

Coating Films Prepared by Photoreactions of the Surface-Modified Diamond Powder and PET Film with a Binder Agent

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ABSTRACT: The surface-modified diamond and PET film underwent photopolymerization rapidly with a binder agent to afford coating films of interpenetrating network (IPN) structure. The coating films thus formed exhibit higher tensile strength, thermal stability, and adhesion strength to the PET film. The inert surfaces of pristine diamond (PD) and PET film were modified by different chemicals and procedures to introduce epoxide and methacryloyl groups, respectively, on their surfaces. A coating agent consisting of an epoxide group containing modified diamond (called ED), a binder agent, and photoinitiators was prepared. After applying the coating agent to the substrate (a glass plate or a methacryloyl group containing PET film, MMA-PET) and degassing under reduced pressure, the thin film of the coating agent was exposed to UV light

(λ_{max} ; 365 nm) at room temperature to yield a coating film of IPN-structure. The tensile strength and thermal properties of the ED-containing free coating film (called free film) increased with the amount of ED embedded, whereas the strength of the PD-containing free film decreased with the amount of PD embedded. The adhesion strength of the coating film on the MMA-PET improved significantly by the free radical polymerization of the methacryloyl groups on the MMA-PET and the acrylate resin in the binder agent. The surface photoreactions of ED and MMA-PET with the binder agent were confirmed by modeling. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 693–701, 2011

Key words: surface modification; photoreaction; pristine diamond; coating film; PET film

INTRODUCTION

Diamonds have become one of the most important materials for science and technology because of their proven combination of extreme hardness, chemical inertness, and other unique properties such as optical transparency, and low electrical and high thermal conductivities.^{1,2} Diamonds, because of their extreme hardness, have been traditionally used as abrasives to polish hard metals or ceramics and as cutting tools to cut glass, stoneware, and scratch-resistant surfaces. For these applications, it is necessary to fix the diamond powders on the substrates, the cutting edges of the prefabricated tools, or the cutting devices. Both soldering and bonding, which are preferred techniques for producing stable diamond joints, require a wettable and reactive dia-

mond surface. However, a diamond surface is largely inert to most chemicals, therefore, a diamond is required to be modified to enhance its reactivity by introducing functional groups on its surface. Many methods have been used to modify diamond surfaces. Ando et al.³ prepared diamond surfaces containing OH, NH, and CF groups by the reaction of chlorinated surfaces, obtained by the reaction of hydrogenated diamonds at high temperatures with H₂O, NH₃, and CHF₃. Liu et al.¹ fluorinated nanoscale diamond powder in a fluorine/hydrogen mixture at high temperatures (150–470°C). The corresponding alkyl-, amino-, and amino acid-nanodiamond derivatives were obtained by the subsequent reactions of fluoro nanodiamond with alkyllithium reagents, diamines, and amino acids. Simon et al.² introduced alcoholic OH on a diamond surface by treatment at low-pressure (<10⁻⁷ mbar) oxygen plasma. Cunningham and co-workers⁴ used fluorine gas to fluorinate the diamond surface in the atmosphere pressure plasma system. All the experiments in the studies mentioned above were performed in the vapor phase. They were performed using very expensive experimental apparatus and under severe experimental conditions. Tsubota et al.⁵

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modified diamond surfaces with carboxylic acids and alkylamines by the chemical reaction of hydrogenated diamond powder in peroxide-containing liquid organic solvent. In this method, although the reaction condition is mild, the starting hydrogenated diamond powder is prepared by treating the oxidized diamond powder in a H₂ environment at 800–900°C.⁶ A severe reaction condition is still needed. Visbal et al.⁷ introduced ether and carbonyl groups on the diamond surface after ultrasonic treating of the acid-washed diamond surface in water under bubbling gas (oxygen or argon) at 40°C. The last modification condition noted above is mild and suitable for laboratory or industrial use.

Polyethylene terephthalate (PET) is used in various forms for a very large number of applications. Its intrinsic low surface energy results in poor adhesion, wettability, and biocompatibility, and it has to be surface-modified for many applications.⁸ There are numerous reports on the chemical surface modification of PET film by hydrolysis,^{9,10} reduction,¹¹ or aminolysis.^{12,13} Other techniques including plasma,¹⁴ corona discharge,¹⁵ laser treatment,¹⁶ and photoinitiated graft polymerization¹⁷ have also been used to modify the surface of PET films.

The UV-curing process is a polymerization technique in which radiation is used to induce a very high polymerization rate so that the reaction is completed, or the change in phase from liquid to solid takes place, within a few seconds or even within a fraction of a second.^{18–20} Radical or cationic species are generated by the interaction of UV light with a suitable photoinitiator or photosensitizer. Onium salts initiate both the cationic and free radical curing processes by generating Brønsted acids (or cations) and free radicals upon photodecomposition.^{21,22} Methacryloyl or the acryloyl group containing monomer/oligomer are typical compounds that undergo free radical UV polymerization, while epoxide group containing compounds undergo cationic UV polymerization. Once the acrylate and epoxy monomers are mixed together and undergo UV polymerization using onium salt as a photoinitiator, the polymer thus formed possesses an interpenetrating polymer network (IPN) structure.^{23,24} The main advantage of IPN-structured materials is that they combine the properties of the two kinds of polymer networks.

