

Effect of poly(vinylidene fluoride) binder crystallinity and graphite structure on the mechanical strength of the composite anode in a lithium ion battery

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Abstract

We have evaluated the mechanical strength of a series of composites consisting of carbon particles bound together by poly(vinylidene fluoride) (PVDF), which is closely related to the carbonaceous anode in a lithium ion battery. We used a balanced beam scrape adhesion tester and evaluated the influence of carbon particle structure, the chemical properties of PVDF, and the processing parameters of annealing temperature and casting solvent on the adhesion of the composite film to a copper substrate. The composite prepared with amorphous carbon shows over 10 times higher adhesion strength than those fabricated from other graphite materials. This results from chemical binding that is intermediate between semi-ionic and covalent C–F bonds, as detected by X-ray photoelectron spectroscopy. To address the effect of the crystalline phase of the binder on the adhesion strength, we investigated PVDF crystallinity in the composite films using differential scanning calorimetry. Samples with higher crystallinity show higher adhesion strength, independent of annealing temperature and casting solvent. The scratch adhesion was also measured for swollen electrodes immersed in 3:7 volume ratio of ethylene carbonate:ethyl methyl carbonate (EC:EMC) at different temperatures. After being swollen, the composite films prepared from PVDF modified with hydroxyl functional groups show higher adhesion strengths than the others due to their low uptake of the electrolyte solvent.

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1. Introduction

A typical composite anode film for a lithium ion battery is prepared from a slurry of amorphous carbon or graphite particles bound together by a polymeric binder, which is doctor-bladed onto a copper foil that will act as the current collector. The composite anodes need to have sufficient mechanical stability, including good adhesion of the film to the substrate and high adhesion between the graphite particles and the binder, in order to achieve increased cyclability of the battery. For example, partial delamination of the film, which is related to the formation of a solid

electrolyte interphase (SEI) combined with the swelling caused by lithium intercalation, leads to a decrease in the reversible capacity [1]. The adhesion of the electrode film to the metal substrate after cycling has been qualitatively investigated through observations of the electrode film delamination and through study of electrochemical performance [1–7]. Carbonaceous anodes with modified poly(vinylidene fluoride) (PVDF) [7] and silica gel binder [1] have been studied previously, and oxide films have also been examined as anodes [2–4] and cathodes [2,5,6]. However, these studies evaluated adhesion based on the observation of film delamination and cracking after cycling, both of which affect the electrochemical performance, instead of determining the adhesion strength directly.

An evaluation of the adhesion between coating and substrate can be made using the scratch test technique [8–14]. Despite the lack of a fully satisfactory analytical model for its contact mechanics, the scratch test is widely

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used to semi-quantitatively evaluate the adhesion of coatings to substrates. In this test, a stylus is drawn across the film surface, while a vertical load applied to the stylus is gradually increased until the film is completely removed, resulting in a clear channel. The critical load at which a clear track is formed is taken as a measure of the adhesion, which depends not only on the interfacial strength but also on a wide range of parameters, including the tip geometry, coating thickness, flaw size distribution at the substrate-coating interface, mechanical properties of the substrate and coating, internal stress in the coating, and friction between the sliding stylus and the coating [8,11,13]. Only when all other factors remain constant can the values of the critical load be taken to reflect the true adhesion of the coating to the substrate. As a consequence, the measured critical load cannot be correlated in a simple way with the thermodynamic work of adhesion, but it does allow a semi-quantitative comparison of samples having different degrees of adhesion [11]. We use this approach in the current study.

Our main goals were to investigate the adhesion of composite films to a copper substrate by varying the type of carbon particles and PVDF binder and processing parameters, and to relate these results to the surface chemistry of the composite films, PVDF crystallinity, and film roughness. Moreover, since the composite film must withstand extensive swelling in the polar organic electrolyte, the scratch adhesion test was performed for swollen anode films and correlated with the electrolyte solvent uptake of PVDF. As good adhesion is a basic requirement for composite films, the scratch test can be effectively utilized to optimize the processing variables.

