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ORIGINAL REPORT



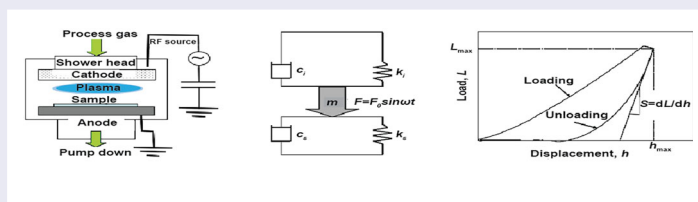
Viscoelastic properties of plasma-treated low-density polyethylene surfaces determined by nanoscale dynamic mechanical analysis

Ayyana M. Chakravartula, Lisa A. Pruitt and Kyriakos Komvopoulos

Department of Mechanical Engineering, University of California, Berkeley, CA, USA

ABSTRACT

Nanoscale dynamic mechanical analysis (nanoDMA) was used to determine changes in surface viscoelastic properties of low-density polyethylene (LDPE) due to Ar plasma treatment. The experimental results show that the exposure of LDPE to high-power plasma produces a more solid-like response compared to low-power plasma. In addition, high-power plasma treatment results in permanent modification of the near-surface microstructure of LDPE, while low-power plasma treatment yields a microstructure that exhibits time-dependent viscoelastic properties. The results of this study show that nanoDMA is an effective method for evaluating changes in surface viscoelastic properties of polymers due to modification of the near-surface microstructure by inert plasma treatment.



IMPACT STATEMENT

This investigation shows that inert plasma treatment can significantly modify the surface properties of polymers and that nanoDMA can differentiate between viscoelastic behaviors of untreated and plasma-treated polymer surfaces.

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KEYWORDS

Dynamic mechanical analysis; low-density polyethylene; nanoindentation; plasma surface treatment; viscoelasticity

1. Introduction

Biopolymers are often modified for use in various medical applications by different surface treatments. Such treatments are intended to change the surface chemistry for the purpose of improving implant biocompatibility, increase the receptiveness to certain drugs, or reduce friction and wear in the body [1,2]. Although it is almost certain that these treatments change the surface microstructure, either through chain scission or through chemical crosslinking, the majority of surface modification studies rely on contact angle and X-ray photoelectron spectroscopy measurements or accepted biological assays to quantify changes in surface chemistry and biocompatibility [3–5]. The tribological characteristics of surface-treated biopolymers are often attributed to changes in bulk mechanical properties [6]; however, since surface treatments only affect the near-surface microstructure (typically, to a maximum depth on the order of $\sim 1 \mu\text{m}$),

traditional measurements of mechanical properties, such as elastic modulus and yield strength, do not capture the effects of surface treatment. With a few exceptions [7,8], surface mechanical testing has rarely been employed to examine the effects of surface modifications at submicrometer scales. In applications where tribological properties, such as friction and wear, are of concern, a changed surface microstructure may be the key to resolving these problems. Therefore, a technique that can accurately measure and discern surface mechanical properties is needed in these application cases.

Nanoindentation has been frequently used to characterize the surface mechanical properties of polymers [9–11]. This method can be used to study the effect of plasma-assisted surface modification on surface viscoelasticity because of its high sensitivity to detect changes in mechanical properties at submicrometer scales. A set of parameters that characterize viscoelastic

behavior includes the storage and loss modulus, E' and E'' , respectively, and the loss tangent, $\tan\delta$. The main difference in the mechanical behavior of polymers and other materials, such as metals and ceramics, is the time-dependent mechanical response of polymers. Because semicrystalline polymers consist of long-chain molecules that exhibit ordered regions of crystallinity and disordered (amorphous) regions, the mechanical interactions at the molecular level cannot be represented by an elastic model. Instead, material parameters such as E' , E'' , and $\tan\delta$ must be used to characterize polymer response at various time scales.

