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# Macroscopic Property Evaluation of Titania Nanocomposite Polymer Capable of Drawing Double-Network Macrostructure Using Photolithography

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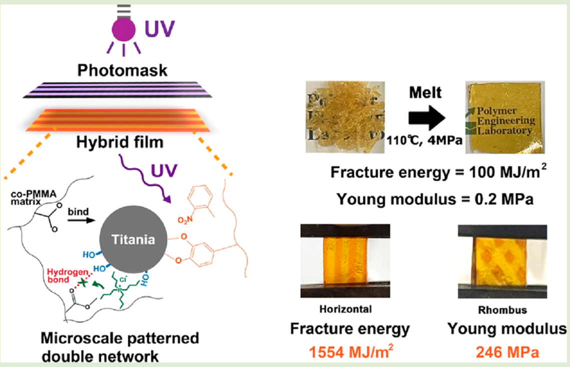
**ABSTRACT:** In this study, we developed a double-network hybrid polymer that controls the strength and density of cross-linking points by utilizing the bonds of titania and catechol groups with an *o*-nitrobenzyl group (ONBg) as the photoreactive cross-linking points. In addition, this hybrid material system, which is composed of thermally dissociable bonds between titania and carboxyl groups, can be molded before light irradiation. The Young's modulus increased by approximately 1000 times upon irradiation with UV light. Moreover, introducing microstructures using the photolithography technique improved the tensile strength and fracture energy by approximately 32 and 15 times, respectively, compared to the sample without the photoreaction. The improved toughness was achieved by the macrostructures, which enhanced the effective cleavage of sacrificial bonds between the carboxyl groups and titania.



By controlling the cross-linking points in double-network polymers, consisting of weak and strong bonds, it is possible to realize materials with both high strength and toughness, which are the characteristic mechanical properties of double-network gels and fiber-reinforced gels.[1−4] Generally, these materials are composed of covalent cross-links that amplify their strength and ion-bonding cross-links that disperse energy. However, it is challenging to apply these systems to general-purpose processing methods, such as melt shaping, because the cross-linking process requires covalent and ionic bonding simultaneously.

To introduce double-network polymers into a normal molding process, it is beneficial to generate cross-linking points after the molding process. The modular patterning of films using photoreactions can add cross-linking points after deposition.[5−9] For example, Clet et al. demonstrated a precise microscale patterning to modify the modulus of silicone elastomers.[10] Furthermore, Sugimoto et al. reported that by designing heat-cross-linking and photo-cross-linking parts, an increase in the Young's modulus by more than 2 orders of magnitude was achieved by performing a photo-cross-linking process after a normal elastomer manufacturing heat process.[11] As an exciting point of this research, the conversion of cross-linked microstructures into macroblock structures was demonstrated to improve their mechanical properties.

These polymers can modify elasticity by adjusting the cross-linking density; they must exhibit improved mechanical properties, including industrially essential functions, such as abrasion resistance and surface hardness. The cross-linking density in hybrid polymer materials can be adjusted by modifying the interaction between the inorganic fillers and polymer chains to satisfy the properties mentioned earlier.[12−14] Furthermore, the addition of inorganic fillers can not only adjust the mechanical properties but also improve the electrical and optical properties of the inorganic materials.[15−18] Moreover, the networks between the polymers and inorganic fillers can suppress the aggregation of the inorganic fillers caused by phase separation. Therefore, the network structures obtained by adding inorganic fillers are essential for maintaining the proper functioning of the hybrid materials.

In this study, we developed a poly(methyl methacrylate) (PMMA)/titania hybrid material that can be melt-molded and cross-linked via micropatterning by photolithography (Figure 1). The strength of this melt-molded hybrid system can not only be adjusted by designing macroscale regions with a Young's modulus increased by the links between titania and

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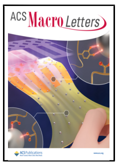

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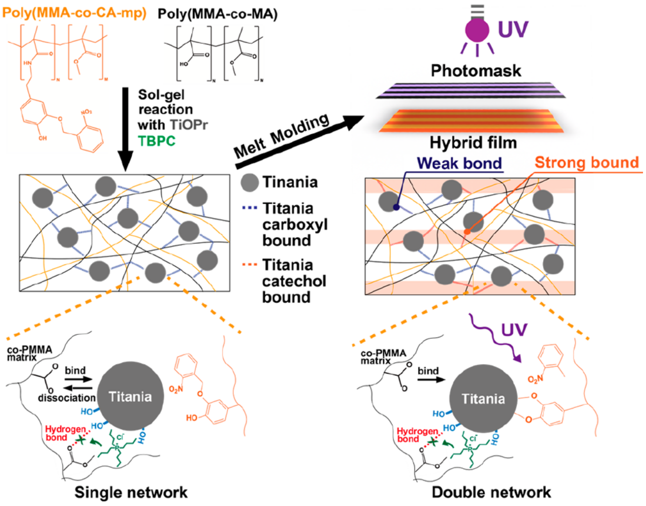