2. Experimental section

2.1. Composite film preparation

We used eight types of carbon particles and three PVDF binders with different molecular weights and functionalities, as listed in Tables 1 and 2, to investigate the effect of the nature of the carbon particles (amorphous vs. graphite) and the chemical properties of PVDF on the scratch adhesion.

Composite films were first prepared by mixing a carbon slurry that contained the carbon particles, 1-methyl-2-pyrrolidinone (NMP) (99.9 + %, Mitsubishi Chemical Corp.) as a carrier, and 10 wt% solution of PVDF binder in NMP solvent. The solid concentration of the slurries was 40 wt%. We spread the slurry using the doctor-blade method on a sheet of copper foil and dried it in an oven at 83 °C in air for 2 h to form a 95/5 wt% graphite/PVDF composite film with around 34.5(±0.5) μm thickness. To study the effect of annealing temperature and casting solvent on the scratch adhesion strength, we also used a annealing temperature of 120 °C and *N,N*-dimethylformamide (DMF) (99.9 + %, Aldrich) as the casting solvent. To provide a reference sample for XPS study, we deposited 5 wt% PVDF/NMP solution on a cleaved, highly ordered pyrolytic graphite (HOPG) substrate (10 mm × 10 mm × 1 mm, Structure Probe, SPI-2 grade) and dried it in the same way.

2.2. Scratch test

The scratch adhesion strength was measured by using a balanced beam scrape adhesion tester (ASTM D2197-98, BYK-Gardner). It can evaluate the adhesion strength of a sliding surface to a stylus pressed against it as a function of normal load, sliding speed, geometry, and material. The tester used a loop stylus consisting of a 0.16 cm drill rod bent 180° to a 'U' shape with a 0.65 cm outside width dimension that was held on a stylus holder mounted at 45° through a pivoted beam. We measured the critical load required for baring the substrate along all portions of the 3-cm path. The critical load, which is related to the adhesion strength, can be altered by surface treatment, the sample platform velocity, and the film thickness. We initially degreased the Cu foil substrate with toluene before depositing the films, used a scratch velocity of 12 cm/min, and maintained the dry film thickness at 34.5(±0.5) μm. Because a rougher substrate surface can cause a rougher interface that can facilitate microcrack initiation when a stylus with a diameter much larger than the film thickness drags on the sample [12], we tried to make the surface of the Cu foil as flat as possible before depositing the films.

Table 1

The manufacturer, type of carbon, average particle size (μm), and BET surface area (m²/g) for eight carbon materials that were used for experiments. Information was provided by the manufacturers

	Manufacturer	Type of carbon	Average particle size (μm)	BET surface area (m ² /g)
MPG-V2	Mitsubishi Chemical Co., Japan	Synthetic graphite	18.4	2.8
MCMB	Oosaka Gas Chem., Japan	Synthetic graphite	7.8	3.3
SFG75	Timcal Co. Ltd, Switzerland	Synthetic graphite	27.0	3.5
MBC-N	Mitsubishi Chemical Co., Japan	Amorphous carbon	18.0	5.0
SFG44	Timcal Co. Ltd, Switzerland	Synthetic graphite	22.0	5.0
SFG15	Timcal Co. Ltd, Switzerland	Synthetic graphite	8.1	8.8
KS15	Timcal Co. Ltd, Switzerland	Synthetic graphite	7.7	12.0
KS6	Timcal Co. Ltd, Switzerland	Synthetic graphite	3.3	20.0

Table 2

Information on PVDF binder used for the experiments. The functionality and molecular weights of PVDF were provided by the manufacturers, and the head-to-head defects were calculated using ^{19}F NMR

