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Comparison of Durability for PUA Type Resin using Wear and Nano-indentation Test

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마모 및 나노 압입 시험을 이용한 PUA계 레진의 내구성 비교

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ABSTRACT

Films with special properties (e.g., water-repellent films, optical films, anti-reflection films, and flexible films) are referred to as functional films. Recently, there has been interest in fine patterning methods for film fabrication. In particular there have been many studies that use a UV nanoimprint process involving a UV curing method. In this paper, a polymer film was fabricated by the UV nanoimprint process with a micro-pattern, and its durability was evaluated by a wear test and a nano-indentation test. The film mechanical properties (such as coefficient of friction, hardness, and modulus of elasticity) were measured. Moreover, the choice of PUA type resin used in the UV nanoimprint process was confirmed to impact the durability of the thin film. Despite making the polymer film samples using the same method and PUA type resin, different coefficient of friction, hardness, and modulus of elasticity values were obtained. PUA 4 resin had the most favorable coefficient of friction, hardness, and modulus of elasticity. This material is predicted to produce a high durability functional film.

Key words : UV Nano Imprint(UV 나노 임프린트), Coefficient of Friction(마찰계수), Nano Indentation(나노 압입시험), Modulus of Elasticity(탄성계수) Durability Test(내구성 테스트)

1. Introduction

Optical, anti-reflection, polarizing, water-repellent, flexible films, and other films with special properties are referred to as functional films. This has emerged as an important field, particularly in the display industry, with films being used as electronic materials. The basic film properties may vary depending on its functions. In addition to the aforementioned functional film properties, durability is also considered to be im portant. In particular, with specially patterned thin

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films, there is the possibility that the pattern may collapse or get damaged with small force. Therefore, a durability test is required to confirm the properties of functional films[1-2].

In this study, the UV nanoimprint process (a next generation micro-patterning method) is used to create a micro-patterned film. Both wear and nano-indentation tests were performed to investigate the durability of the micro-patterned thin film. Polyurethane acrylate (PUA) type resins were cured on PET films by UV light. The film wear characteristics were evaluated by a reciprocating and pin-on-disc test. A nano-indentation test was performed to evaluate film hardness. The most durable polymer film had the lowest friction coefficient and highest modulus of elasticity[3].

2. Basic theory

2.1 UV nanoimprint

The UV nanoimprint technology enables a nano-sized pattern by using a template with nano or micro-sized patterns to pattern to paint on various types of substrates. The nanoimprint process draws attention as a new, alternative technology due to its simple process and low production cost compared to existing semiconductor processes, such as photolithography. In the imprint process, a polymer is drop-casted between a template (where a micro-pattern is formed) and a substrate, making a pattern. The polymer is cured, causing the formation of the reverse phase of the pattern on the template. Depending on the energy source, the polymer curing method is either heating or ultraviolet. In this study, the UV nanoimprint process with a UV curing method was used to create a polymer film[4-5].

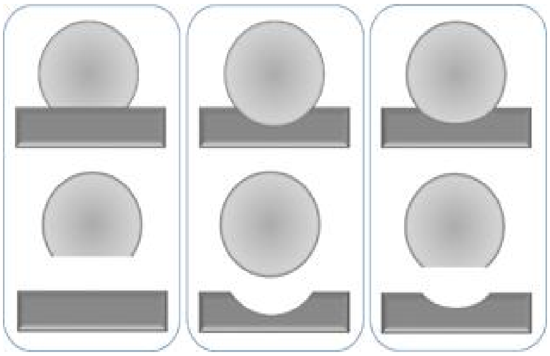
2.2 PUA type resin

UV curing is indispensable in modern industry as a technology that can be applied to paints, inks, adhesives, automobiles and electronic products. UV curing techniques use materials that respond to ultraviolet light. In this process, the monomer, oligomer and photoinitiator are mixed and the curing polymerization reaction is caused by the UV light. The UV-curable material is produced by blending a monomer and an oligomer, which has fundamental characteristics for facilitating polymerization, and a photoinitiator. A PUA type resin (the UV-curable material used in this study) is a material based on a urethane acrylate oligomer and is mainly used in advanced display industrial fields. As urethane bonds are made to hydrogen bonds, with proper bonding force between atoms, the molecular interactions of PUA-type resins are smooth and flexible. In particular, an acrylic ester containing a hydroxyl group (-OH) and an isocyanate functional group counteract to allow an acryloyl group (-acryloyl) at the terminal. This forms a urethane acrylate with an extended chain, which is advantageous as it can make contact with functional groups[6].