**Figure 1.** Schematic illustration of photolithography process for a double network composed with titania−carboxyl and titania−catechol bonds.

catechol groups using photolithography, but the toughness can also be improved by preferentially digesting the bonds between carboxyl groups and titania as sacrificial bonds. Catechol groups protected by an *o*-nitrobenzyl group (ONBg) were used as photochemical regulation units.[19−21] OBNg has received significant attention in polymer chemistry and various fields such as optical and surface pattern materials. Catechol groups form stronger bonds with metal oxides than the carboxyl and hydroxyl groups.[22−25] Moreover, because the carboxyl group was bonded to the catechol group, the links with the carboxyl groups could be switched by heating.[26,27] However, to regulate the interfacial cross-link density between titania and MMA, it is necessary to block unintentional hydrogen bonds between titania and PMMA. We previously reported that the ionic liquid tetrabutylphosphonium (TBPC) explicitly inhibits hydrogen bonding between titania and PMMA. Furthermore, a PMMA−titania hybrid material containing TBPC was melt-molded without phase separation of titanium nanoparticles by designating the interfacial cross-linking between titania and the carboxyl group in poly(MMA-*co*-MA).[27]

The method for synthesizing monocaged catechol monomers (CA-mp) is described in the Supporting Information. Poly(MMA-*co*-CA-mp) was synthesized as shown in Figures S2 and S3. The CA-mp content was determined to be 5 mol % methyl methacrylate, based on the cross-linking density adopted in previous studies.[26,27] The introduction ratio of the monomer was calculated using the integral ratio of NMR (Figure S4). Reversible addition−fragmentation chain-transfer polymerization (RAFT) was adopted as the polymerization method for poly(MMA-*co*-CA-mp). This polymer could not be polymerized by a simple synthetic method using 2,2′-azobis(isobutyronitrile) (AIBN) because of the monomer steric hindrance. Moreover, the catechol hydroxyl group has the potential to inhibit polymerization. However, even the bicaged catechol monomer (CA-Bp), in which the two hydroxyl groups of the catechol groups are protected, did not polymerize using AIBN. In contrast, in RAFT polymerization, the monomer can be added quantitatively and CA-mp can be successfully introduced at a ratio of 5 mol % to MMA. This is due to the excellent reaction properties of RAFT polymerization as well as the high radical stability at the polymer chains, end.[28−31] Subsequently, a sol−gel process was employed to adjust the hybrid films to contain 15 wt % titania relative to the polymer, according to previous studies[27] (the adjustment method is described in the Supporting Information). To confirm the effect of cross-linking more clearly, it is necessary to adjust the Young's modulus of the films because PMMA is a hard and brittle material. In other words, it preferentially cleaves the bonds between the cross-links consisting of titania and PMMA over the cleavage caused by the cross-links owing to the entanglement of the main chain of PMMA when a force is applied to the hybrid film. The composition was examined preliminarily by conducting tensile tests to determine the optimum ratio of TBPC to poly(MMA-*co*-MA), and the Young's modulus and elongation were examined. When 80 wt % TBPC was added to the polymer, a low Young's modulus and high elongation were observed (Figure S5). Therefore, in subsequent experiments, 80 wt % TBPC was added to poly(MMA-*co*-MA).

A photograph of a titania hybrid film composed of equal amounts of poly(MMA-*co*-MA) and poly(MMA-*co*-CA-mp) is shown in Figure 2a (untreated). No phase separation was observed in the mixed film. On the contrary, in the sample formed with only poly(MMA-*co*-CA-mp), phase separation of titania was established (Figure S6). This result indicated that poly(MMA-*co*-CA-mp) did not bind to titania and was effectively protected by the *o*-nitrobenzyl groups (ONBg). The mixed hybrid films, as shown in Figure 2a, were treated under the following three conditions: UV irradiation at 250 W for 3 h at 110 °C, annealing at 110 °C for 3 h, and annealing after UV irradiation. Only two UV-treated samples turned orange. UV irradiation promoted the deprotection of catechol groups and a change in the absorption wavelength of catechol. To confirm the change in cross-linking density, the mechanical properties of the films were measured by dynamic mechanical analysis (DMA) (Figure 2b). The measurement was possible up to 150 °C for untreated, UV-irradiated, and heat-treated samples. However, the film subjected to heat and UV exhibited a plateau, and the measurement was possible up to a higher temperature of 250 °C. These results indicate that the catechol

