rheological crystallization characterization is considered more sensitive than DSC.

The morphology evolution of the blends was obtained by SAXS measurements. Injection-molded samples were measured at room temperature, and the characteristic 2D-SAXS patterns are depicted in Figure 10. For other polymers, the presence of shear structures (shish-kebab) is promoted by addition of a higher molecular weight (viscosity) component.¹⁷ Generally, evolution of such structures is the result of the deformation of the high viscosity component, which promotes nucleation and enhances the crystallization. One may argue that the addition of OXA3,6 and its viscosity suppression effect would hinder the formation of shear-induced structures. However, in a previous study, we proved the opposite; the addition of OXA3,6 into an iPP matrix significantly increased

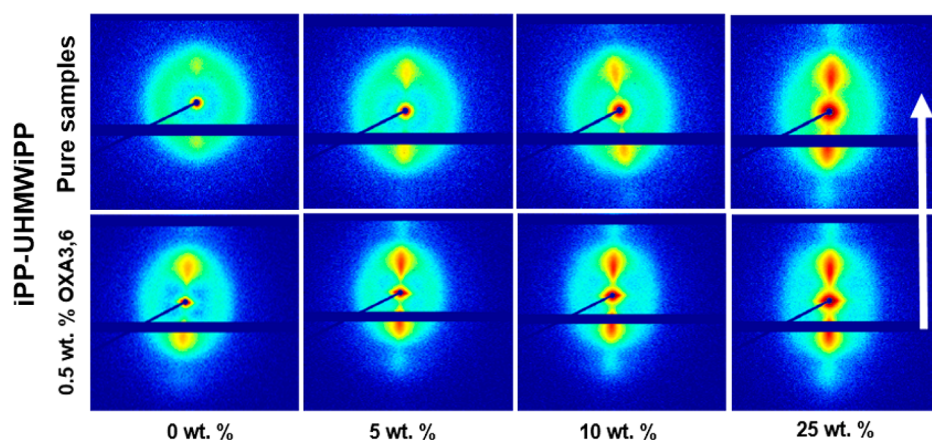


Figure 10. 2D-SAXS patterns of injection-molded iPP–UHMWIPP materials with and without OXA3,6. The arrow represents the flow direction during injection molding.

the formation of shish-kebab structures. Additionally, OXA3,6 also promoted the formation of a multilayer structure rather than the common skin-cored morphology present in the injection-molded samples.⁴⁰ From Figure 10 it is evident that all the samples display a characteristic isotropic halo attributed to isotropically crystallized iPP. In the case of the pure samples, the effect of shear during the injection molding process is evident from the characteristic shish-kebab signals (vertical lobes and equatorial signals). These characteristic features have been reported as skin-core morphology for iPP.⁴⁷ Furthermore, signal intensity is more pronounced as the content of UHMWIPP is increased (10 and 25 wt %). A similar effect has been observed in UHMWPE–HDPE blends and is attributed to a higher number of shish structures created by the alignment of the UHMWPE chains during processing.¹⁷ On the other hand, the addition of OXA3,6 leads to an overall increase in the SAXS intensity over the whole range of UHMWIPP concentrations. Interestingly, in the presence of OXA3,6 all samples displayed an increase in the equatorial signal, which represents the spacing between the shish structures. This suggests a higher density of such structures and an overall increase in the alignment. These results are in agreement with previous findings, where the presence of OXA3,6 increased the overall alignment between the skin and the sample core, in the injection-molded samples, thus increasing the equatorial intensity.⁴⁰ In light of the previous findings, it can be concluded that the viscosity suppression effect of OXA3,6 is accompanied by an enhanced shear-induced morphology for all the iPP–UHMWIPP blends.

To gain further insights into the morphology generated in the presence of OXA3,6, we evaluated the mechanical properties of the injection-molded samples under uniaxial tension (see Figure 11). In general, concerning the comparative blends, we observed an increase in the yield stress of roughly 3 MPa for all the blends having OXA3,6. This reinforcement effect is attributed to the presence of oriented structures along the flow direction. These results agree with the increase in the intensity of the SAXS patterns discussed earlier. In addition to this, Young's modulus (E) of the samples remained somehow constant and independent of OXA3,6 concentration. Finally, a considerable decrease in the strain at break was observed for all the samples containing OXA3,6 (see Table 1). Overall, the effect of OXA3,6 resulted in improved melt processability and the desired self-reinforcement effect.

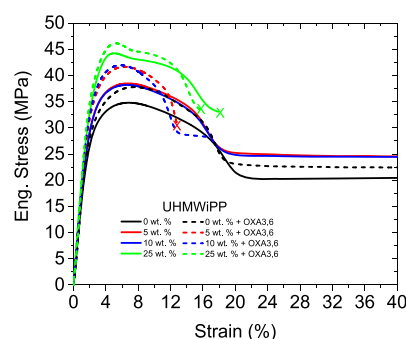


Figure 11. Effect of OXA3,6 in the strain–stress curves at room temperature for different iPP–UHMWIPP samples. The presence of OXA3,6 increases the yield point and lowers strain at break, while maintaining the tensile modulus. This may be attributed to the localized alignment of chains in the presence of OXA3,6.