The dynamic behavior of polymer surfaces is still not well understood. As the surface properties can differ significantly from the bulk properties, knowledge of the dynamic response at the nanoscale is critical. Since dynamic loading is often applied to biopolymers, the dynamic surface response could be the deciding factor for whether or not a biopolymer will be functional *in vivo*. One of the aims of this study was to demonstrate the potential of a surface-sensitive method, known as nanoscale dynamic mechanical analysis (nanoDMA) [12,13], to track the effects of plasma-assisted surface modification on the viscoelastic properties of a common biopolymer, low-density polyethylene (LDPE), in the light of viscoelastic property measurements obtained from indentation depths of $\lesssim 100$ nm.

2. Experimental procedures

Commercially available LDPE pellets (Sigma-Aldrich) were heated until translucent and then pressed onto steel disks with a glass counterface to obtain a smooth and consistent surface. The sample thickness was found to be ~ 1.5 mm. Differential scanning calorimetry showed that the crystallinity of the produced LDPE samples was 27.8%. The fabricated LDPE samples were exposed to inductively-coupled, radio-frequency (RF) Ar plasma for 15 min in a custom-made vacuum system with a base pressure of $\sim 10^{-6}$ Torr. Plasma surface treatments were performed under conditions of 3×10^4 J/m² ion energy fluence, 0.5 Torr chamber pressure, 58 cm sample distance from the plasma source, and RF power P equal to 225, 825, and 1200 W. Control samples were made from LDPE pellets in the same fashion but left untreated. Further details about the plasma-treatment apparatus and the experimental approach specifically developed for plasma-assisted surface modification of polymers can be found elsewhere [14,15].

The surface mechanical properties of LDPE samples were examined with a nanoindentation apparatus (TriboIndenter, Hysitron). Quasistatic tests were

performed for a normal load L of 8–10 μ N applied via a Berkovich diamond tip with a radius of curvature equal to ~ 100 nm, using a trapezoidal loading profile with loading/unloading rates fixed at 20 μ N/s. A trapezoidal loading profile is preferred for testing polymers in order to avoid the development of a ‘nose’ in the force response upon unloading from maximum load [16]. The surface stiffness S was determined from the slope of the line tangent to the beginning of the unloading portion of each load-displacement response [17].

The viscoelastic properties were obtained from frequency-sweep tests in which constant static and dynamic loads of frequency f gradually increasing from 10 to 200 Hz were applied during testing. The amplitude of the dynamic load was $\sim 2\%$ of the static load, which was set equal to 8, 15, and 20 μ N. For this static contact load range, the maximum indentation depth $h_{\max}$ was found to be ~ 100 nm. The viscoelastic measurements were obtained within 1 day and > 7 days from sample preparation. A minimum of 6 nanoindentations were made on each of 3 samples per group at ambient conditions. Statistical results are presented in the form of mean values (discrete symbols) and standard deviation values (error bars).

Atomic force microscope (AFM) imaging of untreated and plasma-treated LDPE samples revealed insignificant changes in surface roughness due to plasma treatment. In particular, nanoscale roughness measurements obtained from $1 \times 1 \mu\text{m}^2$ AFM images showed that the untreated LDPE possessed a root-mean-square (rms) surface roughness of ~ 3 nm, while that of plasma-treated LDPE was in the range of 4–6 nm [14,15], i.e. less than the diamond tip radius and indentation depths by about 1–2 orders of magnitude, implying an insignificant effect of the sample surface topography on the quasistatic and nanoDMA measurements.

3. Analytical method

A dynamic model [18], which includes the stiffness k_i and damping c_i of the indenter and the stiffness k_s and damping c_s of the sample, was used to analyze the nanoDMA measurements. Because the measured stiffness k and damping c include the stiffness and damping of both the indenter and the polymer sample, to extract the polymer properties, the indenter properties k_i and c_i were determined first from nanoDMA experiments performed in air. The measured stiffness and damping of the system-sample assembly are related to the dynamic properties of the sample by $k = k_s + k_i$ and $c = c_s + c_i$. For sinusoidal load amplitude L_0 and driving angular frequency ω , the amplitude of the indenter tip

displacement X_0 and the phase shift ϕ are given by

$$X_0 = \frac{L_0}{\sqrt{(k - m\omega^2)^2 + (c\omega)^2}}, \quad (1)$$

and

$$\phi = \tan^{-1} \left(\frac{c\omega}{k - m\omega^2} \right), \quad (2)$$

where m is the mass of the indenter.

