

Dopamine Acrylamide, as an UV Adhesive Material Found out in Biodiversity

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Abstract-- In a bio-inspired catechol monomer, dopamine acrylamide (DopAm) and 4-(methacrylamido)phenylboronic acid (4-MAPB), those surface affinities were investigated by quartz crystal microbalance (QCM) measurements. To each surface of SiO₂ and Ag, DopAm and 4-MAPB had greater adhesive capacity than 4-hydroxybutyl acrylate (4-HBA), methacrylic acid (MAA), and so on. Subsequently, in UV-curing surface adhesions to ABS, glass, and ITO (coated on glass), a polymer containing only 1wt% of DopAm was adhered more effectively than that containing the same amount of 4-MAPB. Furthermore, when each 0.5wt% of DopAm and 4-MAPB were used at once, the effect was most enhancement for glass and ITO. Finally, in UV-curing tacky adhesions, a co-polymer containing DopAm was also more effective than that containing 4-MAPB for pairs of dissimilar materials, i.e., PET/Cu and PET/Al, in which the synergistic effect of DopAm and 4-MAPB was found in the same as UV-curing surface adhesions.

I. INTRODUCTION

From the perspective of biodiversity, there are various adhesive mechanisms which are in Gecko legs, wild burdock fruit, mussels, etc. In mussels, L-dopa has a catechol group is an important adhesive component [1] (Fig.1).



Fig.1 a) Mussels and each structure of b) L-dopa and c) DopAm.

We focused on L-dopa, dopamine [2], and dopamine acrylamide (DopAm) (Fig.1) as a biomimetic adhesive monomer, which are corresponding to a rare case of an artificially chemical evolution. DopAm and its analogues were studied well about an adhesive gel [3], a nanoimprint lithography [4], a dental adhesive in eugenol monomer [5], and so on. And as another chemistry, catechol groups and boric acid produced corresponding boric acid esters by equilibrium reactions [6], which were used for cross linking in polymers [7] and various applications [8, 9]. From our previous report, in eco-friendly UV curing without solvents, when a small amount of DopAm was used with main monomers, surface adhesiveness to materials and tacky adhesiveness for pairs of dissimilar materials were more improved than those without DopAm [10]. In this study, some synergistic effects were found with DopAm and 4-(methacrylamido)phenylboronic acid (4-MAPB). The properties of DopAm with 4-MAPB were introduced in detail and its application potential was discussed.

II. TECHNICAL WORK PREPARATION

A. Chemicals and Materials

Commercially available chemicals as solvents were reagent grade and used without further purification. 2-Methyl-2-propenoic acid [i.e., Methacrylic acid (MAA)] and its esters (Mitsubishi Chemical Co. Ltd.), N-[2-(3,4-dihydroxyphenyl)ethyl]prop-2-enamide [i.e., dopamine acrylamide (DopAm)] and acrylate esters (Osaka Organic Chemical Industry Ltd.) [11] were also used as received from the manufacturers. [4-(2-methylprop-2-enoylamino)phenyl]boronic acid [i.e., 4-(methacrylamido)phenylboronic acid (4-MAPB)] and 2-[4-(2-methylprop-2-enoylamino)phenyl]-4, 4, 5, 5-tetramethyl-1,3,2-dioxaborolane (pinacol-protected 4-MAPB) were prepared by dehydration of the amines as these precursors and MAA with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl).

In cross-cut peel tests for surface adhesion, ABS resin plates (Type: N, thickness: 2.0mm) (Taiyukizai Co., Ltd.), soda-lime glass plates (thickness: 0.7mm) (Foresight Co., Ltd.), indium tin oxide (ITO)-coated glass plates (thickness: 0.7 mm/glass, 0.13μm/ITO) (EHC Co., Ltd.) were used. In the peel tests for surface adhesion, an adhesive tape (Cellotape™, Nichiban Co., Ltd.) was used. In the 180° peel tack tests, polyester (PET) films (Lumirror 60, thickness: 75μm) (Toray Industries, Inc.), PP plates (Type: N, thickness: 2.0mm) (Taiyukizai Co., Ltd.), Cu plates (Type: FR-4R 1700, thickness: 1.6mm) (Taiyukizai Co., Ltd.), and Al plates (Type: A1050P, thickness: 0.8mm) (Nippon Testpanel Co., Ltd.) were used. The surfaces of these materials were cleaned with acetone or ethanol before use.

B. Instruments and Experiments

A 9 MHz quartz crystal microbalance (QCM) measurements were performed on a SEIKO EG&G QCA922 analyzer. In the UV-curing, monomers or mixtures were coated on sample plates with RDS Mayer Coating Bar No. 10 (coating thickness: 22.9μm) and were exposed to a Heraeus LIGHT HAMMER 10 UV system.

Tension tests were performed using an A&D RTG-1310 testing machine.