2.3 Wear test

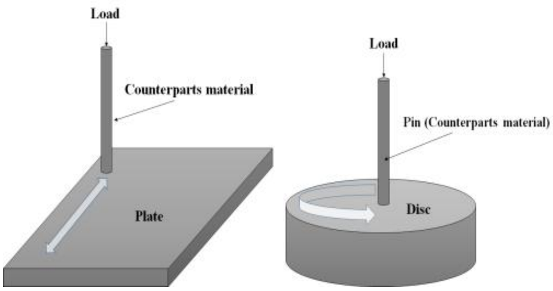
According to the German standards DIN 50320, wear refers to a phenomenon in which objects gradually fall apart due to mechanical motion from the surface of the object, by a contact of liquid or solid. Fig. 1 shows three cases of wear phenomenon. In the case of 1-(a), the hardness of the flat specimen was greater than that of the ball specimen and only the ball specimen had wear marks. In the case of 1-(b), the ball specimen has a greater hardness than flat specimen, and only the flat specimen had wear marks. In the case of 1-(c), the hardness of ball specimen and flat specimen are similar, and there are wear marks on both objects.

The wear test is required to assess the wear resistance of the material and, unlike other material tests, a number of different types of devices are used. This is because abrasion resistance is not inherent to the material, but is relative, and depends on the test



(a) (b) (c)

Fig. 1 Three case of the wear phenomena



(a) (b)

Fig. 2 Schematic of wear test : (a) Reciprocating test, (b) Pin-on-disc test

condition and type of the counterpart material. Herein, we present the trial methodology, the test, the counterpart material, the type of specimen to be tested, and the presence or absence of lubrication to allow for a highly reliable result[7-9].

In this study, two wear tests were performed: a reciprocating wear test (linear motion) and a pin-on-disc test (rotary motion). The reciprocating wear test, as shown in Fig. 2, follows a reciprocating motion, the sample is fixed on the lower flat plate, and the counterpart material of the pin or ball type is fixed at the top, and a fixed load is applied. Afterwards, the counterpart material comes in contact with the surface of the test material and performs a slide motion, and the slide direction is reversed periodically. There are cases where the upper counterpart material moves and the lower plate moves. Unlike the reciprocating test, the pin-on-disc test performs a pivoting movement and can either be considered as a pin-on-disc test or ball-on-disc test according to the shape of the upper counterpart material. The test method specifies whether the upper pin rotates or the lower disc rotates. The wear marks are displayed in a circle. Two wear tests were performed with no lubrication condition. The coefficient of friction is calculated from the test by measuring the abrasion loss amount and the friction force.

2.4 Nano-indentation

To measure mechanical properties, such as the hardness or the modulus of elasticity of a material, Rockwell hardness and Vickers hardness machines are used. However, due to modern improvements as well as the development and integration of nanomaterials in the industry, several methods for measuring the mechanical properties of these materials have been developed.

The nano-indentation test is a method designed to measure the hardness of the material of a thickness less than 1 ㎛, which was previously impossible with large-size hardness testing. In this test, the load is applied after the indenter tip, which has a geometric shape such as a Vickers, Berkovich, or Spherical form, touches the surface of the material. The applied load and depth are continuously measured at the same time and the mechanical properties can be calculated, including the hardness of the material. The nano-indentation test methods can be divided into two types. One type obtains mechanical properties by repetitively pressing one point and the other type, by indentation of several points at once. The test methodology used depends on the kind of material to be tested.

The indenter tip of the nano-indentation used in this experiment was a Berkovich-shaped diamond tip.

The hardness and Young's modulus are calculated by measuring data at multiple points[10-14].

3. Durability test and result

In order to test the durability of a polymer film with micro-patterns, a thin film was manufactured using the UV nano imprint process. The goal of the test is the comparison of PUA type resin which is excellent in flexibility and mainly used in display and semiconductor industry. On the same PET film, we used four kinds of PUA type resins having different viscosity and surface energies. The properties of resins used for the experiments are listed on Table 1.

