Investigation of the extraction process in gel-spinning technology for ultrahigh-molecular-weight polyethylene fibers by low-field nuclear magnetic resonance

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ABSTRACT: A portable, low-field nuclear magnetic resonance scanner, the nuclear magnetic resonance mobile universal surface explorer, is introduced as a tool for investigating the extraction process of mineral oil in the gel-spinning technology of ultrahigh-molecular-weight polyethylene (UHMWPE) fibers. Factors affecting the extraction process were studied systematically; these included the UHMWPE type, extraction agent type, and concentration and ultrasound. We found that the extraction process could be described by a replacement–dilution dual-effect model. The extraction agent not only replaced and extracted the mineral oil but also considerably decreased the viscosity of mineral oil and thus enhanced the molecular motion and diffusion of mineral oil. Although chloroform had a smaller molecular size and lower boiling point, benzene and cyclohexane were found to exhibit more efficient extraction and dilution effects on mineral oil. The extraction efficiency could be characterized by the diffusion of mineral oil in the mineral oil/UHMWPE gel/deuterated extraction agent multicomponent systems during the extraction. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42018.

INTRODUCTION

Ultrahigh-molecular-weight polyethylene (UHMWPE) fibers display a low specific gravity and an extremely high stiffness and strength, which is about 10 times higher than that of steel fibers.[1,2] These excellent properties of the UHMWPE fibers have made them suitable for a wide field of applications, such as aviation, navigation/sailing, communications, sports, and military-grade reinforcements, for example, as armor plates, bullet-proof vests, and helmets. In addition, UHMWPE fibers have attracted much scientific interest in terms of composite material applications.[3] The UHMWPE virgin powder is hard to process directly into UHMWPE fibers because of its high melting point and highly entangled molecular structure. Processing methods include, among others,[4,5] solid-state extrusion,[6,7] gel-spinning ultradrawing,[8,9] hydrostatic extrusion, the drawing of single-crystal mats,[10] and swell drawing.

The only industrial manufacturing process is gel-spinning technology; it was invented by Smith and Lemstra in the late 1970s.[11–13] Nowadays, the gel-spinning technology process mainly consists of the following procedures.[4,13,14] First, typically 10 wt % UHMWPE and 90 wt % solvent are mixed, with either with decalin, as in Smith's original patent, or a less costly mineral oil. After the swelling and dispersion of the UHMWPE, the material is extruded with a screw-type mixer, and the fibers are shaped through a spinneret. This gel-like material is subsequently cooled, and the solvent is extracted by a second solvent with a low boiling point. Drying then removes this extraction agent, and the product is fed into a multistep drawing process.

During the entire sequence, a solvent of nearly 10 times the polymer weight is needed to disentangle the UHMWPE molecule, and consequently, even more extraction agent is required. The large amount of extraction agent leads to high cost and environmental pollution. Apart from these economic aspects,

the details of the extraction procedure play an important role in the UHMWPE fiber productivity and performance. Therefore, it is of considerable interest to investigate and optimize the extraction procedure and to even provide analytical methods during the production process.

The diffusion coefficient (D) is the key parameter for the investigation and optimization of the extraction procedure, which in essence is a mass-transfer process. In the literature, the traditional method used to obtain this quantity for an extraction process is a repeated series of weighing and drying cycles.[15–19] Fick's second law and solutions described in Crank[20] are used for the computation of D. However, the method is time-consuming, requiring a minimum of several days, and is subject to interpretation ambiguity because of the ill-defined and variable boundary conditions. Another weakness of the weighing method is that the value of D obtained is for the solvent–UHMWPE two-component systems without the extraction agent. Therefore, an alternative and more efficient method of determining the diffusion properties during extraction in the UHMWPE gel-spinning technology is of outstanding interest. Ideally, such a method should be applicable during the industrial process with little effort.

In general, diffusion processes in the polymers can also be measured by holographic techniques,[21,22] inverse gas chromatography,[23,24] and nuclear magnetic resonance (NMR)[25,26] apart from the conventional gravity weighing method.[27,28] The transport parameter obtained by the first three methods is the self-diffusion coefficient, whereas that determined by the weighing method is the mutual D. The two Ds are not identical but can be correlated.[29] The holographic approaches are commonly limited by the need for transparent solutions; on the other hand, the size of the UHMWPE fiber is too large to be coated in the column for inverse gas chromatography. NMR is a comparatively fast and appropriate tool for investigating the diffusion in polymer solutions or gels, not only for two-component systems but also for multicomponent systems to separate components either spectroscopically or with multiparameter fitting procedures. With minimal effort, the spin–lattice relaxation time (T_1) and spin–spin relaxation time (T_2) can also be obtained to provide information about the microscopic molecular motion of the solvent and to probe the polymer in a polymer network.[30] Although pulsed-field gradient NMR, frequently combined with high-magnetic field superconducting magnets, has become a standard in determining diffusion properties[31,32] in the laboratory, the possibility of providing online or offline quality studies during the manufacturing process is much facilitated by the more recent development of portable, simple low-magnetic field devices, such as the nuclear magnetic resonance mobile universal surface explorer (NMR-MOUSE). Its one-sided geometry and open access allows the investigation of samples at any stage of the production process.[33,34] At the same time, the contrast of relaxation times, in particular T_1, becomes larger toward lower magnetic fields and thus more sensitive to material properties.

In this study, we proposed the use of the NMR-MOUSE as a desktop tool for measuring the diffusion of mineral oil in a solvent/UHMWPE/deuterated extraction agent system during the

Table I. Characteristics of the UHMWPE Samples

Property	UHMWPE-1	UHMWPE-2	UHMWPE-3
Viscosity molecular weight[a]	3,230,000	4,680,000	6,010,000
Crystallinity (%)[b]	55.4	52.0	49.8

[a] Measured according to GB/T1632.3–2010 with a capillary viscometer.
[b] Determined with differential scanning calorimetry (PerkinElmer 7).

extraction process, and we supported these by relaxation time measurements. This multicomponent system bore a close resemblance to the real system used on an industrial scale. The extraction mechanism was investigated, and the factors affecting the diffusion and extraction efficiency, such as the UHMWPE type, extraction agent type, extraction agent concentration, and extraction duration, were studied.