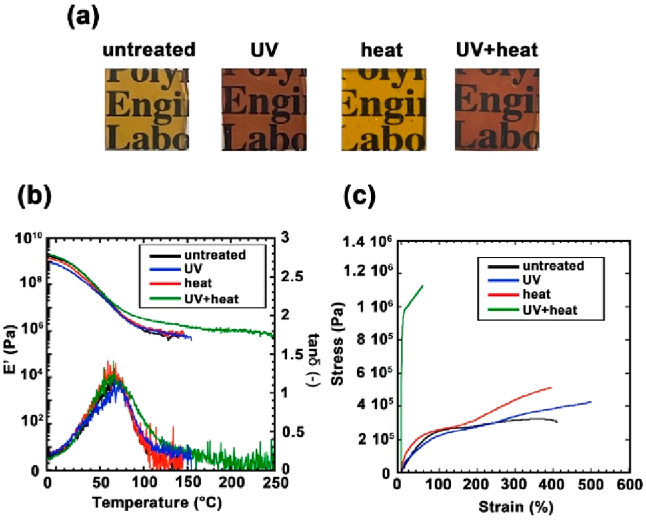

**Figure 2.** Characterization of differently treated titania hybrid films: (a) photographic images, (b) DMA curves, and (c) stress−strain curves.

group bonds with titania were thermally stable and more robust than those of the carboxyl groups. Moreover, the $E'$ of the UV- and heat-treated hybrid film was higher than that of the other hybrid films in the temperature range of 70−150 °C. The $E'$ values in this range correlate with the cross-linking density because PMMA exhibits rubbery elasticity. However, a correct interpretation of this phenomenon requires consideration of the thermal stability effect of the chemical bonds at the cross-links. In this temperature range, the bond between the carboxyl group and titania was in chemical equilibrium, and the apparent cross-linking density decreased. In contrast, the bond between the catechol groups and titania was thermally stable. Therefore, the number of cross-linking points could not be accurately evaluated. Therefore, heat treatment after UV irradiation is essential for the formation of bonds with catechol groups. In other words, this result indicates that the bond between the carboxyl group and titania was switched to the catechol group and heat treatment after UV irradiation was essential for forming bonds with the catechol groups.

Tensile tests were performed to verify the effect of bond exchange with catechol groups (Figure 2c and Table S1). The Young's modulus of the UV- and heat-treated films increased by approximately 170 times compared to that of the untreated film. To exclude the possibility that this was the outcome of the modification of the polymer by UV, a tensile test of the hybrid polymer consisting of only poly(MMA-*co*-MA) was performed (Figure S7 and Table S1). The UV- and heat-treated samples showed a slight increase (1.4 times) in Young's modulus compared to that of the untreated samples. These results suggest that the cross-linking of the titania and catechol groups improves the Young's modulus of the UV- and heat-treated hybrid films. However, it should be noted that an increase in the cross-linking density alone cannot explain this behavior. The number of cross-linking points was equivalent to that of the hybrid film consisting only of poly(MMA-*co*-MA). The difference in Young's modulus was ascribed to the strength of the bond with titania. The bonds of the carboxyl groups of MA are weaker than those of the catechol groups. Weaker bonds disperse a higher mechanical energy. Furthermore, various bonding modes have been proposed for the binding of catechol groups and titania, as discussed below. These bonds are stronger than van der Waals forces, which are intermolecular forces acting on standard polymer matrices. This is strongly suggested by the behavior of the DMAs. In other words, the increase in Young's modulus and breaking strength and the decrease in elongation can be attributed to the cross-linking points switching from MA to catechol groups, which have stronger binding forces.