In this article, we describe the introduction of epoxide and methacryloyl groups onto the surfaces of pristine diamond (PD) powder and PET film, respectively. The epoxy group containing modified diamond (ED) was mixed thoroughly with a binder agent consisting of epoxy and acrylate resins and the photoinitiators to form a coating agent. The coating agent was then applied to the glass plate or the surface of the PET film containing methacryloyl groups (called MMA-PET). After degassing under

reduced pressure, the thin film of the coating agent was exposed to the UV light to develop an IPN-structured coating film. The photoreaction properties of the coating agents, tensile strength, and thermal stability of the free coating film (called free film), and the improvement of the adhesion strength of coating film on MMA-PET were subsequently studied in detail.

EXPERIMENTAL

Materials

PET film (DuPont Melinex 377) with a thickness of 75 μm, the synthetic diamond powder (called pristine diamond, PD; Diamond Innovations MBM) with a grain size of 3–5 μm, and the UV-curable acrylate resin (Agi-Arocoat-5500) were kindly supplied by Kinik Co. (Taiwan). A 2-hydroxy-2-propylphenyl ketone (Darocur 1173) was used to generate free radicals to initiate the polymerization of the acrylate monomer, and a diphenyliodonium hexafluorophosphate (DIH) was used to generate protonic acid to initiate the cationic ring-opening polymerization of the epoxy monomer. These materials were kindly supplied by Ciba Specialty Chemicals. 3,4-Epoxy cyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (EEC), and 1,1,1,3,3,3-hexafluoro-2-propanol [HFP] were purchased from Aldrich Co. and used as received.

Surface modification of diamond

Half a gram of PD was washed with 20 mL of concentrated H₂SO₄/HNO₃ acid solution (v/v: 3/1) at 100°C for 24 h, and was then centrifuged and subsequently rinsed with distilled water until the pH reached a value of 7, and then dried at 120°C for 2 h. The acid-washed diamond powder was exposed to ultrasound in distilled water (20 mL) under bubbling oxygen (0.5 l/min) at room temperature for 30 min using a 43 kHz ultrasonic apparatus. The modified surface of the diamond was characterized by the FTIR and SEM/EDX methods.

Surface modification of PET film

PET film (20 mm x 70 mm) was treated in 0.1 wt % cetyltrimethylammonium bromide 0.5 M NaOH solution (100 mL) at 80°C for 2 h. After rinsing with distilled water and drying at 60°C, the PET film was put in the solution of methacryloyl chloride (1.0 mL), ZnCl₂ (0.01 g), and chlorobenzene (10.0 mL) to react with methacryloyl chloride at 50°C for 1 h under nitrogen atmosphere to introduce methacryloyl groups on the surface of the PET film (called MMA-PET). After rinsing with acetone and drying

at room temperature under reduced pressure (2 Torr) for 1 h, the methacryloyl group containing MMA-PET was identified by the FTIR and ESCA.

Preparation of free film

A coating agent consisting of diamond (PD or ED) particles, a binder agent solution and photoinitiators was prepared according to the formulation listed in Table I, and was applied to the glass plate by a wire-wound rod with wire diameter of 0.45 mm. After degassing under reduced pressure, the thin coating agent on the glass plate was exposed to UV light at room temperature in a crosslinker box (Uni Vex-500, Taiwan) for 1 min to allow the formation of a 50- μm -thick coating film. The light intensity at the sample position was 100 mW/cm². The free film was obtained after the cured coating film was removed from the glass plate in water, and dried at 60°C for 1 h.

Degree of conversion of coating agent

The coating agents were coated on the KBr disks and were evaporated and degassed under reduced pressure. The samples were recorded on a Digilab FTS-1000 FTIR with a resolution of 4 cm⁻¹ before and after UV curing. The total area of the $\nu_{\text{asC-H}}$ and $\nu_{\text{sC-H}}$ absorptions at 2850 and 2950 cm⁻¹ was considered the internal standard (IS).²² The change in the peak area due to the carbon-carbon double bond (C=C) at 1637 cm⁻¹ before and after the reaction was monitored, and the degree of conversion (DC) of acryloyl group in acrylate resin was determined using the following equation:

$$\text{DC}(\%) = [1 - (A_{1637}/A_{\text{IS}})_a / (A_{1637}/A_{\text{IS}})_b] \times 100 \quad (1)$$

where $(A_{1637}/A_{\text{IS}})_a$ is the ratio between the area of C=C absorption at 1637 cm⁻¹ and the area of internal standard absorption after polymerization; $(A_{1637}/A_{\text{IS}})_b$ is the ratio between the area of C=C absorption at 1637 cm⁻¹ and the area of internal standard absorption before polymerization. DC (%) of 3,4-epoxycyclohexyl group (absorption at 795 cm⁻¹)²⁵ in EEC was determined using the following equation:

$$\text{DC}(\%) = [1 - [(A_{795}/A_{\text{IS}})_a / (A_{795}/A_{\text{IS}})_b]] \times 100 \quad (2)$$

Tensile strength of free film

The tensile strengths of the free films were measured with the Universal Testing Machine (Shimadzu AG-1, Japan) at room temperature with a crosshead speed of 1.0 mm/min in accordance with ASTM method D638. A minimum of five specimens were tested in each case to obtain the average value.