	Product name, Manufacturer	Functionality	Molecular weight	H–H defects (%) (from ^{19}F NMR)
PVDF350	KF1300, Kureha	N/A	~ 350,000	4.22(\pm 0.53)
PVDF350M	MKB212A, Atofina	–OH (a little –COOH)	~ 350,000	5.54(\pm 0.67)
PVDF500	Kynar301F, Atofina	N/A	~ 500,000	6.55(\pm 1.24)

2.3. Crystallinity of PVDF

To determine the crystallinity of the PVDF binder in the composite films, differential scanning calorimetry (DSC) (DSC 910S, TA Instruments) was used. Each sample was prepared in an aluminum pan with a lid. It was heated to 250 °C at 10 °C/min and, after melting, held isothermally at 250 °C for 1 min, and then cooled down to 25 °C at 10 °C/min. The heat of fusion calculated from the melting peak area of the first scan was used to calculate the degree of crystallinity (X_c) as follows:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0 W} \times 100 (\%) \quad (1)$$

where ΔH_f is the heat of fusion of the sample, ΔH_f^0 is the heat of fusion of 100% crystalline PVDF, which is 105 J/g [15], and W is the PVDF fraction in the PVDF/graphite composites.

2.4. Film surface characterization

The surface chemical composition of the graphite anodes was measured by X-ray photoelectron spectroscopy (XPS) (S-Probe, Surface Spectrometer) with an aluminum anode and a quartz monochromator that selects Al K α X-ray radiation (1486.6 eV). The X-ray source was operated at 10 kV, and the electron take-off angle was 35° from the sample surface. Survey scans (0–1000 eV) were first performed, followed by detailed scans of C_{1s}, O_{1s}, and F_{1s}. The spot size was 250 μm \times 1000 μm for survey scans with 22 mA of current and 150 μm \times 800 μm for detailed scans with 11 mA current. For the PVDF sample on HOPG, charge neutralization was achieved by an electron flood gun set at 1 eV.

The surface of the composite film after the scratch tests was observed using scanning electron microscopy (SEM) (JSM-5600LV, JEOL) with a gun voltage of 15 kV.

The roughness of the composite films was determined using a profilometer (Dektak 3, Veeco) with a scan speed of 10 $\mu\text{m/s}$ and horizontal resolution of 0.250 μm . In operation, a stylus is placed in contact with and then gently dragged along the surface of the film.

2.5. Swollen electrode preparation and electrolyte solvent uptake measurement

The prepared electrodes were immersed in an electrolyte solvent mixture of ethylene carbonate (EC) (98 + %, Aldrich):ethyl methyl carbonate (EMC) (electrolyte grade,

Ferro Corporation) of 3:7 volume ratio from 1 to 7 days at 25 and 50 °C, and then the scratch test on the swollen electrodes was performed. We investigated the swelling effect caused solely by the electrolyte solvent without adding the lithium salt, which is very sensitive to humidity and thus inappropriate for the scratch test that is performed in the air.

To measure the liquid weight absorbed by the film, pieces of the composite anodes (1.9 \times 1.9 cm²) were first accurately weighed and then immersed in the electrolyte solvent mixture for up to 3 days. At regular intervals, the samples were taken out, pressed lightly between two sheets of clean filter paper to remove surface liquid, and then weighed.

3. Results and discussion

3.1. Adhesion strength and surface chemistry

The adhesion strength of the composite film to the copper foil was determined using the balanced beam scrape adhesion tester with varying carbon materials and PVDF binders. Table 3 shows the critical loads for baring the substrate along all portions of a 3-cm path in terms of carbon materials and PVDF. MBC-N and MCMB show much higher adhesion strengths than the others; in fact, the critical load of MBC-N was out of range of the scratch tester capability (10,000 g). This high adhesion strength is apparently due to the structure of the amorphous carbon, as discussed in the following.

