Entanglement dynamics in ultra-high molecular weight polyethylene as revealed by dielectric spectroscopy

Stavros X. Drakopoulos a,*, Georgios C. Psarras b, Giuseppe Forte a, Ignacio Martin-Fabiani a, Sara Ronca a

a Department of Materials, Loughborough University, Leicestershire, LE11 3TU, United Kingdom
b Smart Materials & Nanodielectrics Laboratory, Department of Materials Science, University of Patras, Patras, 26504, Hellas, Greece

A R T I C L E  I N F O
Article history:
Received 21 May 2018
Received in revised form 3 July 2018
Accepted 5 July 2018
Available online 6 July 2018
Keywords:
Ultra-high molecular weight polyethylene
Entanglement formation
Broadband dielectric spectroscopy

A B S T R A C T
With the help of Broadband Dielectric Spectroscopy, it has been possible to study the molecular dynamics of disentangled Ultra High Molecular Weight Polyethylene in a wide temperature and frequency range. Catalytic ashes of aluminum oxide act as dielectric probes, allowing the identification of five different processes: an α-process due to movements in the crystalline phase, two γ-processes attributed to amorphous chain portions close to the crystalline lamellae, and two β-processes that we have attributed to the disentangled and entangled amorphous phases. The entanglement formation has been followed by isothermal runs and a model that predicts the energy spent to form entanglements as a function of time and temperature is thereby proposed. This model allowed us to calculate the associated activation energy of the entanglement process.

Our work advances further the understanding of entanglement dynamics of ultra-high molecular weight polymers, and the proposed model could prove useful to describe other similar processes such as cross-linking.

© 2018 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is an engineering polymer that finds application in a wide range of fields such as biomedical products, soft ballistic protection and automotive parts [1–3]. UHMWPE differs from high density polyethylene (HDPE) in the average chain length, where it exhibits 10 to 100 times higher degree of polymerization, resulting in average molecular weights above 10^6 g/mol [4,5]. As a result, UHMWPE is difficult to process with conventional thermoplastic methods due to the extremely high viscosity of the highly entangled melt [5–7]. In order to overcome this issue, advances in the chemical synthesis of ultra-high molecular weight polyethylene with a reduced number of entanglements (dis-UHMWPE) have been made by means of metallocene and post-metallocene catalysts [8–11]. Dis-UHMWPE presents significantly improved processability when compared with entangled UHMWPE. Solid-state compression moulding and stretching result in highly oriented uni-axially or bi-axially stretched tapes and films, yielding high values of strength/modulus [12] and thermal conductivity [13].

However, this disentangled state is metastable above the melting temperature of the polymer (>140 °C). The dynamics of polymer chains in the melt have been a topic of intense discussion for a long time. The most accepted model was proposed by De Gennes, in which the polymer chain is trapped in a tube that constrains its movement [14]. The dominating mechanisms for chain dynamics in this model are: (i) Rouse motion at short times and (ii) chain progression by reptation along the tube, until it escapes. Chain reptation results in formation of new entanglements, progressively increasing the viscosity of the polymer. Hence, molten dis-UHMWPE should be considered a material in a non-equilibrium state, where the kinetics of entanglement formation are governed by several factors such as temperature, molecular weight, initial number of entanglements and presence of fillers.

Rheology has proved to be an effective method to follow the formation of entanglements in the melt, both in the presence or absence of fillers [12], [15,16]. It has been reported that the value of G’ of dis-UHMWPE approaches that of entangled UHMWPE once the equilibrium, fully-entangled state is reached [15–17].
Rheological studies have also allowed to determine molecular weights and their distributions of such polymers [15], [16–18].

One major limitation of the dynamic rheological analysis is the upper frequency limit since most rheometers can reach up to 100 Hz, although the use of piezoelectric resonators can extend the frequency range [19]. This limitation is crucial in the study of processes with very short relaxation times were higher frequencies are required.

Broadband dielectric spectroscopy (BDS) is a powerful experimental technique to investigate the interaction of electromagnetic waves with matter in the frequency range of 10^-6 to 10^12 Hz. Combining the broad frequency range with temperature variations, BDS can identify different processes in polymers and polymer composites such as polarization and conductivity phenomena, molecular dipolar fluctuations, thermal transitions, charge transport and interfacial polarization [20,21]. Dielectric and mechanical dynamic analysis can be employed in parallel to either analyze the same processes or explore new ones like interfacial polarization and DC conductivity. In some cases, processes arising from the same phenomena might appear in different relaxation times [22].

The dielectric data can be interpreted in terms of different equivalent formalism like dielectric permittivity, electric modulus, ac conductivity and impedance. A particular formalism might be needed in cases where parasitic effects like electrode polarization partially masks the specimen's dielectric behavior in the studied frequency and temperature range, or when relaxation processes cannot be fully discerned [20] [21], [23]. In addition, interfacial phenomena play a significant role on the properties of heterogeneous materials like polymer composites, semi-crystalline or polymer blends materials and they can also be analyzed using BDS [20], [23–25]. Some of these models have been proven useful in the analysis of mechanical and rheological data as well [26–28]. To identify and analyze the different processes which are superimposed in the experimental data, semi-empirical formulations that deviate from the ideal Debye behavior have been proposed over the years in both the form of dielectric permittivity and electric modulus. These models differentiate from each other in terms of the symmetry of the distribution of relaxation times [23], [29–31]. Relaxation molecular dynamics can be analyzed using Arrhenius and Vogel-Fulcher-Tammann (VFT) equations to elucidate the temperature dependence by providing the values of the activation energy and Vogel temperature (ideal glass-to-rubber temperature) respectively [20] [21], [32]. The dielectric behavior of unentangled and entangled polymers has been interpreted by both the Rouse model and the tube-reptation model respectively [33–35]. In addition, BDS has been a valuable tool to understand the evolution of cross-links in curing resins [36–38]. Considering the two, Nicolai et al. in their study of poly (oxypropylene) melts reported that the dynamics of covalent cross-link and entanglement formation are identical [39].

