The Effect of Processing Conditions on the Rheological Properties of Blends of Ultra High Molecular Weight Polyethylene With High-Density Polyethylene

Krishnaroop Chaudhuri ⁽¹⁾,^{1,2} Suparna Poddar,¹ Harshawardhan Pol,^{1,2} Ashish Lele,¹ Ajit Mathur,³ Gandham S. Srinivasa Rao,³ Rakshavir Jasra³

¹Polymer Science and Engineering Division, CSIR - National Chemical Laboratory, Pune, 411008, India ²Academy of Scientific and Innovative Research (AcSIR), CSIR-HRDC Campus, Ghaziabad, 201 002, India ³Reliance Industries Ltd., Reliance Research and Development Center, Reliance Corporate Park, Navi Mumbai, 400701, India

Blends of high-density polyethylene (HDPE) with small amounts of ultra-high molecular weight polyethylene (UHMWPE) were prepared by melt mixing in a twin-screw microcompounder. Two types of UHMWPE differing in their states of chain entanglement were used. The blend composition, time of mixing, and rotation speed of the screws were varied. Rheological properties of the blends were studied in oscillatory shear and uniaxial elongational tests. Reduction in phase angle measured in dynamic shear rheology and increase in extensional strain hardening were found to be useful indicators for quantifying the extent of mixing of the two components. Although the disentangled UHMWPE showed reasonable mixing with HDPE during typical residence times of melt compounding operations, the entangled UHMWPE remained essentially undissolved. The extent of mixing increased with mixing time and screw speed. POLYM. ENG. SCI., 59:821-829, 2019. © 2018 Society of **Plastics Engineers**

INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) is well known for its superior mechanical and tribological properties and is used in ballistic protection, defense applications and medical devices [1–5]. The enhanced properties of UHMWPE arise from its molecular weight, which is of the order of 10^6 g/mol. The large chain lengths lead to a large number of entanglements per chain, thus creating a dense entanglement network resulting in very high elastic modulus. Recently, the feasibilities of employing UHMWPE as an additive in polymer blends have been explored to improve the properties of the blend [6–12]. In particular, UHMWPE has been mixed in varying quantities with highdensity polyethylene (HDPE) in order to improve the mechanical properties of the latter [13–18], which can be beneficial for various applications such as high strength pipes [19].

There is a large body of work dedicated to exploring various methods such as melt blending [13–15, 20–23], solution blending [4, 14, 16, 17, 24–26, 30–32], in-reactor blending [27–29], and

some unorthodox techniques [17, 30–32] which would give UHMWPE-HDPE blends of optimum mechanical properties. While the large chain length of UHMWPE is necessary to improve the properties of the blend, the same large chain length is also the biggest impediment in blending UHMWPE in HDPE. Being chemically identical, the two components should form a miscible blend at equilibrium. Thus, while no thermodynamic barrier exists for dissolving UHMWPE in HDPE, there are two kinetic barriers to achieving molecular mixing of the two components: (1) dispersion of molten droplets of UHMWPE in HDPE matrix, and (2) diffusion of UHMWPE chains into the HDPE matrix.

It is well known that dispersion of a minor polymeric component of high melt viscosity in a matrix polymer of low melt viscosity is difficult if the shear viscosity ratio of the minor component to the major component exceeds 3 [33–35]. For typical commercial UHMWPE and HDPE of molecular weights $M_{\rm w}\sim5 \times 10^6$ and $M_{\rm w}\sim5 \times 10^4$ g/mol, respectively, the viscosity ratio can be estimated to be $\frac{\eta_{\rm UHMWPE}}{\eta_{\rm HDPE}} \sim \left(\frac{M_{\rm UHMWPE}}{M_{\rm HDPE}}\right)^{3.4} \sim 6.3 \times 10^6$, where the scaling of 3.4 is based on the classical reptation models developed by de Gennes [36], Doi and Edwards [37], and Doi [38]. Because of such high viscosity ratio, dispersing molten UHMWPE droplets in HDPE melt presents a significant challenge.