Table 3

The critical loads of composite films cast from NMP at 83 °C for different carbon and PVDF materials

	Critical load (g)		
	PVDF350	PVDF350M	PVDF500
MBC-N	> 10,000	> 10,000	> 10,000
MCMB	1350	950	1350
MPG-V2	340	290	350
SFG44	250	110	280
SFG75	240	120	310
SFG15	200	120	340
KS6	150	130	390
KS15	50	170	270

Table 4

Binding energies and relative percentages of each element measured in each carbon sample containing PVDF350 cast from NMP at 83 °C

Binding energy (eV)	Assignment	Relative percentage (%)								
		PVDF on HOPG	MBC-N	SFG44	KS6	SFG75	MPG-V2	KS15	SFG15	MCMB
Carbon										
284.32(± 0.02)	C H=; (C=; =C=)	0	49.07	62.50	62.93	63.12	67.18	67.98	71.87	72.90
285.50(± 0.13)	C H ₂ –CF ₂ ; C–O	53.12	15.40	18.56	16.01	17.70	16.01	15.03	12.48	14.65
286.42(± 0.16)	C=O	0	12.42	8.48	8.65	8.39	6.18	8.18	7.07	5.65
287.97(± 0.03)	Between semi-ionic and covalent C–F bond	0	6.66	0	0	0	0	0	0	0
290.47(± 0.07)	C F ₂ –CH ₂	46.88	16.46	10.46	12.41	10.79	10.63	8.81	8.59	6.80
Oxygen										
531.20(± 0.29)	O=C	0	53.54	52.04	45.75	47.73	57.70	35.34	59.61	65.53
532.80(± 0.30)	C–O–H	0	46.46	47.96	54.25	52.27	42.30	64.66	40.39	34.47

The nature of the chemical bonding in carbon particle/PVDF composites was studied using XPS. Table 4 shows the binding energies and their relative percentages for XPS spectra. The graphite samples except MBC-N show four peaks in C_{1s} spectrum [16,17]: the first peak at 284.32 eV corresponds to graphite itself, the second peak centered at 285.5 eV is due to C–O bonds and carbon atoms adjacent to C–F bonds, the third peak centered at 286.42 eV is due to C=O bonds, and the fourth peak at 290.47 eV indicates CF₂ bonds. O_{1s} peaks at 531.2 and 532.8 eV indicate carboxyl and hydroxyl groups, respectively. They are observed at slightly higher binding energies than those in usual carbon materials due to the fluorine of the composite surface [16]. A peak shift to lower binding energies was observed after etching that leads to a lower concentration of fluorine. Finally, F_{1s} is centered at 687.7 eV.

In the PVDF sample, the C H₂–CF₂ and C F₂–CH₂ peak areas are almost equivalent (relative percentages of 53.12 and 46.88), as expected. However, this is not observed in the samples containing graphite/PVDF mixtures. The ratio of areas of these two peaks exceeds 1 and sometime approaches 2 due to surface oxygen components (C–O bonds). The amorphous MBC-N shows a much smaller percentage of the first peak corresponding to the graphite (284.32 eV) than the other samples and also exhibits a peak at 287.97 eV, which does not appear in the other samples. This binding energy is intermediate between the semi-ionic and covalent C–F bonds, which is found in highly fluorinated materials [16,18]. This bonding was observed in a fluorine–graphite intercalation compound [18] and in fluorinated carbon black [19] with increasing fluorine content. We suggest that this binding energy in the MBC-N composite may reflect the structure of amorphous carbon, which contains a number of imperfect hexagonal graphene rings. According to Wang et al. [20], many carbon atoms with dangling bonds exist at the edges of amorphous carbon and around inner micro- or nanopores where neighboring carbon atoms are connected with weak C–H bonds. We [21] and others [22] have established that polymer is preferen-

tially adsorbed onto these imperfect sites, which can lead to a high fluorine–carbon ratio in MBC-N. The occurrence of a bond intermediate between semi-ionic and covalent C–F may lead to a stronger interaction between amorphous carbon particles and PVDF than that observed for physisorption and/or oxygen bonding in graphite/PVDF composites [21]. This may be one of the sources of the high adhesion strength observed for MBC-N. Also, Charitidis et al. [10] showed that a sputtered amorphous film that is rich in sp³ content showed higher scratch adhesion strength than a film rich in sp².