The values of k and c , obtained from Equations (1) and (2) in terms of measured X_0 and ϕ , were used to compute k_s and c_s , which are related to viscoelastic parameters by

$$E'_r = \frac{\sqrt{\pi} k_s}{2\sqrt{A}}, \quad (3)$$

$$E''_r = \frac{\sqrt{\pi} \omega c_s}{2\sqrt{A}}, \quad (4)$$

$$\tan \delta = \frac{E''_r}{E'_r} = \frac{\omega c_s}{k_s}, \quad (5)$$

where A is the contact area (determined from the indenter's tip geometry and indentation depth) and E'_r and E''_r are the reduced storage and loss modulus, respectively, which depend on the elastic modulus and Poisson's ratio of the indenter and the sample.

The storage modulus E'_r is a measure of the energy stored and recovered during each loading cycle, whereas the loss modulus E''_r is a measure of the energy lost or dissipated in the material during each loading cycle. This dissipation is normally attributed to internal friction related to molecular chain rearrangement and reconfiguration during dynamic loading or energy absorption by the increased chain mobility in the polymer. As shown by Equation (5), $\tan \delta$ is independent of A ; therefore, the loss tangent (defined as the loss-to-storage modulus ratio) is an indicator of the viscoelastic behavior of a dynamically indented material. A low $\tan \delta$ implies predominantly elastic behavior (low damping), whereas a high $\tan \delta$ indicates a viscous-dominant behavior (high damping). Peaks representing various polymer transitions are observed when $\tan \delta$ is plotted against frequency (or temperature). The largest peak is associated with the glass transition temperature, whereas smaller peaks are representative of smaller-scale molecular motions, such as rotation around the main chain or cooperative motion of a few main-chain atoms [19,20].

4. Results and discussion

Figure 1(a) shows representative quasistatic nanoindentation force versus displacement responses for control ($P = 0$ W) and plasma-treated ($P = 225$, 825, and

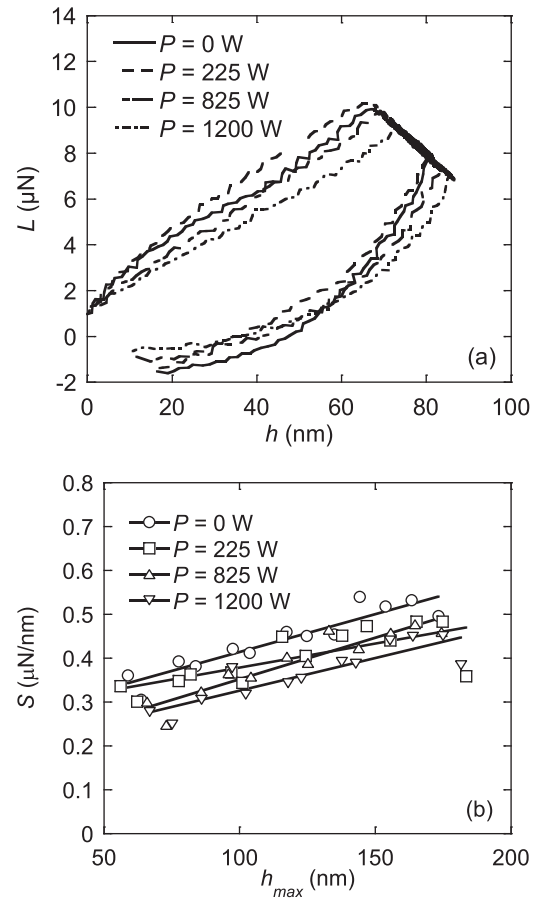


Figure 1. Quasistatic nanoindentation results of untreated LDPE ($P = 0$ W) and plasma-treated LDPE ($P = 225$, 825, and 1200 W): (a) normal load L versus indentation depth h and (b) elastic stiffness S versus maximum indentation depth h_{max} .

