

Spectroscopic Studies of Microwave Plasma Reactions of Maleic Anhydride on Poly(vinylidene fluoride) Surfaces: Crystallinity and Surface Reactions

Yaqiu Zhao and Marek W. Urban*

Department of Polymers and Coatings, North Dakota State University,
Fargo, North Dakota 58105

Received September 22, 1998. In Final Form: March 2, 1999

These studies show that maleic anhydride and carboxylic acid groups can be chemically bonded to poly(vinylidene fluoride) (PVDF) surfaces with the use of microwave plasma energy. Maleic anhydride reacts with the PVDF surface through a C=C bond opening of the maleic anhydride ring, and its hydrolysis results in chemically attached carboxylic acid groups on the PVDF surface. The extent of the surface reactions can be monitored using attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy. These studies also show that maleic anhydride C=O groups are preferentially parallel to the PVDF surface, and molecular mechanics force field calculations indicate that the most favorable angle between maleic anhydride and a polymer backbone is 25°. Quantitative spectroscopic analysis shows that before hydrolysis, volume concentrations of maleic anhydride vary from 1.32×10^{-5} to 7.94×10^{-5} mg/cm³ (surface concentrations from 1.8×10^{-9} to 6.67×10^{-9} mg/cm²), whereas the carboxylic acid content changes from 8.67×10^{-5} to 2.7×10^{-4} mg/cm³ (1.18×10^{-8} to 2.27×10^{-8} mg/cm²) depending on the reaction conditions and depth from the surface. After hydrolysis, the carboxylic acid content changes from 9.1×10^{-5} to 3.15×10^{-4} mg/cm³ (1.24×10^{-8} to 2.65×10^{-8} mg/cm²).

Introduction

Modifications of polymer surfaces using microwave and radio frequency gas plasma techniques are advantageous because usually minimal altering of bulk properties is anticipated.^{1,2} For that reason, plasma surface reactions, including film and nonfilm forming processes, became attractive in numerous applications, ultimately altering such surface properties as polymer biocompatibility,³ adhesion,⁴ hydrophilicity,⁵ friction,⁶ and other surface properties. Previous studies on poly(dimethylsiloxane) (PDMS)^{7,8} showed that maleic anhydride solid-state monomers can be reacted on PDMS elastomer surfaces, and surface reactions are accomplished by the C=C bond opening of maleic anhydride. Since attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy provides adequate surface sensitivity for functional group analysis and the ability to quantify newly formed species,⁹ the content of maleic anhydride was analyzed using this method.

With this background in mind, let us focus on surface modifications of PVDF. Dehydrofluorination reactions of poly(vinylidene fluoride) (PVDF) are attractive because of the possibility of creating polymer surfaces with modified dielectric properties,^{10,11} and the two most commonly used methods to obtain dehydrofluorinated

surfaces are thermal degradation of PVDF^{12,13} and phase-transfer catalysis (PTC) surface reactions.^{10–11,14} In these reactions, the primary process is elimination of HF units and formation of the C=C double bonds along the polymer backbone. It has been proposed that surface reactions proceed according to a “zipper” mechanism, in which HF elimination is initiated at a certain point, and propagates along the polymer chain.¹² Although one would anticipate infinitely long conjugated chains, the presence of head-to-head (HH) or tail-to-tail (TT) surface defects prevents from achieving longer than 30–40 C–C conjugated segments.^{10,11}

Although the effect of polymer composition on surface reactions has been addressed in our earlier studies on PDMS,¹⁵ for thermoplastic polymers such as PVDF, this effect is particularly important due to a unique behavior of crystalline and amorphous surface components of PVDF.¹⁶ Three crystal forms of PVDF are known as α , β , and γ phases,^{17,18} and detailed morphological studies have shown that thermal degradation occurs preferentially in β and γ phases, rather than the α phase because of adverse electrostatic and van der Waals interactions along crystalline phases. In this study, we will address the issue how crystalline phase resulting from melt crystallization¹⁹ may affect dehydrofluorination and the surface reactions

* To whom all correspondence should be addressed.

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on PVDF utilizing maleic anhydride. Due to the effectiveness of microwave energy in the presence of inert and/or reactive gases and surface species, microwave plasma will be applied to conduct surface reactions. Quantitative ATR FT-IR spectroscopy will be used for analysis of newly created surfaces at various depths. An ultimate goal of this study is to determine the nature and extent of polymer surface reactions under microwave plasma conditions and how α -type crystalline/amorphous components may affect newly formed species.

Experimental Section

Substrate Preparation and Surface Reactions. PVDF films were prepared from PVDF powder (Aldrich Chemical Co., MW = 530 000) by melting PVDF powder in a hot pressed plate at 2500 psi for 10 min at 200 °C, followed by annealing them to ambient temperature (approximately 27 °C). The second set of specimens was prepared by quenching PVDF prepared in the same way to a liquid N₂ temperature.

Plasma reactions were conducted using closed reactor conditions described elsewhere.⁸ The PVDF film thickness was about 200 μ m with approximate dimensions of 40 \times 25 \times 0.5 mm. In a typical experiment, a specimen was placed in a microwave plasma reactor, followed by its evacuation to 2 mTorr and purging a sample chamber with gas to a desired experimental pressure, typically about 200 mTorr. At this point, microwave radiation (KMC Model KMO-24G) to induce plasmas was turned on. The same procedure was utilized for reacting maleic anhydride (Aldrich Chemical Co.) monomer. In this case, prior to purging and evacuating the reaction chamber, 50 mg of a solid monomer along with the PVDF were placed in a reactor. Since under such vacuum conditions maleic anhydride monomers will be partially in a gas phase, its supply is sufficient for surface reactions. A similar approach was utilized in the studies of PDMS surface reactions.⁷ In an effort to establish stability of surface treatments on the PVDF surface, after microwave plasma reactions, the samples were boiled in water for 30 min. To obtain acid functionalities on the PVDF surface, after microwave plasma reactions, the samples were boiled in water for 5 min. After drying, the samples were stored in a desiccator under ambient conditions.

