

Surface Free Energy Changes of Stainless Steel after One Atmospheric Pressure Plasma Treatment

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Abstract—Stainless steel plates (AISI 304L) were treated by an atmospheric pressure plasma treatment at room temperature in order to modify the surface properties. After plasma treatment, the surface wettability and the surface free energy were both improved. The wettability and the surface free energy of stainless steel plates before and after plasma treatment were measured from the results of contact angle test. Through the results of contact angle and surface free energy, optimum plasma treatment conditions were obtained, such as the treatment time of 60 sec and the treatment power of 120 W. In addition to this, the optimum aging time was 3 to 5 min in air.

Key words: Atmospheric Pressure Plasma, Contact Angle, Surface Free Energy, Aging Effect

INTRODUCTION

Stainless steel can be used in micro-channel chemical reactors as catalytic supporter and main framework because of the special properties of corrosion resistance and thermal stability [Rouge et al., 2001]. The surface properties are very important for stainless steel as applied in this field. It has been proved that nearly all good adhesion behaviors are accompanied with surface pretreatment first [Kinlich, 1987; Petrie, 2000]. In the micro-channel reactor industry, good adhesion between two plates is basically needed [Benz et al., 2001], so during the adhesion process of stainless steel plates with other substrates, the surface pretreatment is usually indispensable. In fact, the term “adhesion” can be loosely defined as the attraction between two substances and the mechanical resistance to the separation of a system of bonded materials [Kinlich, 1987; Wertheimer et al., 1999]. Since adhesion largely depends on the surface property of materials, it is necessary to modify this near-surface region without affecting the bulk properties of material. Therefore, the surface modification of stainless steel is a quite important process in order to apply the material in the micro-channel industry.

Plasma treatment has been an efficient method for modifying the surface properties of many materials and offers a possibility to create a surface with new functions. Nowadays, a great deal of research has been performed to improve the surface properties of polymers and metals by using plasma treatment. Sohn et al. [2000] studied the permeation of simple permanent gases and their mixtures. He utilized the plasma polymerization of fluorocarbon compounds to form membranes such as pentafluorotoluene and pentafluoropyridine on Celgrad, by which the permeabilities of gases were measured. Kim et al. [1999] made a polymeric composite by low temperature plasma, and also modified the surface properties of the plasma-polymerized membrane by plasma re-treatment. He indicated that the plasma re-treatment had dramatic effect on the physical and chemical properties of polymeric membrane surface. Wertheimer

et al. [1999] reported the merits and drawbacks of industrial plasma processes in comparison with other competing technologies especially those based on ultraviolet radiation, and predicted that both plasma and ultraviolet photochemical processes had a promising future in the industrial processing of polymers. Øiseth et al. [2002] utilized Ar and O₂ plasma to modify polyethylene (PE) film, respectively, and proved that argon plasma was quite useful to modify the surface of PE film. When the Ar-plasma-treated PE was exposed to air, the surface incorporated more oxygen from air. This theory had significant meaning for the surface modification industry. Chung et al. [2003] investigated the surface activation of polyvinylalcohol (PVA) film by using Ar and Ar+O₂ plasma, respectively, and proved that Ar+O₂ plasma was more efficient for PVA surface modification. Sprang et al. [1995] discussed the plasma and ion beam surface treatment of PE, and mentioned that the etch rate, surface structure and roughness of the PE surface were influenced by different plasma treatment parameters. Dilsiz et al. [1995] showed the roughness changes of carbon fiber after plasma treatment and proved that plasma coating had a deep influence on the surface energy of carbon fiber. Kim et al. [2003] discussed the polymer surface modification and metal surface decontamination by using atmospheric pressure ejected plasma, and also studied the plasma effect under various plasma treatment conditions. Kim et al. [2003] used atmospheric pressure plasma jet to modify the surface of stainless steel to make the surface more hydrophilic, and proved that new functional groups were generated after plasma treatment according to XPS analysis.