EXPERIMENTAL

Preparation of the UHMWPE Gel
The UHMWPE gels were prepared by a gel-spinning method described in the literature.[13] Three types of commercial-grade UHMWPE (see Table I) were used in this study. A mineral oil (J&K Chemical Co., Shanghai, China; flash point = 220°C, density = 0.88 g/mL at 25°C) was used as a solvent. The mass ratio of UHMWPE to the solvent was 10:90. The obtained UHMWPE gel was cut into small pieces with uniform sizes for extraction and NMR measurements.

Extraction Process
The extraction processes were carried out with these steps. First, the UHMWPE gel was immersed in the extraction agent for a defined period of time, and then the free solvent was removed from the surface. Second, the sample was positioned on the NMR-MOUSE scanner to measure the NMR relaxation times and self-diffusion coefficients. Third, we repeated the extraction for a second period of time and then performed a further measurement cycle. In this way, it was possible to investigate the relaxation and diffusion properties of the mineral oil in the same UHMWPE gel after different extraction durations. The operating parameters used in the extraction experiments are presented as follows:

1. The extraction durations were 1.5 min for the first interval, 4.5 min for the second interval and 20 min for the third interval.
2. The extraction agent concentrations (i.e., liquid extraction agent-to-solid gel ratios) were 2, 5, and 10 mL/g.
3. The extraction agents were chloroform d ($CDCl_3$), benzene-d_6 (C_6D_6), and cyclohexane-d_{12} (C_6D_{12}). The deuterated extraction agents were chosen to eliminate interference from hydrogen protons.

NMR-MOUSE Measurements
The diffusion and relaxation NMR measurements were performed in the stray field of a single-sided NMR sensor, the profile NMR-MOUSE (Magritek GmbH, Germany) with a ^{1}H resonance frequency of 11.7 MHz, and a constant magnetic field gradient (G) of 11.5 T/m. The magnet and sample were kept at
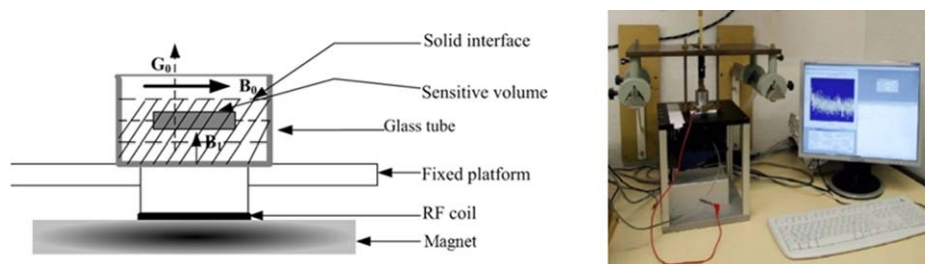
Figure 1. Scheme of the experimental setup, where B_0, B_1 and G_0 indicate the directions of the main magnetic field, the radio frequency (RF) field, and the B_0 field gradient respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

300 ± 0.5 K. The scheme of the experimental setup is shown in Figure 1.

The T_2 decays were obtained with a Carr–Purcell–Meiboom–Gill (CPMG) sequence, that is, a train of $180°$ pulses of a pulse duration of 2.8 μs, which was preceded by the preparation of a $90°$ pulse. The T_1 buildup curves were obtained with a saturation recovery ($90–180°$) pulse sequence followed by a CPMG train to increase the signal-to-noise ratio.

The diffusion decays were obtained with a constant-gradient stimulated spin-echo sequence, as shown in Figure 2, with the same parameters as used in the corresponding relaxation experiments; the diffusion time (Δ) was kept constant at 50 ms, and the pulse separation was varied between the first and the second $90°$ pulses (τ) up to a maximum of about 1 ms. This ensured that the signal decay was unaffected by transverse relaxation, which was found to be $T_2 > 16$ ms in all of the samples.

The relaxation times (T_2 and T_1) and D values were obtained by the fitting of the detected curves according to the following equations:

$$1 \propto \exp\left(-\frac{t}{T_2}\right) \quad (1)$$

$$1 \propto 1 - \exp\left(-\frac{t}{T_1}\right) \quad (2)$$

$$1 \propto \exp\left[-\gamma^2 G^2 \tau^2 \left(\Delta + \frac{2}{3\tau}\right)\right] \quad (3)$$

where I is the signal intensity as a function of the time variable, t is time, and γ is the gyromagnetic ratio. The pulse separation in the CPMG sequence was set as short as possible, that is, to 54 μs, to prevent an additional contribution due to diffusional signal decay. In all analyses, the signal dependence was fitted by mono-exponential and bi-exponential decay functions, and the results were interpreted by two components if the residuals
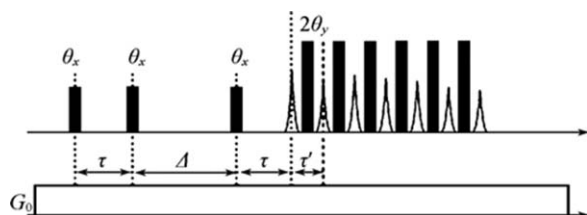
were found to be significantly smaller than in the monoexponential case. For the UHMWPE samples, a two-component fit was probably representative for a continuous distribution of Ds, which could be assigned to the heterogeneous nature of the gel. The values of the diffusion coefficients (large and small components of diffusion, D_1 and D_2) should, therefore, be understood in this way. In general, the ratio D_1/D_2 remained approximately constant; this was to the finding that the shape of the distribution function of Ds did not change significantly. With the experimental method applied in this study, a detailed inversion of the distribution function was not feasible.