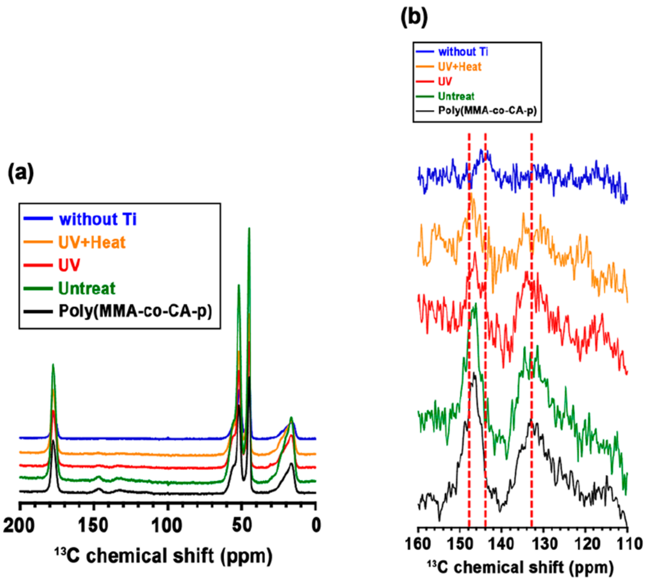

**Figure 3.** $^{13}$C CP-MAS spectra of differently treated titania hybrid films. The ranges (a) 0 to 200 ppm and (b) 110 to 160 ppm traces are offset vertically for clarity.

Solid-state $^{13}$C NMR measurements were performed to observe the switching reaction between titania and catechol groups. Powders for solid-state NMR measurements could not be produced using a hybrid sample with TBPC. Therefore, to remove TBPC, the hybrid films were washed with methanol before pulverization. Typical PMMA peaks were observed for all of the samples. These results indicate that the UV irradiation and heating processes did not affect the PMMA matrix (Figure 3a). In contrast, catechol forms very strong bonds with metal oxides such as titania, and these interactions can be assessed using solid-state NMR methods. Shapiro et al. combined solid-state NMR methods with density functional theory (DFT) to provide a detailed evaluation of molecular binding modes from a computational chemistry perspective.[32] The molecular, monodentate, bidentate, and chelated adsorption modes of catechol groups and titania were proposed as possible binding modes. These binding modes can be inferred from the chemical shift of the $\alpha$ carbon of the catechol groups. For the poly(MMA-*co*-CA-mp) and untreated samples, a peak derived from the $\alpha$ carbon of the catechol groups was observed at 146 ppm (Figure 3b). However, compared to the untreated sample, a downfield shift of the catechol-derived peak (144 ppm) was observed in the sample without titania. This chemical shift is consistent with the discussion in the previous reference[32] and can be understood. This result indicates that UV irradiation induced the deprotection of the catechol groups. Compared to the untreated sample and the UV-irradiated sample (146 ppm), only the UV-irradiated and heat-treated samples were observed at 148 ppm. Moreover, by incorporating the combined analysis of the $^{13}$C CP-MAS experiments of Shapiro et al. and DFT-GIPAW chemical shift predictions, this result suggests that the binding mode in these hybrid membranes is molecular adsorption. This pronounced upfield shift of the $\alpha$-carbon of the catechol groups indicates strong binding of the catechol groups to thermomechanical properties.

A feature of our system is its ability to imprint strong cross-links after melt molding films, which consist of cross-links of weak bonds that can thermally dissociate. Figure 4a shows the melt-formed hybrid film prepared by using the heat-press method at 110 °C for 3 h. Phase separation of titania could not be confirmed in the melt-shaped hybrid film. This result indicated that the TBPC−carboxyl system had a thermally dissociable cross-linked structure, as previously reported.[26] Next, the films were subjected to UV irradiation to create a double network in the molded hybrid films (Figure 4b). In addition to the irradiation of the entire film, horizontal lines and rhombus structures were printed in the pulling direction of tensile testing using photomasks to evaluate the toughness improvement after introducing the macro-cross-linking structures. Tensile tests were conducted to assess the differences in the mechanical strengths of the structures (Figure 4c and Table 1).