By summarizing previous investigations, it is not hard to see that the surface pretreatment is normally necessary before application. Plasma treatment is quite an efficient method to modify the surface properties just like wettability, permeability, conductivity, adhesion and biocompatibility. However, there are few reports related with the surface modification of stainless steel before binding with polymers [Kim et al., 2003]. In this paper, we studied the surface modification of stainless steel by using an atmospheric pressure plasma treatment and discussed the effect of plasma treatment time, plasma treatment power and aging time in air on the wettability and surface free energy in detail.

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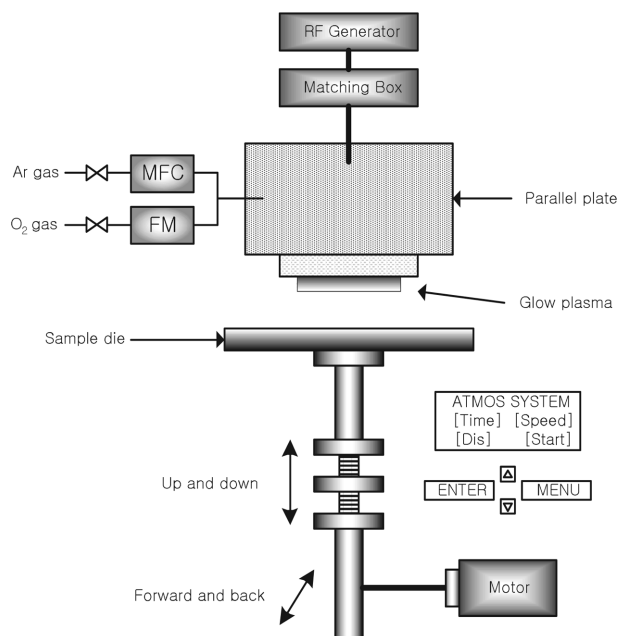


Fig. 1. The atmospheric pressure plasma system used in our research.

EXPERIMENTAL

The stainless steel plates (AISI 304L) (Duwon Company in Daejeon) were washed with 1% HCl/distilled water solution, distilled water and ethanol, followed by drying with a stream of nitrogen gas.

The experiments of surface modification of stainless steel were carried out by the atmospheric pressure argon plasma (Model ATMOS, Plasmart Inc. Korea) (See Fig. 1). The ultra high purity argon purchased from Praxair Korea Co. Ltd. was used as initiating gas. The previously prepared stainless steel plates were treated by one atmospheric pressure argon plasma followed by exposure to air for a few minutes. The distance between plasma discharge source and the stainless steel substrate was fixed at 7 mm.

The contact angle test was performed on the FACE contact-angle meter made by Kyowa Interface Science Co. Ltd. The deionized water and diiodomethane were used as polar and dispersion components, respectively. After plasma treatment the deionized water and diiodomethane were dropped onto the surface of stainless steel plate; then the angles were read through the lens. In this experiment, eight point measurements on each sample were randomly performed, and the average value of the eight point measurements was regarded as the average contact angle of the sample.

The surface free energy of stainless steel after plasma treatment was calculated from the results of contact angle test by using Owen's method [Zenkiewicz, 2001]. The surface free energy (γ) of a solid is equal to the sum of both dispersion (γ^d) and polar (γ^p) components:

$$\gamma = \gamma_s^d + \gamma_s^p \quad (1)$$

and the following relation has been used:

$$\gamma_i = \gamma + \gamma - 2[(\gamma_s^d \gamma_i^d)^{0.5} + (\gamma_s^p \gamma_i^p)^{0.5}] \quad (2)$$

Table 1. The dispersion (γ_i^d), polar (γ_i^p) components and ω_{1-4} coefficients for the probe liquids (Distilled water and diiodomethane are used as polar and dispersion components, respectively)

Liquid	γ_i^d	γ_i^p	ω_1	ω_2	ω_3	ω_4
Water	21.8	51.0				
Diiodomethane	48.5	2.3				
Water and diiodomethane			1.53	7.80	0.22	3.65