The reason for the enhanced adhesion for MCMB (mesocarbon microbead) material may arise from a different source. In this case, the MCMB material has a turbostratic structure to some extent, where graphite sheets are randomly stacked and pinned to each other, and also contains micropores formed between crystallites [23], which is considered to lead to a harder structure [24]. As a consequence, MCMB shows a higher critical load than the other graphite materials. Also, there is a PVDF crystallinity effect on the high critical loads of MCMB samples, which will be discussed later.

Table 3 shows that for all samples, except those involving KS15, PVDF500 exhibits the highest adhesion strength in each composite, perhaps due to its higher molecular weight, followed by PVDF350 and PVDF350M. Although the modified PVDF (PVDF350M) was expected to exhibit higher adhesion strength than does PVDF350 since it showed higher interaction between carbon particles and PVDF through enhanced hydrogen bonding capability [21], this was not observed. This could be due to variation in the friction force between the stylus and the composite sample in the scratch adhesion test. Table 5 presents the relative percentage of carbon, fluorine, and oxygen atoms in different PVDF samples, as measured by XPS. When the modified PVDF (PVDF350M) is used as a binder, more fluorine and oxygen polar groups exist at the surface of the final films compared to those with PVDF350. The polar functional groups at the surface of the coating introduced by the PVDF350M may cause an increase in the friction by

Table 5
Atomic percentage (%) of carbon, fluorine, and oxygen in each sample

Graphite	Binder	Relative percentage (%)		
		C	F	O
MPG-V2	PVDF350	81.03	17.33	1.64
	PVDF350M	69.33	27.09	3.59
MCMB	PVDF350	87.65	9.84	2.51
	PVDF350M	72.46	25.49	2.05

enhanced interaction with the stylus [11], leading to lower scratch adhesion strength. Also, PVDF crystallinity can play a role in the low adhesion strength of the PVDF350M sample, which will be discussed later.

Fig. 1 shows a SEM picture of a composite film after the scratch test. Spalling appears around the clear channel as a result of the compressive stress field preceding the moving stylus. At the critical load, failure predominantly occurs ahead of the moving stylus where the generated compressive stresses are at a maximum. The coating ahead of the stylus can thus reduce its stored elastic energy by buckling or spalling from the substrate at the critical load [8].

3.2. PVDF crystallinity effect

The scratch test evaluates not only the adhesion of the film to the substrate but also the adhesion between particles and polymer, both of which can be influenced by the crystallinity of the PVDF binder. Since the morphology of the polymeric binder can be affected by processing parameters such as annealing temperature and casting solvent, we examined the effect of PVDF crystallinity on the critical load with different annealing temperature (83 and 120 °C) and casting solvent (NMP and DMF). Fig. 2(a) and (b) shows the dependence of critical loads on the PVDF crystallinity for SFG15 and MCMB graphite samples,

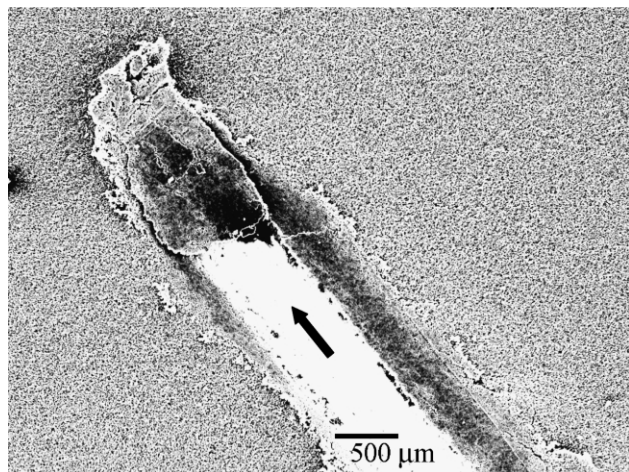


Fig. 1. SEM picture of a MPG-V2/PVDF350 sample cast with NMP at 83 °C after the adhesion test. The other samples show the same profile. The arrow indicates the sliding direction.