Dissolution of UHMWPE into HDPE will require diffusion of the long chains from within a UHMWPE droplet to the surface, and from there out into the HDPE matrix. The time required for a UHMWPE chain to diffuse from within its droplet to the surface can be estimated using classical reptation theories [39]. Talebi et al. [40] have reported the reptation time of a UHMWPE of molecular weight $M_w \approx 2.8 \times 10^6$ g/mol to be $\tau_{rep} = 391$ s. From this value, the reptation time of a UHMWPE of $M_w \sim 5 \times 10^6$ g/mol can be estimated to be ~2807 s. The number of Kuhn monomers can be calculated as $N = M_w/M_0 = 33333$, where the molar mass of a PE Kuhn monomer is taken as $M_0=150$ g/mol [39]. So the center of mass diffusion coefficient can be estimated to be $D_{rep} \approx \frac{R^2}{\tau_{rep}} \approx \frac{(b\sqrt{N})^2}{\tau_{rep}} \approx 2.3 \times 10^{-17} m^2/s$, where the PE Kuhn

to be $D_{\text{rep}} \approx \frac{R^2}{\tau_{\text{rep}}} \approx (2.3 \times 10^{-17} \text{ m}^2/\text{s})$, where the PE Kuhn length is taken as b = 14 Å [39]. Thus for a chain to move a distance of the order of the radius of a UHMWPE particle, say $R_p =$ 1 µm, the time taken will be $t = \frac{R_p^2}{D_{\text{rep}}} \approx 12$ h. Clearly, this is much longer than time scales available for mixing in typical industrial melt compounders. The above estimate is however applicable for quiescent mixing. Ranade and Mashelkar [41] showed that

Correspondence to: K. Chaudhuri; e-mail: k.chaudhuri@ncl.res.in

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application of a convective field (usually manifested as shearing by the screws of a compounder) can lead to faster dissolution when intra-particle diffusion of polymer chains to the surface of the dispersed particle is faster than the disengagement of chains from the surface into the matrix [42, 43]. This would happen only when the dispersed particles are below a certain critical size (typically <1 μ m), which happens to be much smaller than what can be achieved during melt compounding. It is thus evident that complete dissolution of fully entangled UHMWPE droplets in HDPE is difficult to achieve over typical residence time available in a melt compounder. Evidence for this will be presented later in this article.

One plausible way to circumvent the problem of slow dissolution is to use a "disentangled" UHMWPE, which is a metastable state in which the long chains are not as entangled as in conventional UHMWPE [44, 45] and therefore could have lower melt viscosity and higher self-diffusion coefficient than entangled UHMWPE. Disentangled UHMWPE is synthesized using homogeneous [40, 46] or supported [47, 48] single site catalyst in dilute solution wherein individual growing chains crystallize at a rate faster than the rate of polymerization thereby avoiding entanglements until they precipitate out of solution [49, 50]. Disentangled UHMWPE is known to show improved processability [51-54] because of its lower elasticity and viscosity. These rheological properties can be expected to accelerate blending of disentangled UHMWPE in HDPE. Indeed one recent report shows that addition of disentangled UHMWPE to HDPE in a melt compounding process increases the storage and viscous moduli of the blends more than that of conventional entangled UHMWPE and HDPE blends [55]. There are however no reports so far on the effects of the compounding parameters on the efficacy of mixing of the two components.

In this study, we have investigated the effects of melt compounding parameters on the rheology of HDPE/disentangled UHMWPE blends. We use rheology as a tool to infer the extent of mixing in these blends. Indeed, none of the usual characterization methods for measuring the morphology of polymer blends such as microscopy and scattering can be easily applied to this blend, especially in the melt state, because of the identical chemical nature of the two components. On the other hand, melt rheology can be an exceptionally sensitive technique to infer the extent of mixing of the two species because of the strong dependence of rheological parameters such as relaxation spectrum on the molecular weight distribution of the blend. In this study, we have investigated the effects of mixing time, screw speed and content of disentangled UHMWPE on the linear viscoelastic and non-linear extensional rheology of the HDPE/disentangled UHMWPE blends.

