Engineering of Durable Antifog Thin Coatings on Plastic Films by UV-Curing of Proteinoid Prepolymers with PEG-Diacrylate Monomers

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Supporting Information

ABSTRACT: Fog formation on transparent surfaces constitutes a major challenge in several optical applications, such as plastic packaging, lenses, mirrors, and windshields. To overcome this problem, we prepared and characterized durable antifog thin coatings on plastic films such as polyethylene terephthalate (PET). Proteinoids are biocompatible random polymers made of α-amino acids by thermal step-growth polymerization. Proteinoid prepolymers were prepared by adding activated double bonds to proteinoids via the Michael addition reaction. A series of thin antifog cross-linked coatings were prepared by spreading on PET films with a Mayer rod various mixtures of the proteinoid prepolymers, polyethylene glycol diacrylate, and a photoinitiator, followed by UV-curing of the dried coatings. The antifog properties of the coatings were determined by the contact angle, roughness, haze, and gloss measurements, as well as hot and cold fog tests, to examine the optical properties of the films under fog formation conditions. Mechanical properties such as adhesion, robustness, and abrasion resistance of the antifog coatings were examined by tape, knife-scratch, and sandpaper abrasion tests. The effect of coating composition, wettability, and roughness on the antifog properties of the coated PET films was elucidated. The formula was optimized, and the corresponding UV-cured antifog cross-linked thin coating exhibited transparency with good adhesion and excellent durable antifog performance.

1. INTRODUCTION

In certain conditions of temperature and humidity, fog can be created. Fog is an accumulation of small droplets of water that condense on solid surfaces such as plastic films, lenses, mirrors, and windshields. The small droplets on the surface scatter light and reduce light transmission, hence damaging the transparency of the product surface. This may cause significant damage in many fields: in food packaging, the esthetics of the package are compromised, and the quality of the food may decrease to the point where it can no longer be sold because of the accumulated moisture; in agricultural films, fog droplets reduce light transmission, inhibit growth of crops, and harm plant top leaves. One way to avoid fog formation is to control the temperature and humidity of the environment. Another approach is to use antifog coatings, which are preferable because of lower cost and energy consumption. Antifog coatings can be external, where the antifog is applied using spray or dip coating on the surface, or internal, where the antifog is incorporated by compounding. Such coatings prevent water condensation, maintain optical clarity, and increase the surface energy of the films, causing water droplets to rapidly spread into a uniformly thin and non-light-scattering film. In this case, although condensation still occurs, the surface remains optically clear, without disruption of light transfer. In the past three decades, the common method to obtain antifog properties was by hydrophilic coatings with polymers that contain hydrophilic functionalities, such as hydroxyl (OH), carboxylic (COOH), and amine (NH₂) groups. For example, coatings were prepared with poly(ethylene glycol), poly(vinyl alcohol), or acrylic resin with pending OH or COOH groups and glycidyl derivatives. Comparisons with main recent previously reported materials, systems, and substrates are shown in Table S1 in the Supporting Information. The table indicates that the most common substrate used for thin functional coating is glass, as opposed to plastic used in the present study. This is due to the relative ease with which different reagents can react with the surface hydroxyl groups of glass. The use of proteinoid prepolymers for antifog coatings is also new.

Recently, we reported on novel antifog coatings applied to polypropylene films, prepared from a mixture of A131-X, a typical adhesive aqueous solution of polyethyleneimine, and proteinoid polymers or particles. However, these antifog coatings were not durable, as shown by different mechanical tests including immersion in water, adhesion tests, and rub resistance tests, after which they were not stable and showed poor antifog properties. In contrast, the present manuscript...
describes the formation of a simple durable antifog thin coating on polyethylene terephthalate (PET) films.

Water-wetting properties (e.g., low water contact angle) are affected by the surface roughness and/or chemical composition. Rough surfaces cause fog to accumulate in craters on the surface, which contain water droplets.1–7 In addition, the chemical composition of the substrate surface is important for designing optimal antifog coatings. Low water contact angles on surfaces with appropriate roughness and chemical composition usually yield good antifog films.1–7 However, in spite of great efforts, preparation of optical quality thin-film coatings with good antifog characteristics and mechanical durability remains a great challenge.1