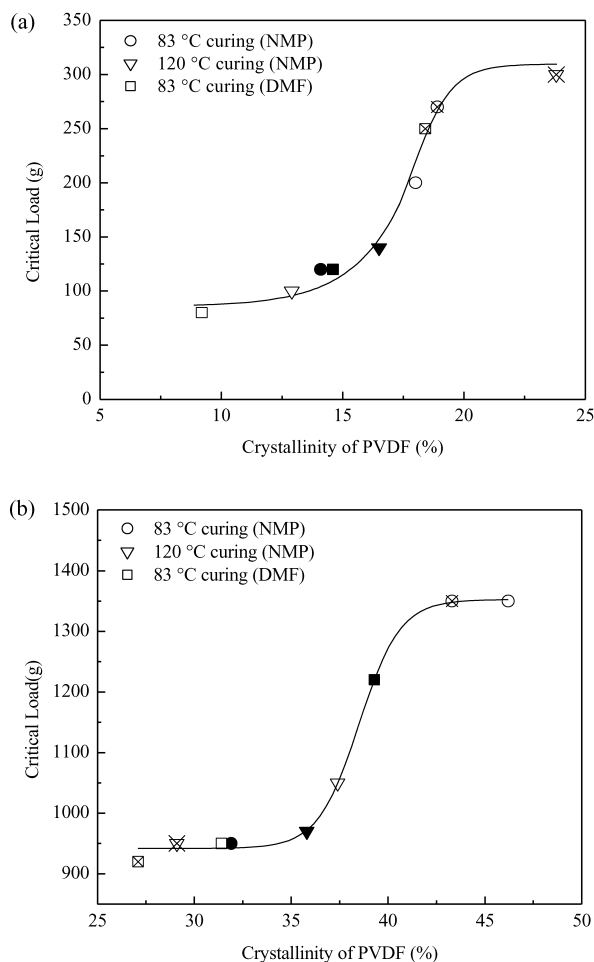


Fig. 2. The relationship between the critical load and the crystallinity of (a) SFG15 and (b) MCMB samples with different processing conditions and PVDF, illustrating that a higher crystallinity film shows higher adhesion strength. Open points indicate films with PVDF350, closed with PVDF350M, and crossed with PVDF500.

respectively. These two systems were selected for more detailed study because they show relatively low and high critical loads (see Table 3). Both figures indicate that a film with higher crystallinity exhibits higher scratch adhesion strength. MCMB samples in Fig. 2(b) show much higher PVDF crystallinity than SFG15, leading to much higher adhesion strength. MCMB particles consist of an aggregate of graphitic crystallites whose edge surface normals are oriented radially. This morphology leads to significant exposure of graphite crystalline edges [25]. Since PVDF preferentially adsorbs onto such edges [21], this large edge area can generate an increase in the nucleation sites for PVDF crystallization at the interface between polymer and graphite particles, consequently leading to an increased crystallinity. The effect of crystallinity on the mechanical strength of films has been studied for polymer blends [26], one-component polymer surfaces [27], and the interface between polymer film and a substrate [28]. In all cases, the occurrence of a crystalline structure leads to a higher adhesion strength.

Fig. 2(a) and (b) shows that all the samples except MCMB/PVDF350M exhibit lower critical loads when DMF solvent is used for casting compared to NMP. This is attributed to the fact that the morphology of PVDF can be changed with a different solvent. Use of DMF solvent leads to more homogeneous PVDF distribution on the graphite surface due to rapid solvent evaporation rate [29], which may affect the adhesion strength. Also, the slower solvent evaporation of NMP [29] can result in solvent-induced crystallization of the PVDF [30], leading to the high critical loads for composite films cast from NMP compared to DMF. Note that, regardless of the processing parameters and the type of PVDF, we observe that samples with higher crystallinity result in higher critical loads, indicating that the crystallinity is the most important factor in determining the adhesion strength, even though the PVDF concentration is relatively low.