The dielectric response of polyethylene has been a subject of research for decades. Polyethylene (PE) presents a very small dipole moment because of its non-polar chemical structure. For this reason, obtaining a complete relaxation map is a challenge that is usually overcome by: (i) addition of probes with a permanent dipole moment [40], (ii) oxidation/chlorination to produce dielectrically active chains [41], or (iii) induced oxidation in the presence of metal oxide fillers [42]. The dielectric spectrum of PE is known to exhibit three main processes. The \( \alpha \)-process is related to molecular fluctuations in the crystalline part (namely \( \alpha-C \)-process). This nomenclature is contrary to the convention used for most polymers where the \( \alpha \) relaxation is associated with chain dynamics in the amorphous region. The \( \beta \)-process is assigned to the amorphous regions [42–45], and the \( \gamma \)-process is related with mobile parts of the amorphous chains in the vicinity of the crystalline lamellae. Often two, or even three types of \( \gamma \)-processes are observed but their assignment to specific molecular processes is not fully clear yet. [20], [46–48]. Moreover, the entanglement dynamics of UHMWPE have not been studied using dielectric spectroscopy to our knowledge.

In the present work, we have studied dis-UHMWPE samples by means of dielectric spectroscopy in a broad frequency and temperature range to further elucidate the process of entanglement formation. The dis-UHMWPE shows additional dielectric processes with respect to the entangled one that we have attributed to the presence of two distinctive amorphous phases with different degree of entanglement. By following the evolution of these phases with temperature, we have been able to formulate a model to estimate the activation energy of the entanglement formation process. Our work advances further in the understanding of entanglement dynamics of ultra-high molecular weight polymers and provides valuable information on how to control their processability. Moreover, the model that we propose might find application to describe the entanglement formation or crosslinking of other polymers.

2. Experimental

2.1. Chemical synthesis of dis-UHMWPE

Disentangled ultra-high molecular weight polyethylene was synthesized following the procedure described elsewhere [49,50]. Samples were taken from the reactor at different times, resulting in three molecular weights (Table 1). Quenching the polymerization reaction with methanol resulted in the presence of traces of catalytic ashes of aluminium oxide (\( \text{Al}_2 \text{O}_3 \)) derived from the methylaluminoxane (MAO, 10 wt% solution in toluene, Albermarle) co-catalyst used. As the amount of MAO is kept constant for all polymerizations, the content of \( \text{Al}_2 \text{O}_3 \) is lower for the longer polymerization times, where more polymer is produced. For sample PE_60 MG acidified methanol (methanol/37% wt HCl 95/5 v/v) was used instead, to completely avoid the formation of \( \text{Al}_2 \text{O}_3 \). For all the other samples the theoretical amount of \( \text{Al}_2 \text{O}_3 \), as calculated by the amount of co-catalyst used in the reaction, is presented in Table 1. It should be considered that this amount is calculated on the assumption that all the MAO added as co-catalyst does react during quenching to form \( \text{Al}_2 \text{O}_3 \), so it is in fact the maximum amount that can be realistically found in the sample. According to an older study of polyethylene – TiO\(_2\) dielectric probes systems, the addition of 1–10 wt% has a minor effect to molecular dynamics of the recorded relaxations but significantly increases the dielectric strength and tan\( \delta \) values. This supports our choice of PE 30, where the maximum amount of \( \text{Al}_2 \text{O}_3 \) is \( < 2.6 \text{ wt}\% \) [42].

2.2. Specimen manufacturing

Specimens for BDS were prepared by moulding the samples in Table 1 into discs of 34 mm in diameter with an average thickness of 1.4 mm. The moulding temperature was kept at 125 °C, below the melting temperature of UHMWPE, to ensure that the minimum amount of entanglements would form during the processing of the specimens. Fully sintered specimens were obtained by applying a load of 5 tonnes for 5 min, 10 tonnes for 10 min and 20 tonnes for 5 min. During cooling, between 1 and 5 tonnes were applied to achieve permanent deformation. The same protocol was followed to prepare the rheology samples having 1 mm thickness and 10.00 mm diameter.
2.3. Characterization techniques

Dielectric Spectroscopy. The dielectric response of the samples was investigated by means of BDS using an Alpha-N Frequency Response Analyzer. The voltage amplitude of the applied field was kept constant at 1 V and frequency varied from $10^3$ Hz to $4.29 \times 10^6$ Hz employing a two-parallel gold-plated electrode capacitor BDS-1200. The temperature was controlled employing a Novotherm system where the isothermal scans were performed in a temperature range of 50–160 °C, in steps of 10 °C. All the BDS parts were supplied by Novocontrol Technologies (Hundsagen, Germany). In order to determine the entanglement formation at 160 °C, 21 consecutive frequency sweep cycles were performed with a total duration of approximately 1 h. To analyze the temperature dependence of the entanglement formation in PE_30, more tests were performed at different temperatures using a new specimen for each temperature. The temperatures selected for these experiments were 80, 100, 120, 140, and 160 °C. The specimens were analyzed again for 21 frequency sweep cycles in the same frequency range as described above. To compare the dielectric and the rheological build-ups of PE_30, a dielectric test at 10 and 100 Hz at 160 °C for over 12 h (~45,000 s) was performed.