In the present study, a new durable thin cross-linked antifog coating on PET films was designed, based on the assumption that a cross-linked polymeric network is essential in order to maintain long-term antifog properties and enhance coating resistance.8 For this purpose, a series of thin cross-linked coatings were prepared by spreading various mixtures of proteinoid prepolymers, polyethylene glycol diacrylate (PEGDA), and a photoinitiator with a Mayer rod on corona-treated PET films, followed by UV-curing of the dried coatings to generate a cross-linked network of polymers by initiating a photochemical reaction. UV-curing is a rapid technology applicable to virtually any substrate, including plastic, metal, composite, wood, paper, leather, glass, magnetic recording tape, and even human teeth.9,10 Proteinoids are polymers made from natural amino acids by thermal bulk step-growth polymerization; they are nontoxic and non-immunogenic and therefore potential candidates for a variety of applications such as specific cell labeling, drug delivery, and diagnosis of diseases.11–14 For the present study, the proteinoids were synthesized using glutamic acid or lysine as solvents for the random polymerization process. These amino acids consist of carboxylic and amine hydrophilic functional groups, thereby the antifog properties are ascribed to the proteinoid. To obtain good mechanical and surface compatibility properties, phenylalanine and isoleucine were added to the proteinoid backbone. Furthermore, in this study, proteinoid prepolymerizations with activated double bonds were prepared by Michael addition of acidic or basic proteinoids with excess PEGDA. The activated prepolymerizations were then UV-cured with PEGDA to achieve optimal thin coatings that exhibit durable antifog properties.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Proteinoids and Proteinoid Prepolymers. Proteinoids were prepared by thermal step-growth polymerization of different amino acids and characterized for their molecular weights and polydispersity, as shown in Table 1. The synthesized proteinoids were of relatively high molecular weight with relatively narrow polydispersity index (PDI)—36 kDa and 1.02 PDI, 68 kDa, and 1.04 PDI, and 95 kDa and 1.09 PDI for poly(KI), poly(EI), and poly(KF), respectively. This indicates that the simple thermal step-growth polymerization procedure used here provides relatively long polymer chains with narrow PDI, as reported in previous studies by our group.11–14 Furthermore, Table 1 shows that all proteinoids exhibit optical activity, although the monomers are known to racemize during the thermal process.20 Proteinoids and proteinoid prepolymers were characterized by Fourier transform infra-red (FTIR). Typical spectra are illustrated in Figure 1, panels A and C, respectively. Figure 1B illustrates the spectrum of PEGDA. All proteinoids spectra (Figures 4A, S1A and S2A) show characteristic peaks of NH stretching at 3300 and 2930 cm⁻¹, amide CO stretching at 1514–1579 cm⁻¹, amide NH bending band at 1449 cm⁻¹, and CO bending at 500–700 cm⁻¹. The PEGDA spectrum shows characteristic peaks of C=O stretching at 1640 cm⁻¹, carbonyl groups at 1724 cm⁻¹, and C=O–C stretching at 1110 cm⁻¹. All proteinoid prepolymers showed a combination of the characteristic peaks of both proteinoid and PEGDA monomers. Hence, it can be assumed that the preparation of proteinoid prepolymers (Figures 1C, S1B and S2B) via the Michael addition reaction indeed was successful.

2.1.1. NMR Analysis of Amino Acid Composition. For a quantitative view of the relative incorporation rates of amino acids into the proteinoids, we employed 1H NMR spectroscopy. The analysis is based on the strictly quantitative nature of the spectrum—the signal is directly proportional to the number of nuclei of a certain type—and on the fact that...
amino acid side-chains have sufficiently unique NMR footprints to afford in most cases unambiguous assignment of the observed signals. Proteinoids were dissolved in neat $^2$H$_2$O at a concentration of 10 mg/mL, and 1D $^1$H spectra were acquired with presaturation of the residual HDO peak. Results for the poly(KF) proteinoid are shown in **Figure 2** and are representative of all measurements; results for the poly(KI) and poly(EIF) proteinoids are shown in the Supporting Information (Figures S3 and S4). Comparison of the spectra to characteristic average chemical shifts reveals that in the aliphatic proteinoids the vast majority of the signal (98–99%) appears in the expected frequency ranges. In contrast, the poly(KF) spectrum exhibited a small amount (5%) of up-shifts that are consistent with ring-current effects. In both cases, the spectra were divided into regions in which the spin assignment was clear, and signals and integrated intensities were assigned to amino acids. Molar ratios were calculated for each pair of residues based on the known initial ratios within the proteinoids, as well as relative incorporation rates observed. Taken together, these observations are consistent with addition of PEGDA groups to the proteinoid.

### 2.1.2. NMR Analysis of Proteinoid Prepolymers

Proteinoid prepolymer samples were analyzed by NMR to observe the incorporation of the cross-linking diacrylate moiety. A comparison of 1D $^1$H NMR spectra before and after coupling to PEGDA is shown in **Figure 3** for the poly(EIF) proteinoid. While the ratio of Glu-to-Ile peaks appears to be similar in both cases, the spectrum shows clearly the addition of protons signals expected for polyPEGDA. The 6.0–6.4 ppm region exhibits signals with chemical shifts and J-couplings typical of an $\alpha$-$\beta$-unsaturated carbonyl moiety present in the acrylate group before Michael addition. Peaks typical of the ethylene glycol moiety and $\alpha$-protons of an ester group can also be observed. Taken together, these observations are consistent with addition of PEGDA groups to the proteinoid.

### 2.2. Characterization of Uncoated and Coated PET Films

#### 2.2.1. Fourier Transform Infra-red

FTIR spectra of PET films, uncoated and coated with PEDGA (PET/PEGDA) before and after UV-curing are shown in **Figure 4**.

**Figure 4A**D exhibits the spectrum of corona-treated PET film with main absorption bands at 1712 cm$^{-1}$ of C=O stretching, 1409 cm$^{-1}$ of ring C–H in-plane bending and ring stretching, 1409 cm$^{-1}$ of ring C–H out-of-plane bending, and 1637 cm$^{-1}$ of aromatic out-of-plane bending.