RESULTS AND DISCUSSIONS

Component Analysis of Mineral Oil

The diffusional decay of the mineral oil as a bulk liquid and mineral oil in UHMWPE-1 before the extraction treatment was measured, and the normalized signal results are shown in Figure 3. The signal curves were tentatively fitted according to eq. (3) by mono-exponential and bi-exponential decays, and only a negligible difference in the fitting quality was found. Because of this small difference, we concluded that to a good approximation, (1) the mineral oil could be considered a pseudo-one-component system, although the mineral oil was, in fact, a mixture of hydrocarbons, and (2) the diffusion inside the polyethylene (PE) was suitably well approximated by a monoexponential behavior and, therefore, by a single self-diffusion coefficient.
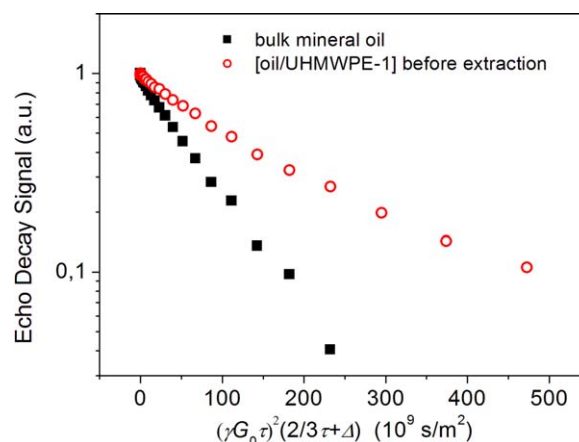

Figure 3. Normalized signal of the diffusion echo decay of mineral oil in the bulk and UHMWPE-1 before extraction, where G_0 is the magnetic field gradient. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. NMR-stimulated spin-echo sequence for measuring D, where θ_x and θ_y correspond to radio frequency flip angles theta and pulse phase x and y, respectively, and τ is the echo pulse separation.

Table II. *D* Values of Mineral Oil in Different Systems

No.	Components	Extraction duration (min)	T_1 (ms)	D or D_1 and D_2 (10^{-11} m²/s)	
1	Mineral oil/UHMWPE-1/CDCl$_3$	1.5	82.2	2.7	0.81
2	Mineral oil/UHMWPE-1/CDCl$_3$	6	140	4.1	0.96
3	Mineral oil/UHMWPE-1/CDCl$_3$	26	212	5.6	1.27
	Mineral oil (bulk)	—	34.1	1.69	
	Mineral oil/UHMWPE-1	—	30.7	0.78	

A comparison of the results of the mineral oil in bulk and in PE revealed that the relaxation times were reduced only minimally (from 34 to 31 ms in T_1 and from 20 to 16 ms in T_2, respectively) and that the D was reduced by about 50% from a bulk value of 1.69×10^{-11} to 0.78×10^{-11} m²/s (see Table II); this corresponded to an effective tortuosity of 2.2. This assumption required that the polymer matrix be considered as a porous medium with the solvent diffusing in between; this had to be an approximation because the concept of tortuosity is conventionally defined by the path length of a fluid molecule in a solid matrix. However, within this picture, for a mass ratio of 10:90, the tortuosity is expected to be closer to unity. We could, thus, expect that the reduction in D was at least partially a consequence of fast exchange with a fraction of molecules entering the solid polymer phase where the mobility was restricted as a function of the solvent molecule size.[24,31,33]

Extraction Mechanism
Replacement Effect of Extraction Agent. The diffusion and relaxation behavior of mineral oil in the mineral oil/UHMWPE-1/CDCl$_3$ three-component system was measured for different extraction durations, with CDCl$_3$ being the extraction agent, and a liquid-to-solid ratio of 2 mL/g. The extraction durations were 1.5 min for the first interval, 4.5 min for the second interval, and 20 min for the third interval.
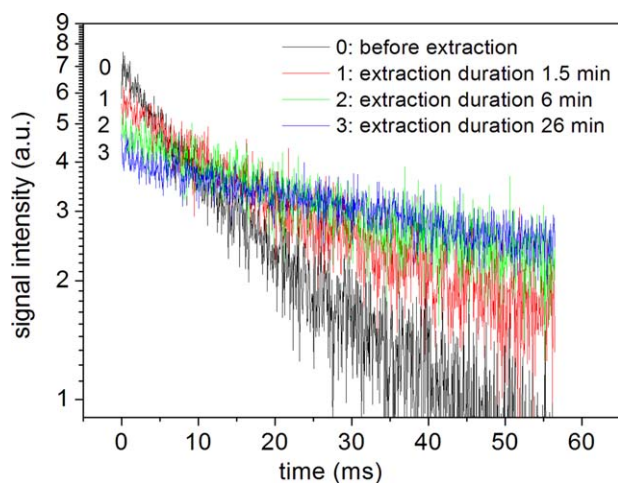
Figure 4 shows the signal decay of the CPMG sequence, from which the transverse relaxation time (T_2) was obtained. We observed that under identical experimental conditions, the initial signal intensity decreased with increasing extraction duration. The NMR signal was proportional to the number of hydrogen atoms, which in this system, corresponded to the concentration of mineral oil to a good approximation because long-chain PE contributed only negligibly to the signal because of its short relaxation time. We, thus, concluded that with increasing extraction duration, the amount of mineral oil remaining in the UHMWPE gel decreased and was replaced by CDCl$_3$.

Furthermore, the weight losses of the UHMWPE gel after different extraction durations were obtained by the traditional drying–weighing method; this included the heating of the sample after extraction in a vacuum oven for at least 24 h at 60°C to completely remove the extraction agent and the comparison of the weight with that before extraction. The weight losses were 24.0, 32.9, and 42.3%, respectively; this indicated that mineral oil was gradually replaced by the extraction agent.

Dilution Effect of the Extraction Agent. *Mineral oil/UHMWPE/CDCl$_3$ three-component system.* The original signal results were normalized for the purpose of directly comparing the diffusion behavior, as shown in Figure 5.
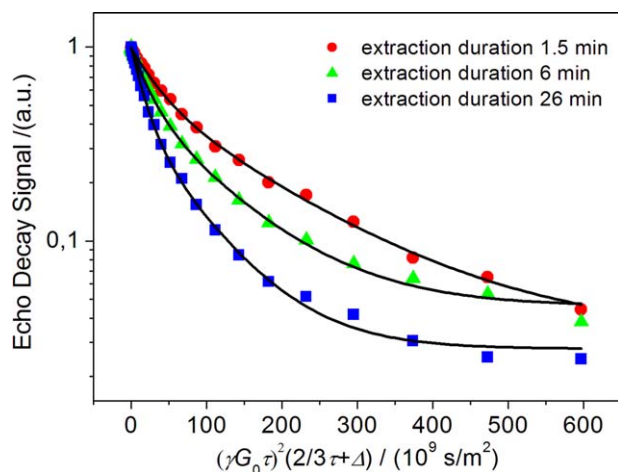