The self-reinforced materials displayed a considerable increase in the yield stress while maintaining the elastic response (Young's modulus), most likely the localized chain alignment and chain adsorption reduce the strain at break in the presence of OXA3,6.

CONCLUSIONS

This work aimed to evaluate the influence of oxalamide-based nucleating agent OXA3,6 on the viscoelastic and mechanical properties of iPP–UHMWIPP mixtures. In the samples without OXA3,6, as anticipated, the viscosity increases with the increasing concentration of UHMWIPP. Surprisingly, a drop in viscosity is observed over the whole range of blends having OXA3,6, when compared with the samples without OXA3,6. These findings were much pronounced in the blends having less than 6 wt % of UHMWIPP. Similar to our earlier studies, we attribute this viscosity drop to the enhanced reptation time of the long chains. A speculative mechanism for the enhanced reptation time is the partial alignment of chain segments mediated by adsorption/desorption events of UHMWIPP chain segments on OXA3,6 nanoparticles and the subsequent alignment (friction reduction) of these segments. Another possible explanation is that the alignment is induced by a shear amplification mechanism, i.e., the amplification of the local shear rate in the vicinity of the OXA3,6 nanosurfaces. In addition, the presence of OXA3,6 promoted the formation of shish structures, illustrated by the

Table 1. Average Mechanical Properties of Uniaxial Tensile Test for Different iPP–UHMWiPP with and without OXA3,6

UHMWiPP	average Young's modulus (GPa)	standard deviation (MPa)	average yield stress (MPa)	standard deviation (MPa)	average strain at break (%)	standard deviation (%)
0 wt %	1.4	16	34	0.2	449	13.0
0 wt % + OXA3,6	1.2	158	38	0.9	114	0.8
5 wt %	1.6	22	37	0.6	316	73.0
5 wt % + OXA3,6	1.6	922	41	1.0	15	0.1
10 wt %	1.7	81	39	2.0	155	125.0
10 wt % + OXA3,6	1.7	164	42	0.4	11	0.1
25 wt %	1.9	26	45	1.0	19	1.0
25 wt % + OXA3,6	1.7	346	47	0.9	15	0.3

increase in the equatorial scattering intensity of the SAXS patterns of the blends. These findings are further supported by the mechanical properties where the blends having OXA3,6 under uniaxial tension show an increase in the yield stress and a decrease in the strain to break, whereas the tensile modulus remains independent of the additive.

Additional studies are required to identify the molecular mechanism causing the viscosity suppression. For example, the self-assembly of the OXA3,6 molecules and their interaction with (relatively short) iPP chains could be investigated by molecular dynamics simulations. Such simulations could shed light on the exact molecular mechanism that causes the viscosity suppression in the linear flow regime. Moreover, measurements under constant, nonlinear shear flow could be performed to examine how the nucleating agent molecules affect the size and the width of the viscosity overshoot as well as the steady state response of the iPP melts. This kind of information could be correlated to the alignment state of the chains. Under fast shear, although edge fracture and other instabilities will prohibit such measurements on UHMW melts, commercial iPP grades of relatively low M_w could be studied with cone-partitioned-plate geometry. Capillary measurements may also provide more insight into the melt processability of these OXA3,6-containing iPP materials. From an application perspective, the use of high UHMWiPP contents in the blends of existing commercial grades has the potential to increase several properties. This in turn can make the fiber-reinforced polymer composites by using inorganic fibers (i.e., glass, carbon) unnecessary. Such composites are very difficult to recycle due to the need to separate the polymer matrix from the fibers. In contrast, the UHMWiPP–low molecular weight grade PP composite is made from 100% PP and therefore easy to recycle.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.1c02042>.

Thermal degradation of the sample (SI-1), melt miscibility of iPP–UHMWiPP blends (SI-2), modeling of the samples without OXA3,6 using the tube model (SI-3), effect of OXA3,6 on the melt properties of iPP–UHMWiPP blends (SI-4), effect of OXA3,6 crystallization on the viscoelastic properties of iPP–UHMWiPP blends (SI-5) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Sanjay Rastogi – Department of Biobased Materials, Maastricht University, 6167 RD Maastricht, The Netherlands; Division of Physical Sciences and Engineering, Department of Chemical Sciences, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia; orcid.org/0000-0002-7804-7349; Email: sanjay.rastogi@kaust.edu.sa

Authors

Ramiro Marroquin-Garcia – Department of Biobased Materials, Maastricht University, 6167 RD Maastricht, The Netherlands; orcid.org/0000-0003-2328-1178

Nils Leone – Department of Biobased Materials, Maastricht University, 6167 RD Maastricht, The Netherlands

Laurence G. D. Hawke – Department of Biobased Materials, Maastricht University, 6167 RD Maastricht, The Netherlands; Bio-and Soft Matter, Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

Dario Romano – Department of Biobased Materials, Maastricht University, 6167 RD Maastricht, The Netherlands; Division of Physical Sciences and Engineering, Department of Chemical Sciences, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia; orcid.org/0000-0001-7326-3037

Carolus H. R. M. Wilsens – Department of Biobased Materials, Maastricht University, 6167 RD Maastricht, The Netherlands; Sabic Technology & Innovation, STC Geleen, 6160 AL Geleen, The Netherlands; orcid.org/0000-0003-3063-9510

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.macromol.1c02042>

Notes

The authors declare no competing financial interest.

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