To determine the durability of the manufactured polymer film sample, the reciprocating test and pin-on-disc test were both conducted during the wear test and the mechanical properties of polymer films were compared and analyzed using a nano-indenter. The micro-pattern, having a pillar structure of 5 ㎛ in diameter, 10 ㎛ in height and 40 ㎛ in pitch, was constructed on the PET film.

3.1 Wear test

The reciprocating test and pin-on-disc test were performed using wear test equipment (UFW-200 model (NEOPLUS Co. Ltd)). Fig. 3 shows the counterpart material of the equipment used for each wear test, the ball type counterpart of reciprocating test and the pin type counterpart of pin-on-disc test. The reciprocating test was conducted in accordance with ASTM G133 standards. This test uses a counterpart material known as high carbon chromium bearing steel (SUJ-2) in the upper ball shape, 5 mm in diameter. As shown in Table 2, the test load was 2 N, the reciprocating frequency was 1 Hz (reciprocates once per second), the reciprocating distance was 10 mm, and the test time was 60 seconds. The reciprocating test was conducted without lubrication. The pin-on-disc test was conducted in accordance with ASTM G99 standards, and the upper counterpart material of the pin was heat-treated martensite stainless steel (SUS 440C). The pin end had a diameter of 5 mm. As shown in Table 2, the test load was 2 N, the test frequency was 1 Hz, the track radius was 11.5 mm, and the test time was 60 seconds, and test was also conducted without lubrication.

It should be noted that at the time of the wear test, the wear ratio is calculated using the difference between the mass before wear test and the mass after the test. It is common to compare the calculated wear rate with the wear resistance of each material[9].

However, in this study, it was difficult to measure the mass before and after the wear test of the polymer film. Therefore, the coefficient of friction

Table 1 Polymer specification

PUA resin	PUA 1	PUA 2	PUA 3	PUA 4
Coating method	Dispensing & rolling, Spin coating			
Process conditions	UV exposure : < 365 nm			
Appearance	Clear yellowish liquid		Clear liquid	
Viscosity (@25℃)	37.4 cPs	7.2 cPs	363.1 cPs	70.6 cPs
Surface energy	30.8mN/m	19.8mN/m	79.1mN/m	27.7mN/m

Fig. 3 Universal function wear tester & ball specimen (SUJ-2) & pin specimen (SUS440C)

Table 2 Experimental condition (wear test)

Factor	Reciprocating test	Pin-on-disc test
Test load	2 N	2 N
Test frequency	1 Hz	1 Hz
Test stroke / Test radius	10 mm	11.5 mm
Test time	60 s	60 s
Ball diameter / Pin diameter	5 mm	5 mm

(load ratio of the frictional force) is used to compare wear resistance.

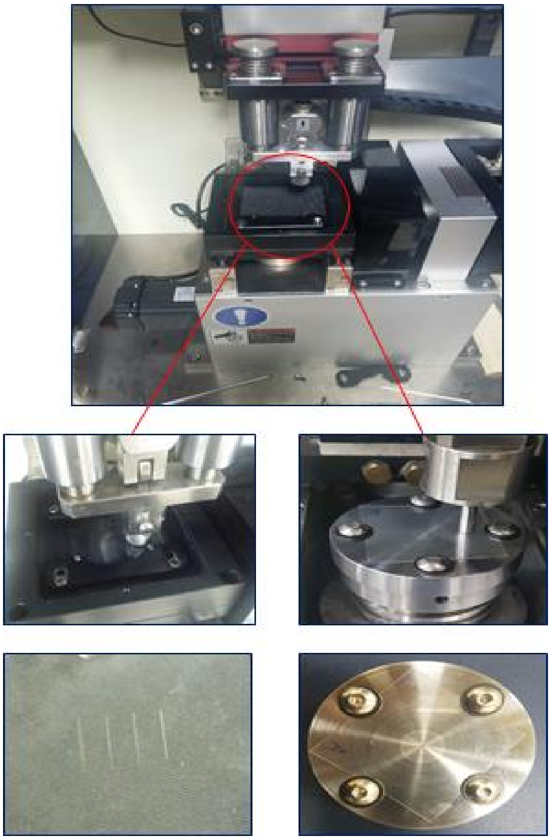
Fig. 5 reveals an SEM photograph of the wear track after the reciprocating test. Damage occurred in all the patterns of the two films, but it can be observed that the pattern of PUA 3 is less degraded than the pattern of PUA 2.