QCM measurements were performed using quartz oscillators on which inorganic oxides or metals were deposited. For comparison with DopAm, the same measurement was performed for 4-hydroxybutyl prop-2-enoate (4-HBA), MAA, phenyl prop-2-enoate (PHMA), and butyl prop-2-enoate (BMA). Furthermore, instead of DopAm, 4-MAPB was also investigated. Each 1 wt% solutions of monomers in ethanol were flowed through a cell for 360 seconds, after silicon dioxide (SiO₂) or Ag coated oscillator was set in the cell. Resonance frequency change (Δf), -1 Hz is equivalent to mass change (Δm), 1.071ng.

UV-curing polymerization for cross-cut and peel tack tests was as follows. On a sample plate (ABS polymer, glass, or ITO-coated glass), a mixture of 4-HBA/[2-(hydroxymethyl)-3-prop-2-enoyloxy-2-(prop-2-enoyloxy-methyl) propyl] prop-2-enoate [i.e., trimethylolpropane triacrylate (TMP-3A)]/DopAm/diphenylphosphoryl-(2,4,6-trimethylphenyl)methanone (TPO) (ratio: 94/5/1/10) was coated with the RDS bar coater. The coated mixture was then exposed to a UV-curing system (3000mJ/cm²). In a mixture of 4-HBA/TMP-3A/TPO (ratio: 95/5/10) without DopAm, the procedure was the same as described above. Cross-cut and peel tests were performed in accordance with the Japanese Industrial Standards (JIS) K5600-5-6.

UV-curing polymerization for 180° peel tack tests was as follows. On a PET film, a mixture of oxolan-2-ylmethyl prop-2-enoate[tetrahydrofurfuryl acrylate (THFA)]/DopAm/TPO (ratio: 99/1/10) was coated with the RDS bar coater. Another PET film was lightly placed

on the coated surfaces of the PET film. Similar to the PET/PET described above, PET/PP, PET/PE, PET/Cu, and PET/Al were also prepared. All of samples were exposed to the PET film side using a UV-curing system. The coated mixture was then exposed to a UV-curing system (3000mJ/cm²). The procedure without DopAm for a mixture of THFA and TPO (ratio: 100/10) was the same as described above. The peel tack tests were performed in accordance with the JIS Z 0237.

III. RESULTS AND DISCUSSION

A. Each Surface Affinities of DopAm and 4-MAPB with Inorganic Oxides and Metals on These Surfaces by QCM

The data of surface affinities for SiO₂ and Ag were shown below in Fig. 2. DopAm adhered well to those surfaces in contrast to other monomers. Namely, it was found that a catechol monomer, DopAm had greater adhesive capacity than 4-HBA, MAA, PHMA, and BMA, which had hydroxyl, carboxyl, phenyl, and alkyl groups, respectively. In addition, the frequency of DopAm gradually decreased on the surface of the oscillator. In other words, DopAm laminated over time. DopAm also showed specific adhesion to ITO, copper, and gold. Those phenomena were not observed for the other monomers described above.

The surface affinity of 4-MAPB for SiO₂ was almost the same as that of DopAm. And in case of Ag, the affinity of 4-MAPB was greater than that of DopAm. On the other hand, in the pinacol ester protected boronic acid group of 4-MAPB (Fig.3), the surface affinities were more less than those of 4-MAPB.