Here, γ_{sl} is the free energy related with the interface between solid and probe liquid, and γ is the surface free energy of liquid, and γ_i^d and γ_i^p are the dispersion and the polar component of the surface free energy of liquid, respectively. When Eqs. (1) and (2) are combined with the Young equation [Stokes and Evans, 1996],

$$\gamma_{sl} = \gamma_s + \gamma_l \cos \theta \quad (3)$$

where θ is the contact angle between the probe liquid and the surface of examined material, the following expression could be obtained:

$$\gamma(1 + \cos \theta) = 2(\gamma_s^d \gamma_i^d)^{0.5} + 2(\gamma_s^p \gamma_i^p)^{0.5} \quad (4)$$

So, according to Eq. (4), two unknowns (γ_s^d and γ_s^p) can be deduced by the results of contact angle for the given substrate using two different liquids with known values of γ_i^d and γ_i^p . Thus, the following equations are finally obtained:

$$(\gamma_s^d)^{0.5} + \omega_1 (\gamma_s^p)^{0.5} = \omega_2 (1 + \cos \theta_1) \quad (5)$$

$$(\gamma_s^d)^{0.5} + \omega_3 (\gamma_s^p)^{0.5} = \omega_4 (1 + \cos \theta_2) \quad (6)$$

Here, ω_n with $n=1-4$ are the coefficients dependent on the nature of probe liquids used, and θ_1 and θ_2 are the contact angles relating to the used liquids. And this Owen's method was usually widely used in the researches of surface free energy. In this experiment, we used water and diiodomethane as two known liquids and the values of γ_i^d , γ_i^p and ω_{1-4} are shown in Table 1. After calculation, both γ_s^d and γ_s^p were obtained and then the surface free energy was easily obtained too.

RESULT AND DISCUSSIONS

During the contact angle test, we observed that after plasma treatment the contact angles of the probe liquids decreased and the surface free energy of stainless steel increased. These changes can be attributed to the effect of plasma. The plasma effect on different materials has been investigated by many researchers [Vallon et al., 1996; Choi et al., 1997; Duca et al., 1998; Mahlberg et al., 1998; Kaczmarek et al., 2002; Kim and Lee, 2002; Kaminska et al., 2002; Kim et al., 2003]. It was considered that plasma can improve the surface wettability and surface free energy. When we modified the surface of stainless steel by plasma, we paid much attention to some crucial plasma parameters which could have considerable influence on the treatment effects: plasma treatment time, treatment power, and aging time in air after plasma treatment.

1. Effect of Plasma Treatment Time

Fig. 2 shows the effect of different plasma treatment times on the change of contact angle. When the plasma treatment time is 60

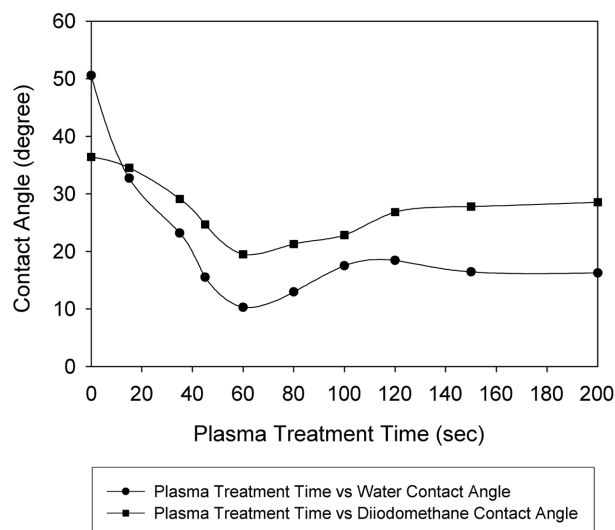


Fig. 2. Changes of contact angles with respect to the plasma treatment time (Plasma treatment power: 100 W, aging time in air after plasma treatment: 3-5 min).