X-ray Diffraction Measurements. In an effort to determine the content of crystalline and amorphous phases in annealed and quenched specimens, X-ray diffraction measurements were performed on annealed and quenched PVDF films. All diffractograms were collected on a Philips diffractometer (Xpert-MPD) using a long fine focus Cu tube operated at 45 kV and 30 mA. The samples were scanned over the 2θ range from 2 to 50° 2θ , with steps of 0.02 2θ and 1 s collection intervals. While annealed PVDF is anticipated to have a higher crystalline content that develops during the slower cooling process, the quenched PVDF will be primarily amorphous due to "freezing" of the amorphous melt. To determine the amount of crystalline phase present in PVDF, the method described by Alexander²⁰ was used. This approach relates intensities of the X-ray diffractogram to the degree of crystallinity.²¹ The degrees of crystallinity determined for annealed and quenched specimens were 64% and 25%, respectively. The observed d spacings and their peak relative intensities are shown in Table 1. According to the results in Table 1, 25% crystalline samples are composed primarily of α -type crystalline phase, whereas 64% crystalline samples are composed of combinations of α and γ crystalline phases.^{17–19,22} It should be noted that the reported crystallinity data were obtained from the bulk, and it is assumed that the surface crystalline content is similar.

Spectroscopic Measurements. ATR FT-IR spectra were collected on a Nicolet Magna-850 FT-IR single beam spectrometer using 4 cm⁻¹ resolution and a mirror speed of 0.1581 cm s⁻¹. A KRS-5 crystal with 45° angle 50 \times 20 \times 3 mm was used. Each spectrum represents 200 co-added scans ratioed against a

Table 1. Observed d Spacings in 25% and 64% Crystalline PVDF

crystallinity	d (Å)	rel intens
25%	4.83	0.771
	4.44	1.00
	3.34	0.252
	2.71	0.126
	2.50	0.126
64%	4.83	0.423
	4.75	1.00
	4.40	0.713
	3.34	0.231
	3.30	0.382
	2.75	0.102
	2.67	0.153
	2.46	0.114
	2.37	0.140
	2.29	0.191

reference spectrum obtained by recording 200 co-added scans of an empty ATR cell. All spectra were corrected for spectral distortions and optical effects using Q-ATR software.⁹ For energy calculations, the HyperChem software package (Hypercube, Inc.) was used and utilized molecular mechanical force field MM+ based on the Polak–Ribiere algorithm method with a total root-mean-square (RMS) gradient of 0.01 kcal/(Å mol).

Results and Discussion

Our earlier studies^{7,23–25} indicated that microwave plasma energy can be successfully used for reacting monomers to elastomeric surfaces, revealing that there are numerous advantages of microwave plasma reactions, and the effect of surface morphology of polymeric substrates appeared to be particularly important.¹⁵ For example, in elastomeric poly(dimethylsiloxane) (PDMS), homogeneously dispersed SiO₂ may form PDMS-rich and SiO₂-rich domains, and aggregates formed in the SiO₂-rich domains result in a crack formation, which ultimately inhibit PDMS surface reactions with imidazole. In the case of thermoplastic polymer surfaces, these issues may be further complicated due to the presence of crystalline and amorphous components, which may inherently alter surface reactivity.

With this background in mind, let us analyze how the 25% α crystalline PVDF surface responds to Ar microwave plasma exposure. Figure 1 illustrates ATR FT-IR spectra of 25% α crystalline PVDF surfaces obtained by microwave plasma reactions in the presence of Ar. In this case, the microwave plasma reaction time was 20 s. While trace A illustrates the spectrum of unreacted 25% α crystalline PVDF surface, trace B is the spectrum of the Ar plasma reacted surface. As seen, after Ar microwave plasma reactions, new bands at 1595 and 1670 cm⁻¹ are detected and their appearance indicates formation of conjugated C=C double bond $-(CH=CF)-$ units along the polymer backbone of dehydrofluorinated PVDF.^{10,13} While the C—C skeletal band of PVDF at 1069 cm⁻¹ remains the same, the band at 1402 cm⁻¹ becomes weaker after plasma reactions. This band is attributed to a combination mode of H—C—H, C—C—H, and C—C normal vibrations.^{27,28} Other notable changes are observed for the bands associated with the C—H, F—C—F, and C—F vibrational

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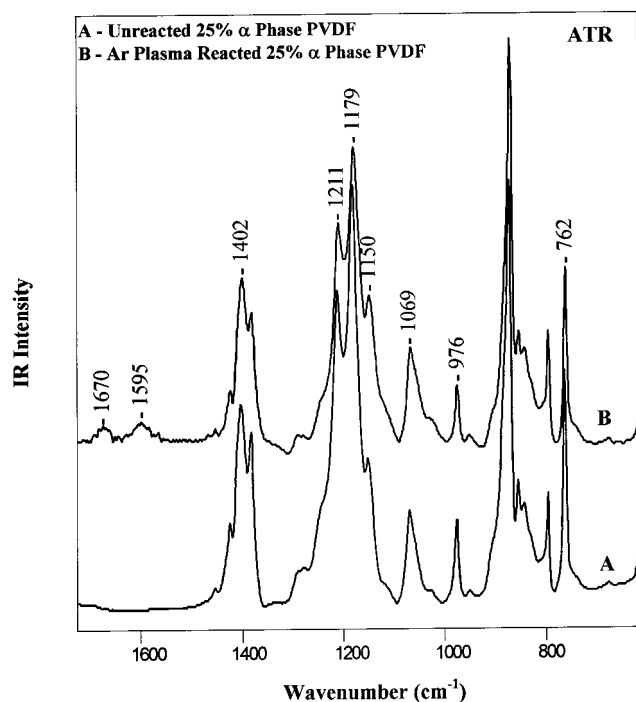