![Figure 2. NMR analysis of proteinoid amino acid composition. 1D $^1$H NMR spectrum of 10 mg/mL poly(KF) in $^2$H$_2$O acquired at 300 K and 16.4 T. Signals emanating from lysine, phenylalanine, and HDO protons, as well as integrated signal areas, are shown.](image-url)

![Figure 3. Comparison of NMR spectra for poly(EIF) (black) and poly(EIF-PEGDA) (red). 1D $^1$H NMR spectra were acquired for 10 mg/mL samples in $^2$H$_2$O at 300 K and 16.4 T. Characteristic signals are indicated.](image-url)

**Table 2. NMR Analysis of Amino Acid Composition in the Proteinoids**

| Proteinoid | Sig-1 | Sig-2 | Sig-ratio | mol/mol ratio $^d$ |
|------------|-------|-------|------------|-------------------|
| poly(KF)   | 1.00  | 6H Lys(H$^\beta$H$^\gamma$H$^\delta$) | 0.41 | 5H Phe(H$^\delta$H$^\epsilon$H$^\zeta$) | 2.44 | 2.03:1 |
| poly(KI)   | 1.71 $^d$ | 6H Lys(H$^\beta$H$^\gamma$H$^\delta$) | 1.00 | 6H Ile(H$^\gamma$H$^\delta$H$^\epsilon$H$^\zeta$) | 1.21$^d$ | 1.21:1 |
| poly(EIF)  | 1.18 $^d$ | 4H Glu(H$^\delta$H$^\beta$H$^\alpha$) | 1.00 | 6H Ile(H$^\gamma$H$^\delta$H$^\epsilon$H$^\zeta$) | 1.01$^d$ | 1.52:1 |

$^a$Sig-1 and Sig-2 represent the relative signals from the first and second amino acid, respectively. $^b$Nuc-1 and Nuc-2 are the nuclei contributing to the signals in the designated spectral regions. $^c$Mol/mol ratio is calculated by dividing Sig-ratio by the ratio between the number of protons that contribute to the signals of the solvent (K/E) and the other amino acid (F/I). $^d$Because of overlap in the 1.2–2.0 (1.8–2.5 ppm) region between the K/I (E/I) frequencies, the relative contribution of each amino acid was deduced from the signal in the Ile methyl spectral region and stoichiometry.
C–C stretching, 1338 cm$^{-1}$ of CH$_2$, O–C–H bending, 1099 cm$^{-1}$ of C–O stretching, 1017 cm$^{-1}$ of ring C–C–C bending, ring C–C stretching, and ring C–H in-plane bending, 870 cm$^{-1}$ of ring C–H out-of-plane bending, ring ester C–C out-of-plane bending, C=O out-of-plane bending and ring torsion, and 722 cm$^{-1}$ of C=O out-of-plane bending, ring torsion, and ring C–H out-of-plane bending.21-22

Figure 4B, E and 4F exhibits spectra with PEGDA coating before and after UV-curing, respectively. Figure 4B exhibits main absorption bands at 1620, 1636–1647, and 810 cm$^{-1}$ of C=O stretching of terminal acrylate group. These peaks were not observed after UV-curing (Figure 4C), showing that all double bonds of the PEGDA monomer reacted during the polymerization process.23 Other prominent peaks were observed at 1731 cm$^{-1}$ of C=O stretching, 2885–2287 cm$^{-1}$ of C–H stretching, 1351–1352 cm$^{-1}$ of C–O asymmetric bending, 1243–1283 cm$^{-1}$ of C–O asymmetric bending, and 1107–1194 cm$^{-1}$ of C–O–C symmetric stretching.

2.2.2. Atomic Force Microscopy. PET films were coated by solutions of PEGDA (5, 10, 15, and 20% w/v) or PEGDA and proteinoid prepolymer, followed by UV-curing of the dried coatings, as described in the experimental part. Table 3 and Figure 5 illustrate the measured surface roughness and water contact angles of the uncoated and coated films. Roughness measurements clearly show that coating by polyPEGDA improve the smoothness of the film. Corona-treated PET films showed high roughness of 3.6 nm because of collisions of oxygen and nitrogen ions with the film, creating pores in the surface. Coating the films with polymers with increasing concentrations of PEGDA systematically reduced the roughness, for example, the roughness decreased to 2.3 and 0.4 nm in polymers made of 5 and 20% PEGDA, respectively, as shown in Table 3. Corona-treated PET films coated with polymers comprising proteinoid prepolymer–PEGDA mixtures display different surface roughness, depending on the type of proteinoid used. Coatings made of poly(KI-PEGDA) or poly(EI-PEGDA) yielded high surface roughness, surpassing uncoated PET films. On the other hand, PET films coated with poly(KF-PEGDA) displayed lower roughness than uncoated films, in the range of 0.2–1.1 nm. This may be explained by the significance of incorporating phenylalanine in the proteinoid backbone, which improves the hydrophobic interaction between poly(KF-PEGDA) and the PET film surface. The similarity in the chemical structure between the phenylalanine group and PET film (aromatic rings) led to improved compatibility, compared with the isoleucine side chain in poly(EI-PEGDA) and poly(KI-PEGDA).