Figure 4. Original signals of the T_2 echo decays (mineral oil in the PE1 gel with a liquid-to-solid ratio of 2 mL/g and CDCl$_3$ as the extraction agent). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Normalized echo decays for the different extraction times, where G_0 is the magnetic field gradient. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
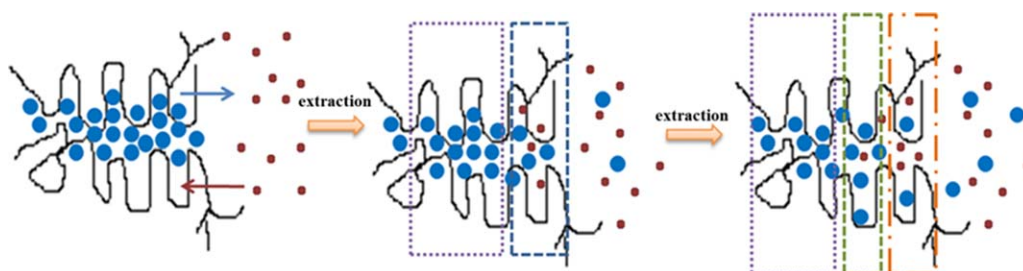
Figure 6. Schematic diagram of the distribution of the solvent and the extraction agent in the gel system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We noticed that the diffusion curves significantly deviated from the monoexponential decays and exhibited multiexponential decays. During the extraction, mineral oil and $CDCl_3$ could not reach the equilibrium in a short time and distribute nonuniformly in the UHMWPE gel, as schematically shown in Figure 6. Consequently, mineral oil was confined in several different domains and exhibited multiple diffusion behaviors.

Although the ternary exponential fitting gave slightly lower residuals than the biexponential fitting, to facilitate the analysis and because of the small dynamic range of the data, the diffusion curves were fitted by a biexponential model, to label D_1 and D_2, respectively. The relative proportion of D_1 increased slightly from 45 to 60% with increasing extraction duration. The larger D_1 represents the diffusion in the less confined domain, where one should keep in mind that in reality, a continuous distribution of Ds may exist. The average root mean square displacement within the experimental encoding time of 50 ms was about 1–2 μm; for any domain sizes much smaller than this value, an averaging to a single D would be observed. This would put a lower limit to the spatial heterogeneity of the sample. The corresponding fitted values are listed in Table II, together with those for the mineral oil bulk liquid and in the UHMWPE gel before extraction. The longitudinal relaxation times (T_1) were obtained from monoexponential fits and are shown for comparison.

In comparison to the two-component system before extraction, the diffusion of mineral oil was enhanced. This was only partially due to a slight swelling of the polymer matrix (i.e., reduction in tortuosity), but mostly it was determined by the presence and diluting effect of the extraction agent, $CDCl_3$. In the biexponential fit, this became most obvious in the higher component D_1, which was even larger than the bulk liquid D. The trend was confirmed by a similar observation of T_1, which was approximately proportional to D_1. This was expected because both D and the relaxation time were inversely proportional to the viscosity, and the reduction in the viscosity brought about by the presence of the extraction agent affected both quantities in the same manner. In a comparison of the three chosen extraction times, we found that the diffusion and relaxation were generally enhanced with growing extraction duration. On the one hand, mineral oil was gradually replaced by $CDCl_3$, whereas the available pore space in the UHMWPE gel was almost maintained in the presence of $CDCl_3$. Less solvent in the same space resulted in larger Ds.

On the other hand, an increase in the concentration of the extraction agent that diffused into the gel led to a more pronounced dilution effect.

Mineral oil/UHMWPE two-component system after extraction drying. The mineral oil/UHMWPE two-component system after extraction drying was obtained by the heating of the sample (after the third 20-min extraction) in the vacuum oven for at least 24 h at 60°C to completely remove the extraction agent chloroform. The diffusion signal echo decay of mineral oil is presented in Figure 7 and is compared with the result of the mineral oil/UHMWPE/$CDCl_3$ three-component system before drying.

After drying for more than 24 h, the mineral oil was uniformly distributed in the UHMWPE gel. Thus, the diffusion curve exhibited a nonexponential decay, which was, however, dominated (ca. 75%) by a slow component of about 3×10^{-12} m^2/s. This value was considerably lower than the one found for the two-component system before extraction (7.8×10^{-12} m^2/s). This was in accordance with a significant reduction in the free volume accessible for the mineral oil, which was not necessarily equivalent to a porosity change of identical magnitude. Rather, the remaining oil was redistributed in the matrix, whereas before extraction, oil was filling voids with a range of diameters in the UHMWPE gel. The remaining oil after extraction was preferentially located in small pores and, thus, possessed a lower mobility. This was possibly enhanced by an attractive
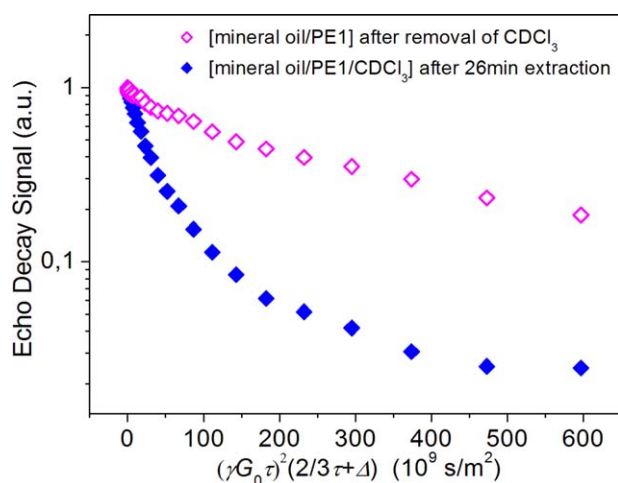