Figure 1. ATR FT-IR spectra in the 1800–700 cm^{-1} region: (A) 25% α phase PVDF; (B) 25% α phase PVDF treated with Ar plasma. Conditions: microwave plasma 600 W, discharge pressure 200 mTorr, reaction time 20 s.

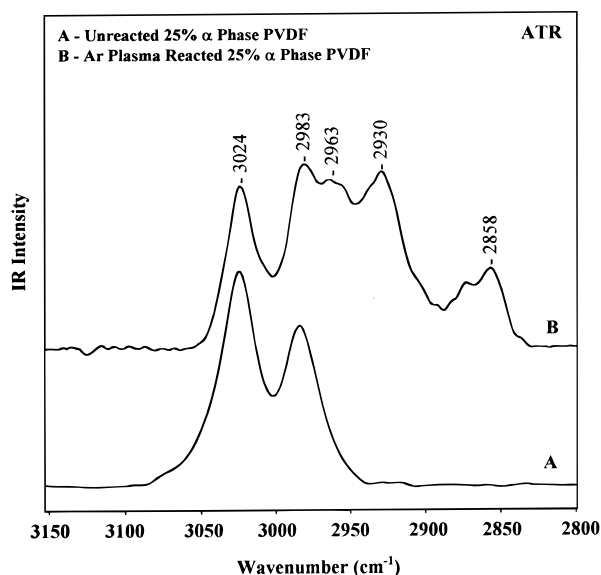


Figure 2. ATR FT-IR spectra of PVDF in the 3150–2800 cm^{-1} region: (A) 25% α phase PVDF; (B) 25% α phase PVDF treated with Ar plasma. Conditions: microwave plasma 600 W, discharge pressure 200 mTorr, reaction time 30 s.

modes^{28,29} at 1211, 1179, and 976 cm^{-1} and also appear to decrease. The above spectral changes indicate that the structural changes at the PVDF surface due to microwave reactions result in dehydrofluorination. If indeed dehydrofluorination reactions lead to the formation of new structures on the PVDF surface, these changes should be also detected in the C–H stretching region. As shown in Figure 2, traces A and B are ATR FT-IR spectra of unreacted 25% α crystalline PVDF and Ar plasma exposed 25% α crystalline PVDF, respectively. After Ar microwave

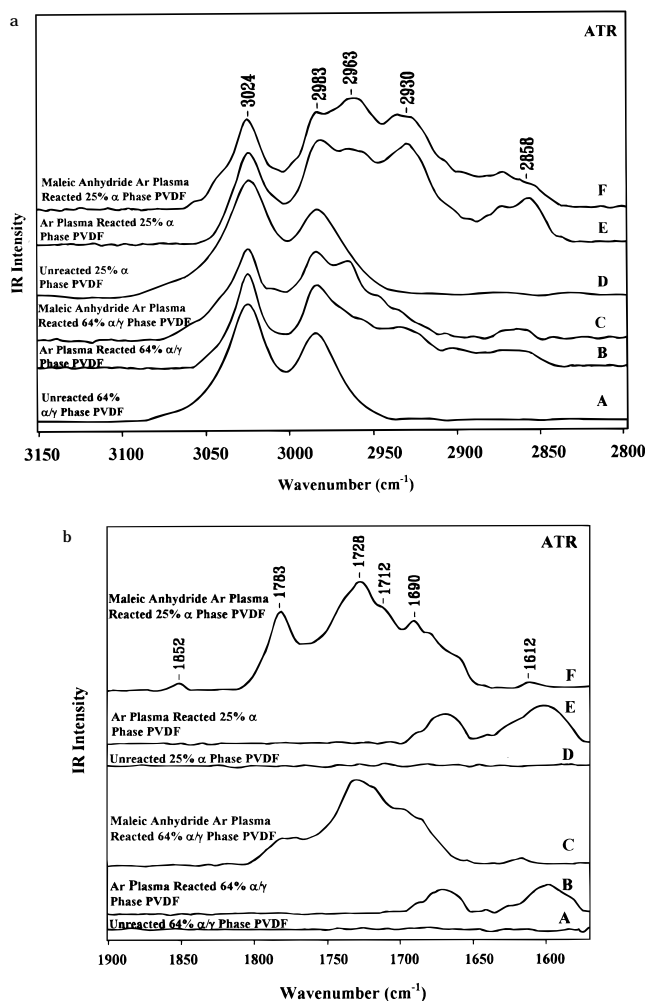


Figure 3. (a) ATR FT-IR spectra of PVDF in the 3150–2800 cm^{-1} region: (A) unreacted 64% α/γ phase PVDF; (B) 64% α/γ phase PVDF treated with Ar plasma; (C) 64% α/γ phase PVDF treated with maleic anhydride Ar plasma; (D) unreacted 25% α phase PVDF; (E) 25% α phase PVDF treated with Ar plasma; (F) 25% α phase PVDF treated with maleic anhydride Ar plasma. Conditions: microwave plasma 600 W, discharge pressure 200 mTorr, reaction time 30 s. (b) ATR FT-IR spectra of PVDF in the 1900–1580 cm^{-1} region: (A) unreacted 64% α/γ phase PVDF; (B) 64% α/γ phase PVDF treated with Ar plasma; (C) 64% α/γ phase PVDF treated with maleic anhydride Ar plasma; (D) unreacted 25% α phase PVDF; (E) 25% α phase PVDF treated with Ar plasma; (F) 25% α phase PVDF treated with maleic anhydride Ar plasma. Conditions: microwave plasma 600 W, discharge pressure 200 mTorr, reaction time 30 s.