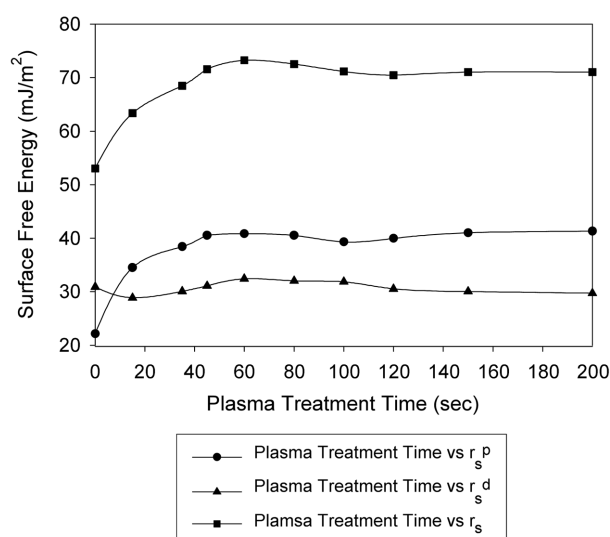


Fig. 3. The effect of plasma treatment time on surface free energy of stainless steel plate (Plasma treatment power: 100 W, aging time in air: 3-5 min).

sec, the contact angles of both polar and dispersion components decrease to the minimum, and then, after 60 sec, they gradually increase with increasing plasma treatment time. Fig. 3 shows the effect of plasma treatment time on the change of surface free energy. As shown in Fig. 3, at the beginning stage, both γ_s^d and γ_s^p increase with increasing plasma treatment time. At the time of 60 sec, they reach maximums. Then, with further treatment, the γ_s^d and γ_s^p tend to be stable, and even a little decreased. The changes in Fig. 2 and Fig. 3 were thought to be caused by the new oxides, nitrides and radicals on the surface of stainless steel which were generated by plasma treatment, and these new oxides, nitrides and radicals would result in the decrease of contact angles and the increase of surface free energy.

In this experiment, at the beginning, the amount of oxides, nitrides

and radicals on the surface of stainless steel increased with extending the plasma treatment time, so the contact angles kept on decreasing and the surface free energy kept on increasing. When the plasma treatment time was extended above a certain time, the oxides and nitrides on the surface would not keep on increasing any more because some of the oxides and nitrides may transfer into non-active particles due to long time exposure to plasma [Suzuki et al., 1986; Ito et al., 1999]. These non-active particles were thought to have adverse influences on the contact angle and the surface free energy. So, after 60 sec, the contact angles of both polar and dispersion components increased instead of keeping on decreasing, and the surface free energy did not increase any more, either. On the other hand, it was also considered that many oxides and nitrides could be generated during the process of exposure to air after plasma treatment [Suzuki et al., 1986; Kühn et al., 1999]. This phenomenon could be attributed to the radicals, which were also generated by plasma treatment. When these radicals were exposed to air after plasma treatment, they could react with N_2 and O_2 in air and generate more oxides and nitrides on the surface, which was beneficial for the surface wettability and free energy. But, if the plasma treatment time was too long, the amount of active radicals would also decrease because of the appearance of non-active particles, so the amount of oxides and nitrides, which were generated by the radicals, also decreased. This result also led to the decrease of surface wettability and free energy.

Furthermore, as shown in Fig. 3, at the beginning of plasma treatment, the free energy of polar components- γ_s^p kept on increasing until the treatment time reached 60 sec. After 60 sec, the γ_s^p nearly showed no apparent changes. In the case of dispersion components- γ_s^d , when the plasma treatment time was short, the changes were not so distinct, and only when plasma exposure time reached 60 sec, was a relatively small increase observed. However, the increase of polar components- γ_s^p was more than dispersion components- γ_s^d . This meant that changing plasma exposure time had more influence on polar components than dispersion components on stainless steel. So, from this point, we can deduce that, in the case of stainless steel, the plasma treatment time mainly affected the polar components rather than the dispersion components.

