

Development of Bio-inspired Monomer, Dopamine acrylamide

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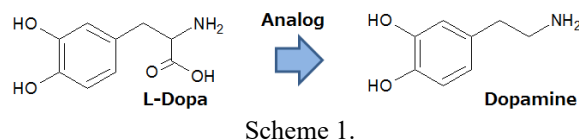
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In Quartz crystal microbalance (QCM) analysis, Dopamine acrylamide (DopAm) accumulated on the surface of SiO₂, ITO, and Ag over time. These results suggest that the scaffolds on these surfaces are formed with the catechol groups and DopAm accumulates by the intermolecular hydrogen bondings. And in the investigation of the surface adhesion and the tackiness, by adding only 1% of DopAm to UV curing monomers, DopAm was effective to several materials and several pairs of dissimilar materials. Considering the behavior of the QCM, these results suggest that DopAm has the effect of resin reinforcement by intermolecular hydrogen bondings with the functional groups of other monomers as well as scaffolding by catechol groups. To further applications, a redox characterization of DopAm was investigated by a cyclic voltammogram (CV).

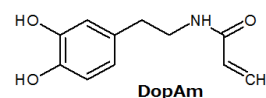
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1. Introduction

Bio-inspired chemistry is a fascinating field. In adhesion and coating, Dopamine structure [1,2] and polymers containing Dopamine analogs have been used well [3,4], which were developed as alternatives of L-Dopa [5] (Scheme 1). J. H. Waite et al. reported about the adhesive mechanism of marine mussels [6,7] (Scheme 2) and its applications [8-10]. A. Takahara et al. investigated adhesive gels of co-polymers with Dopamine acrylamide (DopAm) [11] (Scheme 3). H. Yabu et al. studied catechols applied DopAm in a nanoimprint lithography [12]. Recently, we synthesized DopAm at large scale as few Kgs so that we could examine about its characterization more easily. In QCM analysis, the interactions of DopAm with inorganic oxides and metals on those surfaces were confirmed by comparison with other monomers. And about co-polymers containing a few amount of DopAm, we also investigated surface adhesions and tackinesses between different materials with UV curing system. And to further applications, a redox characterization of DopAm was investigated by CV.



Scheme 2.
Marine Mussels



2. Experimental_ Chemicals

Tetrahydrofuran (THF) (Kishida Chemical Co. Ltd.), Dimethylsulfoxide (DMSO) (Tokyo Chemical Industry Co., Ltd.), Dopamine hydrochloride (Tokyo Chemical Industry Co., Ltd.), tetrabutylammonium perchlorate (TBAP) (Tokyo Chemical Industry Co., Ltd.), 2,4,6-trimethylbenzoyl-diphenyl phosphine

oxide (TPO) (IGM Resins B.V.) as an UV-initiator, Silver Nitrate (AgNO_3) (Sigma-Aldrich Co. LLC.) and other chemicals of reagent grade were used without further purification. Methacrylic acid and its esters (Mitsubishi Chemical Co. Ltd.), Dopamine Acrylamide, i.e., N-[2-(3,4-dihydroxyphenyl)ethyl]acrylamide (DopAm) and Acrylate esters (Osaka Organic Chemical Industry Ltd.) were used as received.

Materials

In cross-cut peel tests about surface adhesive, ABS resin plates (Type; N, thickness; 2.0mm) (Taiyukizai Co., Ltd.), glass plates (soda-lime glass, thickness; 0.7mm) (Foresight), ITO coated glass plates (thickness; 0.7mm/glass, 0.13 μm /ITO) (Electronics Harmonious Chemicals Co., Ltd.) were used. To the peel tests, an adhesive tape (Cellotape™) (Ncthiban Co., Ltd.) was used. And in 180° peel tests about tackiness, PET films (Lumirror 60, thickness; 75 μm) (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.), Al plates (Type; A1050P, thickness; 0.8mm) (Nippon Testpanel Co., Ltd.) were used. The surfaces of these materials were cleaned up with acetone or ethanol before use.

Instruments

9MHz Quartz crystal microbalance (QCM) analysis were carried out on a SEIKO EG&G QCA922 analyzer. Monomers or mixtures of them were coated on sample plates with RDS Mayer Coating Bar No.10 (coating thickness 22.9 μm) and were exposed by a Heraeus LIGHT HAMMER 10 UV-system. Tension tests were carried out on an A&D RTG-1310 testing machine. Cyclic voltammetry (CV) was measured by an ALS Electrochemical Analyzer, Model 612D.