Rheological measurements. The oscillatory time sweep experiments were conducted at 160 °C by means of rheology employing a TA Instruments ARES-G2 for the same sample in two frequencies, 1 and 10 Hz at 0.5% strain located in the linear viscoelastic region for almost 100 h (~350,000 s).

3. Results & discussion

3.1. Effect of catalytic ashes on the dielectric strength of dis-UHMWPE

The dielectric response of all dis-UHMWPE samples is shown in Fig. 1, where the real and imaginary parts of dielectric permittivity at 160 °C are presented in Fig. 1a and b respectively. The complex dielectric permittivity $\varepsilon^*$ is defined as:

$$
\varepsilon^* = \varepsilon' - i\varepsilon''
$$

where, $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of dielectric permittivity respectively. Fig. 1a shows how the dielectric strength increases with increasing Al$_2$O$_3$ content. For samples PE_30 and PE_15, the values of dielectric permittivity in the low frequency range are due to the dielectric contribution of the catalytic ashes. This can be better appreciated in Fig. 1b, where the imaginary part of the dielectric permittivity is presented. The PE_60_MG sample exhibits a close to zero dielectric loss behavior in the middle and high frequency range were all the relaxation processes are located, thus confirming that the presence of dielectric probes is paramount to yield the UHMWPE dielectrically active, as discussed elsewhere for the case of PE [40–42]. However, this sample exhibits relatively higher values of losses combined with an increase in the real part of dielectric permittivity in the low frequency edge which could be ascribed to interfacial polarization between the crystalline and the amorphous phases of polyethylene. This effect seems to be less intense in the rest of the samples in the window of observation, since the whole process has moved to lower frequencies due to the increased heterogeneity from the presence of Al$_2$O$_3$ catalytic ashes. As the concentration of catalytic ashes increases, the dielectric loss values increase as well. It is interesting to note that the loss peak maximum tends to shift to lower frequencies with the increase of molecular weight, as bigger chains require more time to react to the applied electric field. To follow the formation of entanglements, we have decided to focus on sample PE_30. This sample balances a strong enough dielectric strength to perform dielectric studies with a concentration of catalytic ashes that is not expected to affect strongly the entanglement topology in the melt.
3.2. Connection between electric modulus and mechanical shear modulus

Dielectric data can be presented using different formalisms, such as electric modulus, dielectric permittivity, impedance and ac conductivity, and the choice mainly depends on the materials used and on the specific phenomena that are observed [21], [23].

The complex electric modulus $M^*$ is defined according to Equation (2):

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - i\varepsilon''} = \frac{\varepsilon' + i\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M + iM''$$

(2)

where $M'$ and $M''$ are the real and the imaginary parts of the electric modulus respectively, $\varepsilon^*$ is the complex permittivity and $\varepsilon'$ and $\varepsilon''$ are the corresponding real and imaginary parts, in analogy to the complex modulus defined for other types of dynamic measurements. In Fig. 2, the real part of electric modulus as a function of time at 160°C for PE_30 at 10 and 100 Hz is presented. For comparison, the real part of mechanical shear modulus $G'$ for the same sample at the same temperature at 1 and 10 Hz is presented in the inset of Fig. 2. An increase in elastic shear modulus $G'$ is observed as time proceeds due to the progressive increase of entanglements [51]:

$$G_N^0 = \frac{8\pi \rho RT}{M_e}$$

(3)

where $G_N^0$ is the plateau modulus at thermodynamic equilibrium state, $\rho$ is a numerical factor, $\rho$ is the density of the material at the absolute temperature $T$, $R$ is the gas constant and $M_e$ is the molecular weight between entanglements and it is inversely proportional to the entanglement density. This increase is in agreement with other studies in the literature [15–17]. As it can be appreciated, the same behavior is observed in the electrical modulus as well, due to the formation of entanglements, although the timescales involved appear to be faster. The formed entanglements restrict the motion of polar parts hindering their ability to be aligned with the field. Consequently, polarization and permittivity diminish approaching a constant value. Electric modulus being the inverse quantity of permittivity increases with time reaching a plateau. The different timescale reflects the disparity of the excited substances in the two techniques, i.e. masses and dipoles respectively as previously discussed by Pakula [22].