TABLE I
Formulations of Coating Agents and the Properties of the Corresponding Free Films at a Thickness of 50 μm after Photopolymerization

Formulations	Binder agent (%) ^a	PD _(phr)	ED _(phr)	Tensile strength (N/mm ²)	T _{d5}
CF-0	100	–	–	12.67 ± 3.82	277.3
CF-PD-10	100	11.1	–	11.54 ± 1.88	251.3
CF-PD-30	100	42.9	–	8.29 ± 0.83	257.3
CF-PD-50	100	100.0	–	7.49 ± 3.63	263.4
CF-ED-10	100	–	11.1	17.13 ± 1.48	286.5
CF-ED-30	100	–	42.9	19.09 ± 3.63	292.5
CF-ED-50	100	–	100.0	22.09 ± 3.48	298.9

^a consisted of 78.8 wt % of UV-curable acrylate (Agi-Arocoat-550) with the major component of TEGDMA and 1,1,1-trimethylol propane triacrylate, 19.7 wt % of EEC, 0.5 wt % of DIH, and 1.0 wt % of Darocur 1173.

Thermogravimetric analysis of free coating films

The thermogravimetric analyses (TA Instruments Q500) of free films were carried out at a heating rate of 20°C/min under nitrogen atmosphere (flow rate of 40 mL/min) in the thermal range of 25–600°C. The sample sizes were in the range of 6–10 mg.

Preparation of coating film on PET film

A coating agent was applied to the MMA-PET or untreated PET films with the thickness of 6 μm by a wire-wound rod with wire diameter of 0.08 mm. After evaporating and degassing under reduced pressure, the coating film was exposed to UV light under the same condition as mentioned above.

Adhesion of coating film on PET film

The adhesion of the coating film on the MMA-PET and untreated PET films was analyzed in accordance with the cross-cut tape test method in ASTM method D 3359-08. The cutter was moved on the coating film to make a lattice pattern, 1 mm² being the area of each lattice. After brushing the surface lightly with a soft brush to remove loose flakes of coating, a 3M Scotch 610-1 PK tape was applied to the lattice pattern and then removed quickly. The results observed on the lattice pattern were compared to the "classification of adhesion test results" listed in the protocol. The grade of adhesion between the coating film and the PET film was classified in order of increasing strength from 0B, 1B, 2B, . . . to 5B.

Measurements

The FTIR spectra of the samples were recorded on a FTIR (Digilab FTS-1000) with a resolution of 4 cm⁻¹. Liquid samples for FTIR measurement were

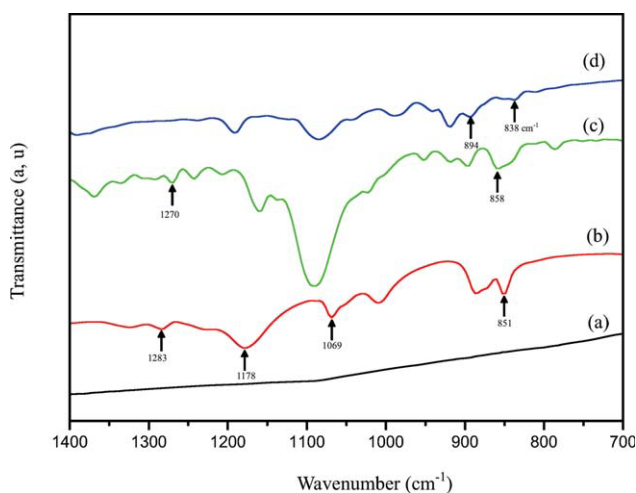


Figure 1 IR spectra of (a) PD, (b) ED, (c) cyclohexene oxide, and (d) ED after photoreacting with cyclohexene oxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

prepared by coating the polymer or homogeneous mixtures on the KBr disks followed by vacuum drying (<5 Torr) at 40°C for 5 h. Solid samples were mixed and ground with dry KBr powder and then pressed into a transparent disk. Scanning electron microscopy (SEM) was performed with a 20 kV beam energy using a scanning electron microscope (Cambridge SEM S360, Britain) equipped with an energy-dispersive X-ray analyzer (EDX; Link-AN10-85S, Britain). The surface composition of the modified PET sample was investigated by ESCA using a VG ESCA Scientific Theta Probe 2002 (Britain) apparatus, equipped with an Al K α anode. Contact angle determinations were performed with distilled water on a FACE CA-5 150 (Kyowa Interface Science Co.) goniometer. The data presented are the average of at least five measurements.