Figure 7. Normalized echo decays for the mineral oil in PE1 before and after the removal of $CDCl_3$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
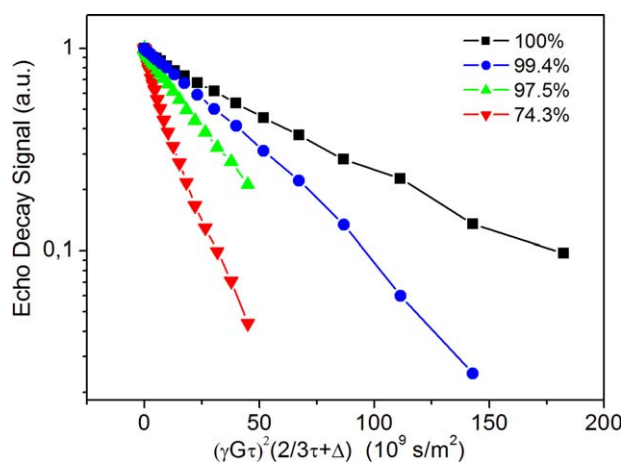
Figure 8. Normalized echo decays for the mineral oil and CDCl₃ mixtures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interaction with the matrix. This picture is analogous to the unsaturated porous media, where the wetting fluid preferentially filled the smallest pores and pore throats first.

Mineral oil/CDCl₃ liquid mixtures. To confirm the relation between D of the mineral oil and its dilution in CDCl3, samples with corresponding amounts of the latter were prepared. The mineral oil/chloroform d two-component systems were prepared by the mixture of the two liquids with the concentrations of mineral oil being 74.3, 97.5, and 99.4%, respectively. We noticed that the viscosity of mineral oil was significantly reduced when it was mixed with chloroform. The measured diffusion behaviors of the liquid mixtures were compared with that of the pure mineral oil, as presented in Figure 8 and Table III. In the homogeneous mixtures, the diffusional decay was monoexponential as expected.

According to the Einstein–Stokes equation

$$D = \frac{k_B T}{6\pi\eta R_h} \tag{4}$$

where k_B is the Boltzmann constant, η is the viscosity, R_h is the hydrodynamic radius of the molecular, and T is the temperature. D was inversely proportional to the viscosity. The diffusion of mineral oil was accelerated as a result of decreasing viscosity with increasing CDCl₃. The results further prove the dilution effect of the extraction agent and provide an estimate of the concentration of extraction agent at the three different extraction periods, but a direct comparison was not possible because

Table III. D Values of Mineral Oil in the Mineral Oil/CDCl₃ Mixtures

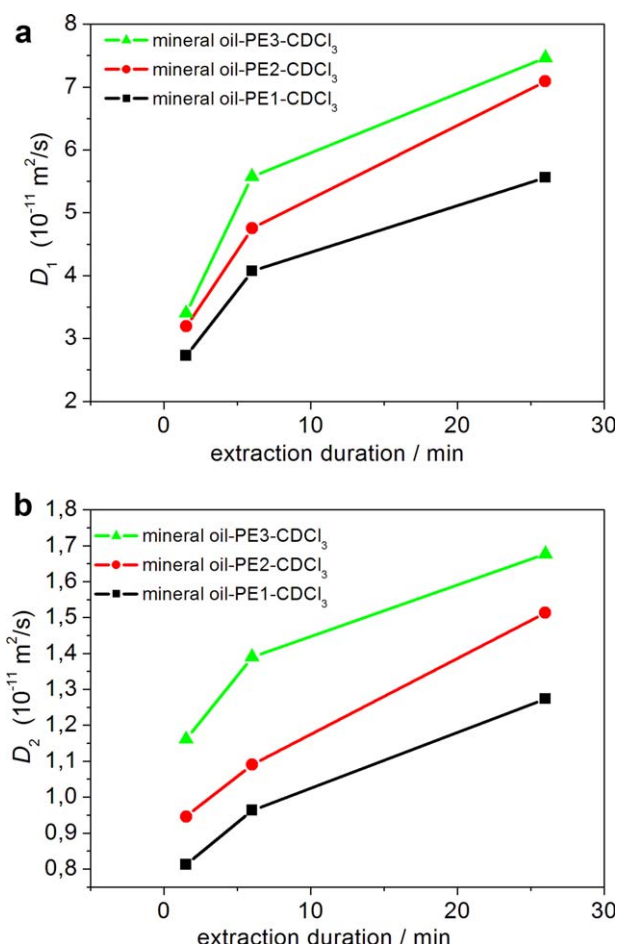| No.	Concentration of mineral oil (%)	D (10^{-11} m²/s)
1	74.3	10.8 (0.3)
2	97.5	3.85 (0.05)
3	99.4	2.20 (0.02)
4	100	1.69 (0.06)

Figure 9. Effect of the UHMWPE type on the diffusion of mineral oil during extraction (D_1 and D_2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the inhomogeneous nature of the gel (cf. Figure 6 and discussion).

Replacement–Dilution Dual Effect of the Extraction Agent. After the previous results were combined, we concluded that the extraction process could be described by a dual mechanism of replacement and dilution. On the one hand, the extraction agent and the solvent permeated and diffused mutually into or out of the UHMWPE under the concentration gradient during the extraction process. The solvent was replaced and extracted for the desolvation effect of the extraction agent; thus, the concentration of the solvent decreased, and that of the extraction agent increased. On the other hand, the diffused-in extraction agent decreased the viscosity of the solvent. This enhanced the molecular motion and diffusion of the solvent. This could be considered as the dilution effect, which as the results suggests, outweighed the effect of confinement due to the presence of the UHMWPE chains.