2. Effect of Plasma Treatment Power

The plasma treatment power is also an important parameter in the field of plasma surface modification. An increase of plasma treatment power means an increase of the capability of producing oxides, nitrides and radicals on the surface. When the treatment power is low, plasma cannot provide enough energy to produce oxides and nitrides on the surface of substrates and cannot generate enough radicals either. On the other hand, if the plasma treatment power is too strong, the surface would be scathed and the surface uniformity would decrease. In the meantime, more non-active particles would also be generated. Yasuda [1985] once gave good explanations on the effect of plasma treatment power. So, in this experiment, we also discussed the effect of plasma treatment power on the surface modification of stainless steel.

Fig. 4 shows the effect of plasma treatment power on the wettability of stainless steel. At the power of 120 W, the contact angles of both polar and dispersion components fall down to the minimum. In Fig. 5, the surface free energy reaches the maximum value when plasma treatment power is 120 W. We can explain this result

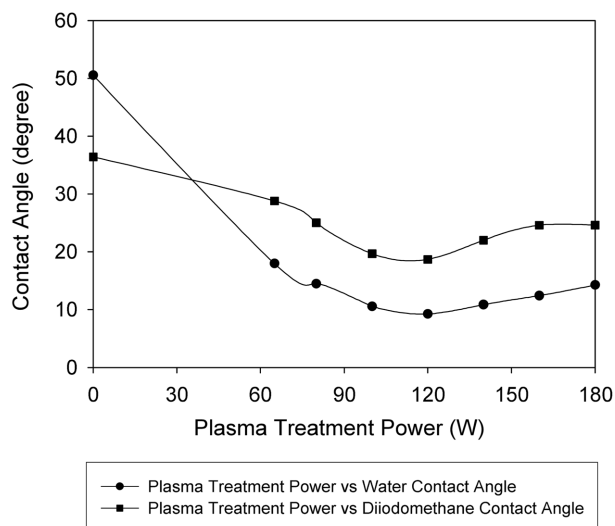


Fig. 4. Changes of contact angles with respect to plasma treatment power (Plasma treatment time: 60 sec, aging time in air after plasma treatment: 3-5 min).

such that, when plasma power was lower than 120 W, the density of nitrides and oxides was low and kept on increasing. Therefore, the contact angles kept on decreasing and the surface free energy kept on increasing. When the power was increased up to 120 W, it was supposed that the oxidation and nitration of the treated surface attained to the saturated state. So the contact angles reached the minimum and the surface free energy the maximum. Further increasing the plasma treatment power after the saturated state, the density of the oxides and nitrides on the surface of stainless steel would not increase markedly any more. However, because of surface scathe under too strong plasma discharge, more non-active particles were generated. So, when the plasma treatment power was stronger than 120 W, the contact angles increased and the surface free energy decreased. On the other hand, when the plasma treatment power was too strong, the active radicals may also have decreased because of non-active particles. This would also lead to the decrease of oxides and nitrides on the surface of stainless steel when exposed to air, which resulted in the decrease of wettability and surface free energy. Therefore, in recent research, low power plasma discharge was usually utilized to reduce the scathe made by plasma bombardment and radiation.

In Fig. 5, when the plasma treatment power was below 60 W, the polar components- γ_s^p kept on increasing. This phenomenon meant that the energy of polar components could be largely enhanced and quickly reached the maximum even at low power of plasma treatment. After that, even if the plasma treatment power increased considerably, the γ_s^p kept stable. Compared with γ_s^p , the changes of the dispersion components- γ_s^d were not so apparent at low power of plasma treatment. Only when the plasma power got to 90 W did the γ_s^d gradually increase. At the power of 120 W, it reached the maximum. From this phenomenon, we can conclude that, at low power plasma treatment, the improvement of surface free energy was mainly attributed to the polar components, whereas, at relatively high power plasma treatment, the increase of surface free energy was mainly due to the dispersion components.