RESULTS AND DISCUSSION

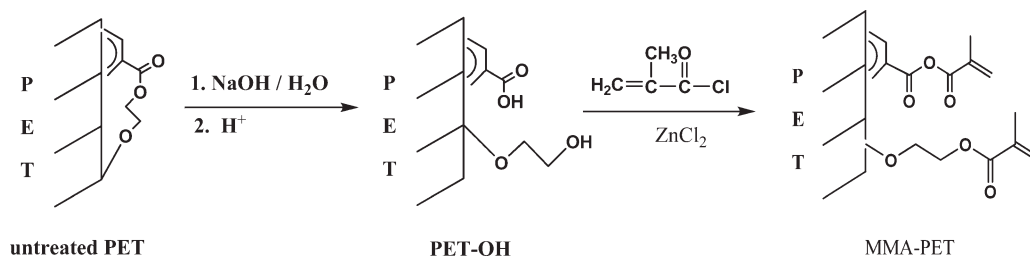
Modification of diamond surface

The ED was obtained when the PD was washed in concentrated H₂SO₄/HNO₃ solution at 100°C, followed by ultrasonic treatment in distilled water with

bubbling oxygen gas.⁷ It was proved by X-ray analysis that the intrinsic crystal structure of the diamond was not changed at all (spectrum not shown here) in this modification procedure. The EDX analysis of the surface of ED showed an increase in the oxygen content from 0.56 to 9.61 atomic% (data not shown here), indicating that oxygen containing functional groups were introduced on the surfaces of diamond particles. The IR spectrum of ED shown in curve **b** of Figure 1, when compared with that of the PD in curve **a**, shows new significant characteristic absorptions. The absorptions at 1069 and 1178 cm⁻¹ could be assigned to ether stretching (ν_{C-O-C}), and the absorptions at 1283 and 851 cm⁻¹ could be assigned to epoxy stretching (ν_{C-O}).^{26,27} The existence of the epoxy group on the diamond surface was further confirmed by the HClO₄/(C₂H₅)₄N⁺Br⁻ titration system using crystal violet as an indicator.²⁸ The epoxide groups on the surface of ED were quantitative titrated with the concentration of 7.8×10^{-3} mmol/g.

Modification of PET film surface

The surface of the PET film was hydrolyzed with aqueous sodium hydroxide by the saponification of ester linkage to increase hydroxyl and carboxyl groups on the surface of the film (PET-OH) (scheme 1). The optimum saponification condition was tried to achieve a PET-OH with a lower water contact angle (WCA) and lower weight and tensile strength losses. The hydroxyl and carboxyl groups on the PET-OH then reacted with methacryloyl chloride under the catalyze of ZnCl₂ to make the MMA-PET. The WCA of the PET film at different modified stages was measured (Table II). It was found that once the highly hydrophobic methacryloyl groups were introduced on the surface of PET, the WCA of the film increased drastically. The ESCA spectrum of untreated PET showed the carbon and oxygen peaks ratio, C/O, was 2.33, and was very close to the theoretical 2.50 value. These findings are indicative of an essentially untreated PET surface. The characteristic carbon 1s peaks at 284.5, 286.4, and 288.9 eV, assigned to the aromatic, ether, and ester carbon atoms, respectively, while oxygen 1s peaks at 532.4



Scheme 1 Reactions at PET film surface for preparing MMA-PET.

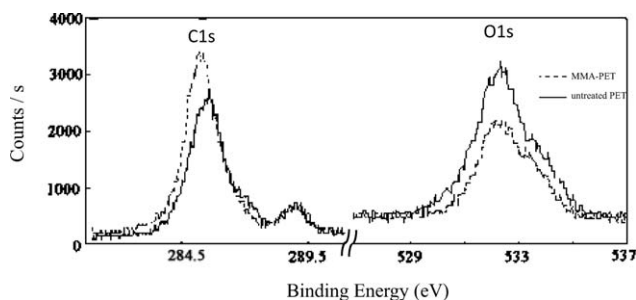


Figure 2 ESCA spectra of C 1s peak and O 1s peak for untreated PET and MMA-PET.

and 535.3 eV, as shown in the spectra shown in Figure 2.^{29,30} The 3.48 (C/O) ratio measured for the MMA-PET is much higher than the 2.33 value. This relative decrease in the oxygen content, when compared with that of untreated PET, is caused by an increasing carbon ratio and a decreasing oxygen ratio on the surface of MMA-PET, because of the presence of the methacryloyl group on the surface of PET film, which has a higher C/O ratio (i.e., 4/1). The MMA-PET film was dissolved in HFP²⁹ and then was coated on the KBr disk. After vacuum drying, the IR spectrum was recorded and the characteristic peaks were treated by the Gaussian peak-fitting method [Fig. 3(b)]. The new characteristic absorptions at 1774 and 1755 cm^{-1} could be assigned to the unsymmetrical (ν_{as}) and symmetrical (ν_{s}) carbonyl stretching of anhydride, while the additional absorptions at 1639 cm^{-1} could be assigned to the stretching of $-\text{C}(\text{CH}_3)=\text{CH}_2$ of the methacryloyl groups.

