Polyethylene Film Surface Metallization Modified by Radiation Grafting of N-vinyl Pyrollidone

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Abstract— **Poyethylene films can be modified by radiation grafting of N-vinyl pyrollidone using γ-radiation. FTIR spectra were used to confirm the modification of PE films. The modified films were activated by two-step and one step methods for electroless Cu plating. Morphology of metallized films has been investigated. Electroless Cu plating onto the modified films depends mainly on the grafting degree and activation type. The conductivity of the metallized films has been investigated.**

I. INTRODUCTION

Copper metallization of polymer has been of great interest to the microelectronics industries [1, 2]. There are several techniques for metal depositions on surface of polymeric materials such as evaporation, sputtering, electroplating and electrolysis. However, due to the surface inertness of the most polymers the adhesion strengths between the metal and plastic is inadequate for practical applications [3-6]

Electroless Cu plating technique has been widely used in the automotive and electronics industry for the metallization of plastics due to its advantages like selectivity, its ability to plate the deep places and vais, low coast, and can be performed at room temperature [7].

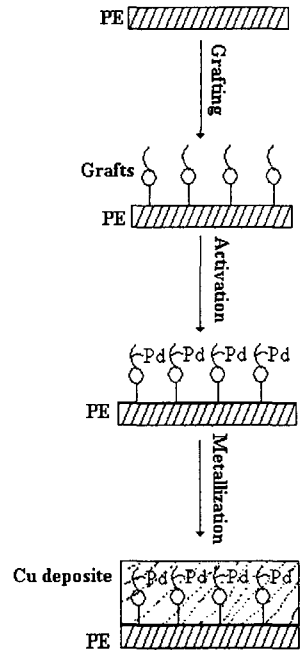
Radiation grafting is one of the promising modern methods for the modification of polymers due to the wide variety of the applications as membranes, catalysts, electronic materials, etc [8, 9]

The aims of this work is to make Cu metallization of PE films modified by grafting of NVP, investigation of the surface activation methods and study of morphology of metallized films in addition to preparing the conductive polymer for application of micro-electronics with their conductivity measurements and investigations of large sized films.

II. RESULTS AND DISCUSSION

Surface metallization of PE films can be performed through the sequence steps listed in Scheme 1. Firstly, PE films were subjected to γ-radiation in presence of NVP to modify the surface of PE.

The modification of PE surface was confirmed by FTIR spectra (figure 1). It can be seen that the spectrum of modified films is characterized by appearance of the new band at 1659 cm^{-1}, which is typical for carbonyl group of NVP.



Schem 1. Steps of surface metallization of PE films

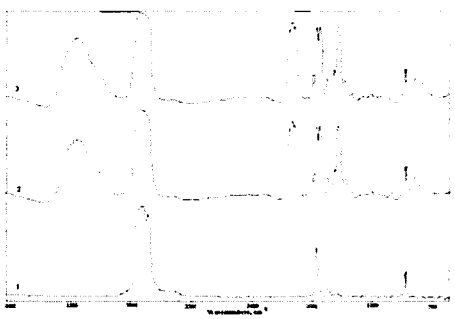


Fig.1 FTIR spectra of PE (1), PE-g-NVP at absorbed dose 54 kGy (2), and PE-g-NVP at absorbed dose 162kGy(3)

The grafting degree of NVP as a function of the absorbed dose has been studied and the results are shown in figure 2. It can be seen that the grafting degree increases with increasing of absorbed dose resulting in higher concentration of NVP content on the PE surface.

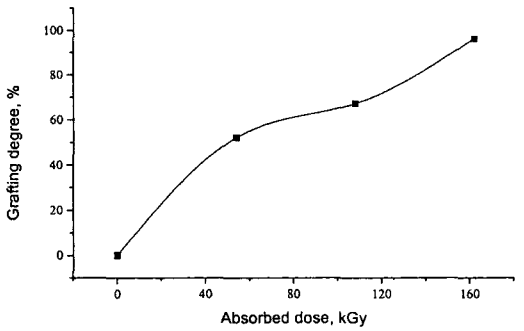


Fig.2 Dependence of grafting degree on absorbed dose

Electroless Cu plating was performed with the modified PE films with different grafting degrees after activation by $PdCl_2$. It was noticed that the electroless plating rate increases with increase of grafting degree (figure 3). This can be explained by enhancing of polycomplex formation between Pd ions and NVP species on the surface in activation step resulting in more active catalytic surface for the plating process.