EXPERIMENTAL DETAILS

Materials

The polyethylene species used in this study were HDPE (Relene 50MA180, MFI 18, $M_w = 8 \times 10^4$ g/mol), termed "HDPE", commercial UHMWPE (UHM2504, $M_w = 3.4 \times 10^6$ g/mol), termed "UHM", and disentangled UHMWPE ($M_w = 5 \times 10^6$ g/mol), termed "dPE". The dPE was synthesized as per procedures outlined in published patents [56–58]. The molecular weight distribution of HDPE was measured using a high temperature size exclusion chromatography (SEC) (Malvern Viscotek Model 430)

equipped with triple detector system of refractive index, viscosity and light scattering (Malvern Viscotek HT-GPC Module 350A). The molecular weights of the UHMWPE samples were too high to be measured accurately by SEC and hence were estimated from rheological data following the experimental protocols of Talebi et al. [40], who estimated the molecular weights of UHMWPE samples of high molecular weight using the method given by Mead [59].

Blending

The dPE was used in powder form as obtained from the reactor directly. The UHM sample was annealed under vacuum for 7 days at 190°C to ensure that it was nearly fully entangled. The sample was then ground under cryogenic conditions (Retsch CryoMill) into a fine powder. We will refer to this sample as the "ePE" sample. The HDPE pellets, which contained additive stabilizer package, were also cryo-ground into fine powder to facilitate mixing with dPE and ePE powders before melt compounding. Scanning electron microscopy on several specimens of the three powdered samples indicated that the particles were <2 µm in size. Additional quantity of antioxidant Irganox 1010 was added (7,000 ppm of total weight of blend) during the melt blending process to minimize oxidative degradation. dPE + HDPE, and ePE + HDPE powders were weighed, mixed and charged into the hopper of a twin-screw co-rotating 5 ml microcompounder (DSM MC5) having a recirculating channel. The dPE amount was varied (0, 0.1, 0.5, 1, 5, and 10% by weight), keeping the total dPE + HDPE mixture weight per batch equal to 4 g. Three different screw speeds (30, 150, and 300 rpm) were used and two different mixing times of 5 and 30 min were used. The total mixing time comprised charging and compounding, of which the charging time was <1 min. It may be noted that the mixing time of 5 min is of the same order as typical residence time in an industrial melt compounder. Thus it was of interest to see if dissolution of UHMWPE samples was possible in this residence time. The temperature of compounding was kept constant at 190°C and an inert atmosphere maintained inside the microcompounder by supply of nitrogen gas. Details of dPE blends and their corresponding nomenclature are given in Table 1. The ePE powder was blended with HDPE at 150 rpm for 5 min to prepare blends of compositions 0, 0.1, 0.2, 0.5, 1, and 10% by weight ePE. The details of these ePE blends and their corresponding nomenclature are given in Table 2. Pure dPE and ePE were not extruded because of limitations of maximum torque that can be imposed and maximum axial load that can be measured by the microcompounder. The blends, which emerge as strands from the microcompounder, were cut into small pieces and compressed using a hot press (Technosearch Instruments PF M15) at 190°C under a pressure of 2,000 psi for 1 min to prepare the following rheology specimens:

- Circular discs of 25-mm diameter and 1-mm thickness (for oscillatory rheology of HDPE–UHMWPE blends).
- 2. Rectangular plates of about 18-mm length × 10-mm width × 0.6-mm thickness (for extensional rheology of HDPE–dPE blends).

Additionally, ePE and dPE powders were compacted by hand at room temperature inside a 12-mm mold to form discs of \sim 1-mm thickness, out of which 8 mm discs were punched out. These were used for time sweep oscillatory shear tests.

TABLE 1. Details of processing conditions and nomenclature of the dPE + HDPE blends used in this article.

Name of sample	Wt % of dPE (D)	Wt % of HDPE	Speed of mixing (<i>r</i>) (rpm)	Time of mixing (<i>t</i>) (min)
0D_30r_5t	0	100	30	5
0D_150r_5t	0	100	150	5
0D_150r_30t	0	100	150	30
0D_300r_5t	0	100	300	5
0.1D_150r_5t	0.1	99.9	150	5
0.1D_150r_30t	0.1	99.9	150	30
0.5D_150r_5t	0.5	99.5	150	5
0.5D_150r_30t	0.5	99.5	150	30
1D_30r_5t	1	99	30	5
1D_30r_30t	1	99	30	30
1D_150r_5t	1	99	150	5
1D_150r_30t	1	99	150	30
1D_300r_5t	1	99	300	5
1D_300r_30t	1	99	300	30
5D_30r_5t	5	95	30	5
5D_150r_5t	5	95	150	5
5D_150r_30t	5	95	150	30
5D_300r_5t	5	95	300	5
10D_150r_5t	10	90	150	5
10D_150r_30t	10	90	150	30

TABLE 2. Details of processing conditions and nomenclature of the ePE + HDPE blends used in this article.