1200 W) LDPE samples. The sloped path corresponding to constant load is attributed to polymer relaxation. The slightly negative load measured before the detachment of the tip from the sample surface is indicative of the adhesiveness of polymer surfaces. The small attractive (adhesive) force (less than $-2 \mu\text{N}$) compared to the applied indentation load ($8\text{--}10 \mu\text{N}$) indicates a secondary effect of surface adhesion on the nanomechanical measurements. The closeness of the loading and unloading curves of various samples shows the difficulty in distinguishing the effect of different plasma treatments by quasistatic nanoindentation. A similar conclusion can be drawn from the results of the elastic stiffness $S = (dL/dh)|_{h_{\text{max}}}$ versus maximum indentation depth h_{max} shown in Figure 1(b). Thus, although other methods reveal changes in the surface chemical structure and nanoscale texturing [14], traditional quasistatic indentation cannot reveal changes in the elastic surface stiffness.

Figure 2 shows nanoDMA results of $\tan \delta$ versus load frequency $f (= \omega/2\pi)$ for the same samples used in the quasistatic nanoindentation results shown in Figure 1.

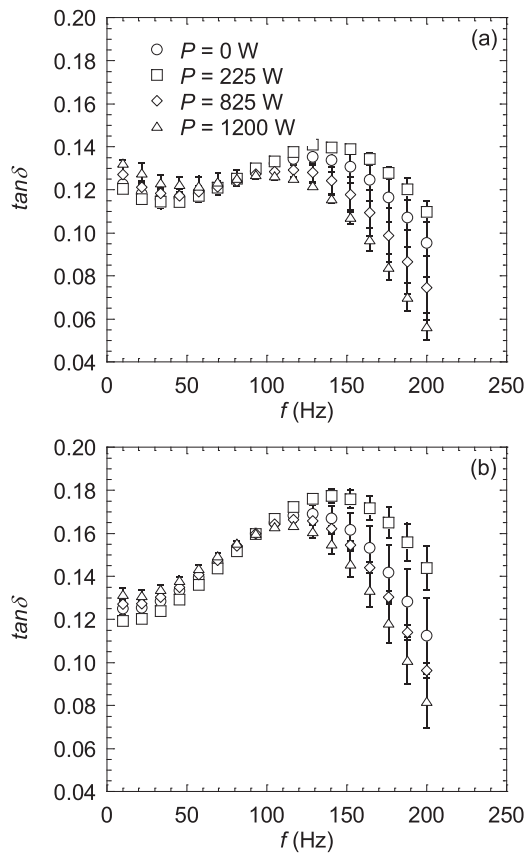


Figure 2. Loss tangent $\tan\delta$ of untreated ($P = 0$ W) and plasma-treated ($P = 225, 825$, and 1200 W) LDPE versus load frequency f for (a) shallow ($h < 35$ nm) and (b) deep ($h > 75$ nm) indentations. All of the measurements were obtained 1 day after Ar plasma treatment.

Dynamic test data are shown for relatively shallow ($h < 35$ nm) and deep ($h > 75$ nm) indentations in Figures 2(a) and 2(b), respectively, for $P = 0$ – 1200 W. Both data sets show significant differences among various plasma treatments, particularly at higher frequencies. Importantly, the results indicate a dependence of the transition frequency $f_{\text{transition}}$ on plasma power. While for higher power treatments ($P = 825$ and 1200 W) $f_{\text{transition}}$ decreased, for the lower power treatment ($P = 225$ W) it increased, indicating the existence of a threshold plasma power. Below this power threshold, polymer damping increased, while above it polymer damping decreased. The lower $f_{\text{transition}}$ for high-power treatments indicates that the energy dissipation mechanisms in untreated and low-power-treated LDPE, such as molecular chain friction and movement, were not available to the samples after high-power plasma treatment.

The $\tan\delta$ versus f responses shown in Figure 2 reveal three characteristic frequency ranges. The decreasing trend of $\tan\delta$ in the low frequency range ($f \lesssim 50$ Hz) is attributed to surface stiffening due to less time available

for molecular chain rearrangement in the region adjacent to the advancing indenter tip. The increasing trend of $\tan\delta$ in the intermediate frequency range ($50 \text{ Hz} < f < 140 \text{ Hz}$) is related to localized softening of the amorphous phase prompted by the increasing energy dissipation in the near-surface region. The latter increased the free volume and, in turn, the chain mobility, resulting in a more viscous-like response. At a critical frequency ($f_{\text{transition}}$), the viscous-like behavior saturated, and $\tan\delta$ began to decrease (high frequency range, $f > 140 \text{ Hz}$) due to stiffening of the molecular chain network produced ahead of the tip in the intermediate frequency range.