3.3. Dielectric spectra of dis-UHMWPE

In Fig. 3, we report the comparison between the imaginary part of dielectric permittivity (Fig. 3a) and electric modulus (Fig. 3b) as a function of frequency and temperature for the PE_30 specimen. The processes that can be found using the complex permittivity formalism are present at very similar frequencies and temperatures range in the electric modulus formalism. For a single process, the relationship between the peak frequencies in both formalisms can be written as:

$$f_{M,\text{max}} = \frac{\varepsilon_s}{\varepsilon_{\infty}} f_{\varepsilon,\text{max}}$$

(4)

where $f_{M,\text{max}}$ and $f_{\varepsilon,\text{max}}$ are the relaxation peak frequencies in the modulus and permittivity formalisms respectively while $\lim_{f \to 0} \varepsilon^* = \varepsilon_s$ and $\lim_{f \to \infty} \varepsilon^* = \varepsilon_{\infty}$. When the ratio of $\varepsilon_s/\varepsilon_{\infty}$ is relatively close to 1, the...
loss peak positions of dielectric permittivity and electric modulus are very similar. For this reason, using the dielectric permittivity or electric modulus formalisms for the analysis in our systems is equivalent. In the supplementary data in Figure SD1 a comparison between the imaginary parts of dielectric permittivity and electric modulus as a function of frequency varying the temperature are presented to highlight this similarity in a 2D representation.

To better discern sub-relaxation processes, the electric modulus formalism will be adopted from now on in this work. To analyze the different processes present in the PE$_{30}$ sample a deconvolution technique that employs frequency-dependent model functions, namely the Havriliak-Negami model function in its electric modulus formalism as developed by Tsangaris et al. [23] was used. Equation (5) provide the expressions for the real and imaginary part of electric modulus:

$$M_0 = M_\infty M_s \left[ \frac{(M_\infty - M_s) \cos \gamma \phi + (M_\infty - M_s)^2}{M_\infty^2 A^2 \gamma^2 + 2 A^\gamma (M_\infty - M_s) M_s \cos \gamma \phi + (M_\infty - M_s)^2} \right]$$ (5a)

$$M' = M_\infty M_s \left[ \frac{(M_\infty - M_s) \sin \gamma \phi A^\gamma}{M_\infty^2 A^2 \gamma^2 + 2 A^\gamma (M_\infty - M_s) M_s \cos \gamma \phi + (M_\infty - M_s)^2} \right]$$ (5b)

where:

$$A = \left[ 1 + 2 (\omega \tau)^\beta \sin \left( \frac{\pi (1 - \beta)}{2} \right) + (\omega \tau)^{2\beta} \right]^{1/2}$$ (5c)

$$\varphi = \arctan \left[ \frac{(\omega \tau)^\beta \cos \left( \frac{\pi (1 - \beta)}{2} \right)}{1 + (\omega \tau)^{2\beta} \sin \left( \frac{\pi (1 - \beta)}{2} \right)} \right]$$ (5d)

For $\beta = \gamma = 1$ the above relations reduce to the Debye function model for a single relaxation time, while for $\beta < 1$, $\gamma = 1$ and $\beta = 1$, $\gamma < 1$ the symmetrical Cole-Cole and asymmetrical Davidson-Cole model functions apply respectively. $M_\infty$ and $M_s$ are the reciprocal values of $\varepsilon_\infty$ and $\varepsilon_s$ respectively. To fit the experimental data in the entire temperature range, a total of six processes were required. The parameters used in the simulations are provided in the supplementary data Table SD1.

In Fig. 4 the imaginary part of electric modulus as a function of frequency for PE$_{30}$ is presented for 50°C (Fig. 4a), 90°C (Fig. 4b), 120°C (Fig. 4c) and 160°C (Fig. 4d). The points represent the experimental data while the interpolating lines are obtained from the computational model.
Interestingly, in the case of the disentangled regions, where the chains can move easier, the entangled amorphous will have longer relaxation times compared to the segmental relaxation of different molecular weight fractions expected to react differently to the electric field. We have observed that the two distinct amorphous regions already appear from 90°C, as a consequence of the application of the electric field. When simulating M' as a function of frequency, it was observed that the relaxation times for this process appear to remain constant between 140 and 160°C, instead of decreasing, which is expressed via shifting the frequency loss peak position to higher frequencies, as would be expected from the increased kinetic energy. According to the literature, this behavior is due to gradual melting of crystals of different dimensions [41]. The intensity of the process also diminishes with the increase of temperature, due to the progressive disappearance of the crystals, although it does not vanish completely, even at 160°C, suggesting the presence of residual crystals.

The β-process of polyethylene is attributed to the molecular fluctuations of the amorphous chain segments above the glass transition temperature [52]. In the case of dis-UHMWPE, we have observed two distinct processes that we have attributed to the two distinct amorphous regions present in this material, namely the entangled amorphous (β_ent-process) and the disentangled amorphous region (β_0-process). The presence of amorphous components with different dynamics in disentangled UHMWPE has been previously observed via 1H NMR T2 relaxometry. Rastogi et al. [53] have reported that, on heating disentangled UHMWPE above 13°C, between a crystalline parts of the polymer melt, and two distinct amorphous components with different mobility can be identified by the presence of two different T2 times. With the help of BDS we have observed that the two distinct amorphous regions already coexist at temperatures below the melting. The two regions are expected to react differently to the electric field, as chains in the entangled amorphous will have longer relaxation times compared to the disentangled regions, where the chains can move easier. Interestingly, in the case of the β_0-process, the relaxation times appear to remain constant when entering the melt state similarly to what happens to the α-process: we ascribe this effect to the progressive melting of the crystalline regions resulting into a higher density of entanglement formation in both the initially disentangled amorphous and the molten crystals. In the case of the β_ent-process instead, the frequency maximum increases with temperature even during the melting, as further entanglement formation is expected to happen in these regions. Both processes are described by the symmetrical Cole-Cole function model, in analogy with the α-process described above.