Name of sample	Wt % of ePE (E)	Wt % of HDPE	Speed of mixing (<i>r</i>) (rpm)	Time of mixing (<i>t</i>) (min)
0E_150r_5t	0	100	150	5
0.1E_150r_5t	0.1	99.9	150	5
0.2E_150r_5t	0.2	99.8	150	5
0.5E_150r_5t	0.5	99.5	150	5
1E_150r_5t	1	99	150	5
10E_150r_5t	10	90	150	5

Rheology

All rheological measurements were done using ARES G2 strain-controlled rheometer (TA Instruments). dPE and ePE discs were subjected to oscillatory time sweep test at 0.5% strain amplitude and 10 rad/s angular frequency to ascertain their states of entanglement. Aluminum parallel plates of 8-mm diameter were used and a normal force of 2 N was applied during the test in order to reduce wall slip experienced by the highly elastic UHMWPE samples. Both time sweeps were carried out at 190°C under nitrogen atmosphere.

The 25 mm discs of blends were subjected to small amplitude dynamic frequency sweeps. Samples were loaded between two 25-mm stainless steel parallel plates. The strain applied to the blends was 15%, which was well within the measured linear viscoelastic regime for the blends. The frequency range of testing was 0.1 to 100 rad/s. Rheological testing was done under nitrogen atmosphere at a temperature of 190° C. In order to prevent slipping of the samples, a small axial force of 0.1 N was constantly applied throughout testing.

Extensional rheometry was performed using the extensional viscosity fixture (EVF) attachment on the ARES G2 rheometer.

The temperature of testing was 137° C, which is just above the melting temperature of HDPE and UHMWPE, respectively. The fixture was first heated to the test temperature, and then the sample was attached onto the fixture. After the temperature had come back up to the set point, the samples were held at the test temperature for 4 min to ensure thermal equilibrium before starting the test. Extensional experiments were done at strain rates of 10, 3, 1, 0.3, 0.1, 0.03, and 0.01 s⁻¹, and the maximum Hencky strain to which samples were stretched was 3. The data generated were analyzed using the in-built Trios software (TA instruments).

RESULTS AND DISCUSSIONS

Dynamic Oscillatory Data

Figure 1 shows time evolution of normalized elastic modulus $\tilde{G}' = \frac{G'}{G_N^0}$ of dPE and ePE samples. Here, G_N^0 is the long time (plateau) modulus of the samples. It is clear that the initial states of dPE and ePE as measured from $\tilde{G}'(t=0)$ are very different. The much lower value of initial normalized elastic modulus of dPE confirms its disentangled state and the evolution of the modulus suggests its metastable nature. On the other hand, the higher value of initial modulus of ePE confirms its entangled nature and the smaller extent of evolution with time suggests that the ePE is closer to its equilibrium structure. For the dPE, the rise in \tilde{G}' occurs more rapidly in the initial 1 h, but it ultimately takes about 7 h to reach the equilibrium entangled state.

The storage modulus (G') and loss modulus (G") of the dPE/HDPE samples blended at 150 rpm for 5 min are plotted versus angular frequency (ω) in Fig. 2a and b respectively. It is observed that as the concentration of dPE increases in the blends, both G' and G" show an incremental trend. To emphasize the impact of long chains of dPE chains in HDPE blends, the tan δ values are plotted in Fig. 2c. Whereas the tan δ values tend to merge at high frequencies for all compositions, the low-frequency loss tangent values are observed to systematically decrease with increasing dPE concentration suggesting that the low-frequency elastic modulus increases to a greater extent than the loss



FIG. 1. Normalized time sweep data for entangled UHM (ePE) and disentangled dPE. Normalization done by $\tilde{G}' = \frac{G'}{G_N'}$ where G' is the storage modulus and G^0_N is the value of the constant storage modulus after equilibration. The dPE has a significant rise from 0.82 for about 4000 s, whereas the ePE has a short rise from 0.91. Inset: The same graph, on a semilog scale.