Factors Affecting the Extraction Process
The extraction duration, UHMWPE type, extraction agent type, and its concentration played important roles in the extraction process of the mineral oil/UHMWPE system and for the properties of the UHMWPE fibers obtained with this process.
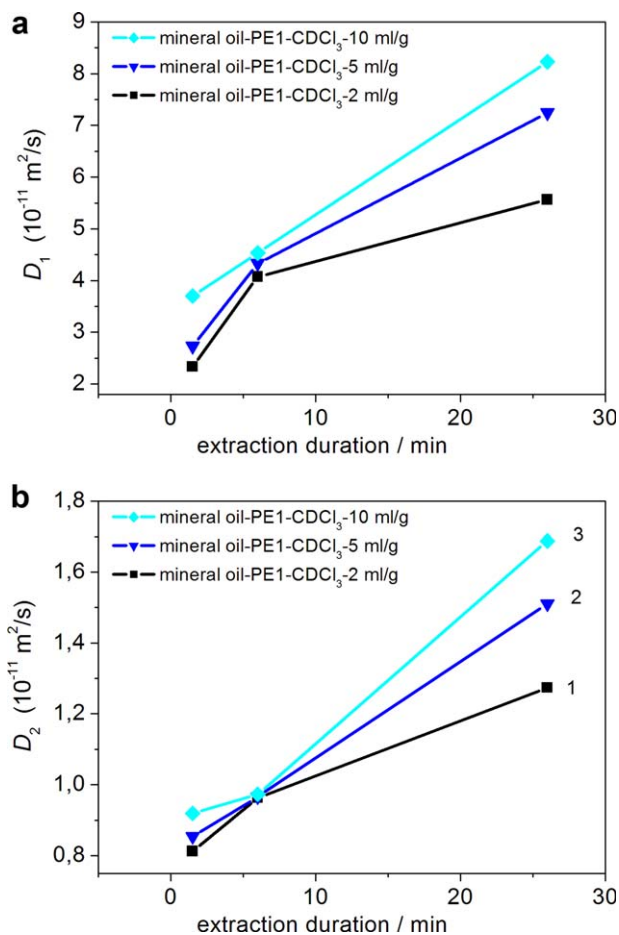
Figure 10. Effect of the extraction agent concentration on the diffusion of the solvent during extraction (D_1 and D_2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The effect of those factors on the relaxation and diffusion of mineral oil in UHMWPE were investigated empirically to identify a correlation between the quantities measured by NMR and the material properties.

Effect of UHMWPE Type. UHMWPE with a higher molecular weight favored an increase in the degree of orientation and crystallinity and thus improved the intensity and abrasion resistance of the UHMWPE fibers. At the same time, the very large molecular weights rendered the extraction process itself exceedingly difficult and cost-intensive. This was the motivation for analyzing the diffusion and extraction process for mineral oil in UHMWPE as a function of the molecular weight.

Three UHMWPEs with different molecular weights were selected, and their characteristics are listed in Table I. The mineral oil/UHMWPE gel samples were extracted by CDCl$_3$ for the diffusion measurements, with an extraction agent concentration of 2 mL/g and extraction durations of 1.5, 4.5, and 20 min. The detected initial and normalized signals followed similar trends to those shown in Figure 5. The NMR Ds were obtained by the biexponential fitting of the curves according to eq. (3), and the results are summarized in Figure 9.

The oil Ds increased with increasing UHMWPE molecular weight. This was in agreement with the assumption that long chains hindered crystallization. As a result, the crystallinity decreased,[36] as shown in Table I. A higher amount of amorphous material, in turn, facilitated diffusion into and within the matrix.[37] Although the addition of solvent led to partial dissolution, the remaining crystallinity was expected to be largest for the lowest molecular weight because this agreed with the highest degree of order. The variation in D with the molecular weight of UHMWPE was in agreement with the variation of crystallinity, but a change in the pore volume available for the mineral oil at each extraction stage, indirectly related to the molecular weight and crystallite size, was also possible because the differences between the sample types were comparatively large.

Effect of the Extraction Agent Concentration. The diffusion of mineral oil in the UHMWPE gel samples extracted by CDCl$_3$ was investigated as a function of the extraction agent concentration, that is, with the liquid-to-solid ratio being 2, 5, and 10 mL/g, respectively. The extraction durations were kept at 1.5, 4.5, and 20 min. The Ds are plotted in Figure 10.

A larger liquid-to-solid ratio was found to result in higher Ds at the same extraction duration. Because a larger liquid-to-solid
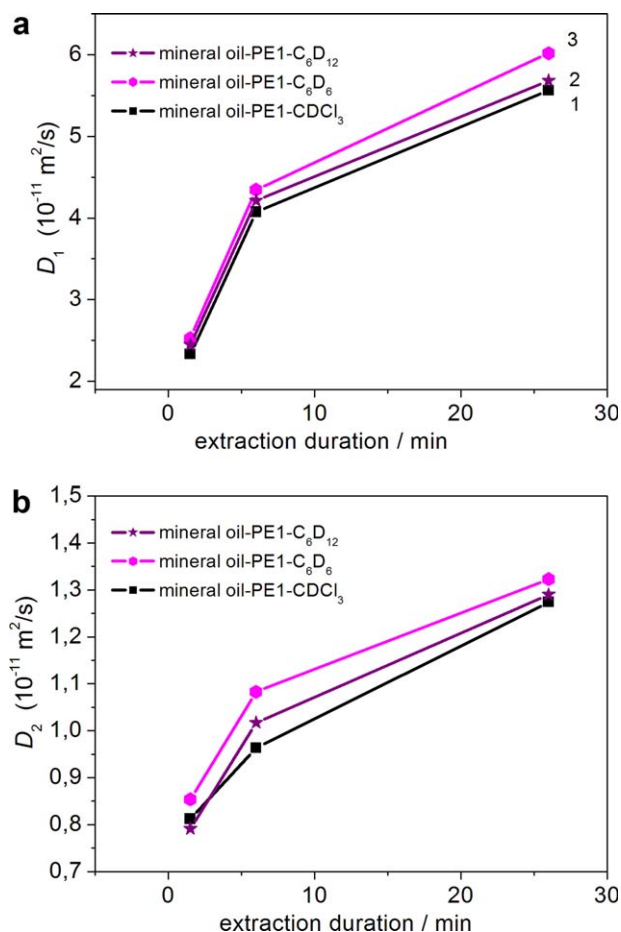