As shown in Fig. 4, the film specimen is fixed to the equipment and each wear test is conducted. The coefficient of friction values are measured at the same time as the test in Fig. 6 are plotted.

The pin-on-disc test results spanned a wide range of values, as compared to the results of the reciprocating test. As the rotational motion is different from the reciprocating motion, the force compounds and the range where the wear phenomenon occurs is larger than that of the reciprocating test. This seems to be a phenomenon caused by various factors.

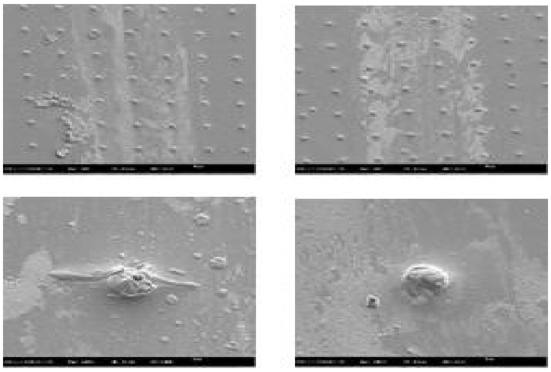
As a result of the wear test, a different value of the coefficient of friction was obtained, depending on the test. The reason for this is believed to be due to the different shape of the relative materials (ball or pin), and the variation in the actual force applied to the specimen, depending on whether the test included a reciprocating motion or a rotary movement

Of the coefficient of friction values calculated as a result of the reciprocating test, PUA 1 has the lowest. value, under 0.1 or less in total. PUA 3 and PUA 4 have similar values between 0.1 and 0.2. PUA 2 had a value of 0.7, which was considerably high.



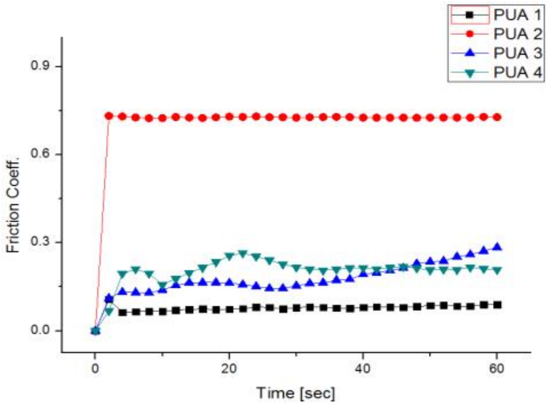
(a) (b)

Fig. 4 Wear test on the film : (a) Reciprocating test, (b) Pin-on-disc test

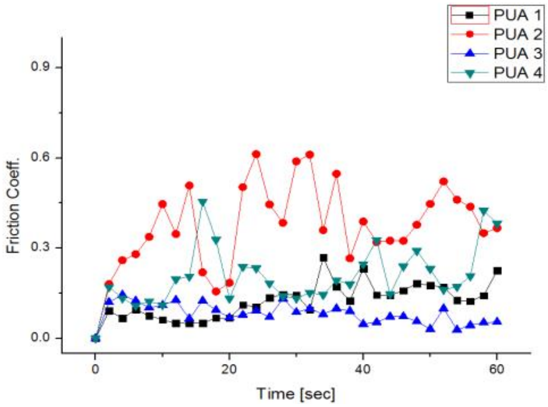


(a) (b)

Fig. 5 Wear track of film (Reciprocating test) : (a) PUA 2, (b) PUA 3



(a)



(b)

Fig. 6 Result of wear test (coefficient of friction graph) : (a) Reciprocating test, (b) Pin-on-disc test

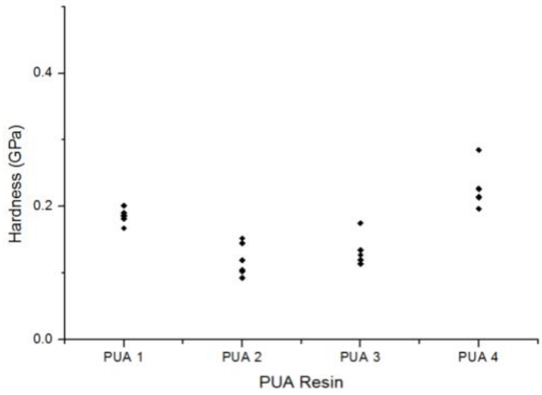
Of the coefficient of friction values calculated as a result of pin-on-disc test, the average coefficient of PUA 1, PUA 3 and PUA 4 were not significantly different and were between 0.1 and 0.2. PUA 3 had relatively high value of 0.4 or higher. In conclusion, PUA 1, PUA 3, and PUA 4 showed better wear resistance than PUA 2.