FIG. 2. SAOS data for dPE + HDPE blends for processing conditions of 150 rpm and 5 min, for all compositions. (a) Storage modulus (G') data (b) Loss modulus (G'') data (c) tan δ data for dPE + HDPE blends for all compositions, and also for pure dPE. (d) tan δ data for ePE + HDPE blends for compositions of 0, 0.1, 0.2, 0.5, 1, and 10% by weight ePE.

modulus. The increased elasticity of the blends is indicative of dissolution of dPE in HDPE under the blending conditions used during compounding. The dissolved dPE chains contribute relatively more at the lower frequencies because of their long relaxation time. The high frequency behavior is dominated by dynamics of shorter chain segments contributed predominantly by the matrix HDPE and also to smaller extent by the dissolved dPE chains. It may be noted that the decrease in tan δ in the lowfrequency range is not due to branching or crosslinking of polyethylene during the 5 min of compounding time. As mentioned earlier, a surplus amount of antioxidant was added to the blends during compounding to quench formation of free radicals. That branching or crosslinking does not happen in the 5 min compounding time is also supported by the results on ePE/HDPE blends compounded under identical conditions as will be seen in the following discussion.

Figure 2d shows tan δ versus frequency data for ePE/HDPE blends of varying compositions prepared at 150 rpm for 5 min of melt compounding. It can be seen that except for the blend containing the highest ePE composition (10%), there is no lowering of *tan* δ for the other blends compared with the 0% ePE data over the entire range of frequencies. In fact, a small increase in loss tangent is observed for some of the blends compared with 0% ePE in the lower frequency range. This is likely due to a small amount of molecular weight degradation of the blend due to the

compounding conditions. This data also rule out the likelihood of forming branched or cross-linked microstructure during compounding for either of the ePE/HDPE and dPE/HDPE blends. The 10% ePE sample shows some lowering of tan δ , albeit very less compared with the lowering of tan δ observed in the dPE blends.

It is evident that the ePE does not contribute to lowering the tan δ of the blend over the entire range of frequencies for any of the other compositions, which is in sharp contrast to the behavior of dPE. This suggests that the fully entangled ePE dissolves to a negligible extent in the HDPE matrix. Thus, linear viscoelasticity can be used to infer qualitatively the extent of dissolution of ultralong PE chains in the HDPE matrix; a lower value of tan δ indicating higher extent of dissolution of these chains. The difference between the extents of dissolution of ePE and dPE is interesting. As argued in the Introduction section, a particle of fully entangled UHMWPE is not expected to dissolve in HDPE due to difficulties in achieving fine dispersion and the long reptation times. This is indeed observed for the ePE/HDPE blends. In contrast, the ability of dPE to blend in HDPE is intriguing because it implies that the chain dynamics of dPE are fast enough to achieve dissolution within the compounding time of as low as 5 min. Moreover, the dissolution dynamics of dPE seems to be faster than the dynamics of self-entanglement, which would in fact hinder the diffusion of dPE chains into the matrix. As can be seen from Fig. 1, the selfentanglement kinetics of dPE occurs rapidly over the first 1 h and

then more slowly over 7 h. Thus, dPE chains diffuse and dissolve faster than entangling with themselves.

Next, we study the effect of mixing speed on the extent of dissolution of dPE in HDPE. For all mixing speeds, the loss tangent values of samples compounded for 5 min in the microcompounder are plotted in Fig. 3. For visual clarity, only blends having dPE concentrations of 0, 1, and 5% by weight are plotted. For the 0% dPE, the tan δ values are almost identical over the entire range of frequencies except in the low-frequency region where the tan δ increases in the order 300 > 150 > 30 rpm. This is likely due to a small amount of chain scission occurring in HDPE at the higher rpm. When 1% dPE is blended with HDPE, the effects of the rpm are clearly seen. The tan δ values of these blends decrease substantially as the mixing speed increases from 30 to 150 rpm. The same trend is also seen for the other dPE/HDPE blend compositions, and it indicates greater extent of dissolution of dPE in HDPE with increased screw speed. At higher mixing speed of 300 rpm the tan δ values do not appreciably decrease relative to 150 rpm for both 1 and 5% dPE containing blends. This suggests that the extent of dissolution does not increase greatly by increasing microcompounder screw speed beyond 150 rpm for the 5 min mixing time.