The γ-process is attributed to the rigid/constrained amorphous parts that are close to the surface of the crystalline lamellae. A very broad asymmetrical distribution of relaxation times is expected for this process, according to the literature [46], [52]. Previous studies have identified in some cases two types of γ-processes, attributed to the segmental relaxation of different molecular weight fractions of the chains [46]. In our case it is possible to recognize two γ processes, both strongly asymmetrical (the asymmetrical γ parameter in γ1-process was found to be 0.658, while in the case of the γ2-process it varied from 0.190 to 0.260 in the considered temperature range), with γ1 showing slightly higher relaxation times than γ2. We attribute the different γ processes to the presence of chains in the close vicinity of a crystalline lamella that have either one or both ends attached to it. The process found in the lower end of the frequency window appears from 90°C and is enhanced especially above 130°C. This process is mainly attributed to polarization at the interface between the polymer chains and the ceramic catalytic ashes. Interfacial polarization arises due to the electrical heterogeneity between a material's constituents. It is possible a contributing interfacial polarization between the crystalline and amorphous regions to exist, however its contribution could not be significant, because of the small difference in dielectric permittivity and conductivity of the amorphous and crystalline parts of UHMWPE.

A pronounced interfacial polarization effect should result in high values of the real and imaginary part of permittivity, leading to low values of electric modulus because of Equation (2). We cannot exclude some contribution from DC conductivity, but this would be minimal due to the highly insulating character of polyethylene. This process is only partially visible in the observation window chosen and is better described employing a Debye function model.

In Fig. 5 are reported the loss peak positions versus the reciprocal temperature for the processes described above, except for the interfacial polarisation. All five processes' frequency loss peak positions follow the Arrhenius equation expressed as:

$$f_{\text{max}} = f_0 e^{\left(\frac{\Delta H}{k_B T}\right)}$$

(6)

where $f_0$ is a pre-exponential factor, $E_A$ is the activation energy, $k_B$ the Boltzmann constant and $T$ the absolute temperature. Calculated values of the activation energy are given in Fig. 6. All the $R^2$ of the fittings can be found in the supplementary data in Table SD2. The activation energy for the α-process is in very good agreement with the literature values, as we estimated to be $E_A = 1.126$ eV against a reported value of 1.036 eV [52]. According to previous studies, the β-process temperature dependency also follows the Arrhenius equation (although a non-linear relation modelled by the Vogel-Fulcher-Tammann equation may be found for low molecular weight samples) with an estimated activation energy of $E_A = 2.280$ eV [42], [52]. In our case, we found that the temperature dependency of the two processes were $E_A = 0.722$ eV for the β_ent and $E_A = 1.104$ eV for the β_0-process. The higher activation energy of the disentangled amorphous regions might arise from the higher concentration of chains compared to the entangled regions. The γ-process is characterized by an activation energy of $E_A = 0.466$ eV according to the literature [52]. However, Kakudate et al., reported two γ-processes, γ1- and γ2-, with activation energies of 0.997 and 0.564 eV respectively [47]. For the same γ-processes our analysis found values of 0.838 and 0.444 eV. The γ1- process is characterized by both larger relaxation times and higher activation energy comparing to the γ2-process and we attributed to either larger amorphous segments or more constrained chain ends close to the lamellae as described above.
3.4. Entanglement dynamics in UHMWPE

To gain a better insight on the mechanism of entanglement formation, isothermal runs at various temperatures of dis-UHMWPE were measured as a function of time. In Fig. 6 the imaginary part of electric modulus as a function of frequency varying the number of frequency sweep cycles at 160 °C for the PE_30 sample analysed before is presented. The points represent the experimental data, while the lines represent the superposition of the computational models. Inset shows the loss peak position of the \( \beta_{\text{dis}} \)-process with the progression of frequency sweep cycles.

\[ f_{\text{max}} = f_0 e^{-\frac{E_D}{k_B T_M}} \]  

(7a)

where \( f_0 \) is an exponential factor, \( T_M \) is the temperature during the isothermal measurement, \( E_D \) is the entanglement formation energy (energy spent by the polymer to entangle at the \( T_M \) temperature), \( n \) is the number of frequency sweeps and \( k_B \) is the Boltzmann constant. The higher the value of \( E_D \), the higher the number of entanglements forming at a constant temperature with the evolution of time.

In Fig. 7a the evolution of the frequency loss peak position of the computed \( \beta_{\text{dis}} \)-process as a function of the number of frequency sweep cycles at 80, 100, 120, 140 and 160 °C is presented and the value of the entanglement formation energy \( (E_D) \) is calculated. All the R\(^2\) of the fittings can be found in the supplementary data in Table SD4. A newly prepared specimen from the same sample was employed for each temperature, to ensure the same starting point.