3. Effect of Aging Time in Air after Plasma Treatment

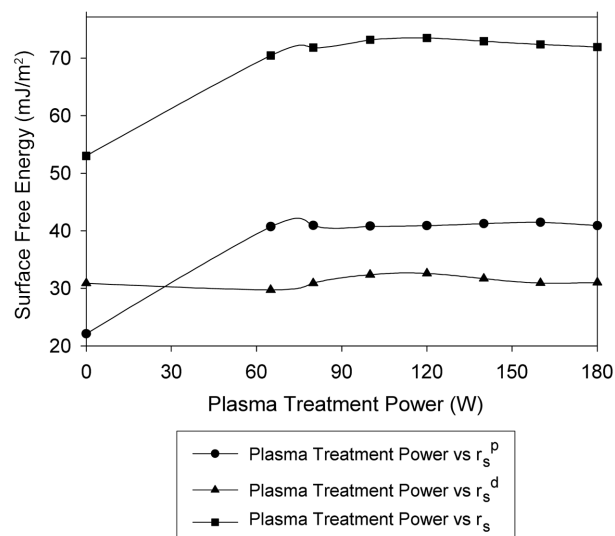


Fig. 5. The effect of plasma treatment power on surface free energy of stainless steel plate (Plasma treatment time: 60 sec, aging time in air: 3-5 min).

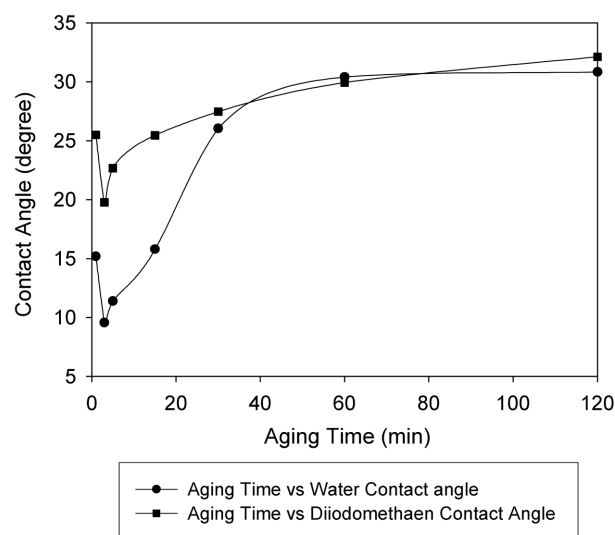


Fig. 6. Changes of contact angles with respect to aging time in air after plasma treatment (Plasma treatment time: 60 sec, plasma treatment power: 100 W).

Aging property is an important factor for maintaining high surface energy of materials. It has a deep significance with production cost and storage. In this experiment, we discussed the aging property of stainless steel after plasma treatment.

Fig. 6 shows the influence of exposure time on the contact angles after plasma treatment. It is easy to see that the contact angles of both polar and dispersion components decrease to the minimum within a short exposure time in air (3-5 min). With extending the exposure time, the contact angle becomes larger and larger. Fig. 7 shows the effect of aging time on surface free energy. When the aging time becomes 3 to 5 min, the surface free energy reaches the maximum.

In previous discussion, it has been stated that the reason for the changes of contact angles and surface free energy was due to the

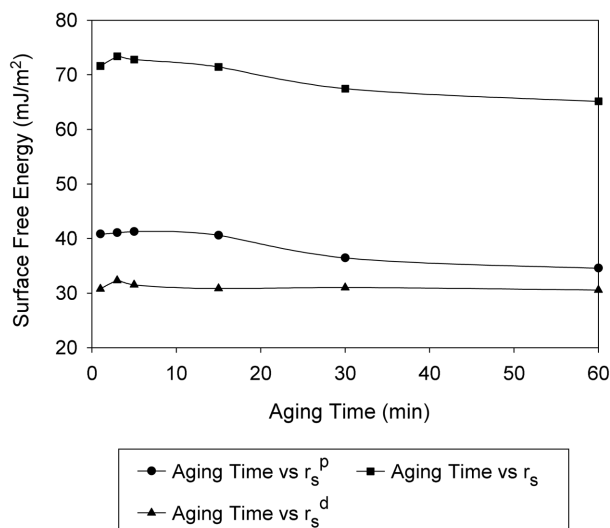


Fig. 7. The effect of Aging time in air on surface free energy of stainless steel plate (Plasma treatment time: 60 sec, plasma treatment power: 100 W).