A plausible mechanism of dissolution of dPE in HDPE can be described as follows. dPE chains from within a molten dispersed particle diffuse to the surface where they form a layer of disentangled chains. Here they entangle with the matrix chains, which pull them away from the surface by convection thereby causing dissolution. At lower rpm, the overall dissolution rate is governed by convection. At higher rpm, the diffusion from within particle to its surface is the likely rate-controlling step.

Figure 4 exhibits the dependency of the extent of dissolution on the mixing time at constant screw speed of 150 rpm. Both blending times, viz. 5 and 30 min are studied for four blend compositions: 0, 0.1, 0.5, and 1% dPE. For the 0% dPE samples, the tan δ for both 5 and 30 min almost coincide, except in the lowfrequency region where the tan δ for 30 min compounding is slightly lower than that for 5 min compounding. This may be attributed to a small amount of branching or crosslinking caused by the prolonged shearing in the microcompounder for 30 min. Even the large amount of antioxidant added to the blend before compounding does not fully prevent the formation of non-linear chain microstructure during the prolonged compounding time.



FIG. 3. For all mixing speeds, tan δ values of those samples processed in 5 min are plotted. For visual clarity, only 0, 1, and 5% dPE by weight blends are represented.



FIG. 4. Keeping the mixing speed constant at 150 rpm, tan δ values of both 5 and 30-min blends are plotted. Inset: 5 and 10% dPE by weight blends are plotted separately.

Upon introduction of dPE (0.1, 0.5, and 1% by weight) in HDPE, the tan δ values for blends compounded for 30 min were always lower than those compounded for 5 min. The reduction of tan δ caused by blending dPE in HDPE is far higher than the reduction in tan δ caused by the enhanced mixing time in the compounder. This suggests greater extent of dissolution of dPE in HDPE with increasing mixing time. In other words, dPE dissolves only partially in HDPE during melt compounding.

Analyzing the data in Figs. 3 and 4, it can be seen that the sixfold increase in mixing time from 5 to 30 min led to a relatively weaker decrease in tan δ compared with that observed by a fivefold increase in the screw rotation speed from 30 to 150 rpm. For example, in the case of 1% dPE, the low-frequency tan δ value dropped by ~4 units as the mixing time was increased from 5 to 30 min keeping screw speed constant at 150 rpm, while in the same frequency range the tan δ values dropped by ~16 units as the mixing speed was incremented from 30 to 150 rpm keeping mixing time constant at 5 min. Thus, screw speed has a bigger influence on the dissolution dynamics of dPE in HDPE than the mixing time. Similar conclusions can be drawn if we examine the effect of mixing time on blends with higher concentration of dPE, viz. 5 and 10% by weight. We see that for a 5% dPE blend the drop in tan δ is even lower (~1 units) for an increase from 5 to 30 min. In contrast for the same blend the drop in tan δ was nearly 10 units when the screw rpm was increased from 30 to 150. This suggests the possibility of optimizing deformation rates and type (shear/extensional/transient) for achieving improved mixing of dPE in HDPE within mixing time of 5 min.

The aforementioned trends are summarized by the data presented in Fig. 5, where we have plotted $tan \delta$ for all the different combinations of blending 1% dPE in HDPE. Interestingly, similar extent of dissolution of dPE in HDPE can be obtained using [30 rpm, 30 min] compounding conditions and [150 rpm, 5 min] compounding conditions. No further benefit in extent of mixing is obtained by using [300 rpm, 5 min], while a small amount of further dissolution is seen by using [150 rpm, 30 min]. The tan δ values for [300 rpm, 30 min] are actually higher than [150 rpm, 30 min] for all frequencies because of the likelihood of shear induced degradation of chains at the high rpm as discussed earlier. All these observations indicate that dPE can be melt blended in HDPE during 5 min of mixing in a microcompounder at a screw



FIG. 5. For 1% dPE by weight blends, tan δ values of all combinations of mixing speed and residence time are plotted. The filled circle graph indicates the optimum processing conditions for the satisfactory blending of dPE and HDPE.

speed of 150 rpm so that partial but sufficient amount of dPE gets dissolved in HDPE to effect significant change in rheology.

