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PLASMA SURFACE MODIFICATION OF POLYMERS

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Translation of "Kobunshi Ryozai no Hyomen Kaishitsu", Purazuma to Kagaku, April, 1980, pp. 58-61

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16. Abstract

This article deals with types of surface modification of polymers (Plasma etching, plasma surface coating, and plasma activation) and the characteristics that this modification brings forth.

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PLASMA SURFACE MODIFICATION OF POLYMERS

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1. Introduction

In a broad sense, plasma surface modification of polymers can be called the functionalization of polymers. The characteristics of this method can improve only the surface section without substantially influencing the volume characteristics of the polymer itself. Moreover, by appropriately choosing the conditions of reactions of gases that are used as the plasma, it is possible to control these surface characteristics. When we taken into consideration the scope of the treatment or the simplicity of the treatment process and treatment method, the surface modification is very unique and can be called remarkable. /58*

2. Classification of Plasma Surface Modification

Surface modification of polymers by plasma can be classified according to the following reactions:

(1) plasma etching,

(2) surface coating by plasma polymerized thin films, and

(3) plasma activation surface graft polymerization.

(1) is the etching of the surface section by gas plasma of nonpolymers. The polymer is usually accompanied by dehydration, etc. and a bridge layer is formed [1]. N_2 and NH_3, which form nitrogen plasma, react with basic materials when they are activated. The nitrogen that is plasma-activated provides a hydrophilic group from the amino group [2].

Even in the case of gas plasma, the polymer surface reacts with O_2

*Numbers in the margin indicate pagination in the foreign text.

after irradiation, when it is placed in the air, by radical activation and gives off an oxide functioning group. When we use O_2 plasma, surface oxidation (or surface combustion) becomes the most important and this is also called "plasma burnoff."

(2) is what is called plasma polymerization and is made possible by the evaporation of organic compounds. The formation of film substances that are thin and free of pinholes is a particular characteristic. This plasma polymerization differs from the usual vinyl or condensation polymerization in that the monomer does not always make the functional group of a polymer necessary. Eventually, the plasma activation of molecules is accompanied by partial fragmentation. In this way, the radical, which is formed without ions, survives by reuniting with the basic material or gas phase. It provides a polymer substance, which is a bridge builder. Consequently, the monomer in this case is not what is called a polymerized unit. Rather it is more appropriately considered as a unit supplied to an element.

The variety of component elements and their ratio has a large function in the properties of a polymerized film, when compared to the chemical composition of the monomer itself. Even among the component elements, there is a difference between the easy polymerizing deposition and the difficult separation. For example, from the results of several amino systems, the ratio of the components in polymers increases in the order of $N<C<Si$ [3]. The behavior of each of these elements in plasma is suggested.

In any event, there is an increase of between 10 and several 1000 Angstroms in the basic material surface by coating treatments with thin polymerized films. From this, the surface characteristics are brought forth. However, there are cases where the plasma polymerized layer on /59
top of the substrate is not necessarily strongly bonded. Problems such as cracking and clinging have occurred.

In (3), plasma irradiates the polymer and forms an activated polymerized substance with radicals on the surface. This is basic graft polymerization [5]. Consequently, we can assume the characteristics of various hydrotaxic and hydrophilic properties from the monomer chain used here. Here the radiation graft polymerization is different and a new polymerized layer is formed only on the surface of the basic material.

Even in these plasma modification methods, the fact that we can be selective in modifying the surface of the basic material is characteristic. As for the surface characteristics of the substance, there are many cases where these characteristics depend on the thickness corresponding to the elements that circulate in the surface layer. Therefore, from these points, we can say that the plasma treatment is valid.

3. Examples of Surface Modification

The surface substances can be characterized by an affinity for the substances that contact the surface or be repelled by substances connecting the surface substances. It is thought that absorbency characteristics are good examples of affinity properties. Examples of repelling properties are waterproofing and dirt and stain repelling characteristics. In order to allow for the characteristics, we will show how the plasma surface modification method can be tried in the several examples given below.

(a) Adhesive Characteristics

Adhesive properties are important in the polymer process. There are many materials in which we allow for improved polytetrafluoroethylene characteristics. With regard to these materials, plasma is irradiated and activated layers are formed from bridge building and olefin layers of the polarized particles. The improved adherence can be measured [6]. Hydrophilic properties and adherence can be improved by coating a substance with thin amino polymerization films that will not crack.