plasma reactions, new bands at 2858 and 2930 cm^{-1} are observed, indicating again formation of the $-(\text{CF}=\text{CH}-)$ units. Furthermore, the intensity decrease of the 3024 cm^{-1} band due to asymmetric C–H stretching modes confirms that indeed surface dehydrofluorination occurs.

While the above experiments confirm previous studies that microwave Ar plasma can be used to generate conjugated C=C surface chains, the next question to be addressed is whether such surfaces can be further grafted by reacting maleic anhydride. The choice of maleic anhydride was dictated by the fact that it may not only alter surface polarity but also form a bonding site for further surface reactions. Figure 3 illustrates ATR FT-IR spectra of maleic anhydride reacted on a PVDF surface in the presence of Ar microwave plasma. Traces A, B, C, D, E, and F are ATR FT-IR spectra of unreacted 64% α/γ crystalline PVDF (A), Ar plasma reacted 64% α/γ crystal-

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line PVDF, maleic anhydride Ar plasma reacted 64% α/γ crystalline PVDF (C), unreacted 25% α crystalline PVDF (D), Ar plasma reacted 25% α crystalline PVDF (E), and maleic anhydride Ar plasma reacted 25% α crystalline PVDF (F), respectively. After the 64% α/γ crystalline PVDF surface (trace A) is exposed to Ar plasma (trace B), conjugated C=C bands at 1595 and 1670 cm^{-1} , and newly formed C—H stretching bands at 2858 and 2930 cm^{-1} due to $-(\text{CF}=\text{CH})-$ units, are detected. When such a specimen is further exposed to maleic anhydride Ar plasma (trace C), the bands at 1595 and 1670 cm^{-1} due to conjugated C=C bonds are eliminated, and a new band at 1612 cm^{-1} due to nonconjugated C=C bonds is observed. Furthermore, the bands at 2858 and 2930 cm^{-1} due to C—H stretching modes in the $-(\text{CF}=\text{CH})-$ units decrease, whereas the band intensity at 2963 cm^{-1} increases.

Although these results suggest that maleic anhydride reacted to the PVDF surface through the C=C bond opening, resulting in nonconjugated C=C linkages and new C—H species, further evidence for the presence of maleic anhydride reactions is observed. In the 1900–1580 cm^{-1} region, shown in Figure 3, trace C, new bands at 1783, 1728, and 1690 cm^{-1} are detected. The band at 1783 cm^{-1} is attributed to symmetric anhydride C=O stretching modes of the maleic anhydride ring,³⁰ and the band at 1728 cm^{-1} is due to the C=O stretching modes of $-\text{COOH}$ resulting from the maleic anhydride ring-opening reactions on the PVDF surface.³¹ However, in the 3150–2800 cm^{-1} region, the C—H stretching band due to C=C—H units of maleic anhydride is not detected, thus indicating that maleic anhydride reacts with the PVDF surface through the C=C opening.

While the above results were obtained for 64% α/γ crystalline PVDF, analysis of ATR FT-IR spectra of maleic anhydride plasma reactions conducted on 25% α crystalline PVDF surfaces illustrate other features. As shown in Figure 3, trace F, as a result of microwave plasma experiments, the band at 1852 cm^{-1} is present, and the intensity of the 1783 cm^{-1} is significantly stronger. The presence of the band at 1852 cm^{-1} attributed to asymmetric anhydride C=O stretching modes of the maleic anhydride ring indicates that, for 25% α crystalline PVDF under the same microwave plasma conditions, reactions of maleic anhydride in the presence of Ar plasma yield a higher content of anhydride functionalities. In contrast, when the PVDF crystalline content increases, the amount of maleic anhydride reacted is diminished, thus indicating that the crystalline content of PVDF indeed affects the extent of microwave plasma reactions. A proposed mechanism leading to maleic anhydride surface reactions in the presence of Ar plasma is shown in Figure 4a. As illustrated, the first step involves formation of the conjugated C=C bonds as a result of surface dehydrofluorination of PVDF treated with Ar plasma. When maleic anhydride Ar plasma is introduced, C=C bonds open to form anhydride radicals and dicarboxylic acid radicals capable of reacting with PVDF through conjugated C=C bonds.

While initial surface reactions result in the presence of surface acid, there is also maleic anhydride attached to the surface. In an effort to convert maleic anhydride to acid functionalities and to establish stability of the reaction products, the next step involved hydrolysis of microwave plasma-maleic anhydride modified PVDF surfaces. For

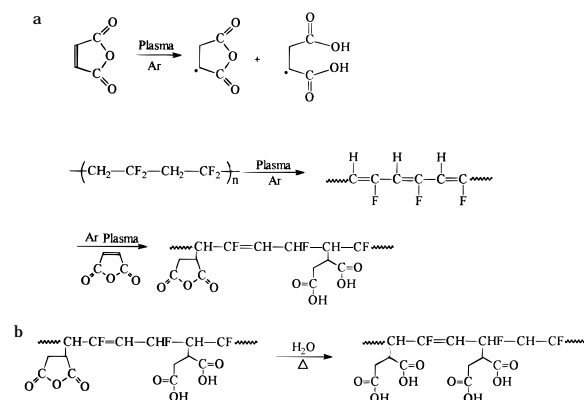


Figure 4. (a) Proposed mechanisms of maleic anhydride reactions to PVDF surfaces in the presence of Ar gas in the closed plasma chamber. (b) Surface modified PVDF hydrolysis reactions.