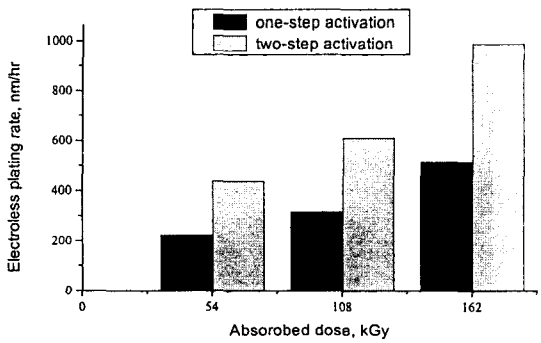


Fig.3 Dependence of electroless plating rate on activation type

Activation of the modified films was performed by two methods; one-step and two-step activation. In two-step method, the polymer surface was immersed successively in $SnCl_2$ and then $PdCl_2$ solution where the Pd ions displaced the Sn ions according to the equation (1) with the formation of catalytic surface of Pd metal atoms [10]

$$Pd^{+2} + Sn^{+2} \longrightarrow Pd^{0} + Sn^{+4} \qquad (1)$$

The one-step process is based on colloidal catalyst composed of mixed tin-palladium colloid. However $SnCl_2$ is not active catalyst for electroless process. So it is important to develop tin free bath to avoid the side effects of tin. In this case, the reduction of Pd ions will take place in the electroless copper bath consuming longer time to form catalytic surface with Pd metal atoms [11]. Figure 3 demonstrates the effect of activation type on the electroless plating rate. It was found that the two-step activation is more effective than the one-step activation.

The surface morphology of metallized films modified by different grafting degrees is shown in figure 4(a, b). The white clusters representing metallic copper demonstrate good coverage and uniformity of the deposited metal. Moreover, microanalysis of metallized films shows that the atomic percent of Cu metal on the film surface is 99.8%.

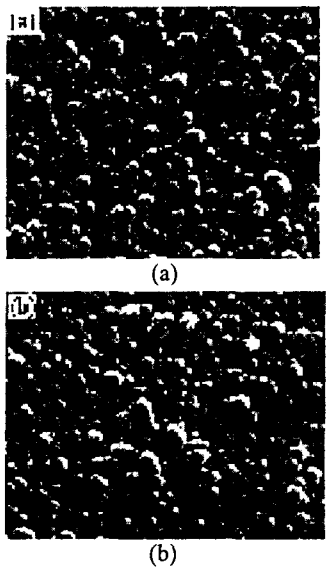
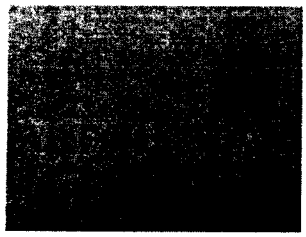
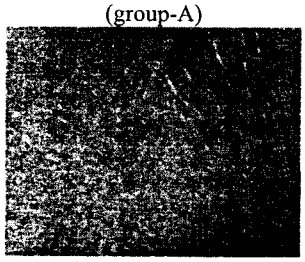


Fig.4. Morphology of the metallized films with grafting degree 52% (a) and 98% (b)

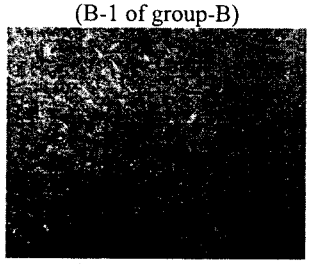
For the investigation of electric conductivity and adhesion of the grafted and metallized PE films, those were prepared with group-A of pure polyethylene, and group-B of polyethylene films grafted with NVP at lower grafting degree of B-1 and at higher grafting degree B-2. Also, polyethylene films of group-C grafted with NVP and followed by metallization at lower grafting degree of C-1, at medium grafting degree of C-2 and at higher grafting degree of C-3 were prepared. Finally, those were investigated and tested by electronic multi-meter and vacuum tester. The adhesion property of electroless plating of metallization was normally good enough for all kinds of PE samples, however, the electric conductivity could be found only on the PE samples of group-C as like with normal metal films after medium to higher grafting degree of C-2 and C-3 samples.