Extensional Flow Data

Figure 6 is a combined plot of the extensional data for pure HDPE, and 1, 5, and 10% dPE in HDPE blends compounded at 150 rpm for 30 min. These data have been vertically shifted for clarity as mentioned in the figure caption. Although the elongation viscosity $\eta_E^+(t)$ of the blends was found to increase with increase in concentration of dPE in the blend, a more striking feature of the extensional data is the significant strain-hardening observed for the blends across almost all strain rates in comparison with HDPE which does not show any strain-hardening. The Hencky strain for the onset of hardening was found to decrease with increase in dPE content in the sample. Diop et al. [17] reported



FIG. 6. Extensional flow data for blends of 150 rpm and 30-min processing conditions. For blends, pure HDPE (\Diamond), 1% (\triangle), 5% (\bigcirc), and 10% dPE (\square) by weight data is plotted. The zero-shear viscosity value for HDPE is indicated by the dotted line. The values on each graph correspond to the Hencky strain rate (s⁻¹) applied. Temperature of EVF testing was 137°C, while the zero-shear viscosity has been measured at 190°C, which is why it has been shifted using TTS data. Some data have been smoothed out to reduce noise without much loss in information about trend. The onset of strain hardening in blends has been indicated by circles for each composition. For the sake of clarity, data for the blends have been vertically shifted by factors viz. pure HDPE (×1), dPE blends: 1% (×5), 5% (×10), and 10% (×50).

strain-hardening in UHMWPE + HDPE blends containing as high as 20% by weight of UHMWPE. Here we have found strain-hardening with as low as 1% dPE in HDPE.

For the blends prepared at [150 rpm, 5 min] the extensional flow data are plotted in Fig. 7. Here again, the blends show a clear strain-hardening tendency, although in this case the increase in elongation viscosity and the extent of strain-hardening across all samples is slightly less than that for blends prepared at [150 rpm, 30 min] (Fig. 6). As discussed earlier, the extent of dissolution of dPE in the [150 rpm, 30 min] blends was greater than for the [150 rpm, 5 min] blends, which results in the increased strain-hardening tendency for the former blends. To study the pattern of neck formation and breaking in the blends, the samples were photographed after the experiments were completed (Fig. 8).

We compared the extensional viscosity data with predictions of a discrete multi-mode Lodge model. Discrete relaxation spectra (DRS) were calculated from the dynamic oscillatory data using the method by Baumgartel and Winter [60]. Since the dynamic oscillatory experiments were performed at 190°C, the data were first shifted to 137°C using shift factors obtained from timetemperature superposition (TTS) experiments. Figure 9 shows the DRS for blends containing 0, 1, 5, and 10% dPE by weight prepared at [150 rpm, 5 min] and [150 rpm, 30 min]. The relaxation spectra for all blends tend to merge with the HDPE spectrum for smaller relaxation times because of the predominance of shorter chain segment dynamics. For longer relaxation times, as the dPE content increases the value of the relaxation mode G_k increases because of the increasing influence of the dissolved dPE which has slower relaxing modes. These relaxation spectra values were used in the discrete multi-mode Lodge model to predict the transient extensional viscosity data as per the equation below:

$$\eta_{e}^{+} = \sum_{k} \frac{3\eta_{k}}{(1-2\dot{\varepsilon}\lambda_{k})(1+\dot{\varepsilon}\lambda_{k})} - \sum_{k} \frac{2\eta_{k}}{(1-2\dot{\varepsilon}\lambda_{k})} e^{-\frac{(1-2\dot{\varepsilon}\lambda_{k})^{r}}{\lambda_{k}}} -\sum_{k} \frac{\eta_{k}}{(1+\dot{\varepsilon}\lambda_{k})} e^{\frac{-(1+\dot{\varepsilon}\lambda_{k})^{r}}{\lambda_{k}}}$$
(1)

Here $\eta_e^+(t)$ is the transient extensional viscosity, $\eta_k = G_k \lambda_k$, where G_k is the strength of *k*th relaxation mode and λ_k is the *k*th relaxation time as obtained from the DRS, and $\dot{\epsilon}$ is the strain rate applied in the experiment.