Preparation of free coating film

When a 50- μm -thick film of coating agent, prepared according to the formulation listed in Table I, was applied to the glass plate and exposed to UV light, the EEC/ED and acrylate resin components in the binder agent underwent respective cationic and free radical polymerizations simultaneously to form an IPN-structured coating film (scheme 2). The free film was obtained by removing the cured coating film from the glass plate. The degree of conversion (DC) of both the epoxy group and acrylate group in the coating agent with film thickness of 15 μm were measured.^{23,25} Figure 4 shows the DC of EEC and acrylate resin in the binder agent with the UV exposure times for various contents of PD. Photopolymerizations of both the EEC and acrylate components were found to proceed extensively in air,²³ especially in the presence of PD. The DC of both components could reach higher than 80% within 1 min of exposure, and increase with the optimum amount of PD added. Obviously, the rates of polymerization of

both components increase with the amount of PD added from 0 to 30 wt % then start to decrease.

Properties of free films

In addition to the high DC of the binder agent after UV curing, the dispersion of the diamond powder in the coating agent and the interfacial force between diamond powder and the cured binder agent matrix (called matrix) have an influence on properties such as the tensile strength and thermal stability of the free films thus formed.³¹

Tensile strength and thermal stability

The tensile strength of free films prepared from the binder agent and the respective PD and ED of

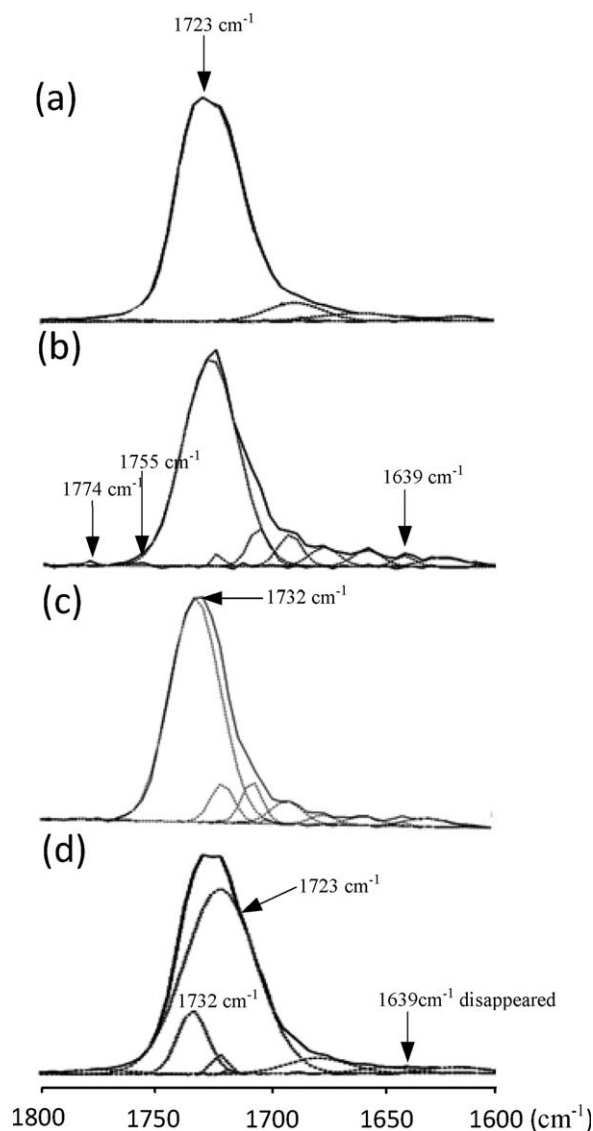
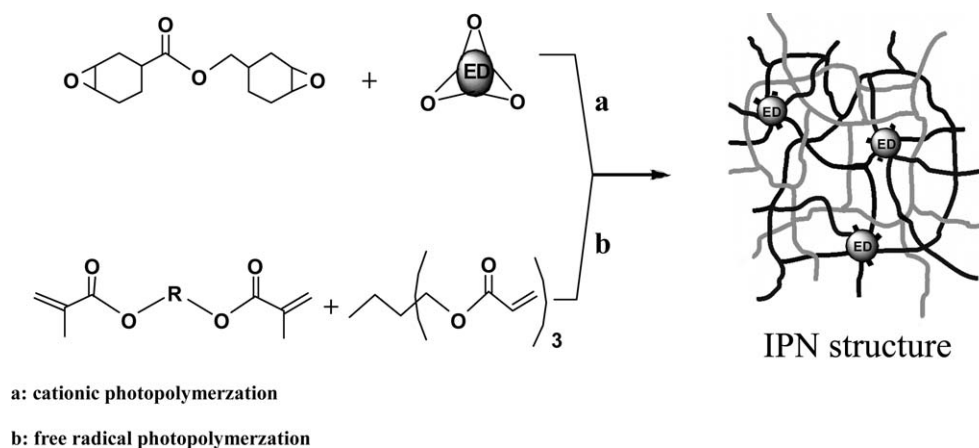


Figure 3 IR spectra (treated by Gaussian peak-fitting method) of (a) untreated PET, (b) MMA-PET, (c) PMMA, and (d) MMA-PET after reacting with MMA.