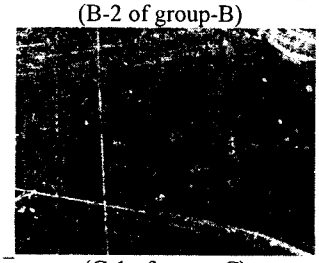
(group-A)



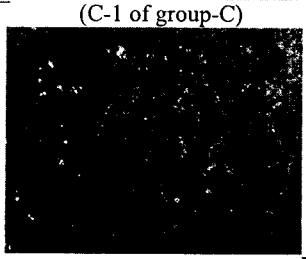
(B-1 of group-B)



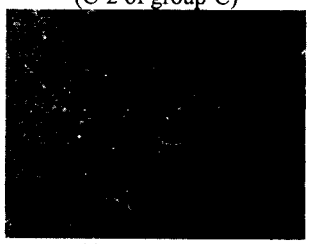
(B-2 of group-B)



(C-1 of group-C)



(C-2 of group-C)



(C-3 of group-C)

Fig 5. Photographs of metallization samples

III. CONCLUSION

It was investigated and confirmed by the method of radiation grafting with N-vinyl pyrollidone(NVP) using γ-ray radiation to prepare the thin metal film on the flexible polyethylene films for the useful application in many kinds of microelectronics.

FTIR spectra was used to confirm the modification of PE films, and the modified films were activated by one-step or two-step methods for electroless Cu plating on the polyethylene.

Morphology of metallized films has been investigated with the white clusters on the films which was representing the metallic copper in samples showing good coverage and uniformity of the deposited metal with the atomic percent of 99.8% on the Cu metal film surface.

Metallization by electroless Cu plating onto the modified films depends mainly on the grafting degree and activation types. The electrical conductivity and adhesion of the metallized films has been investigated and tested in regard of grafting degree of samples. The adhesion property of electroless plating metallization was normally good enough for all kinds of prepared PE samples, however, the electric conductivity could be found only on the PE samples of group-C as like with normal metal films after medium to higher grafting degree of C-2 and C-3 samples with good availability in practical use.

REFERENCES

[1] Rye R.R., Ricco A.J., In: Mitall K.L., editor, Metallization plastics: fundamental and applications, New York: Marcel Decker, 1998.

[2] Rober M.G., Wiliam T.M., Yoshio N.,Robert D., editor. Handbook of semiconductors manufacturing technology, New York : Marcel Decker, 2000.

[3] K.W. Lee, S. P. Kowalczyk, J.M. Shaw. Langmuir, 7, 2450 (1991)

[4] N. Inagaki, S.Tasaka, K. Hibi. J Polym. Sci. Polym. Chem, 30, 399 (1992)

[5] G. Rozovskis, J. Vinkevicius, J Adhes. Sci. Technol., 10, 399 (1996)

[6] J.Y.Zhang, H. Esrom, U. Kogelschatz, G.Emig. J. Adhes. Sci. Technol., 18, 1179 (1994)

[7] N. Inagaki, S. Tasaka, T. Umehara, J.Appl.Polym.Sci. 71, 2191 (1999)

[8] V.Ya.Kabanov, Vysokomolek. Soed. B. 37, 6 (1995).

[9] Kato K., Uchida E., Kang E.-T., Uyama Y., Ikada Y., Prog. Polym.
i. Sci. 28 (2003)

[10] 10. Muller, G.;Baudrand, D. W. Practical Handbook on Plating on plastics. -Robert Draper Ltd.: Teddington, 1971.

[11] 11. Meek, R. L. J. Elechrochem. Soc, 122, 1478 (1971)