3.2 Nano-indentation

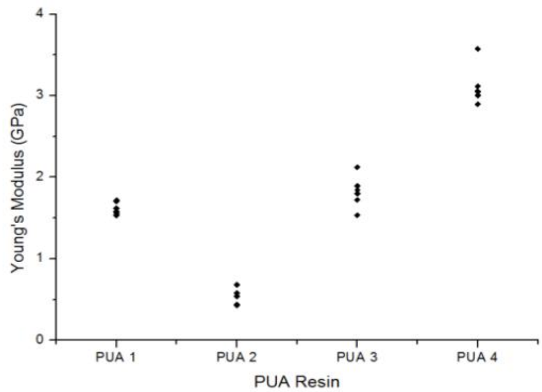
The equipment used for nano-indentation is the NHT model (CSM Instrument Co. Ltd). In this experiment, the surface of the polymer film was randomly indented at 3 - 5 points by the indenter. In order to reduce the effect of film material, the polymer film was fabricated to have a thickness of 20 ㎛ or more and the test was carried out on the polymer film with a micro-pattern. As shown in Table 3, the maximum load applied by indenter tip

Table 3 Experimental condition (nano-indentation)

Factor	Value
Maximum load	5 mN
Approach speed	2000 nm/min
Loading/Unloading rate	10 mN/min
Poisson’s ratio	0.3



(a)



(b)

Fig. 7 Result of polymer film measured by nano-indentation : (a) Hardness, (b) Young’s modulus

after contact with the surface was set to 5 mN, and the Poisson's ratio was set to 0.3 which is the same as ordinary ceramic.

The hardness values and Young's moduli were calculated by the nano-indentation results. In terms of hardness, all PUA type resin had similar values between 0.1 and 0.3 GPa, but the Young's moduli were quite different. In particular, the Young's modulus of PUA 4 was measured to be about 3.12 GPa which is approximately six times higher than the average of PUA 2, which was 0.54 GPa.

4. Conclusion

In this study, polymer films with micro-patterns were formed on PET film using the UV nanoimprint process. The mechanical properties of four different types of PUA resins were obtained. The reciprocating test and pin-on-disc test were conducted to obtain the coefficient of friction of the materials. The nano-indentation test was carried out to measure material hardness and modulus of elasticity of polymer film. The film characteristics were compared and analyzed according to the types of PUA resin. Depending on the type of PUA resin, each property confirmed the difference; the summary of the measurement results is the same as those listed in Table 4.

It was observed that there was large variability in friction coefficient, hardness and modulus of elasticity between the four types of resin, even though they are made up with same PUA material.

The PUA type 2 resin had a low Young's modulus value and a high friction coefficient, so it can be expected to have poor durability. The PUA type 4 resin had a low coefficient of friction and a higher Young’s modulus, thus it can be considered the most durable material.

With regards to the coefficient of friction, all resins, except PUA type 2, had values lower than 0.2. Therefore, we can expect that they have

Table 4 Mechanical properties of polymer film

Material	Coefficient of friction		Hardness (GPa)	Young’s modulus (GPa)
	Reciprocating test	Pin-on-disc test		
Si wafer	-	-	5.1	190
PUA 1	0.0787	0.1270	0.186	1.619
PUA 2	0.7275	0.4151	0.120	0.542
PUA 3	0.1819	0.1012	0.134	1.535
PUA 4	0.2092	0.2131	0.227	3.116

relatively good wear resistance. Low hardness values were obtained as on the whole because the materials are polymeric. However, PUA type 4 resin had a high Young's modulus value (over 3 GPa), thus is predicted to greatly improve the durability of a PUA type resin. Overall, this study revealed that wear tests and nano-indentation tests can be helpful to determine the durability of polymer film.

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