Insight into the effect of plasma power on surface viscoelasticity of LDPE can be obtained in the light of the nanoDMA results shown in Figure 3. All of the results exhibit initially an increasing trend followed by a decaying trend with increasing frequency. The variation of $f_{\text{transition}}$ with RF power P shown in Figure 3(a) is consistent with the interpretation of the results shown in Figure 2. The results shown in Figures 3(b)–3(e) are for the maximum frequency ($f_{\text{max}} = 200 \text{ Hz}$) used in this study for which the largest differences in the measurements were obtained. The viscoelastic measurements for the higher power cases are similar to or less than those of untreated LDPE (control), indicating that these plasma treatments induced surface crosslinking. In surface-crosslinked polymers, the molecular chains at the surface are constrained, resulting in decreased amounts of damping; hence, lower E'_r and $\tan\delta$ values. It is possible that low-power plasma treatment contributed more to chain scission at the surface than crosslinking, which explains the increase of E'_r in these treatments. The decrease of E'_r at higher powers may be attributed to the decrease of surface crystallinity due to the formation of molecular defects during the intense Ar^+ ion bombardment at high RF powers. The increase of E'_r and $\tan\delta$ in the case of the low-power plasma treatment suggests an increased mobility of surface molecular chains, possibly due to chain scission induced by the bombarding energetic Ar^+ ions. This further supports the existence of a threshold power of Ar plasma treatment above which crosslinking dominates and below which chain scission dominates.

The effect of driving (load) frequency f on $\tan\delta$ is shown in Figure 4 for $P = 0$ – 1200 W. To examine the stability of the plasma-modified surface microstructures, experiments were performed after 1 and > 7 days from plasma treatment. To minimize the contribution of unmodified bulk material to the measurements, only results from shallow indentations ($h < 35 \text{ nm}$) are shown in Figure 4. The variation of $\tan\delta$ with f shown in Figure 4 is in agreement with the findings of a previous study [12]. For untreated LDPE (Figure 4(a)) and