2.2.3. Contact Angle. The water contact angles of the film surfaces, shown in Table 3, clearly indicate that all polymeric coatings led to a decrease in the contact angle, compared with the uncoated Corona-treated PET films. The reduced contact angle yields a range of required values for antifog properties. Low contact angles indicate a high hydrophobic character of the coated films, hence achieving good water-wetting surface properties. Corona-treated PET films possess a water contact angle of 69°, while coatings with PEGDA polymer alone reduced the contact angle to 28.3–33.6°, and coating with proteinoid prepolymer–PEGDA polymer mixtures reduced the contact angle further to very low values, down to 5.6°. Table 3 also demonstrates that increasing the concentration of PEGDA polymers from 5 to 20% does not affect or decreases

Table 3. Surface Roughness and Contact Angle of the Various Films

| coating type   | roughness (nm) | contact angle (deg) |
|----------------|----------------|---------------------|
| uncoated PET   | 3.6 ± 0.1      | 69.3 ± 1.0          |
| poly(PEGDA 5%) | 2.3 ± 0.3      | 33.6 ± 1.0          |
| poly(PEGDA 10%)| 1.0 ± 0.5      | 32.3 ± 1.2          |
| poly(PEGDA 15%)| 0.1 ± 0.4      | 28.5 ± 0.5          |
| poly(PEGDA 20%)| 0.4 ± 0.1      | 28.3 ± 1.4          |
| poly(KI-PEGDA 5%)| 7.1 ± 2.7 | 7.1 ± 0.5          |
| poly(KI-PEGDA 10%)| 7.4 ± 2.7  | 8.5 ± 0.7          |
| poly(KI-PEGDA 15%)| 8.7 ± 0.6  | 7.3 ± 2.7          |
| poly(KI-PEGDA 20%)| 15.8 ± 9.4 | 8.0 ± 1.6          |
| poly(KF-PEGDA 5%)| 0.2 ± 0.0   | 22.7 ± 0.4          |
| poly(KF-PEGDA 10%)| 0.3 ± 0.0   | 20.7 ± 0.4          |
| poly(KF-PEGDA 15%)| 0.3 ± 0.6   | 20.8 ± 1.0          |
| poly(KF-PEGDA 20%)| 1.1 ± 0.6   | 25.4 ± 2.2          |
| poly(EI-PEGDA 5%)| 4.2 ± 1.4   | 10.9 ± 2.6          |
| poly(EI-PEGDA 10%)| 5.4 ± 0.4   | 10.5 ± 0.1          |
| poly(EI-PEGDA 15%)| 6.4 ± 2.2   | 7.1 ± 1.5           |
| poly(EI-PEGDA 20%)| 10.2 ± 5.1  | 5.6 ± 1.4           |

*All samples refer to corona-treated PET films (30 μm) coated with polymers made of PEGDA solutions (5, 10, 15, and 20% w/v) and preproteinoid–PEGDA mixtures, as described in the experimental part. Each result represents an average of three measurements at three different areas of the film.*
the contact angle only slightly. For example, coatings made of 5 and 20% poly(KF-PEGDA) display water contact angles of 22.7 ± 0.4 and 25.4 ± 2.2°, respectively, while coatings made of 5 and 20% poly(EI-PEGDA) attain contact angles of 10.9 ± 2.6 and 5.6 ± 1.4°, respectively. As mentioned above, to achieve a good antifog coating, reaching low contact angle is important. Surfaces which exhibit water contact angles of less than 40° are often considered as candidates for being antifog coatings. The lowest water contact angles were achieved by poly(KI-PEGDA) and poly(EI-PEGDA) as shown in Table 3. Figure 6 illustrates the visual difference in the contact angle between uncoated PET films and PET films coated with proteinoid prepolymer–PEGDA polymer mixtures. As seen, the water spreads into a continuous and uniform layer only on the coatings made from proteinoid–PEGDA (C–E) with contact angle in the range of 8.5–20.7°. Nevertheless, on uncoated corona-treated PET films, the water formed ball-shaped droplets on the surface (A) with contact angle of 69.3°. The coating changes the interfacial tension between the water and the PET surface and enables strong connectivity between the film and water droplets.

Table 3 indicates that the relationship between roughness and contact angle is also dependent on the composition of the coatings. For example, it is difficult to understand why increasing the roughness of the poly(EI-PEGDA) coatings leads to a decrease in the contact angle, while increasing the roughness of the poly(KI-PEGDA) coatings has little effect on the contact angle. These results should be further investigated.

2.2.4. Optical Activity. The haze, gloss, and light transmission of UV-cured coated and uncoated PET films are shown in Table 4. PET films coated by polymers made of 5–20% PEGDA exhibit similar values of haze and transmission as uncoated PET film, in the range of 7.6–8.2 and 91.0–92.1, respectively. On the other hand, the gloss reduced slightly from 150 to the range of 120–130. Table 4 also illustrates that in the coatings with proteinoid prepolymer–PEGDA polymer mixtures, the haze values of the films with poly(KI-PEGDA) and poly(EI-PEGDA) increased, while that of the poly(KF-PEGDA)-coated film remained unchanged, the gloss values decreased, and the transmission remained unchanged relative to the uncoated PET film. It is possible that the increase in haze of the poly(KI-PEGDA) and poly(EI-PEGDA) coatings is due to the relatively low compatibility of the proteinoids with the PET film. On the other hand, poly(KF-PEGDA) coatings exhibit low values of haze, similar to uncoated PET, because of the better compatibility with PET discussed above.