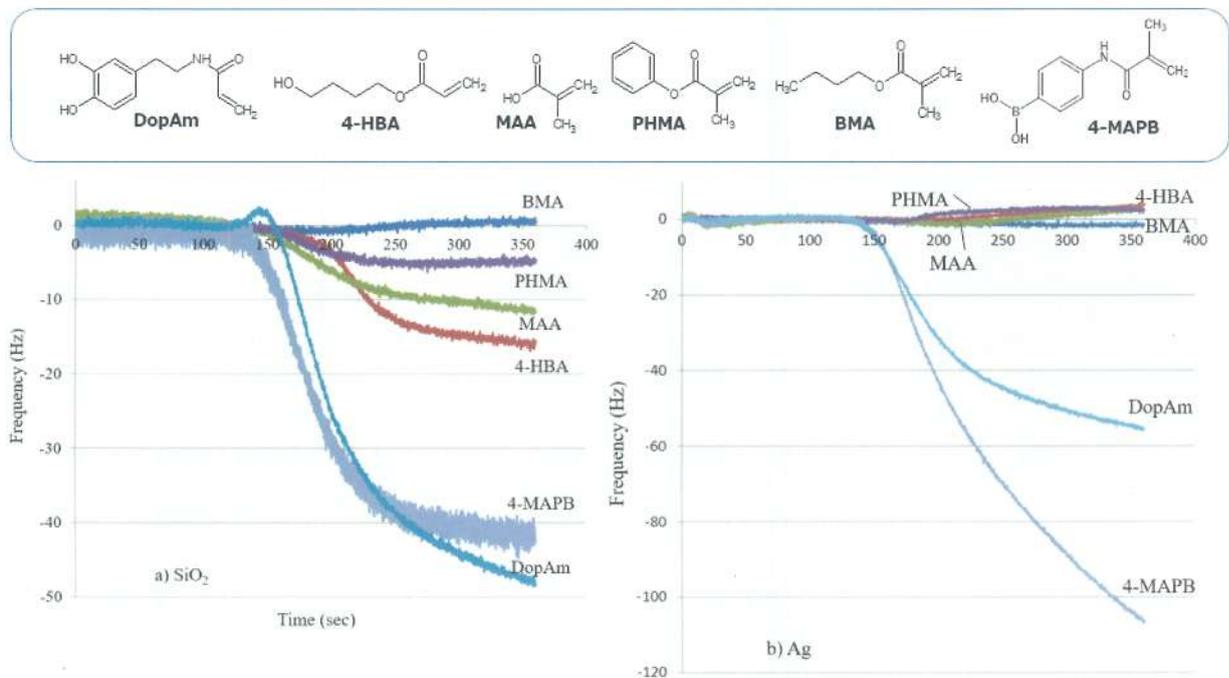


Fig. 2 Comparison of surface affinities of monomers to a) SiO₂ and b) Ag by QCM measurement.

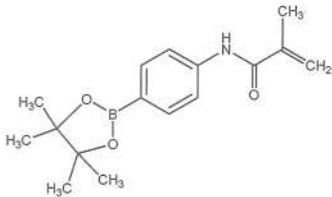


Fig. 3 Structure of pinacol-protected ester.

B. UV-Curing Surface Adhesions of Co-polymers Containing DopAm and or 4-MAPB

In the surface adhesion tests, a co-polymer of 4-HBA and TMP-3A (Fig. 4) was used for a general-purpose hard coat composition. A mixture of monomers was coated on each plate of ABS, glass, and ITO (coated on glass) and exposed to UV light during the polymerization process. After making a grid-shaped cut, a commercially available adhesive tape was attached to the coating films.

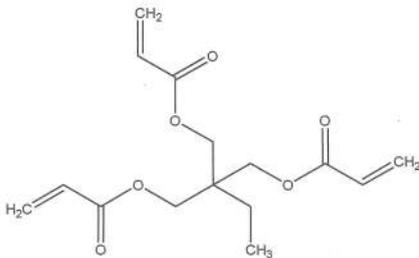


Fig. 4 Structure of TMP-3A

After detaching the adhesive tapes in ABS, glass, and ITO, it was found that the surface adhesion were improved by the addition of only 1wt% of DopAm (Fig. 5). Without DopAm, the co-polymer was almost peeled

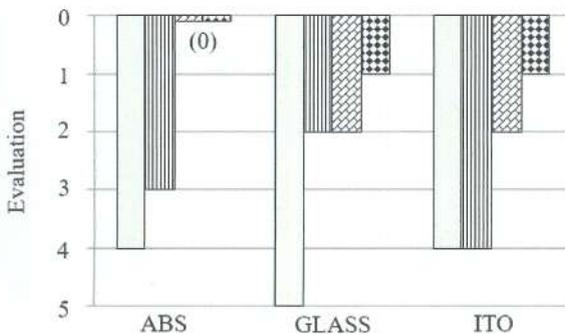


Fig. 5 Cross-cut and peel test
 □ Blank. 4-HBA/TMP3A/UV-Initiator (wt. ratio: 95/5/10). ▨ 4-MAPB (1wt% vs. all monomers) was added. 4-HBA/4-MAPB/TMP3A/UV-Initiator (wt. ratio: 94/1/5/10). ▩ DopAm (1wt% vs. all monomers) was added. 4-HBA/DopAm/TMP3A/UV-Initiator (wt. ratio: 94/1/5/10). ▪ DopAm (0.5wt% vs. all monomers) and 4-MAPB (0.5wt% vs. all monomers) were added. 4-HBA/DopAm/4-MAPB/TMP3A/UV-Initiator (wt. ratio: 94/0.5/0.5/5/10). JIS K5600-5-6 (ISO2409). UV curing film; thickness ca. 20 μ m. Evaluation (unchanged: 0 ~detachment > 65%; 5).

off along with the adhesive tape after cross-cutting. In case of 4-MAPB, the surface adhesion was improved for glass in the same condition with DopAm. In contrast to those results, when each 0.5wt% of DopAm and 4-MAPB

were used at once, surface adhesions of the copolymer became more strongly than that containing DopAm or 4-MAPB. TPO was used as the UV initiator (Fig. 6).