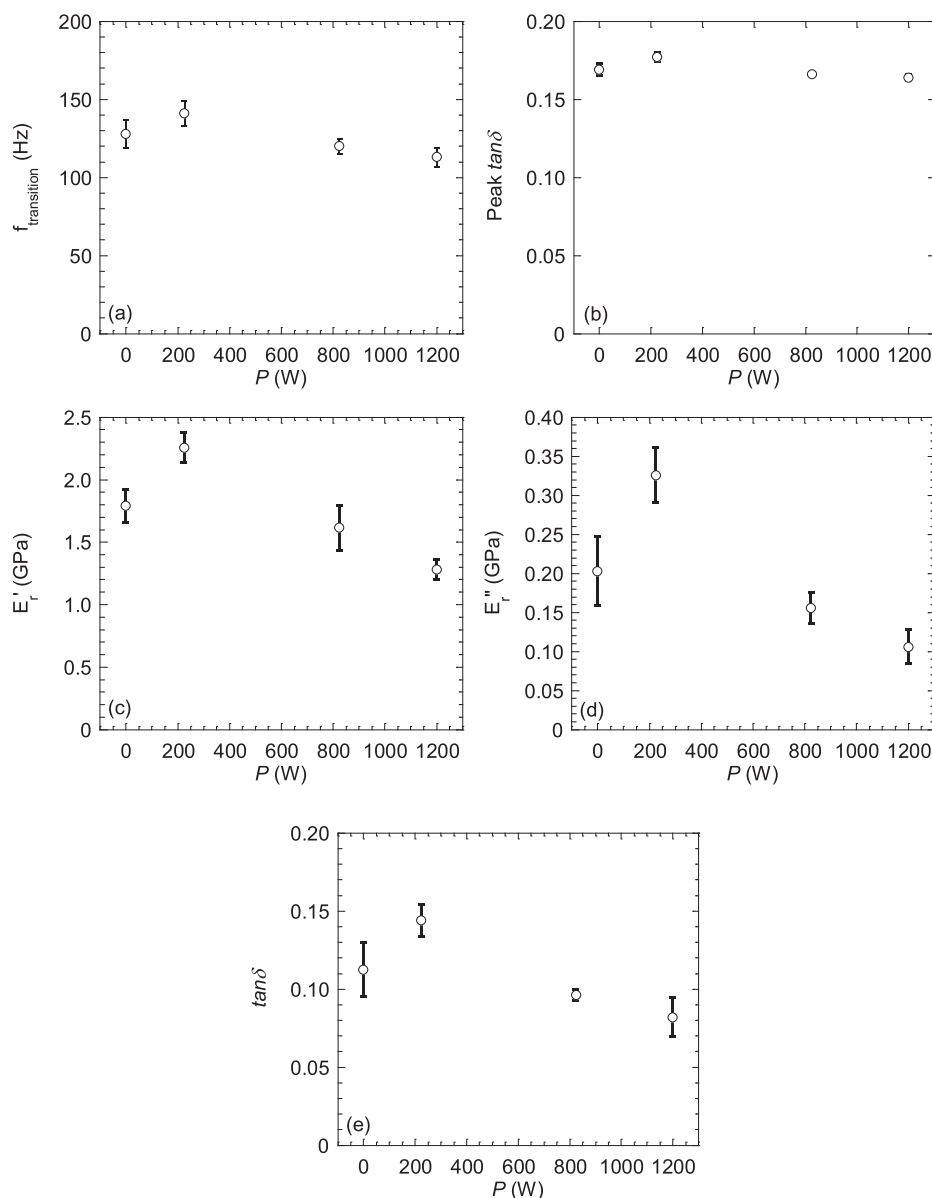


Figure 3. (a) Transition frequency $f_{\text{transition}}$, (b) peak $\tan\delta$, (c) reduced storage modulus E'_r , (d) reduced loss modulus E''_r , and (e) loss tangent $\tan\delta$ of LDPE versus plasma power P . The results shown in (b)–(d) were obtained at $f_{\text{max}} = 200$ Hz, which is the frequency that resulted in the greatest differences in the results. All of the measurements were obtained 1 day after Ar plasma treatment ($h > 75$ nm).

low power plasma-treated LDPE (Figure 4(b)), the 1 day and > 7 day curves are distinctly different, especially at higher frequencies, whereas for the higher power treatments (Figures 4(c) and 4(d)), the responses corresponding to 1 day and > 7 days after plasma treatment are practically identical. This indicates that high-power plasma treatment permanently modified the near-surface microstructure of LDPE, providing further support to crosslinking at higher powers as evidenced by the $\tan\delta$ responses. Because the surfaces of the control and low-power plasma-treated LDPE were not constrained by crosslinks, they exhibited molecular rearrangement over time. As mentioned earlier, the low-power plasma

treatment might have contributed more to chain scission at the surface than crosslinking, which explains why the surface viscoelastic properties demonstrate a more viscous response compared to the control material. Thus, the shorter chains were more likely to rearrange under cyclic indentation, absorb energy, and, hence, yield higher E''_r .

The potential differences between untreated and plasma-treated LDPE are the molecular weight and the degree of crosslinking. The molecular weight at the polymer surface is likely to decrease with increasing plasma power due to chain scission caused by the bombardment of energetic Ar^+ ions, leading to a more fluid-like