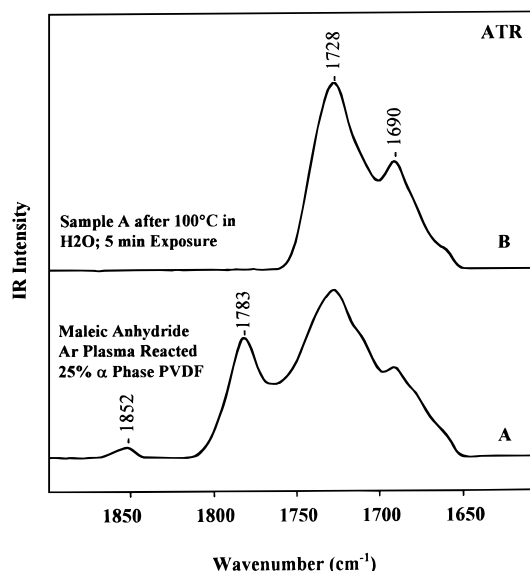


Figure 5. ATR FT-IR spectra in the 1900–1600 cm^{-1} region: (A) maleic anhydride reacted on 25% α phase PVDF in the presence of Ar microwave plasma; (B) sample A after exposure to 100 $^{\circ}\text{C}$ in H_2O for 5 min.

this purpose, we boiled microwave surface modified PVDF specimens in H_2O for 5 and 30 min. While the first experiment (5 min) allows converting maleic anhydride to acid groups, the purpose for the second treatment (30 min) was to determine the stability of newly formed species.

Figure 5 illustrates ATR FT-IR spectra in the 1900–1580 cm^{-1} region of maleic anhydride reacted on 25% α crystalline PVDF in the presence of Ar microwave plasma after 5 min exposure to 100 $^{\circ}\text{C}$ H_2O . While trace A shows the spectrum of PVDF before, trace B illustrates the results after boiling. As seen in trace A, the asymmetric anhydride C=O stretching band at 1852 cm^{-1} and the symmetric anhydride C=O stretching band at 1783 cm^{-1} of maleic anhydride ring are detected. However, after boiling (trace B), both bands are not present, and instead, intensities of the band at 1728 cm^{-1} due to C=O stretching modes of maleic acid became stronger. Furthermore, the OH stretching band at 3410 cm^{-1} is observed (not shown), which indicates that for 25% α crystalline PVDF, maleic anhydride is hydrolyzed to form acid functionalities after 100 $^{\circ}\text{C}$ exposure to H_2O . Reactions leading to the formation of these species are shown in Figure 4b. As indicated above, the second step was boiling for 30 min in H_2O , and this

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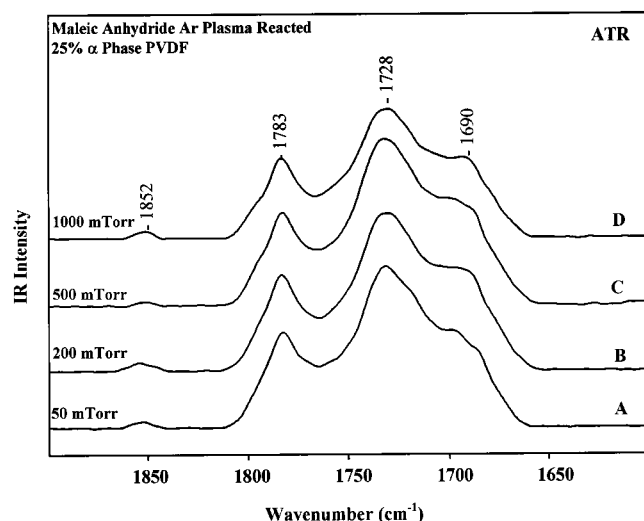


Figure 6. ATR FT-IR spectra in the 1900–1600 cm^{-1} region of maleic anhydride reacted on 25% α phase PVDF in the presence of Ar plasma under different pressures: (A) 50 mTorr/30 s; (B) 200 mTorr/30 s; (C) 500 mTorr/30 s; (D) 1000 mTorr/30 s.

step did not alter the species formed after 5 min exposure to 100 $^{\circ}\text{C}$ H_2O , indicating that acid groups exhibit hydrolytic stability and are chemically bonded to the PVDF surface.

Our previous studies on PDMS and PVC also indicated that discharge pressure in a microwave reactor may influence surface reactions.^{15,32} Figure 6 illustrates ATR FT-IR spectra in the C=O stretching region for maleic anhydride reacted on 25% α crystalline PVDF under various discharge pressures ranging from 50 mTorr (trace A) to 1000 mTorr (trace D). As shown, the amount of maleic anhydride reacted on the PVDF surface increases with decreasing discharge pressure, which is illustrated by the increased intensity of the band at 1728 cm^{-1} . The highest concentrations of monomer at lower pressure are most likely attributed to enhanced monomer abundance in the gas phase and, at lower initial pressure, solid monomer will be more readily evaporated into a gas phase when microwave plasma is generated, leading to a higher partial vapor pressure of the gas-phase monomer. Table 2 lists the band assignments for PVDF, Ar plasma reacted PVDF, and maleic anhydride, respectively.