(b) Dye Properties and Printing Properties

The fact that printing and dyeing of textiles and polymerized materials can be done easily is related to the high value of these materials. Base properties are introduced from the gas plasma of ammonia, etc. and, on the other hand, acid properties are introduced from plasma treatment of SO_2, etc. We will show that we can improve dye properties by acid and base dyes [7].

There are also examples which measure the improvement of dye characteristics by surface graft polymerization layers. However, this is not an example that allows for dye properties. Therefore, we use plasma irradiation in the desizing stage after dye treatment. We also presented the method which effectively excludes PVA glue [8]. If we pyrolize an element with O_2 plasma and the pyrolysis occurs only on the surface area, the damage to the basic textiles is highly limited. These are also characteristics of the plasma method.

(c) Hydrophilic Characteristics

With N_2 and NH_3 or rare gases, we can bring out the hydrophilic characteristics of polymerized surfaces by many gas plasmas. This has already been explained as the hydrophilic action of polarity. Here the problem is the slow change of the substance with polyethylene and silicon resins. The hydrophobic change, which progresses with time, is observed in a substance that was once hydrophilic.

In the silicon treatment, the [term unknown] layer, which was formed by the radiation graft polymerization treatment of HEMA and AM, degenerates under dehydration conditions. This is explained by the fact that a polarized substance creeps in below the surface [9]. It is possible to explain the occurrence of hydrophilic properties with plasma treatment in the same way.

(d) Waterproof Characteristics

The thin plasma polymerized films from fluoride and silicon compounds show a waterproof characteristic. These polymers coat glass materials and this characteristic can change. Porous materials treated with these thin, waterproof polymer films also have interesting characteristics.

(3) Insulating Properties

In order to protect lenses and glass material from the cold, they are coated with silicon polymerized films [11]. The advantage of this plasma polymerization is extremely small. We have been able to make each layer of coating similar, especially in the case of silicon, in order to form the polymer by Si-Si bonding. Therefore, we can use this process in optical materials that demand transparency [12]. /60

(f) Others

As one interesting analysis, we have the application of plasma to the production of medical supplies. Because of the advantages of its low price and processing, plastic is used on a vast scale, even in the production of medical supplies. We can note several examples that measure the efficiency of plastic by plasma surface modification.

For example, the hydrophilic characteristics and easywear characteristics in contact lenses are improved with plasma treatment [13]. Plasma bridge-building layers and polymerized film layers are formed in the soft polyvinyl chloride surface that is used to improve contact lenses and blood bags. There are substances from these raw materials that will prevent the melting of these plastics [14] and will regulate small doses of medicine [15]. There are several examples of the use of plasma etching for cleaning various raw material surfaces, such as activation of carbon electrode surfaces by plasma.

4. Conclusion

Thin plasma polymerization films have been discussed from the viewpoint of simplicity in production stages. The application of selective, absorbent films and films used in selective permeability has been tested.

However, contrary to the results that have been announced, questions are raised concerning physical and chemical strengths (cracking and decomposition in ion oxidation solvents) and the aspect of permeability.

The most recent substitution for these are the plasma modifications of raw materials which are first made into polymers. This fact is also brought forth in recent patents. In Table 1, Japanese patents involving plasma, corona and spattering discharges, which were disclosed several years ago, are summarized and classified. The actual number is thought to be somewhat larger than that shown here. It is inferred that there is a strong tendency to measure surface modification of functionalization of raw material surfaces.

However, there are not many examples of the actual use of plasma reaction involving surface modification of polymers. The reason for this is that there are problems in assessing the treatment test materials, the control of the reaction conditions, the equipment (for example, the magnification and continuation of systems), etc.

It goes without saying that plasma surface modification must be improved for each purpose and it is necessary that we search for applications of the smallest amounts of materials which produce the optimum results in the laboratory.

Further reading and study must be done on polymers to fully understand the significance of plasma surface modification.

Table 1. Classification of Japanese Patents, Which Were Disclosed Earlier, Involving Plasma, Corona and Spattering (1977-1979)

	Subject	Total Number
(1)	Functionalization of the surface, formation of the protective layer	22
(2)	Surface modification (dyeing, adherence, hydrophilic properites, etc.)	14
(3)	Metal evaporation by spattering	8
(4)	Film materials	2
(5)	Medical materials	3
(6)	The practical application of inorganic materials	2
(7)	Patents related to treatment methods and equipment	4
(8)	Others	2

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