To study the dynamics of entanglement formation a new model based on two equations is hereby proposed. The natural logarithmic loss peak position \( \ln f_{\text{max}} \) of the \( \beta_{\text{dis}} \)-process versus the number of frequency sweep cycles \( n \), is presented as an inset in Fig. 6 and it is linear. Therefore, the frequency loss peak position as a function of the frequency sweep cycles follows an Arrhenius type trend and so we propose a linear model of isothermal entanglement formation. From this equation, the amount of energy that is spent at constant temperature to trigger the transition can be calculated according to:

\[ f_{\text{max}} = f_0 e^{-\frac{E_D}{k_B T_M}} \]  

(7a)
was present in all measurements (minimum number of entanglements). By increasing the measurement temperature ($T_M$) we observed that the entanglement formation energy ($E_D$) is linearly increasing since there is more available energy for entanglements to form. Only in the case of 140 °C the value is deviating from the linear increase, but this should be expected since the crystalline parts are melting and most of the energy is spent for this transition. The values of the entanglement formation energy are found to be very low compared to the dynamics of the relaxation processes discussed in Fig. 5 and this is attributed to the fact that they are measured isothermally.

In Fig. 7b the values of the entanglement formation energy ($E_D$) are plotted as a function of the measurement temperature. The entanglement formation energy ($E_D$) exhibits a linear behavior with temperature (the value at 140 °C was excluded from the fitting for the reasons explained above). The linear relationship between the entanglement formation energy ($E_D$) and temperature can be described by:

$$E_D(T_M) = ST_M - E_A$$ (7b)

where $S$ is the slope in Fig. 7b. The minus symbol in front of the activation energy describes the energetic barrier. The intercept of the line is the energy barrier of the entanglement formation, calculated to be $E_A = 13.480$ meV. The limit temperature at which $E_D = 0$ where the formation of entanglements is energetically favourable, was found to be $T_0(E_0 = 0) = 331$ K (58 °C) which according to previous studies from our group is close to the temperature where the thermal conductivity of an uni-axially stretched UHMWPE sample starts to decrease [55]. In addition, the slope ($S$) of the line was calculated to be $4.069 \times 10^{-2}$ meV/K which is in the same order of magnitude of the Boltzmann constant ($k_B = 8.617 \times 10^{-2}$ meV/K). According to De Gennes the energy $k_BT$ is a function of the molecular mass and the mobility of a single polymer chain following Equation (8) [56]:

$$k_BT = \frac{D_0N}{B}$$ (8)

where $D_0$ is the diffusion coefficient and is inversely proportional to the molecular mass, $B$ is the mobility of one monomer while $N$ is the polymerization index. The overall mobility of a single chain corresponds to the ratio $B/N$. It is reasonable to think that a deviation from Equation (8) could be expected in the presence of interchain interaction.

The temperature dependency of the entanglements formation as presented from our model would also explain the challenges that melt processing of dis-UHMWPE presents, which usually occurs at temperatures as high as 260 °C (533 K) [57]. According to Equation (7b), at 260 °C the entanglement formation energy equals $E_D = 9.5$ meV which is over twice the amount at 160 °C (Fig. 7b). In addition, the mechanical stirring coming from extrusion techniques would feed the melt with extra energy resulting to even faster entanglement formation. This is why a short residence time (30 min) in the melt processing of dis-UHMWPE is suggested even at those temperatures where re-entanglement according to rheology should take place in the range of hours [58].

4. Conclusions

The application of broadband dielectric spectroscopy (BDS) to disentangled UHMWPE has allowed us to further expand our understanding of both its solid and metastable melt states. The presence of Al$_2$O$_3$ catalytic ashes oxidizes some of the polymer chains rendering them dielectrically active. We have identified three main relaxation processes, two of which are composed of two sub-relaxations. One attributed to the crystalline part ($\chi_1$ process), a second one associated with the disentangled ($\beta_{dis}$) and entangled ($\beta_{ent}$) amorphous phase, and another to the constrained amorphous chains ($\gamma_1$ and $\gamma_2$). By following the evolution of the $\beta_{dis}$ process as a function of both time and temperature, we have been able to formulate a model to estimate the activation energy related to the entanglement formation process in UHMWPE ($E_A = 13.480$ meV), as well as the minimum temperature at which this process will start appearing (58 °C). We also introduce the entanglement formation energy ($E_D$) which is the remaining thermal energy after the subtraction of the activation energy. The $E_D$ is responsible for the amount of entanglements forming in a given temperature.

Our work advances further in the understanding of entanglement dynamics of ultra-high molecular weight polymers and provides valuable information on how to control their processability. Our linear model of isothermal entanglement formation can be proven useful to describe the dynamics of cross-linking or entanglement formation in other polymers.

Acknowledgement

This project has been funded by the Engineering and Physical Science Research Council (EPSRC), grant EP/K034405/1.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2018.07.021.