2.2.5. Fog Test. The coated films were subjected to hot and cold fog tests, as described in the Experimental Section. All results were obtained during 1 day of heating in 60 °C or cooling in 4 °C, as shown in Table 5 and Figure 6. Figure 9 shows the range of optical visibility through the PET films, ranked A–D, where A denotes excellent visibility, while D denotes poor visibility. Uncoated corona-treated PET films show poor visibility even after 1 day (see Table 5 and Figure 6A). Coating the films with polymers made of PEGDA at different concentrations (5–20%) did not significantly improve the visibility observed during the first few hours in the cold tests, while in the hot tests there was improvement with increasing PEGDA concentration. For instance, after 3 h, the visibility in the hot fog test improved from D to C, B, and A/B for coatings with 5, 10, and 15% PEGDA. Thus, higher PEG percentage in the coating produces faster improvement in visibility, which is reasonable, as PEG increases the water-wetting properties of the coatings. Still, Table 5 illustrates that coating PET films with high percentage of poly(PEGDA) is not sufficient for obtaining good antifog coatings.

Significant improvement in optical visibility was observed when the PET films were coated with polymers made of proteinoid prepolymer–PEGDA mixtures, as shown in Table

**Figure 6.** Hot fog test after 1 h in 60 °C of (A,B) uncoated PET films and (C,D) poly(KI-PEGDA 10%)-coated PET films. Immediately after heating, the films were placed over a written paper and the optical properties were observed (panels B and D). “Photograph courtesy of Elisheva Sason”. Copyright 2019.

**Table 4.** Haze, Gloss, and Light Transmission of the Various Films

| coating type | haze (°) | gloss (%) | transmission (%) |
|--------------|---------|-----------|------------------|
| uncoated PET | 7.4 ± 0.1 | 150 ± 2 | 91 ± 1 |
| poly(PEDG 5%) | 7.6 ± 0.2 | 120 ± 1 | 92 ± 1 |
| poly(PEDG 10%) | 7.7 ± 0.2 | 128 ± 1 | 91 ± 1 |
| poly(PEDG 15%) | 8.1 ± 0.1 | 120 ± 1 | 91 ± 1 |
| poly(PEDG 20%) | 8.2 ± 0.1 | 130 ± 2 | 91 ± 1 |
| poly(KI-PEDG 5%) | 9.2 ± 0.2 | 120 ± 4 | 91 ± 1 |
| poly(KI-PEDG 10%) | 10.8 ± 0.6 | 120 ± 1 | 91 ± 1 |
| poly(KI-PEDG 15%) | 11.7 ± 0.2 | 110 ± 5 | 91 ± 1 |
| poly(KI-PEDG 20%) | 20 ± 1 | 120 ± 5 | 91 ± 1 |
| poly(KF-PEDG 5%) | 7.1 ± 0.1 | 136 ± 1 | 91 ± 1 |
| poly(KF-PEDG 10%) | 7.2 ± 0.1 | 136 ± 1 | 91 ± 1 |
| poly(KF-PEDG 15%) | 7.6 ± 0.1 | 137 ± 2 | 91 ± 1 |
| poly(KF-PEDG 20%) | 7.3 ± 0.2 | 138 ± 3 | 90 ± 1 |
| poly(EI-PEDG 5%) | 8.7 ± 0.0 | 103 ± 3 | 92 ± 1 |
| poly(EI-PEDG 10%) | 10.0 ± 0.4 | 106 ± 2 | 91 ± 1 |
| poly(EI-PEDG 15%) | 11.7 ± 0.1 | 103 ± 7 | 91 ± 1 |
| poly(EI-PEDG 20%) | 14.0 ± 0.4 | 105 ± 3 | 91 ± 1 |

*a All samples refer to corona-treated PET films coated with polymers mad of 5–20% PEGDA and proteinoid prepolymer–PEGDA mixtures, as specified. b Each result represents an average of three measurements at three different areas of the film.
Table 5. Hot and Cold Fog Tests of Uncoated and Coated PET Films Over 1 day

| coating type* | hot test | cold test |
|---------------|----------|-----------|
|               | 5 min    | 60 min    | 180 min | 1 day | 5 min | 60 min | 180 min | 1 day |
| uncoated PET  | D        | D         | D       | D     | D     | D      | D       | A/B   |
| poly(PEGDA 5%)| D        | C         | C       | C     | D     | D      | D       | A    |
| poly(PEGDA 10%)| D      | C         | B       | B     | D     | D      | D       | A    |
| poly(PEGDA 15%)| D      | D         | A/B     | A/B   | D     | D      | D       | A    |
| poly(PEGDA 20%)| D      | D         | A/B     | A/B   | D     | D      | D       | A    |
| poly(KI-PEGDA 5%)| A       | A         | A       | B/C   | A     | A      | A       | A    |
| poly(KI-PEGDA 10%)| A      | A         | A       | A     | A     | A      | A       | A    |
| poly(KI-PEGDA 15%)| A      | A         | A       | A     | A     | A      | A       | A    |
| poly(KI-PEGDA 20%)| A      | A         | A       | A     | A     | A      | A       | A    |
| poly(KF-PEGDA 5%)| B       | B         | B/C     | B/C   | B/C   | B/C    | B/C     | A    |
| poly(KF-PEGDA 10%)| B      | B         | B/C     | B/C   | B/C   | B/C    | B/C     | A    |
| poly(KF-PEGDA 15%)| B      | A/B       | A       | A     | A     | A      | A       | A    |
| poly(KF-PEGDA 20%)| A      | A         | A       | A     | B     | B      | B       | A    |
| poly(EI-PEGDA 5%)| A       | A         | B/C     | C     | A     | A      | A       | A    |
| poly(EI-PEGDA 10%)| A      | A         | A       | B     | A     | A      | A       | A    |
| poly(EI-PEGDA 15%)| A      | A         | A       | A     | A     | A      | A       | A    |
| poly(EI-PEGDA 20%)| A      | A         | A       | A     | A     | A      | A       | A    |