oxidization and nitration of surface by plasma treatment. We also mentioned that, after plasma treatment, the active radicals could keep on reacting with the O_2 and N_2 in air, through which more oxygen and nitrogen components could be incorporated onto the surface. In this experiment, at the beginning of the aging process, the surface after plasma treatment was so activated that surface radicals could react rapidly with stable components in air. This meant that new oxides and nitrides could be promptly formed on the surface. Therefore, the contact angles rapidly decreased while the surface free energy rapidly increased in this period. With further extending the exposure time in air, the activated surface was more and more stable due to the reaction with the stable components in air. At last, the oxides and nitrides on the surface approached to the saturation state. At this saturated state, the contact angles fall down to the minimum and the surface free energy increases to the maximum. In this experiment, the aging time at the saturated state was 3 to 5 min (Shown in Fig. 6 and Fig. 7). After 3 to 5 min, if further extending the exposure time, the contaminations and stable components in air would form undesired impurities on the saturated surface and these undesired compounds can make the surface more passive, which is disadvantageous for surface wettability and free energy. Therefore, when exposure time was over 3 to 5 min, contact angles increased and surface free energy gradually decreased.

In Fig. 7, the increase of surface free energy, when the aging time was around 3 min, was mainly caused by the changes of dispersion components- γ_s^d , and the decrease of surface free energy as extending the aging time was mainly caused by polar components. This result indicated that, when the surface of stainless steel was exposed to air after plasma treatment, the new functional groups generated by active radicals had more influence on the dispersion components as enhancing the surface free energy. The surface passivation caused by long-term exposure to air was mainly influenced by polar components.

In this research, the aging time is the value representing a period of time (3-5 min), rather than a specific point of time. When the contact angle test was conducted, a short period of time was neces-

sary to read the values of eight drops. Therefore, the aging time obtained for representing the contact angles was taken from the mean value of eight measurements of drops. As a consequence, the optimum aging time in air has been determined between 3 and 5 min.

CONCLUSION

The surface free energy of stainless steel plate was successfully improved by using atmospheric pressure plasma treatment. The contact angle test and the calculation of surface free energy have proved that a more wettable surface was obtained after plasma treatment and the optimum plasma treatment conditions were a treatment time of 60 sec, treatment power of 120 W, and aging time of 3 to 5 min in air.

From this research, we also draw the following conclusions. Firstly, the effect of plasma treatment time on the surface free energy of stainless steel is mainly due to the contribution of polar components but not dispersion components. Secondly, the polar components mainly contribute to the improvement of surface free energy under low power plasma treatment, whereas the dispersion components can contribute to the small increase of surface free energy under relatively high power plasma treatment. Thirdly, short time exposure of plasma treated surface in air can improve the surface free energy. And, in this period, the dispersion components mainly contribute to the enhancement of surface free energy when the aging time is short, whereas the polar components dominantly affect the decrease of surface free energy during long time exposure in air.

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NOMENCLATURE

Greek Letters

- γ_s : surface free energy
- γ_s^d : free energy of dispersion components
- γ_s^p : free energy of polar components
- γ_{sl} : free energy related with the interface between the solid and the probe liquid
- γ_l : surface free energy of the liquid
- γ_l^d : free energy of the dispersion component of the liquid
- γ_l^p : free energy of the polar component of the liquid
- θ : contact angle between the probe liquid and the surface of the stainless steel
- θ_1 : contact angle between the water and the surface of the stainless steel
- θ_2 : contact angle between the diiodomethane and the surface of the stainless steel
- ω_{1-4} : coefficients dependent on the nature of probe liquids used

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