One of the aspects of surface/interfacial chemistry that is not often addressed is orientation of surface/interfacial groups. Because orientation of surface groups will affect numerous surface properties, let us examine the preferential orientation, if any, of the surface groups generated by microwave plasma reactions. Figure 7 illustrates ATR FT-IR spectra in the C=O stretching region for maleic anhydride reacted on 25% α crystalline PVDF recorded using 90 $^{\circ}$ (TE) and 0 $^{\circ}$ (TM) polarizations. As we recall, polarization experiments allow determination of preferential surface group orientation.³³ Following commonly accepted nomenclature, TE polarization refers to parallel orientation of the electric vector of electromagnetic radiation, whereas TM is perpendicular to the film surface. Comparison of ATR FT-IR spectra of the 25% α crystalline PVDF specimen analyzed with TM (trace A) and TE (trace B) polarizations shows that the band intensities at 1783 and 1728 cm^{-1} (trace A) are significantly weaker, thus

Table 2. Tentative Band Assignments for PVDF, Plasma Reacted PVDF, Maleic Anhydride (MA), Plasma Reacted Maleic Anhydride, and Hydrolyzed PVDF Surface

PVDF PVDF ^a	plasma reacted ^a	MA MA ^b	plasma reacted ^b	PVDF hydrolyzed ^b	assignments ^c
3024	3024				$\nu_a(\text{CH}_2)$
2983	2983				$\nu_s(\text{CH}_2)$
	2930				$\nu_a(\text{CH})(\text{CF}=\text{CH})$
	2858				$\nu_s(\text{CH})(\text{CF}=\text{CH})$
		1852	1852		$\nu_a(\text{C}=\text{O})$
		1783	1783		$\nu_s(\text{C}=\text{O})$
			1728	1728	$\nu(\text{C}=\text{O}) (\text{COOH})$
			1690	1690	$\nu(\text{C}=\text{O}) (\text{COOH H-bonded})$
	1670				$\nu(\text{CF}=\text{CH}, \text{conjugated})$
	1612				$\nu(\text{CF}=\text{CH})$
	1595				$\nu(\text{CF}=\text{CH}, \text{conjugated})$
1402	1402			1402	$\omega(\text{CH}_2) + \nu_a(\text{CC}) + \delta(\text{CH})$
1211	1211			1211	$\nu_a(\text{CF}_2) + \omega(\text{CH}_2)$
1179	1179			1179	$\nu_a(\text{CF}_2) + \gamma(\text{CF}_2) + \gamma(\text{CH}_2)$
1069	1069			1069	$\nu_a(\text{CC})$
976	976			976	$\tau(\text{CH}_2)$

^a Reference 33. ^b Reference 7. ^c key: ν_a , asymmetric stretching; ν_s , symmetric stretching; δ , bending; ω , wagging; τ , twisting; γ , rocking.

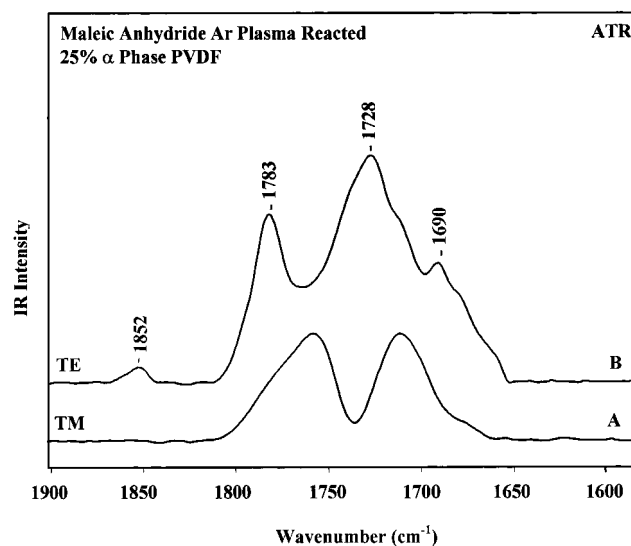
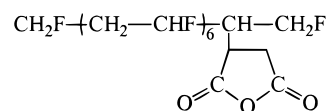


Figure 7. ATR FT-IR spectra in the 1900–1580 cm^{-1} region of maleic anhydride reacted on 25% α phase PVDF in the presence of Ar microwave plasma: (A) TM polarization; (B) TE polarization. Conditions: microwave plasma 600 W, discharge pressure 200 mTorr, reaction time 20 s.

indicating that C=O groups are preferentially parallel to the surface. Since ATR FT-IR spectra recorded for 64% α/γ crystalline PVDF exhibit the same behavior (not shown), it appears that surface orientation is not affected by the content of crystalline/amorphous components.

Assuming that the maleic anhydride molecule attached to the PVDF surface exhibits the lowest energy, let us establish the angle for the lowest energy state on the surface. For that reason we used the following model compound



and calculated energy changes resulting from the maleic anhydride angle changes with respect to a polymer backbone. The energy curve as function of the angle between the maleic anhydride ring and polymer backbone is depicted in Figure 8a, and as seen, for angles between