UV Curing Polymerization for Cross-cut and Peel Test

On a sample plate (ABS polymer, glass, or ITO coated glass), a mixture of 4-hydroxybutyl prop-2-enoate (4-HBA) / [2-(hydroxymethyl)-3-prop-2-enoyloxy-2-(prop-2-enoyloxymethyl)propyl] prop-2-enoate (TMP-3A) / DopAm / TPO (ratio was 94/5/1/10) was coated with the RDS bar coater. And the coated solution was exposed by UV curing system.

The procedure without DopAm about a mixture of 4-HBA / TMP-3A / TPO (ratio was 95/5/10) was the same as described above.

UV Curing Polymerization for 180° Peel Test in Tackiness

On a PET film, a mixture of oxolan-2-ylmethyl prop-2-enoate (THFA) / DopAm / TPO (ratio was 99/1/10) was coated with the RDS bar coater. And another PET film was lightly placed on the coated surfaces of the PET film. As the similar with the PET/PET described above, PP/PET, Cu/PET, and Al/PET were prepared. These samples were exposed from the PET film side by UV curing system. The procedure without DopAm about a mixture of THFA / TPO (ratio was 100/10) was the same as described above.

Cross-cut and Peel Test

Cross-cut and peel test was accordance with JIS K5600-5-6.

180° Peel Test about Tackiness

The peel test about tackiness was accordance with JIS Z 0237.

Cyclic Voltammogram (CV) of DopAm

In CV measurement, Ag/10mM AgNO_3 as reference electrode, Pt as working electrode, and Pt coil as counter electrode were used. In 0.1M of TBAP/DMSO, 3.3 μM of DopAm was used. Scanning range was -1.5V to 1.5V vs Ag/ AgNO_3 at 20°C. Scanning rate was 0.1V/s.

3. Results and discussion

3.1. Strategy

At first, we confirmed the surface affinities of DopAm with inorganic oxides and metals on those surfaces by the QCM. Then, co-polymers containing DopAm prepared by UV curing were investigated in surface adhesions and tackinesses. To further applications, an electrochemical behavior of DopAm was characterized by the CV.

3.2. Confirmation of surface affinities of DopAm with inorganic oxides and metals on those surfaces by QCM.

QCM measurement was performed using quartz oscillators on which an inorganic oxides or metals were coated. For comparison with DopAm, the same measurement was performed for 4-HBA, 2-methylprop-2-enoic acid (MAA), phenyl 2-methylprop-2-enoate (PHMA), and butyl 2-methylprop-2-enoate (BMA). Each 1 wt% solutions of monomers in ethanol were flowed through a cell for 350 seconds. In the cell, silicon dioxide (SiO_2) or Ag coated oscillator was set. Resonance frequency change (Δf); -1 Hz is equivalent to mass change (Δm); 1.071ng. The data for SiO_2 and Ag are shown below in Fig. 1. As a result, it was found that DopAm adhered

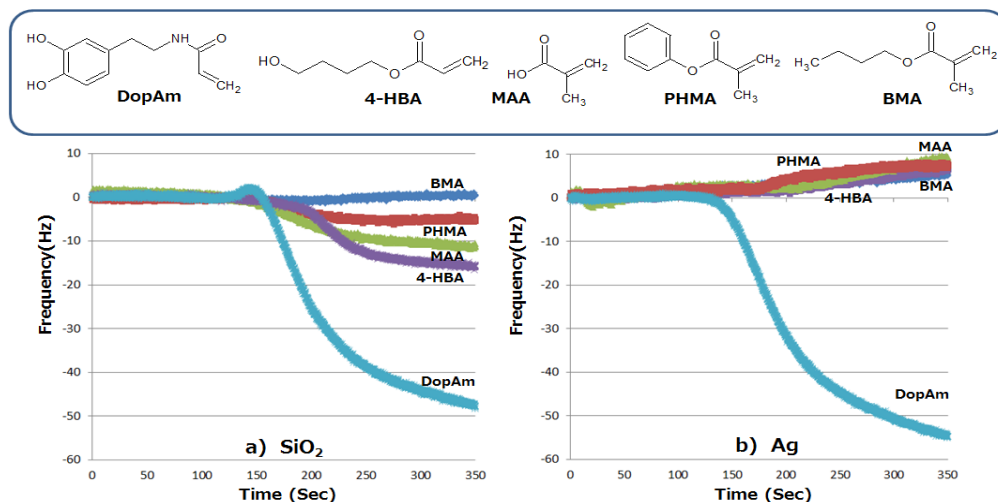


Fig. 1. Comparison of Surface Adhesions of monomers to SiO₂ and Ag by QCM measurement

several times to several tens times comparing with 4-HBA, MAA, PHMA and BMA, which have the hydroxyl group, the carboxyl group, the phenyl group, and the alkyl group. In addition, the frequencies in DopAm were gradually reduced on the surface of the oscillators. In other words, DopAm was laminated with time. DopAm also showed specific adhesions for indium tin oxide (ITO) and gold. These phenomena were not found in other monomers described above.