*All samples refer to corona-treated PET films coated with polymers made of 5−20% PEGDA or protein prepolymer−PEGDA mixtures, as specified.

5. For coatings composed of poly(EI-PEGDA 5−20%), the visibility rank after 5 min and throughout the day was A in the cold test, while in the hot test higher PEG content yielded better optical visibility, for example, after 3 h, B/C and A were obtained with EI and 5 and 10% PEGDA, respectively, while coatings with 15 or 20% PEGDA attained a visibility rank of A after 5 min that persisted throughout the day. Table 5 also illustrates the importance of the proteinoid composition of the coatings; substituting isoleucine for phenylalanine deteriorates significantly the antifog properties. The source of this behavior is still not clear to us. While in both tests, poly(KI-PEGDA 10−20%) coatings rapidly attained excellent visibility, poly(KF-PEGDA 5−20%) attained optical visibility of A only after a day, while in the hot test poly(KF-PEGDA 5−10%) only reached visibility of B even after 1 day.

Figure 6 illustrates the visual differences in optical properties between the uncoated corona-treated PET films (panels A and B) and corona-treated PET films coated with polymers made of poly(KI-PEGDA 10%) (panels C and D). In panels A and C, the films were placed over a beaker filled with water and kept at 60 °C. As illustrated in Figure 6C, the water spread into a continuous and uniform layer only on the poly(KI-PEGDA 10%-coated film, obtaining a ranking of A. On the other hand, on the uncoated corona-treated PET films (Figure 6A), the water formed tiny droplets on the surface that damaged the clarity of the PET film, obtaining a poor ranking of D. Immediately after heating, the films were placed over a written paper, and the optical properties were observed (Figure 6, panels B and D). It is clear that the writing observed through the film coated with poly(KI-PEGDA 10%) is completely clear, while the writing covered by the uncoated film is obscure.

2.2.6. Durability of the Coatings. The stability of the coatings was examined, as mentioned in the Methods section. All samples exhibited similar results following 20 cycles of the hot fog test. Furthermore, similar results were obtained following the overnight soaking test in water after the first cycle and then drying in an oven at 80 °C. Hence, the coatings are stable and durable in water, and the antifog properties are preserved for a relatively long term.

2.2.6.1. Mechanical Properties of Coatings. As mentioned in the Materials and Experimental Section, tape, knife-scratch, and sandpaper abrasion tests were performed on the coated films after which the films were introduced to the hot fog test. All coatings exhibited the same antifog properties as shown before the tests (as shown in Table 5), indicating that the coatings are resistant to different types of mechanical abrasions while maintaining their antifog properties.

3. EXPERIMENTAL SECTION

3.1. Materials. The following analytical-grade chemicals were purchased from commercial sources and used without further purification: L-glutamic acid, L-phenylalanine, L-isoleucine, and L-lysine from Sigma (Rehovot, Israel); PEGDA 400 Da from Polysciences (Germany); bisacrylphosphate oxide—a photoinitiator named IRGACURE 819-DW, from BASF (Germany); PET films (air corona-treated) of A4 size and 36 μm average thickness from Hanita Coatings Ltd. (Israel); and tape from 3M (USA). Water was purified by passing deionized water through an Elgastat Spectrum reverse osmosis system (Elga Ltd., High Wycombe, UK).

3.2. Methods. 3.2.1. Preparation of Proteinoids by Thermal Step-Growth Polymerization. A selection of L-amino acids was used to prepare a series of proteinoids: L-glutamic acid, L-phenylalanine, L-lysine, and L-isoleucine from Sigma (Rehovot, Israel); PEGDA 400 Da from Polysciences (Germany); bisacrylphosphate oxide—a photoinitiator named IRGACURE 819-DW, from BASF (Germany); PET films (air corona-treated) of A4 size and 36 μm average thickness from Hanita Coatings Ltd. (Israel); and tape from 3M (USA). Water was purified by passing deionized water through an Elgastat Spectrum reverse osmosis system (Elga Ltd., High Wycombe, UK).
The following proteinoids were prepared: poly(KI) with 1:1 w/w lysine/isoleucine, poly(KF) with 1:1 w/w lysine/phenylalanine, and poly(EI) with 1:1 w/w glutamic acid/isoleucine.