Scheme 2 IPN-structured coating film

various weight percentages is listed in Table I. It is found that the tensile strength of ED-containing CF-ED series free films (CF-ED-10 ~ 50) is much higher than that of the blank free film (sample CF-0). The strength of the film increases with the amount of the ED embedded, that is, tensile strength of CF-0 < CF-ED-10 < CF-ED-30 < CF-ED-50. Whereas the strength for PD-containing CF-PD series free films (CF-PD-10~50) is much lower than that of CF-0, and the strength decreases with the amount of PD embedded, that is, the strength of CF-0 > CF-PD-10 > CF-PD-30 > CF-PD-50. Figure 5 shows the TGA thermograms of free films of the CF-0 and CF-ED and CF-PD series. The temperatures of 5% weight loss (T_{d5}) for CF-ED series free films are not only higher than that of CF-0, but these films also have a higher ED content (Table I). An increase of T_{d5} is generally considered as an indication of enhancement of thermal stability.^{32,33} The T_{d5} for CF-PD se-

ries free films, however, is lower than that of the free films of CF-0 and CF-ED series of corresponding diamond content. Several possible causes can be suggested for this enhancement of tensile strength and the thermal stability of CF-ED series free films, such as the incorporation of the ED particles in the binder agent matrix, the reaction of the epoxide group on the ED surface with the EEC component in the binder agent to enhance the interfacial force between the ED and the matrix, or the increase of the interfacial force with the amount of ED added. A possible reason that could explain the decrease of tensile strength and thermal stability of CF-PD series free films is that the PD particles have a poor adhesion to the matrix, and the polyhedral edges of PD particles act as stress raisers for crack nucleation at the diamond/matrix interface.³⁴

Morphology

The experimental results shown above have proved that CF-ED series free films are of higher tensile strength and thermal stability than the CF-PD series of corresponding PD content. This observation suggests that in the ED-containing coating agent, the epoxy group on the ED powder might react (cationic ring-opening polymerization) with the EEC during the period of UV curing to enhance the interfacial force between the diamond and the matrix, while in the PD-containing coating agent, the PD only acts as

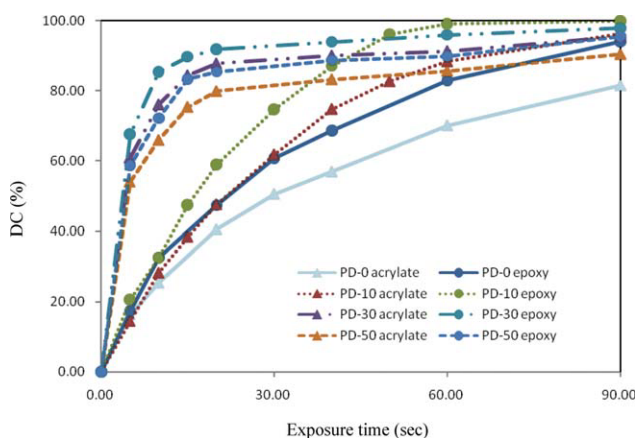


Figure 4 The DC of both epoxide and acrylate groups of binder agents with UV exposure time in the presence of PD of various contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Water Contact Angles of PET Film at Various Stages of Modification

PET film	untreated	PET-OH	MMA-PET
WCA (°)	79 ± 0.43	56.5 ± 0.90	99.5 ± 1.39

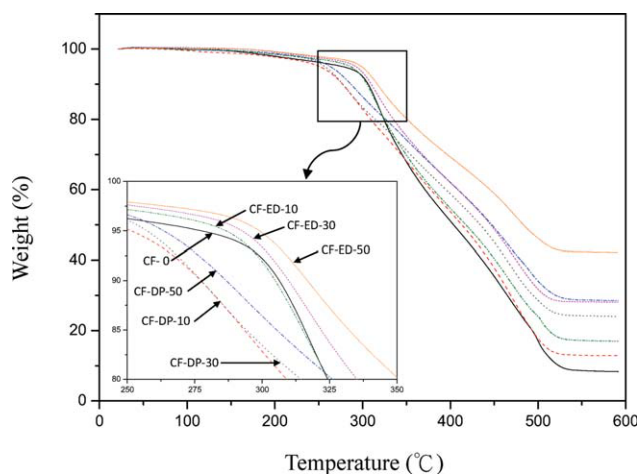


Figure 5 TGA curves of free films of CF-0, CF-ED, and CF-PD series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a nonreinforcing filler, which disperses in the matrix without any chemical reaction with the binder agent during the UV-curing reaction. The interaction between the diamond and the binder agent could be confirmed by investigating the morphology of the fracture surface of the free film (Fig. 6). Figure 6(a) is the fracture cross-section of PD-containing CF-PD-50 free film. It can be seen that the PD particles are partially detached from the matrix and directly associated with the cavities. The interfacial boundary between the diamond and the matrix is clear. All of the above indicate a weak interfacial force between the two phases.³⁴ Figure 6(b) is the fracture cross-section of ED-containing CF-ED-50 free film. No diamond particle detached from the matrix is found on the fracture surface, and the boundary between the diamond and the matrix is ambiguous, indicating that all ED particles were wetted, coated, and reacted with the matrix. The interfacial force between the ED and the matrix is strong enough to prevent the diamond from separating from the matrix, because of chemical bonding between the two phases.