3.3. Roughness effect

Since the adhesion strength, as evaluated by the scratch test, is influenced by friction between the electrode surface and the stylus, the condition of the electrode surface can play an important role in evaluating the critical load [14]. Therefore, the effect of surface roughness of the composite films on the scratch adhesion strength should also be considered. Table 6 shows normalized film roughness. Note that the film roughness depends on average carbon particle size; therefore, we normalized the data by dividing the film roughness by the average particle size. As noted earlier, we could not evaluate the critical load for MBC-N, and that for MCMB is much higher than those of the other graphite samples. Therefore, to compare the influence of film roughness for similar critical loads, they are not listed in Table 6. Our normalization procedure is clearly imperfect because we used the average particle sizes, but each sample does show a general relationship with the critical load (see Table 3); as the roughness increases, the scratch adhesion strength decreases. For a rough surface, a microcrack can be initiated when the stylus slides over the coating surface, leading to lower scratch adhesion strength.

Since this surface roughness can be influenced by the PVDF interfacial morphology, we measured the surface

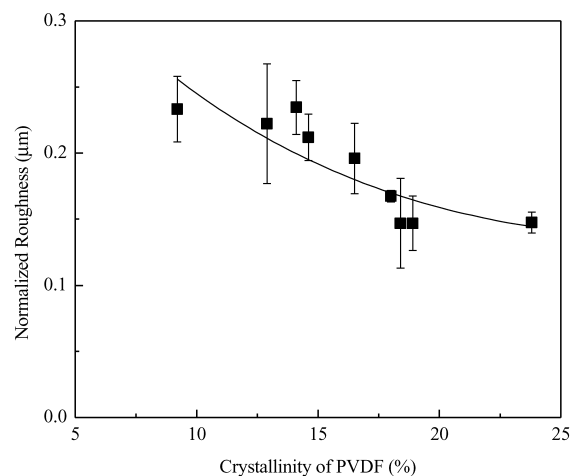


Fig. 3. The dependence of normalized roughness on the crystallinity of PVDF. SFG15 samples with different PVDF, curing temperature, and casting solvent are used.

roughness of SFG15 samples of Fig. 2(a) and related this to the PVDF crystallinity, with the result shown in Fig. 3. We observe that less crystalline morphology with lower adhesion strength can result in a rougher surface. Therefore, the surface roughness can also be influenced by PVDF crystallinity.

3.4. Adhesion strength of swollen electrodes

The composite electrode needs to maintain adhesion to the substrate throughout many electrochemical cycles in order to be useful. However, during Li^+ ion insertion, electrolyte solvent molecules can also enter the graphite layers, leading to delamination of the anodes. Thus, the binder must counteract the dispersive forces caused by the graphite layers expanding due to Li^+ ion intercalation. It must also withstand extensive swelling in the polar organic electrolyte, because both effects would result in loss of internal contact. Since it is impractical to monitor adhesion strength after electrochemical cycling because the sample size for the electrochemical experiment is very small, we immersed the anodes into electrolyte solvent and investigated the swelling effect on the adhesion.

Fig. 4(a) and (b) shows the critical loads after samples were immersed in 3:7 (volume) EC:EMC up to 1 week at 25 and 50 °C, respectively. At 25 °C, the critical load decreases slightly after 1 day, but after being immersed for 3 days, the critical load decreased rapidly and there was little change for longer immersion time. In general, the critical load of all the samples at 25 °C is higher than that at 50 °C. Moreover, electrodes at 50 °C show much lower adhesion strength after being immersed for 1 day compared to samples immersed at 25 °C as a result of fast solvent diffusion into anodes at higher temperature. There is little change in the critical load up to 7 days. Therefore, solvent diffusion seems to be saturated after 1 day at 25 °C and before 1 day at 50 °C.