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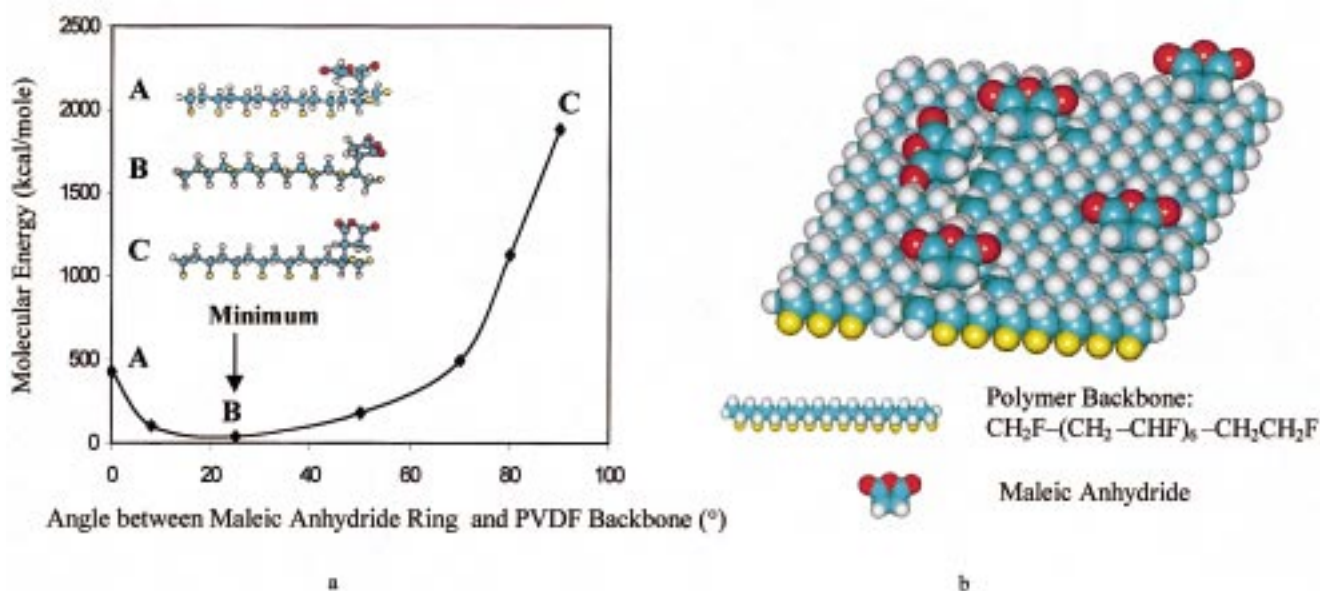


Figure 8. (a) Model compound energy curve as function of an angle between maleic anhydride and the polymer backbone. (b) Diagram of the maleic anhydride ring surface reacted with the PVDF surface with a 25° orientation of maleic anhydride with respect to the polymer surface.

10° and 40°, the total energy of the system reaches a minimum at 38 kcal/mol, which corresponds to a 25° angle. In contrast, for a maleic anhydride ring parallel or perpendicular to the polymer backbone, the energy is significantly higher at 428 or 1881 kcal/mol, respectively. Based on the above molecular mechanics force field calculations, a pictorial representation of the maleic anhydride ring surface reacted on the PVDF surface was generated, with the most favorable angle of 25° illustrated in Figure 8b. These results are in good agreement with the ATR FT-IR results, which showed that C=O groups are preferentially parallel to the surface.

Since ATR FT-IR spectroscopy also allows determination of surface content at various depths,⁹ let us examine how the content of newly formed species change as a function of distance from the surface. We will analyze the results of the experiments summarized in Figure 4a,b. In an effort to obtain such information, it is necessary to change the angle of incidence in an ATR experimental setup.⁹ To eliminate effects of band distortions resulting from optical effects in an ATR experiment, ATR spectra should be corrected.⁹ Although this method is suitable for quantitative ATR analysis using the Beer–Lambert law, it is necessary to know an absorption coefficient. The extinction coefficient for the 1783 cm⁻¹ C=O stretching band of maleic anhydride⁸ is 1148 L/(mol cm) and has been used to quantify maleic anhydride surface reactions on the PVDF surface. Because the extinction coefficient of the 1728 cm⁻¹ C=O stretching band to quantify acid groups on the PVDF surface is not known, a series of known concentrations of hydrolyzed maleic acid solutions were prepared and a plot of the absorbance of the 1728 cm⁻¹ C=O stretching band as a function of maleic acid concentration was generated. Using these data, the extinction coefficient for the 1728 cm⁻¹ C=O stretching band was determined to be 544.32 L/(mol cm). Using the double KKT approach, it is thus possible to determine maleic anhydride and carboxylic acid concentrations on the PVDF surface at various depths.⁹ These results are shown in Figure 9 and indicate that, for 25% α crystalline PVDF specimens before hydrolysis, as the depth of penetration increases from 0.84 to 1.36 μ m, volume concentrations of maleic anhydride reacted on the PVDF