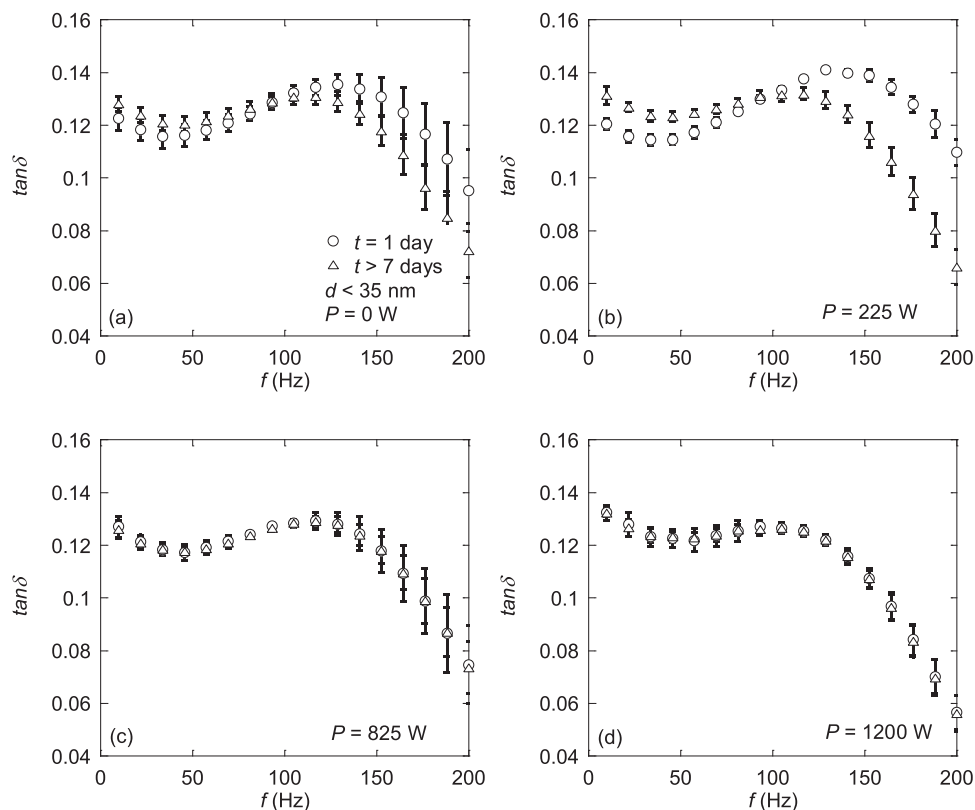


Figure 4. Loss tangent $\tan\delta$ of LDPE versus load frequency f for plasma power P equal to (a) 0 W (control), (b) 225 W, (c) 825 W, and (d) 1200 W. The results were obtained 1 and > 7 days after Ar plasma treatment ($h < 35$ nm).

response during dynamic testing. Conversely, a more solid-like response is expected from increased chain crosslinking in the high-power plasma treatments. The obtained results indicate a more solid-like response for high-power plasma treatment, which was consistent over a period of > 7 days. In the present study, nanoDMA measurements were acquired predominantly from the near-surface region of LDPE samples, where the viscoelastic properties differed significantly from those of the bulk due to molecular reorganization at the surface induced by the bombarding Ar^+ ions. Thus, significant changes in surface viscoelastic properties cannot be obtained from bulk measurements, because they do not capture the effects associated with hindered molecular chain mobility and rearrangement.

5. Conclusions

The results of this study demonstrate that nanoDMA is a surface-sensitive method that enables the detection of small but nevertheless important changes in the viscoelastic properties of polymer surfaces. It was shown that nanoDMA can differentiate between viscoelastic behaviors of untreated and plasma-treated LDPE

indented to very small depths and discern the depth to which the plasma treatment causes significant structural modification. As plasma treatments are becoming more common to biomedical polymeric components to improve biocompatibility, lubricity, or receptivity to certain drugs, the high surface sensitivity of nanoDMA provides an effective means of tracking changes in surface mechanical properties of biopolymers. If the dynamic properties and the threshold of transition frequency can be related to crystallinity or molecular weight, it will be much easier to tailor these properties with other treatments. A limitation of the present technique is its relatively small frequency range for testing. While much published dynamic data are taken over significantly broader frequency ranges, the entire $\tan\delta$ response that captures many different types of molecular motions cannot be generated in the frequency range of this system. Thus, future studies should focus on extending the work presented herein to broader frequency ranges and other polymers. Nevertheless, the current nanoDMA system enables facile identification of a shift in the $\tan\delta$ response or specific changes in other surface viscoelastic properties due to surface-confined structural changes induced by inert plasma treatment.

