



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

ARTICLE INFO

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

ABSTRACT

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_c -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].

* Corresponding author.

E-mail address: s.drakopoulos@lboro.ac.uk (S.X. Drakopoulos).

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 where 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 formalisms: 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 α -process is related to molecular fluctuations in the crystalline part (namely α_c -process). This nomenclature is contrary to the convention used for most polymers where the α relaxation is associated with chain dynamics in the amorphous region. The β -process is assigned to the amorphous regions [42–45], and the γ -process is related with mobile parts of

the amorphous chains in the vicinity of the crystalline lamellae. Often two, or even three types of γ -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 cross-linking 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 (Al_2O_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 Al_2O_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 Al_2O_3 . For all the other samples the theoretical amount of Al_2O_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 Al_2O_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 Al_2O_3 is ≤ 2.6 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.

Download English Version:

<https://daneshyari.com/en/article/7818996>

Download Persian Version:

<https://daneshyari.com/article/7818996>

[Daneshyari.com](https://daneshyari.com)