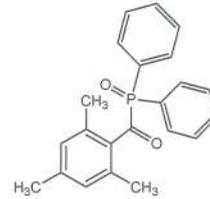


Fig. 6 Structure of TPO.

C. UV-Curing Tacky Adhesions of Co-polymers Containing DopAm and or 4-MAPB

In the 180° peel tack tests, THFA (Fig. 7) was used as a general-purpose tacky adhesive. According to the

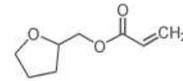


Fig. 7 Structure of THFA

experimental section described above, pairs of PET/PET, PET/PP, PET/PE, PET/Cu, and PET/Al were prepared with THFA by UV curing for the peel tack tests (Fig. 8).

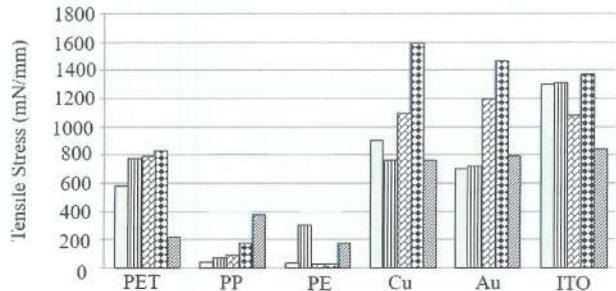


Fig. 8 180°Peel tack tests using PET film.
 □ Blank. THFA/UV Initiator (wt. ratio: 100/10). ▨ 4-MAPB (1wt% vs. all monomers) was added. THFA/4-MAPB/UV-Initiator (wt. ratio: 99/1/10). ▩ DopAm (1wt% vs. all monomers) was added. THFA/DopAm/UV-Initiator (wt. ratio: 99/1/10). ▪ DopAm (0.5 wt% vs. all monomers) and 4-MAPB (0.5 wt% vs. all monomers) were added. THFA/DopAm/4-MAPB/UV-Initiator (wt. ratio: 99/0.5/0.5/10). ▫ Commercial silylated urethane adhesive. JIS Z0237. UV curing adhesion; thickness ca. 20 μ m.

In comparison with the tests without DopAm, the adhesions of PET/PET, PET/Cu, and PET/Al were improved by adding only 1wt% of DopAm. In contrast to DopAm, 4-MAPB was not so effective for those pairs except for PET/PET. Interestingly, using each 0.5% of DopAm and 4-MAPB at a time improved the adhesions for PET/Cu and PET/Al over using 1wt% of them respectively. When 5wt% of DopAm was added, the effects were not significantly different from those with 1wt% DopAm. And about the solubility, it was difficult that 4-MAPB was solved more than ca. 1wt% in THFA. In PET/PP and PET/PE, DopAm and or 4-MAPB were found to be slightly or no effective. Those results indicated that DopAm was more effective on polar

surfaces including oxide layers on metals. Considering the QCM results, DopAm and 4-MAPB may have the effect of resin reinforcement by intermolecular hydrogen bonding with the functional groups of other monomers, as well as scaffolding by catechol group or boronic acid group. In copolymers containing DopAm or its methacrylamide, adhesivenesses were known about surface adhesions [4, 12] and lap shear adhesive strength of some pairs of single materials [3]. The interaction of catechol and boronic acid group is well known as described in introduction, and as an additional example, the pair of two polymer brushes containing each group to glue the surface each other [13].

In DopAm, those properties and low oxidation potential by catechol group in cyclic voltammetry (CV) [10] will be used to resin reinforcement systems, eco-friendly adhesives and coatings.

IV. CONCLUSIONS

In the QCM measurements, DopAm accumulated on the surfaces of SiO₂ and Ag over time. Those results suggest that the scaffolds on these surfaces were formed with catechol groups, and DopAm accumulated by intermolecular hydrogen bonds. The surface affinities of 4-MAPB with boronic acid group weren't similar to that of the pinacol protected 4-MAPB, but to those of DopAm with the accumulation. In the cross-cut and peel tests for ABS, glass, and ITO-coated glass, the surface adhesion with UV-curing was improved by adding only 1wt% of DopAm to the acrylates. Furthermore, when both of DopAm and 4-MAPB were used, the surface adhesions of the corresponding copolymer became more strongly than that with DopAm or 4-MAPB. Finally, in the 180° peel tack tests, the UV-curing tackinesses were also improved by adding only 1wt% of DopAm to THFA. DopAm was effective for pairs of dissimilar materials (PET/Cu, PET/Al). Those results suggest that DopAm has the effect of resin reinforcement by intermolecular hydrogen bonding with the functional groups of other monomers, as well as scaffolding by catechol groups. In the same as the surface adhesions, the synergistic effect of DopAm and 4-MAPB was also observed for PET/Cu and PET/Al. These phenomena will be applied to adhesions of dissimilar materials in the fields of electricity, automobiles and dentistry.

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