3.3. UV Curing Surface Adhesions of a Co-polymer Containing DopAm

In the surface Adhesion tests, a co-polymer of 4-HBA and TMP-3A was used as a general-purpose hard coat composition. The co-polymer was coated on each plates of ABS, Glass and ITO (coated on a glass), and were exposed by UV light. After making a grid-shaped cut, to the coating films were attached commercial adhesive tapes. After deattaching the adhesive tapes, in ABS, Glass, and ITO, surface adhesions were improved by the addition of only 1wt% of DopAm (Fig. 2). Without DopAm, the co-polymer were almost peeled off with the adhesive tape after the cross cutting. As a UV-initiator, a typical phosphine oxide, TPO was used (Scheme 4).

3.4. UV Curing Tacky Adhesions of a Co-polymer of THFA Containing DopAm

In the 180° peel tests, THFA was used as a general-purpose tacky adhesive. According to the experimental section described above, the pairs of PET/PET, PET/PP, PET/Cu, and PET/Al

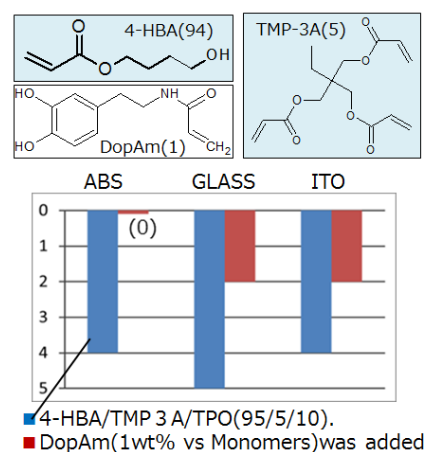
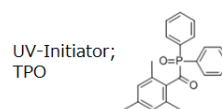


Fig. 2. Cross-cut Adhesion Test
JIS K5600-5-6(ISO2409)
UV Curing Film; Thickness ca.20μm
Evaluation (Unchange;0~Detachment > 65%;5)



Scheme 4.

were prepared using THFA for tests of tackiness (Fig. 3). 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 using 5wt% of DopAm, the effects weren't so different from those at 1wt%. In the test of PET/PP, DopAm was slightly effective. These result shows that DopAm is effective on the polar surfaces. Considering QCM results, these result suggest that DopAm has the effect of resin reinforcement by intermolecular hydrogen bondings with the functional groups of other monomers as well as scaffolding by catechol

groups. The effects of DopAm and its analogues were known about adhesive lap shear strength tests of some pairs of single material [13,14].

3.5. Redox Characterization of Dopam by Cyclic Voltammetry.

To further applications, a redox characterization of DopAm was investigated by CV. The oxidation potential of DopAm (0.37V vs Ag/AgNO₃) is relatively lower than that of Dopamine (0.42V vs Ag/AgNO₃) [15-18]. Dopamine is famous about nano-coating [19] and reduction of metal ions [1,20] used the low oxidation potential. There are potentials in DopAm and its polymers for these applications.

4. Conclusion

In QCM analysis, DopAm accumulated on the surface of SiO₂, ITO, and Ag over time. These results suggest that the scaffold on these surface is formed with the catechol groups and DopAm accumulates by the intermolecular hydrogen bondings. In the tests of cross cut and peel for ABS, Glass and ITO coated glass, the surface adhesion with UV curing were improved by adding 1wt% of DopAm to the acrylates. In 180 °C peel tests, the tackinesses were also improved by adding 1wt% of DopAm to THFA. DopAm was effective to several pairs of dissimilar materials (Cu/PET, Al/PET, PP/PET). These result suggest that DopAm has the effect of resin reinforcement by intermolecular hydrogen bondings with the functional groups of other monomers as well as scaffolding by catechol groups. In the redox characterization of DopAm, the oxidation potential of the CV was relatively lower than that of Dopamine.

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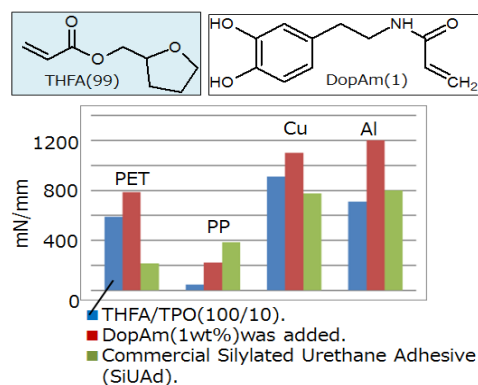


Fig. 3. 180° Peeling Test Using PET Film JIS Z 0237
UV Curing Adhesion; Thickness ca.20µm

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