3.2.2. Preparation of Proteinoid Prepolymers. Proteinoid prepolymers were prepared via Michael addition reaction, by interacting free primary amino groups of the proteinoids with double bonds belonging to the cross-linker monomer PEGDA, as shown in Figure 7. Briefly, crude proteinoids were dissolved in water (100 mg in 1 mL), and the pH was adjusted to 8–9 in the acidic poly(EI) proteinoid solution by adding NaOH (1 M, 400 μL). PEGDA (10% w/w, 10 mg in 0.2 mL ethanol) was added to the proteinoid aqueous solution, and the mixture was heated to 50 °C and stirred for 120 min to yield the proteinoid prepolymers.

3.2.3. Characterization of Proteinoids and Prepolymers. The molecular weights and polydispersity indices of the proteinoids were determined using gel permeation chromatography (GPC) comprising a Waters Spectra Series P100 isocratic high-performance liquid chromatography (HPLC) pump with an ERMA ERC-7S10 refractive index detector and a Rheodyne (Coatati, CA, USA) injection valve with a 20 μL loop (Waters, MA, USA). The samples were eluted with superpure HPLC water through a linear BioSep SEC-s-3000 column (Phenomenex) at a flow rate of 1 mL/min. The molecular weights were determined relative to poly(ethylene glycol) standards (Polymer Standards Service-USA, Silver Spring, MD, USA) with a molecular weight range of 100–450 000 Da, human serum albumin (67 kDa, Sigma-Aldrich), and bovine plasma fibrinogen (340 kDa, Sigma-Aldrich), using Clarity Chromatography software (DataApex, Prague, Czech Republic).

The optical activities of the formed proteinoids were determined using a PE343 polarimeter (PerkinElmer). The measurements were done in water, at 589 nm and 25 °C.

FTIR measurements of the crude proteinoids and prepolymers were done by the attenuated total reflectance (ATR) technique, using a Bruker ALPHA-FTIR QuickSnap sampling module equipped with a Platinum ATR diamond module.

1H NMR characterization of proteinoids and prepolymers was performed on a Bruker DRX700 spectrometer using a cryogenic TCI probehead equipped with z-axis pulsed field gradients. Measurements were conducted at 300 K on 5–10 mg/mL proteinoid samples in 2H2O using a 1D-1H NMR sequence with presaturation of the residual water signal. Typical total measurement times were 30–60 s per sample. Spectra were processed and analyzed using the Bruker TopSpin 3.5 platform.

3.2.4. Preparation of Antifog Thin Coatings. Thin antifog coatings on PET films were prepared by spreading with a Mayer rod (Figure 2B) various mixtures containing the selected proteinoid prepolymer, photoinitiator, and different concentrations of PEGDA, followed by UV-curing of the dried mixtures. Briefly, in the first step, to improve the adhesion of the coating on the plastic, PET films were pretreated by corona with iCorona-1 (VETAPHONE Corona & Plasma, Denmark) at 300 W-min/m². Then, 1 mL of mixtures containing different concentrations of PEGDA (5, 10, 15, and 20% w/v) and 1% (relative to the PEGDA) of the photo-initiator IRGACURE 819-DW (Figure 8A) were added to a 1 mL aqueous solution containing 100 mg of the selected proteinoid prepolymer. In the next step, the different mixtures were spread on PET films by a Mayer rod (Figure 8B) with 6 μm thickness.5,43 Following this process, the coating was dried in a heating oven at 80 °C for a few minutes and cured by UV (testing model RW-UVA 201-20 with 220 V ac 50 Hz power supply) at speed of 35 m/min, under high-pressure mercury UV lamp with 100 W/cm power and main wavelength of 365 nm to achieve dried coated films.

Similar coating was done with ethanol solutions containing different concentrations of PEGDA and photoinitiator without proteinoid prepolymer.

3.2.5. Characterization of Antifog Coatings. FTIR measurements were performed as described in Section 3.2.2 on uncoated and coated PET films with PEGDA (20% w/v) before and after UV-curing.

Surface topography analysis of the coated and uncoated PET films was obtained using atomic force microscopy (AFM, NanoScope 9, Bio FastScan, Bruker AXS, Santa Barbara, CA). All images were obtained in soft tapping mode with a FastScan-B (Bruker) silicon probe. The images were captured in the retrace direction with a scan rate of 1.4 Hz. Scans for each film were performed on an area of 3 μm × 3 μm. Height images were captured with 512 scans/line image resolution. AFM images were obtained in air at room temperature. Before analysis of the images, second-order “flattening” and first-order “planefit” functions were applied to each image. Analysis of the height images was done using the NanoScope Analysis software. The morphological changes of the films were determined by averaging the root mean square roughness (Rq) values over three different regions on each film. The reported values are an average of at least three different points of four different films.

Figure 7. Michael addition reaction of proteinoid with PEGDA 400.