References

[1] S.A. Taylor, D.J. Carr, Post failure analysis of 0 degrees/90 degrees ultra high molecular weight polyethylene composite after ballistic testing, J. Microsc. 196 (1999) 240–256, https://doi.org/10.1046/j.1365-2818.1999.00632.x.
[2] S.M. Kurtz, O.K. Muratoglu, M. Evans, A.A. Edidin, Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty, Biomaterials 20 (1999) 1659–1688, https://doi.org/10.1016/S1359-6462(99)00053-8.
[3] G. Lewis, Properties of crosslinked ultra-high-molecular-weight polyethylene, Biomaterials 22 (2001) 371–401, https://doi.org/10.1016/S1359-6462(00)00195-2.
[4] J.M. Kelly, Ultra-high molecular weight polyethylene*, J. Macromol. Sci. Polym. Rev. 42 (2002) 355–371, https://doi.org/10.1081/MA-100006452.
[5] S. Ronca, G. Forte, H. Tjaden, Y. Yao, S. Rastogi, Tailoring molecular structure via nanoparticles for solvent-free processing of ultra-high molecular weight polyethylene composites, Polym. (United Kingdom) 53 (2012) 2897–2907, https://doi.org/10.1016/j.polymer.2012.04.031.
[6] R.W. Rendell, K.L. Ngai, G.B. McKenna, Molecular weight and concentration dependences of the terminal relaxation time and viscosity of entangled polymer solutions, Macromolecules 20 (1987) 2250–2256, https://doi.org/10.1021/ma00175a033.
[7] S. Padmanabhan, K.R. Sarma, S. Sharma, Synthesis of ultrahigh molecular weight polyethylene using traditional heterogeneous Ziegler–Natta catalyst systems, Ind. Eng. Chem. Res. 48 (2009) 4866–4871, https://doi.org/10.1021/ie802006v.
[8] P. Selg, H.H. Brintzinger, R.A. Andersen, I.T. Horváth, Coordination of CD to the alkaline earth metalloene ([Me5C5]2Ca), Angew Chem. Int. Ed. Engl. 34 (1995) 791–793, https://doi.org/10.1002/anie.199507911.
[9] V.C. Gibson, S.K. Spitzmesser, Advances in non-metalloene olefin polymerization catalysis, Chem. Rev. 103 (2003) 283–315, https://doi.org/10.1021/cr980461c.
[10] S. Rastogi, D.R. Lippits, G.W.M. Peters, R. Graf, Y. Yao, H.W. Spiess, Heterogeneity in polymer melts from melting of polymer crystals, Nat. Mater. 4 (2005) 635–641, https://doi.org/10.1038/nmat1437.
[11] D. Romano, E. Andablo-Reyes, S. Ronca, S. Rastogi, Aluminoxane co-catalysts for the activation of a bis phenoxime titanium (IV) catalyst in the synthesis of disentangled ultra-high molecular weight polyethylene, Polym. (United Kingdom) 74 (2015) 76–85, https://doi.org/10.1016/j.polymer.2015.07.039.
[12] S. Rastogi, Y. Yao, S. Ronca, J. Bos, J. Van Der Eem, Unprecedented high-modulus high-strength tapes and films of ultrahigh molecular weight polyethylene via solvent-free route, Macromolecules 44 (2011) 5558–5568, https://doi.org/10.1021/ma200687m.
[13] S. Ronca, T. Igarashi, G. Forte, S. Rastogi, Metallic-like thermal conductivity in a
lightweight insulator: solid-state processed ultra high molecular weight polyethylene tapes and films, Polym. (United Kingdom) 123 (2017) 203–210, https://doi.org/10.1039/c7py00733c.

[14] P.G. De Gennes, Reptation of a polymer chain in the presence of fixed obstacles, J. Chem. Phys. 55 (1971) 572–579, https://doi.org/10.1063/1.1675899.

[15] K. Liu, E.L. De Boer, Y. Yao, D. Romano, S. Ronca, S. Rastogi, Heterogeneous distribution of entanglements in a nonequilibrium polymer melt of UHMWPE: influence on crystallization without and with graphene oxide, Macromolecules 49 (2016) 7497–7505, https://doi.org/10.1021/acs.macromol.6b01173.

[16] K. Liu, S. Ronca, E. Andablo-Reyes, G. Forte, S. Rastogi, Unique rheological response of ultra high molecular weight polyethylene in the presence of reduced graphene oxide, Macromolecules 48 (2015) 131–139, https://doi.org/10.1021/ma507279y.

[17] D. Romano, N. Topis, J. Bos, S. Rastogi, Correlation between thermal and mechanical response of nascent semicrystalline UHMWPEs, Macromolecules 50 (2017) 2033–2042, https://doi.org/10.1021/acs.macromol.6b02339.

[18] K. Liu, E. Andablo-Reyes, N. Patil, D.H. Merino, S. Ronca, S. Rastogi, Influence of reduced graphene oxide on the rheological response and chain orientation on shear deformation of high density polyethylene, Polym. (United Kingdom) 87 (2016) 8–16, https://doi.org/10.1039/c6py01056c.

[19] L. Sánz, R. Vogt, J. Meier, D. Auh, E. Van Ruyembeke, C. Friedrich, Entanglement relaxation time of polyethylene melts from high-frequency rheometry in the mega-hertz range, J. Rheol. (N. Y. N. Y.) 61 (2017) 1023–1033, https://doi.org/10.1115/1.4998174.

[20] A. Schönhals, F. Kremer, Analysis of dielectric spectra, in: F. Kremer, A. Schönhals (Eds.), Broadband Dielectric Spectroscopy, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003, pp. 59–98, https://doi.org/10.1007/978-3-642-56120-7.

[21] G.C. Psarras, Conductivity and dielectric characterization of polymer nano-composites, in: S.C. Tjong, Y.-W. Mai (Eds.), Phys. Prop. Appl. Polym. Nano-composites, first ed., Elsevier, 2010, pp. 31–69, https://doi.org/10.1533/9780857090049.1.3.

[22] T. Pakula, Dielectric and mechanical spectroscopy — a comparison, in: F. Kremer, A. Schönhals (Eds.), Broadband Dielectric Spectroscopy, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003, pp. 597–623, https://doi.org/10.1007/978-3-642-56142-8.