Disclosure statement

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ORCID

Kyriakos Komvopoulos  <http://orcid.org/0000-0001-9418-1567>

References

- [1] Yahia L, Lombardi S, Selmani A, et al. Effect of plasma treatment on tribological properties of synthetic ligaments. *Bio-med Mater Eng.* **1994**;4:347–356.
- [2] Favia P, d'Agostino R. Plasma treatments and plasma depositions of polymers for biomedical applications. *Surf Coat Technol.* **1998**;98:1102–1106.
- [3] Lin JC, Cooper SL. Surface characterization and ex vivo blood compatibility study of plasma-modified small diameter tubing: effect of sulphur dioxide and hexamethyldisiloxane plasmas. *Biomater.* **1995**;16:1017–1023.
- [4] Wang P, Tan KL, Kang ET. Surface modification of poly(tetrafluoroethylene) films via grafting of poly(ethylene glycol) for reduction in protein adsorption. *J Biomater Sci, Polymer Ed.* **2000**;11:169–186.
- [5] Pu FR, Williams RL, Markkula TK, et al. Monocyte adhesion and adhesion molecule expression on human endothelial cells on plasma-treated PET and PTFE in vitro. *J Mater Sci: Mater Med.* **2001**;12:971–977.
- [6] Rieu J, Pichat A, Rabbe LM, et al. Ion implantation effects on friction and wear of joint prosthesis materials. *Biomater.* **1991**;12:139–143.
- [7] Tóth A, Bertóti I, Szilágyi E, et al. Surface characterization of ultrahigh molecular weight polyethylene after nitrogen ion implantation. *Surf Interf Anal.* **2000**;30:434–438.
- [8] Klapperich C, Pruitt L, Komvopoulos K. Nanomechanical properties of energetically treated polyethylene surfaces. *J Mater Res.* **2002**;17:423–430.
- [9] Bischel MS, Vanlandingham MR, Eduljee RF, et al. On the use of nanoscale indentation with the AFM in the identification of phases in blends of linear low density polyethylene and high density polyethylene. *J Mater Sci.* **2000**;35:221–228.
- [10] Gilbert JL, Cumber J, Butterfield A. Surface micromechanics of ultrahigh molecular weight polyethylene: microindentation testing, crosslinking, and material behavior. *J Biomed Mater Res.* **2002**;61:270–281.
- [11] Ho SP, Riester L, Drews M, et al. Nanoindentation properties of compression-moulded ultra-high molecular weight polyethylene. *Proc Inst Mech Eng, Part H.* **2003**;217:357–366.
- [12] Chakravartula A, Komvopoulos K. Viscoelastic properties of polymer surfaces investigated by nanoscale dynamic mechanical analysis. *Appl Phys Lett.* **2006**;88:131901.
- [13] Zhou J, Komvopoulos K. Interfacial viscoelasticity of thin polymer films studied by nanoscale dynamic mechanical analysis. *Appl Phys Lett.* **2007**;90:021910.
- [14] Tajima S, Komvopoulos K. Surface modification of low-density polyethylene by inductively coupled argon plasma. *J Phys Chem B.* **2005**;109:17623–17629.
- [15] Tajima S, Komvopoulos K. Effect of ion energy fluence on the topography and wettability of low-density polyethylene exposed to inductively coupled argon plasma. *J Phys D: Appl Phys.* **2006**;39:1084–1094.
- [16] Briscoe BJ, Fiori L, Pelillo E. Nano-indentation of polymeric surfaces. *J Phys D: Appl Phys.* **1998**;31:2395–2405.
- [17] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J Mater Res.* **1992**;7:1564–1583.
- [18] Asif SAS, Wahl KJ, Colton RJ. Nanoindentation and contact stiffness measurement using force modulation with a capacitive load-displacement transducer. *Rev Sci Instrum.* **1999**;70:2408–2413.
- [19] Young RJ, Lovell PA. *Introduction to polymers.* 2nd ed. London: Chapman and Hall; **1991**.
- [20] Ward IM, Sweeney J. *An introduction to the mechanical properties of solid polymers.* 2nd ed. West Sussex: Wiley; **2004**.