Figure 8. (A) Chemical structure of the photo-initiator IRGACUR 819-DW; (B) setup for coating with Mayer rod on plastic films: the PET plastic film was placed on a flat surface, and the rod was pulled over the PEGDA solution with or without proteinoid prepolymer, leaving a uniform layer with wet thickness of 6 μm. "Photograph courtesy of “Elisheva Sason”. Copyright 2019."
Sessile drop water contact angle measurements were done using a Goniometer (System OCA, model OCA20, Data Physics Instruments GmbH, Filderstadt, Germany). Drops of 5 μL of distilled water were placed on five different areas of each film, and images were captured a few seconds after deposition. The static water contact angle values were determined by Laplace—Young curve fitting. All measurements were done at 25 °C and 60% moisture. Each result represents an average of four measurements with up to 5% standard deviation. Uncoated PET was used as a reference.

Haze and transmission measurements were performed using a Haze-Gard Plus 4752 model with ASTM D1003 standard (BYK-Gardner, Germany). The instrument was used to evaluate the degrading visibility of different damage modes by measuring the haze level; the transparent specimen was illuminated at normal incidence, and the transmitted light was measured photoelectrically by an integrating sphere. Haze is caused by wide-angle scattering. According to ASTM D1003, haze is the percentage of transmitted light that deviates from the incident beam by more than 2.58° on average. When total transmittance was measured, the sphere’s normal outlet was closed, and when haze is measured, the normal outlet was open. Increased haze of a transparent sample reduces the contrast of an object viewed through the sample, resulting in a milky or cloudy appearance of the object.

Gloss measurements were performed using a Tri-Gloss-master 20 60–85° model multiance Glossmeter (SH260C, Sheen Instruments, USA).

Antifog behavior of the films was studied using hot and cold fog tests. Briefly, an open 28 mL vial filled with 10 mL water was covered with a 5 cm × 5 cm film and subsequently kept in a 60 °C water bath or at 4 °C in a refrigerator. Variations in the optical visibility of the films were observed and recorded at different time intervals. Ratings of A to D were used, where D denotes zero visibility with an opaque layer of small water droplets and A describes excellent optical visibility where a transparent continuous film of water is displayed, as shown in Figure 9.

Figure 9. Optical visibility ranking: (A) transparent continuous layer of water providing excellent optical performance; (B) large water drops on some parts of the surface allowing partial light transmission; (C) medium water drops on most of the surface allowing partial light transmission; and (D) small water drops on the entire surface causing very poor visibility. "Photograph courtesy of “Elisheva Sason". Copyright 2019.”

3.2.6. Durability of the Coatings. Coating stability was evaluated by repeating the hot fog test 20 times. In each cycle, the sample was cooled overnight to room temperature and exposed to the test the next day. In addition, durability of the coatings in water was tested after completion of the first cycle by soaking the coated films in water overnight and drying in an oven at 80 °C for a few minutes prior to the second cycle.

3.2.6.1. Mechanical Properties of the Coatings. Adhesion tests were done to investigate the strength of the interaction between the coating and the substrate film. Each test was carried out as follows: an adhesive tape was firmly pressed onto the coating film and then slowly peeled off. The process was repeated 10 times after which the tested film was introduced to the hot fog test to insure that the antifog properties were not damaged (Figure S5).

Knife-scratch and sandpaper abrasion tests were performed to evaluate the robustness and abrasive resistance of the coatings. A knife was used to scratch the coatings along several lines after which the tested film was introduced to the hot fog test (Figure S6). The sandpaper abrasion test was carried out as follows: a 35 g weight was placed on a ruler, and the film was attached to the ruler, which was positioned on a sandpaper with the coated side facing the sandpaper (Figure S7A). The ruler with the attached film was moved 10 cm along the sandpaper five times (Figure S7B) after which the film was introduced to the hot fog test.

4. CONCLUSIONS

In this study, a series of thin antifog cross-linked coatings were prepared by spreading on PET films with a Mayer rod various mixtures of proteinoid prepolymer, PEGDA, and a photoinitiator, followed by UV-curing of the dried coatings. The proteinoids, synthesized by thermal bulk step-growth polymerization, were mostly uniform in size distribution with relatively high molecular weights. The proteinoids were activated by Michael addition with PEGDA to yield proteinoids with double bonds, termed proteinoid prepolymers. Then, thin cross-linked coatings were made on corona-treated PET films by UV-curing of mixtures of the proteinoid prepolymer and different concentrations of PEGDA. The coated PET films before and after UV-curing were characterized by FTIR, which indicated full polymerization of the monomers during the UV-curing process. The surface roughness and contact angles of the films were characterized and showed hydrophilic coatings with static contact angles in the range of 5.6–33.6° and surface roughness in the range of 0.37–15.8 nm. The mechanical properties of the coatings were examined by tape, knife-scratch, and sandpaper abrasion tests. After the tests, the coatings kept their mechanical stability and antifog properties. The effect of the proteinoid polymer composition on the antifog properties of the coatings was also illustrated. For example, coatings containing isoleucine illustrated significantly better antifog properties than coatings of similar composition in which isoleucine was substituted by phenylalanine. The optical characteristics of the coatings were determined, with haze in the range of 7.4–20 and good rankings in hot and cold fog tests. This series of UV-curable acrylate polymers containing proteinoids may potentially become useful as antifog material for various devices and potentially also for biological and food-related applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00336.

Comparison table of antifog materials and systems, FTIR, and NMR graphs for various proteinoids and proteinoid–PEGDA, photographs of adhesive test, knife-scratch test, and sandpaper abrasion test (PDF)

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Notes

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