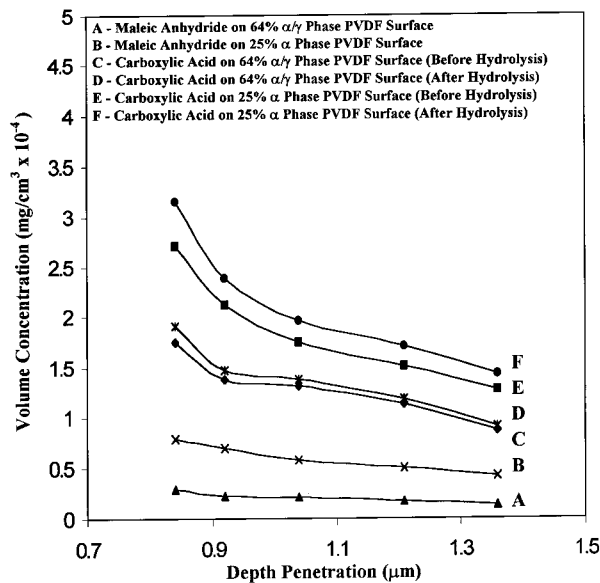


Figure 9. Plots of volume concentrations of maleic anhydride and carboxylic acid reacted on the PVDF surface in the presence of Ar microwave plasma as a function of penetration depth: (A) maleic anhydride on 64% α/γ phase PVDF surface; (B) maleic anhydride on 25% α phase PVDF surface; (C) carboxylic acid on 64% α/γ phase PVDF surface before hydrolysis; (D) carboxylic acid on 64% α/γ phase PVDF surface after hydrolysis; (E) carboxylic acid on 25% α phase PVDF surface before hydrolysis; (F) carboxylic acid on 25% α phase PVDF surface after hydrolysis. Conditions: microwave plasma 600 W, discharge pressure 200 mTorr, reaction time 20 s.

surface decrease from 7.94×10^{-5} to 4.22×10^{-5} mg/cm³, which correspond to surface concentrations of 6.67×10^{-9} to 5.74×10^{-9} mg/cm²,³⁴ and volume concentrations of carboxylic acid decrease from 2.7×10^{-4} to 1.28×10^{-4} mg/cm³ (2.27×10^{-8} to 1.74×10^{-8} mg/cm²); after hydrolysis, carboxylic acid decreases from 3.15×10^{-4} to 1.44×10^{-4} mg/cm³ (2.65×10^{-8} to 1.96×10^{-8} mg/cm²).

(34) To obtain surface concentrations, it is assumed that the density of the surface layer formed on the PVDF surface is equal to 1 within the IR light depth penetration. For volume concentrations, surface concentrations are obtained by multiplying by ATR depth penetrations.⁸

For 64% α/γ crystalline PVDF specimens, similar trends are observed. Before hydrolysis, as the depth of penetration increases from 0.84 to 1.36 μm , volume concentrations of maleic anhydride decrease from 2.84×10^{-5} to $1.32 \times 10^{-5} \text{ mg/cm}^3$ (2.39×10^{-9} to $1.8 \times 10^{-9} \text{ mg/cm}^2$) and volume concentrations of carboxylic acid decrease from 1.75×10^{-4} to $8.67 \times 10^{-5} \text{ mg/cm}^3$ (1.47×10^{-8} to $1.18 \times 10^{-8} \text{ mg/cm}^2$); after hydrolysis, carboxylic acid decreases from 1.91×10^{-4} to $9.1 \times 10^{-5} \text{ mg/cm}^3$ (1.60×10^{-8} to $1.24 \times 10^{-8} \text{ mg/cm}^2$). These results show that the extent of surface reactions for maleic anhydride and carboxylic acid on the 64% α/γ crystalline PVDF surface is lower, thus suggesting that the combinations of the α and γ crystalline phase inhibit surface reactions.

Conclusions

These studies show that PVDF can be surface modified using solid monomer microwave reactions, which are conducted in a closed reactor environment. Under Ar microwave plasma conditions, conjugated $-\text{CH}=\text{CF}-$ linkages resulting from dehydrofluorination are detected on PVDF surfaces, and maleic anhydride is chemically reacted under Ar plasma reactions through the C=C double bond opening. Under the same experimental conditions, a higher content of maleic anhydride and carboxylic acid can be reacted on a 25% α crystalline PVDF surface. These results are consistent with our previous studies,³² where the high crystallinity content of PVC inhibited imidazole microwave surface reactions. Maleic anhydride prefers to take almost parallel orientation with

respect to the surface and the angle between the maleic anhydride and PVDF polymer backbone is 25° , which agrees with ATR FT-IR measurements. Quantitative analysis shows that, for 25% α crystalline PVDF films before hydrolysis, as the depth of penetration increases from 0.84 μm to 1.36 μm , volume concentrations of maleic anhydride reacted on the PVDF surface decrease from 7.94×10^{-5} to $4.22 \times 10^{-5} \text{ mg/cm}^3$ (6.67×10^{-9} to $5.74 \times 10^{-9} \text{ mg/cm}^2$) and volume concentrations of carboxylic acid decrease from 2.7×10^{-4} to $1.28 \times 10^{-4} \text{ mg/cm}^3$ (2.27×10^{-8} to $1.74 \times 10^{-8} \text{ mg/cm}^2$); after hydrolysis, carboxylic acid decreases from 3.15×10^{-4} to $1.44 \times 10^{-4} \text{ mg/cm}^3$ (2.65×10^{-8} to $1.96 \times 10^{-8} \text{ mg/cm}^2$). For 64% α crystalline PVDF films before hydrolysis, as the depth of penetration increases from 0.84 μm to 1.36 μm , volume concentrations of maleic anhydride decrease from 2.84×10^{-5} to $1.32 \times 10^{-5} \text{ mg/cm}^3$ (2.39×10^{-9} to $1.8 \times 10^{-9} \text{ mg/cm}^2$) and volume concentrations of carboxylic acid decrease from 1.75×10^{-4} to $8.67 \times 10^{-5} \text{ mg/cm}^3$ (1.47×10^{-8} to $1.18 \times 10^{-8} \text{ mg/cm}^2$); after hydrolysis, carboxylic acid decreases from 1.91×10^{-4} to $9.1 \times 10^{-5} \text{ mg/cm}^3$ (1.60×10^{-8} to $1.24 \times 10^{-8} \text{ mg/cm}^2$).

Acknowledgment. The authors are thankful to the National Science Foundation Industry/University Cooperative Research Center in Coatings at North Dakota State University and Eastern Michigan University for partial support of this project.

LA981310M