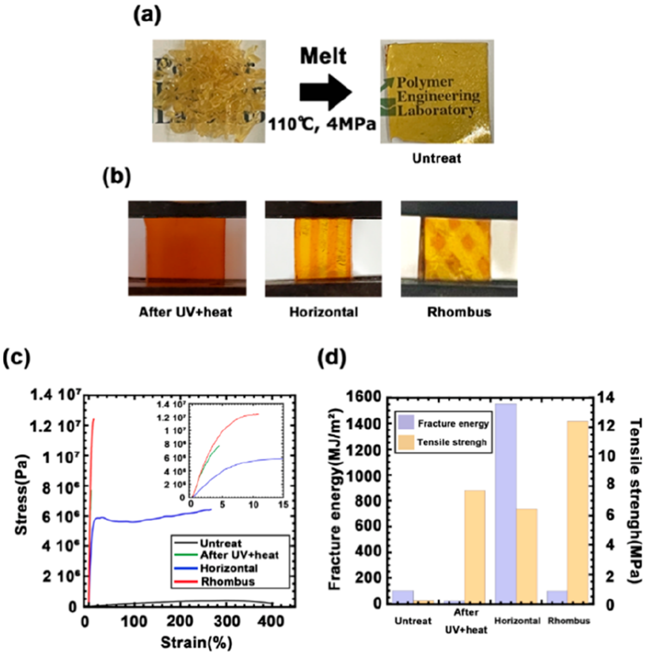

**Figure 4.** (a) Photographic images of titania hybrid films recycled from pulverized as-cast films and reshaped. (b) Photographic images of reshaped titania hybrid films after UV irradiation and heat treatment with photomasks. (c) Stress−strain curves of titania hybrid films irradiated under different UV lights. (d) Fracture energy and tensile strength obtained from tensile tests of titania hybrid films irradiated under different UV lights.

**Table 1. Results of Tensile Testing for Molded Hybrid Films Using Different Processes**

| sample | untreated | after UV + heat | horizontal | rhombus |
|---|---|---|---|---|
| fracture energy (MJ/m$^2$) | 100.3 | 20.16 | 1554.38 | 97.36 |
| tensile strength (MPa) | 0.20 | 7.69 | 6.42 | 12.39 |
| strain (%) | 402.5 | 4.4 | 267.6 | 10.9 |
| Young's modulus (MPa) | 0.21 | 220.86 | 88.08 | 246.38 |

The entire surface of the sample exposed to light showed an approximately 38-fold improvement in tensile strength and a 1000-fold improvement in Young's modulus compared with the untreated sample. However, the breaking energy was reduced to approximately one-fifth that of the untreated film. This behavior differs from that of typical double-network gels. These results indicate that the sacrificial bonds between the carboxyl groups and titania were not broken when double networks were formed over the entire film. This is probably because the cross-link density ratio of the strong bonds of the catechol groups with titania to the weak bonds of the carboxyl groups is not appropriate. These phenomena are frequently observed in double-network gels with different cross-links.[33] In contrast, the sample with stripes lithographed in the tensile direction exhibited approximately 32 times higher tensile strength and approximately 15 times higher fracture energy.

Furthermore, it was revealed that the rhombus structures in a film resulted in a tensile strength 61 times higher, the breaking energy being 0.97 times that of the untreated film, improving strength without sacrificing toughness. In particular, Young's modulus with rhombic structures improved to the same value as that when UV was applied to the entire surface. These results demonstrate that macrostructures are essential for the effective cleavage of sacrificial bonds. The structural dependence of the toughness is reminiscent of the behavior of the fiber-reinforced hydrogels. When fiber-based hydrogel composites are subjected to an external load, the fibers cut off the main chain because the strength of the fibers is much higher than that of the hydrogel. Moreover, the mechanical properties of materials with weak interactions between the fibers and polymer chains depend significantly on the directions of the fibers and applied tension.[34] In addition, an improvement in the material toughness along the orientation direction of the fibers was confirmed in PVA crystal hydrogels.[35] Our hybrid system not only has a large difference in strength and Young's modulus between the UV-irradiated and non-UV-irradiated parts but also can imprint any structure. These results reveal that the macrostructure is an important factor in designing the scission of microstructural interactions between titania and organic matter.

In summary, it was possible to partially increase the cross-linking density and bond strength by utilizing the OBN photoprotecting catechol units. The change in Young's modulus was also supported by the observation of strong binding modes of catechol groups by solid-state $^{13}$C NMR analysis. In particular, Young's modulus increased by a factor of 1000 after UV irradiation and heating. To the best of our knowledge, this is the best light-controlled network polymer with regulatable cross-linking density and strength. Furthermore, macrostructures could be printed after melt processing using this hybrid system, whose mechanical properties depend on the macrostructure. The printing technique significantly improved the Young's modulus, tensile strength, and fracture energy, which was achieved by introducing macroscopic structures to cleave the bonds between carboxyl groups and titania preferentially. This study demonstrates a new class of double-network polymers utilizing the difference in the bonding strength between inorganic fillers and organic substances and provides new ideas for creating materials that combine high strength and toughness.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.3c00230.

Materials, synthesis of monocaged catechol monomer (CA-mp), synthesis of the polymers, preparation of hybrid organic−inorganic films, characterization, $^1$H NMR spectrum, stress−strain curves of the hybrid films composed of poly(MMA-*co*-MA), photographs of each hybrid film (PDF)

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### Notes

The authors declare no competing financial interest.

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