Model reaction

The cationic ring-opening polymerization of the epoxy groups on the ED surface with the EEC in the binder agent could be proved indirectly by the model reaction of ED and cyclohexene oxide, which has the same epoxide structure as the EEC. Blends of respective PD and ED with cyclohexene oxide were applied to the glass plate and were exposed to UV light in the presence of DIH and Darocur 1173. After washing with THF to purge off all soluble organic species including polymer (e.g., polycyclohexene oxide) and other additives, the IR spectrum of the diamond was recorded. The IR spectrum of PD after reacting with

cyclohexene oxide is very similar to that of the PD (curve a in Fig. 1); no additional absorption is found, indicating that PD does not react with cyclohexene oxide at all. Curve d in Figure 1, however, shows the characteristic absorptions of ED (shown in curve b) and cyclohexene oxide (shown in curve c), except for the disappearance of absorptions of their respective epoxy groups at ca. 1270, 1283, 851, and 858 cm^{-1} after exposure to the UV light. The result of the model reaction could be used to prove that the epoxy groups on the surface of ED undergo cationic ring-opening copolymerization with the EEC component of the binder agent to form the chemical bonding between the two phases.

Adhesion of coating agent on the surface of MMA-PET

Studies on how the adhesion strength of the coating film on the surface of PET film is influenced by the strength of the coating film just described above and

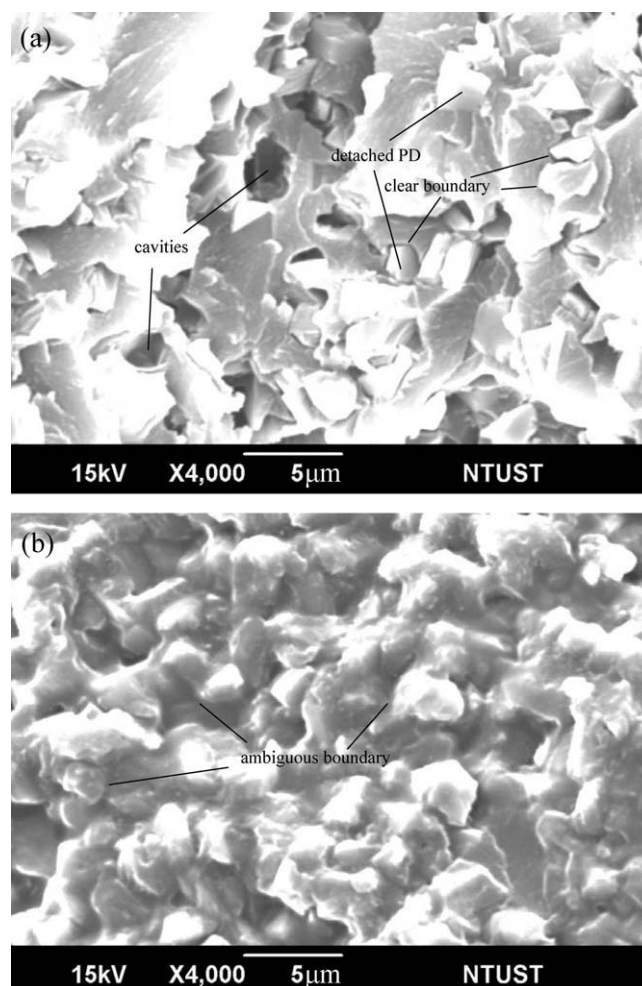


Figure 6 SEM images of the fracture surfaces of the free films of (a) CF-PD-50 and (b) CF-ED-50.