[23] G.M. Tsangaris, G.C. Psarras, N. Kouloumbi, Electric modulus and interfacial influences on crystallization without and with graphene oxide, Macromolecules 37 (2004) 2460–2470, https://doi.org/10.1021/ma0303333.

[24] K. Liu, S. Ronca, E. Andablo-Reyes, G. Forte, S. Rastogi, Comparison of polymer dynamics between entanglements and covalent cross-links, Phys. Rev. Lett. 82 (1999) 863–866, https://doi.org/10.1103/PhysRevLett.82.863.

[25] O. Van Den Berg, W.G.F. Sengers, W.F. Jager, S.J. Picken, M. Wübbenhorst, Dielectric and fluorescent probes to investigate glass transition, melt, and crystallization in polyolefins, Macromolecules 37 (2004) 2460–2470, https://doi.org/10.1021/ma0303333.

[26] K. Schmidt-Rohr, H.W. Spiess, Chain diffusion between crystalline and amorphous regions in polyethylene detected by 2D exchange 13C NMR, Macromolecules 23 (1990) 5288–5293, https://doi.org/10.1021/ma00159a011.

[27] M. Kakiokata, T. Kudekate, T. Hideshima, Comparative study of dielectric, mechanical, and nuclear magnetic relaxations in linear polyethylene. II. Relaxation spectroscopy of the α, β, and γ loss bands with special emphasis on fine structure, J. Polym. Sci. B Polym. Phys. Ed. 23 (1985) 809–824.

[28] F. Audren, D. Ronarc’h, Determination of the chain segment lengths involved in γ relaxation of low-density polyethylene by thermostimulated depolarization measurements, J. Appl. Phys. 60 (1986) 946–954.

[29] T. Kakudate, M. Kakiokata, T. Hideshima, Comparative study of dielectric, mechanical, and nuclear magnetic relaxations of linear polyethylene. I. Broadline NMR investigation of the fine structure of the α and γ loss bands observed by dielectric and mechanical measurements, J. Polym. Sci. B Polym. Phys. Ed. 23 (1985) 787–808.

[30] Y. Ohita, H. Yasuda. The influence of short branches on the α, β and γ-relaxation processes of ultra-high-strength polyethylene fibers, J. Polym. Sci., Part B: Polym. Phys. Ed. 32 (1994) 2241–2249, https://doi.org/10.1002/pol.1994.1803221529.

[31] G. Forte, S. Ronca, Synthesis of disentangled ultra-high molecular weight polyethylene: influence of reaction medium on properties of final products, J. Polym. Sci. 2017 (2017), https://doi.org/10.1002/polb.21343.

[32] S. Ronca, G. Forte, H. Tjaden, S. Rastogi, Solvent-Free solid-state-processed Tapes of ultrahigh-molecular-weight polyethylene: influence of molar mass and molar mass distribution on the tensile properties, Ind. Eng. Chem. Res. 54 (2015) 7737–7738, https://doi.org/10.1021/acs.iecr.5b01469.

[33] J.D. Ferry, Viscoelastic Properties of Polymers, third ed., Wiley, New York, 1980.

[34] A. Schönhals, Molecular dynamics in polymer models systems, in: F. Kremer, A. Schönhals (Eds.), Broadband Dielectric Spectroscopy, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003, pp. 225–324, https://doi.org/10.1007/978-3-642-00900-X.

[35] S. Ronca, G. Forte, H. Tjaden, S. Rastogi, Solvent-Free solid-state-processed Tapes of ultra high-molecular-weight polyethylene: influence of molar mass and molar mass distribution on the tensile properties, Ind. Eng. Chem. Res. 54 (2015) 7737–7738, https://doi.org/10.1021/acs.iecr.5b01469.

[36] K. Schmidt-Rohr, H.W. Spiess, Chain diffusion between crystalline and amorphous regions in polyethylene detected by 2D exchange 13C NMR, Macromolecules 23 (1990) 5288–5293, https://doi.org/10.1021/ma00159a011.

[37] M. Kakiokata, T. Kudekate, T. Hideshima, Comparative study of dielectric, mechanical, and nuclear magnetic relaxations in linear polyethylene. I. Broadline NMR investigation of the fine structure of the α and γ loss bands observed by dielectric and mechanical measurements, J. Polym. Sci. B Polym. Phys. Ed. 23 (1985) 787–808.

[38] Y. Ohita, H. Yasuda. The influence of short branches on the α, β and γ-relaxation processes of ultra-high-strength polyethylene fibers, J. Polym. Sci., Part B: Polym. Phys. Ed. 32 (1994) 2241–2249, https://doi.org/10.1002/pol.1994.1803221529.

[39] G. Forte, S. Ronca, Synthesis of disentangled ultra-high molecular weight polyethylene: influence of reaction medium on properties of final products, J. Polym. Sci. 2017 (2017), https://doi.org/10.1002/polb.21343.

[40] S. Ronca, G. Forte, H. Tjaden, S. Rastogi, Solvent-Free solid-state-processed Tapes of ultrahigh-molecular-weight polyethylene: influence of molar mass and molar mass distribution on the tensile properties, Ind. Eng. Chem. Res. 54 (2015) 7737–7738, https://doi.org/10.1021/acs.iecr.5b01469.

[41] J.D. Ferry, Viscoelastic Properties of Polymers, third ed., Wiley, New York, 1980.