Figure 11. Effect of the extraction agent type on the solvent diffusion during extraction (D_1 and D_2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
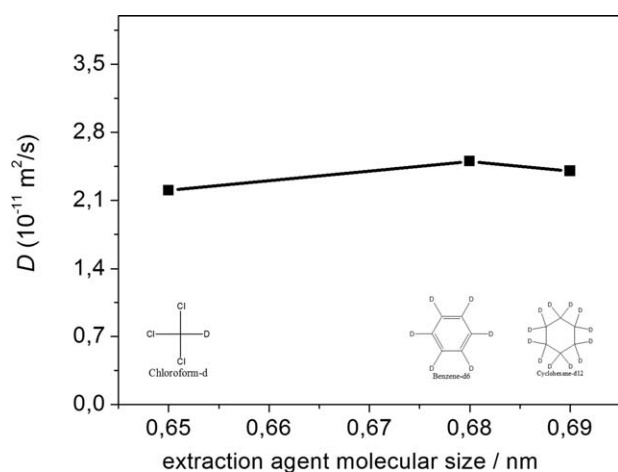
Table IV. Physical Properties of the Extraction Agents[35]

Extraction agent	C_6D_6	C_6D_{12}	$CDCl_3$
Molecular weight	84.15	96.24	120.38
Boiling point (°C)	79	80.7	60.9
Molecular size of corresponding undeuterated solvent (nm)	0.68	0.69	0.65

ratio was equivalent to a larger concentration gradient, the driving force of mass transfer was larger, and it became easier for the chloroform to diffuse into and for mineral oil to diffuse out of the matrix. Under the effect of replacement and dilution, the amount of mineral oil left in the UHMWPE gel became smaller, and the dilution influence of mineral oil got stronger with a larger liquid-to-solid ratio.

Effect of the Extraction Agent Type. The requirements for an optimal extraction agent are usually formulated as follows:[38] (1) excellent compatibility with solvent, (2) low boiling point and high volatility, (3) constant state of macromolecules of the gel during or after the extraction process, and (4) high availability, low price, and feasibility in industrial processes. Halogenated alkanes, xylol, hexane, gasoline, and so on are frequently used as extraction agents. In this study, the self-diffusion coefficients of mineral oil during the extraction process with different extraction agents ($CDCl_3$, C_6D_6, and C_6D_{12}) were measured. The liquid-to-solid ratio was maintained at 2 mL/g, and the extraction durations were chosen as indicated in the Experimental section.

Figure 11 presents the fitted D_1 and D_2 of mineral oil in the UHMWPE gel after extraction by different extraction agents. We observed that the extraction rate of benzene was fastest and that of chloroform was slowest; however, the differences were minor. Generally speaking, an extraction agent of lower boiling point, higher volatility, and smaller molecular size can permeate into the gel more easily. Consequently, it can replace and extract mineral oil more efficiently. C_6D_6 can extract mineral oil somewhat more quickly than C_6H_{12}. However, the extraction efficiency tendency presented in Figure 11 of $C_6D_6 > C_6D_{12} > CDCl_3$ did not follow

the decreasing tendency of the boiling point and molecular size $CDCl_3 < C_6D_6 < C_6D_{12}$, as shown in Table IV. On the one hand, the permeation rate of the extraction agent also depended on the molecular structure and polarity according to the like-dissolves-like rule. C_6D_6 and C_6D_{12} had a more similar structure and non-polarity with C—C of UHMWPE compared with $CDCl_3$. Thus, they could diffuse into the UHMWPE gel network and replace mineral oil faster; this caused a lower oil concentration at any given time and, therefore, a larger self-diffusion coefficient. On the other hand, this was probably a result of the combined effects of dilution and replacement. As mentioned in the extraction mechanism part earlier, the extraction agent not only replaced and extracted the oil from the gel system but also diluted the oil. Figure 12 shows the D of the liquid mixtures of mineral oil and extraction agent with the same oil concentration, 99.4 wt %. This indicated that the dilution efficiency of benzene was strongest, whereas that of chloroform as weakest (cf. the bulk value of mineral oil of 1.69×10^{-11} m^2/s). Thus, benzene enhanced the molecular motion and diffusion of the oil most significantly.

Effect of Ultrasound. Zhou[39] introduced ultrasound to enhance the mass transfer of hydrocarbon in the devolatilization process of polyolefin. Ultrasound was recently applied to improve the
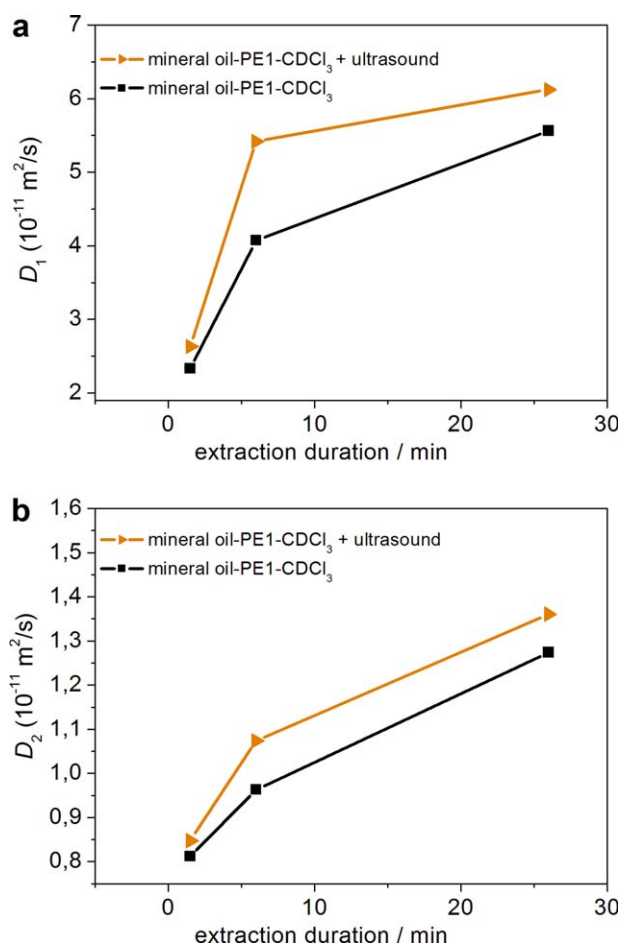
Figure 13. Effect of ultrasound on the solvent diffusion during extraction (D_1 and D_2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
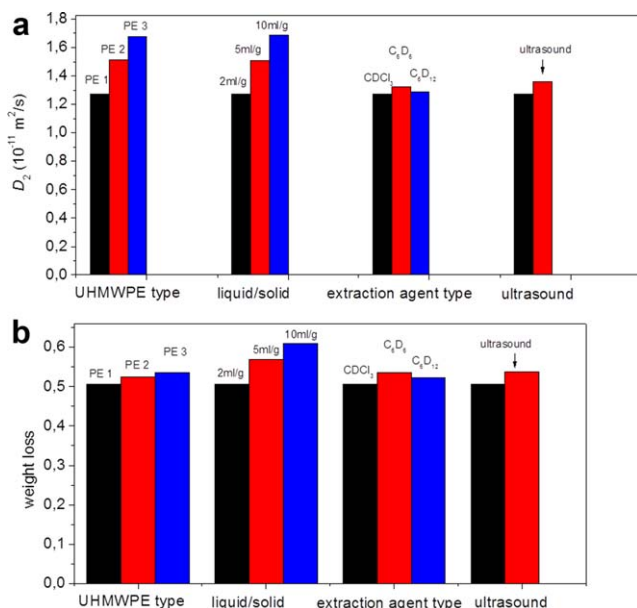