After solvent is incorporated into the anodes and

Table 6

Surface roughness normalized to the average particle size of each carbon sample

	Normalized roughness (μm)		
	PVDF350	PVDF350M	PVDF500
MPG-V2	0.185	0.190	0.121
SFG44	0.183	0.214	0.138
SFG75	0.133	0.167	0.176
SFG15	0.167	0.235	0.147
KS6	0.225	0.237	0.177
KS15	0.219	0.187	0.197

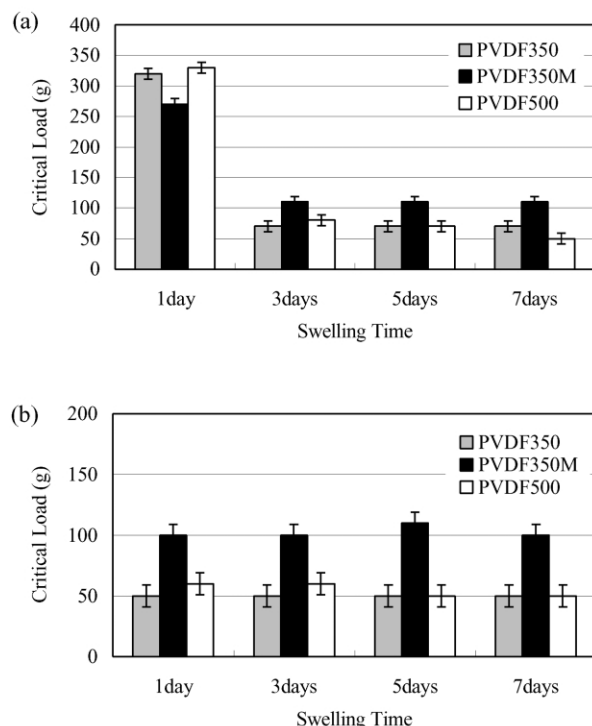


Fig. 4. Dependence of the critical load of the anodes made of MPG-V2 and three kinds of PVDF on swelling time. The anodes were swollen in EC:EMC = 3:7 (vol) (a) at 25 °C and (b) at 50 °C up to 1 week.

saturated, the PVDF350M samples show the highest scratch adhesion strength, nearly twice those of PVDF350 and PVDF500 samples, which are quite similar. The weight percentages of electrolyte solvent uptake of the anode films after 3 days at 25 °C are 38.56, 27.64, and 38.66% for the MPG-V2 sample with PVDF350, PVDF350M, and PVDF500, respectively. Thus, the high adhesion strength of the PVDF350M sample appears to result from the low uptake of electrolyte solvent. The electrolyte solvent uptake of films can cause crystalline regions to become amorphous, which is reflected in the disappearance of the melting peak of PVDF crystalline phase in DSC (not shown), leading to a low critical load.

4. Conclusions

The durability and functionality of coatings critically depend on the adhesion between the coating and an underlying substrate. In this paper, we have demonstrated that the adhesion strength in model carbonaceous anodes depends on the structure of the carbon particles and on the chemical properties of PVDF, suggesting that the film properties can be controlled at the molecular level. Amorphous carbon, which forms a C–F bond having characteristics between semi-ionic and covalent, shows much higher scratch adhesion strength than crystalline carbon, and samples having higher PVDF crystallinity also

show higher scratch adhesion strength. Sample roughness affects the critical load in each carbon sample, which can also be correlated with the crystallinity of PVDF. After being swollen in the electrolyte solvent mixture of EC and EMC, samples with PVDF350M show higher adhesion strength compared to non-modified PVDF due to low solvent uptake of the PVDF350M samples. This study demonstrates that the surface chemistry and the polymer crystallinity of composite films are important for processing a durable coating.

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