FIG. 7. Extensional flow data for blends of 150 rpm and 5-min processing conditions. Symbols and annotations same as Fig. 6.



FIG. 8. Photographs of necking and fracture patterns observed in samples of 5% dPE, blended for 5 min at 150 rpm. These are after extensional viscosity measurements were performed on them. The right images show necking without fracture in lower strain rates, while the left images show fracture before the entire Hencky strain has been covered by the stretching of the sample.



FIG. 9. DRS of dPE + HDPE blends blended at 150 rpm for (a) 5 min, (b) 30 min



FIG. 10. Lodge model fits along with extensional data for 5% dPE by weight blends of (a) 5-min blends at 150 rpm and (b) 30-min blends at 150 rpm.

The results from the Lodge model for both the 5 and 30 min samples for 5% dPE blended at 150 rpm are plotted along with the experimental data in Fig. 10. The model underpredicts extensional viscosity when compared with experimental data for the [150 rpm, 5 min] blends, although it shows reasonable agreement with data insofar as predicting the onset of strain hardening at higher stretch rates. For the [150 rpm, 30 min] blends, the model underpredicts the extensional viscosity more severely possibly because of the small amount of branching/crosslinking in these samples as suggested by the $tan\delta$ data. Another source of error could be the occurrence of considerable necking showed by the samples during extensional tests, as seen in the photographs (Fig. 8) of the 5% dPE [150 rpm, 5 min] samples after experiments were over. The low strain rate samples $(0.01, 0.03, 0.1 \text{ s}^{-1})$ exhibited considerable necking without fracture for the entire Hencky strain while at higher strain rates $(0.3-10 \text{ s}^{-1})$ the tendency to undergo necking decreased and the sample exhibited ductile fracture. Similar behavior was observed for the 5% dPE [150 rpm, 30 min] samples. In an extensional experiment, the calculation of extensional viscosity from measured tensile force is based on the assumption that the area of the sample decreases in proportion to the Hencky strain. However, upon necking, the strain is non-homogeneously distributed across the sample length. Differences between model predictions and experimental data could arise from such differences.

CONCLUSIONS

When compared with conventional methods involving sequential reactors and/or multiple catalysts, additivation of a high molar mass HDPE into a low molar mass HDPE by melt compounding is an alternative simpler method for manufacturing bimodal HDPE grades provided that the different components can be mixed at molecular level. In this work, we have investigated the dissolution of two types of UHMWPE, which differed in their states of entanglement, into a low molar mass HDPE matrix. We showed that melt rheology is a sensitive tool, and perhaps the only available tool, to detect dissolution of UHMWPE in HDPE. We argued that an entangled UHMWPE (ePE) would not dissolve in HDPE to any appreciable extent during typical melt compounding time scales of a few minutes due to the presence of long, entangled chains which lead to high melt viscosity and low selfdiffusion coefficient. This was validated with experimental data for ePE/HDPE blends. In contrast, we showed that a metastable disentangled UHMWPE (dPE) dissolves much more readily in HDPE within just 5 min of melt compounding. Using dynamic oscillatory rheology, we showed that an increase in the screw speed of the microcompounder led to better dissolution, whereas a large increase in residence time may not always be beneficial to the blending process. Our experiments suggest that at low screw rpm of the melt compounder, the overall rate of dissolution of dPE is controlled by the shear induced disengagement of chains from the surface of dispersed droplets whereas at higher screw rpm the rate of dissolution is controlled by diffusion of chains from within the droplet. The extensional strain hardening properties of these blends were tested using elongational rheometry. dPE/HDPE blends having as little as 1% dPE showed considerable strain hardening relative to pure HDPE. This could have interesting implications on melt processing of HDPE for applications in blow molding, extrusion film casting, film blowing, etc.

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