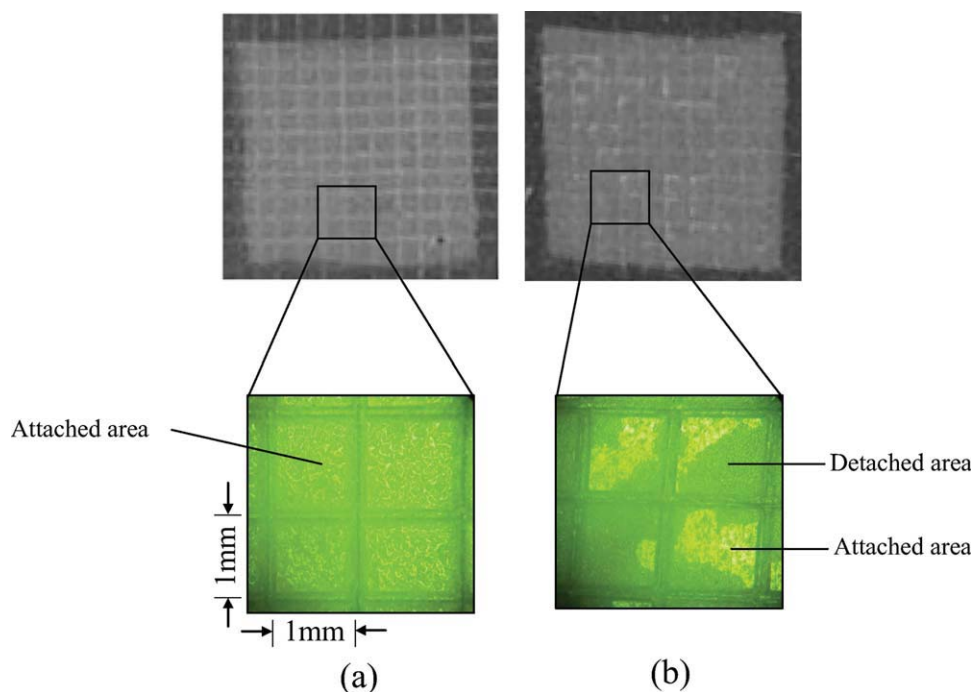


Figure 7 Cross-cut tape test for CD-ED-50 coating film on (a) MMA-PET and (b) untreated PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the interfacial force between the two phases. When the thin film of coating agent (with the thickness of ca. 6 μm) on the MMA-PET was exposed to UV light, the acrylate resin in the binder resin not only underwent free radical polymerization itself, but also copolymerized with the methacryloyl group on the PET film. The adhesion strength between the coating film and the MMA-PET film was determined in accordance with the cross-cut tape test in ASTM method D 3359-08. The cut edges of the coating film were completely smooth, and none of the squares of the lattice were detached [Fig. 7(a)]; therefore the adhesion test could be classified as being in the highest grade, **5B**. However, for the coating film on the untreated PET film, the test is classified as **0B** [Fig. 7(b)], because more than 65% of the square lattices were detached because of the weak interfacial force (without chemical bonding) between the coating film and the PET film. The model reaction for confirming the photoreaction between the surface of MMA-PET and the acrylate resin in binder agent was done by applying the solution of methyl methacrylate (MMA)/cyclohexene oxide (w/w:3/1) monomers, DIH, and Darocur 1173 to the films of MMA-PET and untreated PET, respectively, at the thickness of 6 μm . After degassing and exposing to UV light, the two films were treated subsequently as follows: washing thoroughly with THF to purge off all soluble organic species, dissolving in the HFP, and coating on the KBr disks followed by vacuum drying. The IR spectra of the carbonyl peaks of both the untreated

PET and MMA-PET were recorded and were processed by the Gaussian peak-fitting method. It was found that the carbonyl peak of untreated PET after reacting with MMA is very similar to that of the untreated PET [Fig. 3(a)] indicating that the surface of untreated PET does not react with MMA, whereas carbonyl peak of MMA-PET after reacting with MMA is composed of two carbonyl peaks [Fig. 3(d)]. The peak at 1732 cm^{-1} is the same as that due to the absorption of carbonyl group of PMMA [Fig. 3(c)], while the peak at 1723 cm^{-1} is the same as that due to absorption of carbonyl group of untreated PET [Fig. 3(a)]. The existence of additional carbonyl absorption of PMMA in the MMA-PET carbonyl group and the disappearance of the methacryloyl group absorption at 1639 cm^{-1} reveals that MMA was grafted from the MMA-PET. The result of the model reaction can be used to further prove that the methacryloyl group on the surface of PET undergoes free radical copolymerization with the acrylate component of binder agent to increase the adhesion of the coating film on the surface of the PET film.

CONCLUSIONS

A IPN-structured free film or coating film on the MMA-PET substrate was prepared. The tensile strength and the thermal stability of the free films of the CF-ED series increased with the amount of ED embedded in the matrix, but decreased for the CF-

PD series samples. The increase in the tensile strength and thermal stability of the free films of the CF-ED series was attributed to the chemical bonding between the ED and the cured binder agent matrix, whereas the decrease in the tensile strength of the free films of CF-PD series was attributed to the low interfacial stress between the PD and the matrix. These explanations were confirmed by the model photoreaction of ED with cyclohexene oxide, which has the same epoxide structure as the EEC component in the binder agent, and by SEM investigation of the morphology of the fracture cross-section of samples from the two series. The significant improvement in the adhesion strength of the coating film on the MMA-PET was because of the free radical polymerization of the methacryloyl groups on the MMA-PET film with the acrylate resin in the binder agent. The model reaction of MMA-PET with methyl methacrylate was used to confirm the free radical polymerization between the two phases.

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