Figure 12. Diffusion of the solvent in the solvent/extraction agent mixtures.

Figure 14. (a) Comparison of D_2 after 26 min of extraction. (b) Comparison of weight loss after 26 min of extraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

extraction processes.[40] We investigated the influence of ultrasound on the extraction process of mineral oil in the UHMWPE gel. The ultrasound extraction experiments were carried out in an ultrasound cleaning bath (Fisher Scientific FB15047, 55 kHz) at 300 ± 0.5 K. The extraction agent was $CDCl_3$, the liquid-to-solid ratio was 2 mL/g, and the extraction durations were kept as in the previous experiments. The Ds after extraction are shown in Figure 13.

The diffusion of mineral oil was enhanced to some extent. Extraction appeared to be affected most at intermediate times, but it tended to saturate at longer times. The enhancement effect of ultrasound was partly due to an increase in the temperature. The introduction of ultrasound increased the temperature of the system by up to 5°C. This led to an increase in D of the extraction agent between 5 and 10%. In addition, the mechanical effect of the ultrasound promoted the extraction agent concentration being distributed uniformly, and it increased the concentration gradient near the gel surface.

Comparison of the Affecting Factors. The self-diffusion coefficients, D_1 and D_2, of mineral oil in the UHMWPE gel after 26 min of extraction under different extraction conditions were compared; only D_2 is shown in Figure 14(a) (D_1 is proportional). The weight losses of mineral oil after 26 min of extraction were obtained by the traditional drying–weighing method, and the results are compared in Figure 14(b).

After 26 min of extraction, D_1 and D_2 followed the same tendency as that of the weight losses. The self-diffusion coefficients could thus be used to characterize the extraction efficiency. With the increasing molecular weight of UHMWPE and extraction agent concentration, the self-diffusion coefficients of mineral oil increased. Although chloroform had a smaller molecular size and lower boiling point, benzene and cyclohexane could extract and

dilute the mineral oil more efficiently; thus, the self-diffusion coefficients of mineral oil and extraction efficiency were larger with benzene and cyclohexane than with the extraction agent.

By varying several parameters independently of each other, we found small but statistically significant influences on the extraction efficiency. For all variables that were compared—polymer type, extraction agent concentration and type, and application of ultrasound—the NMR parameters of the self-diffusion coefficient and T_1 were found to be correlated with the weight loss figures obtained after the end of the extraction process.

CONCLUSIONS

The diffusion behavior of mineral oil in the extraction process of the gel-spinning technology of the UHMWPE fibers was investigated by a portable low-cost NMR scanner. The self-diffusion coefficients were obtained from the NMR signal decay in a constant G provided by the device, and the NMR relaxation times were determined for the same samples. The extraction agent was deuterated, and only the signal of mineral oil was detected. The mineral oil could be treated as a pseudo-one-component system despite its composition because a single average D and a single relaxation time were determined in bulk. The effects of various experimental parameters, such as the UHMWPE type, extraction agent type, extraction agent concentration, extraction duration on the diffusion of mineral oil, and extraction efficiency, were investigated systematically. In addition, ultrasound was introduced to enhance the extraction process.

The extraction process could be described by a replacement–dilution dual-effect model. On the one hand, the extraction agent replaced and extracted the mineral oil for the desolvation effect. This caused the amount of mineral oil in the UHMWPE gel to decrease. On the other hand, the diffused-in extraction agent enhanced the molecular motion and diffusion of mineral oil by decreasing the viscosity of liquid in the UHMWPE gel. The dilution enhancement effect was far stronger than the confinement effect of the UHMWPE chains. We concluded from the phenomena that the fastest components of Ds of mineral oil in the mineral oil/extraction agent/UHMWPE gel system were much larger than that of the bulk mineral oil liquid. The dilution effect of the extraction agent promoted the replacement effect. In the extraction process, the mineral oil and extraction agent were not distributed uniformly in the gel. This led to a multiconfined space formed in the UHMWPE gel and multidiffusion behaviors of mineral oil.

The self-diffusion of mineral oil was faster in UHMWPE with a higher molecular weight and under a larger extraction agent concentration. The Ds were slightly larger with benzene and cyclohexane being the extraction agents, although chloroform was of a smaller size and lower boiling point, an effect of the vanishing polarity of the former substances.

The distribution of self-diffusion coefficients brought about by the nonuniform distribution of oil and extraction agent in the gel matrix was successfully approximated by the fitting of a two-component diffusion process, with both components following identical trends during the variation of variables. In

relaxation, the long component of T_1 dominated. For all variables investigated in this study, the self-diffusion coefficients and relaxation times correlated with the weight loss after extraction, itself being a measure for the extraction efficiency. The methods applied, thus, not only provided a noninvasive approach for quantifying the extraction efficiency in such a process but also allowed, in principle, the monitoring of the extractions process itself because the duration of a diffusion and a relaxation experiment could be reduced to a timescale of a few minutes. Although the quantitative correlation of the measured parameters with the sample's weight loss was demonstrated in this contribution, a more thorough understanding of extraction processes requires a detailed study of the heterogeneities in the UHMWPE gel matrix and its influence on the diffusion and relaxation properties of the mineral oil.

ACKNOWLEDGMENTS

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