ESR STUDY ON RADIATION GRAFTING REACTION OF INORGANIC OXIDES

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ABSTRACT

In this paper Al_2O_3 and MgO were studied as targets for the radiation grafting of MAA by electron beams. The reaction conditions and materials were characterized by IR spectroscopy, Scanning electron microscopy, X-ray diffraction methods. It is concluded that grafting copolymerization of inorganic oxides and organic monomers has been confirmed. We focus our attention on using ESR spectrum to study the effects of ionizing radiation on inorganic oxides and the properties of initiating active centers. In addition, the radiation grafting mechanism of inorganic oxides and organic monomers has been primarily investigated.

Keywords: Aluminum oxide Magnesium oxide Methacrylic acid Radiation grafting ESR spectrum

1 INTRODUCTION

Generally speaking, chemical initiation is difficult to accomplish grafts on inorganic materials, but ionizing radiation can make them active. Throughout the grafting reaction, the compound materials not only maintain a stable backbone, but also have some special functions. The production of compound materials made by grafting of organics onto inorganics is an attractive new technology of radiation processing.

2 EXPERIMENTAL

Materials and reagents: Aluminum oxide (AR), Magnesium oxide (AR), Methacrylic acid (CP).

Radiation conditions: The samples were irradiated by being passed under the electron beams of a JJ-2 type (2 MeV) accelerator, operating at a beam energy of 1.5 MeV and with a current of 20 μA. All of the irradiations were carried out under room temperature and in air. The radiation dose was 7 to 84 kGy.

Grafting copolymerization: Mutual irradiation was performed on Al_2O_3 or MgO in aqueous solution of MAA, and the whole system was irradiated. The pre-irradiation was that Al_2O_3 or MgO was irradiated before being brought into contact with aqueous solution of MAA and then grafted under vacuum (13.33Pa) and a fixed temperature.

Calculating graft yield: The products were extracted with distilled water for 24 h and dried; the pures were repeated again until constant mass was achieved. The graft yield may be expressed as follows:

$$G(\%) = [(W_f - W_i)/W_i] \times 100\ \%$$

where W_f = weight of graft copolymer, W_i = initial weight of Al_2O_3 or MgO.

Measurements: The grafted samples were characterized by IR spectroscopy model FT-IR 170EX and scanning electron microscopy model S-450 and X-diffraction instrument model D/mar-rA respectively. The determination of ESR signals used X-band of BRUKER ESR ER 200 DSRC instrument. The value of electron spin concentration (N_x) was calculated as follows:

$$N_x = \{[Y_{max} \cdot (\triangle H_{pp})_x^2]/[W Y_{s,max} \cdot (\triangle H_{pp})_s^2]\} \times (G_s/G_x) \times N_s$$

where Y_{max} is peak-to-peak amplitude, s means standard sample, x is unknown sample, $\triangle H_{pp}$ is peak-to-peak width, G is amplifying times, W is weight of unknown sample, N_s is the electron spin concentration of standard sample.

3 RESULTS AND DISCUSSIONS

3.1 Radiation grafting reaction

Fig.1 illustrates that in the pre-irradiated Al_2O_3 system, the graft yield increases

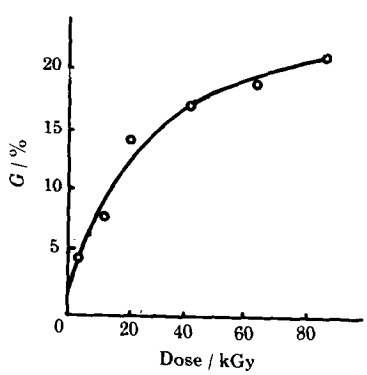

Fig.1 The relationship of dose with grafting yield

Al_2O_3 pre-irradiation

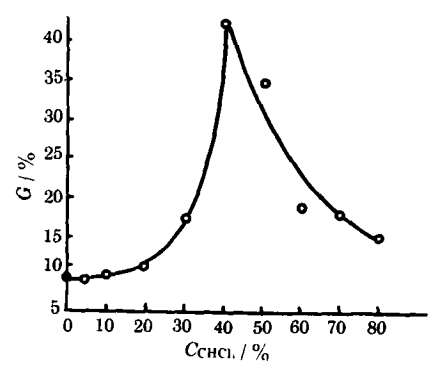

Fig.2 The relationship of C_{CHCl_3} with grafting yield

Al_2O_3 mutual irradiation

with the dose. Fig.2 shows that MAA solutions in the mixture solvent of $CHCl_3$ and H_2O as various volume proportions with $CHCl_3$:H_2O = 2:3, the mutual irradiation graft

yield is greatly enhanced by the presence of $CHCl_3$. It is possible that in mutual irradiation, the free radicals of $CHCl_3$ produced in irradiation can promote the grafting reaction, which will be discussed later.

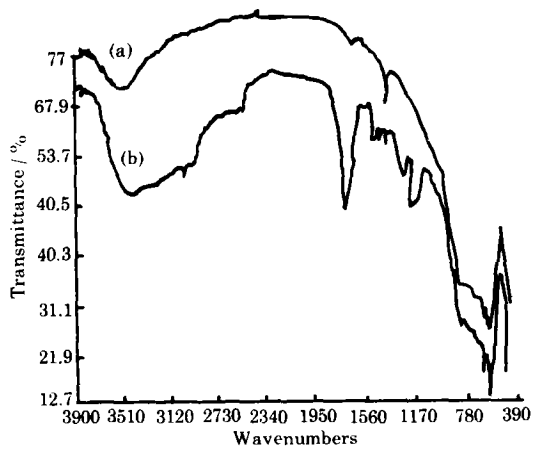

Fig.3 IR spectra of Al_2O_3 (a) and its grafts (b)

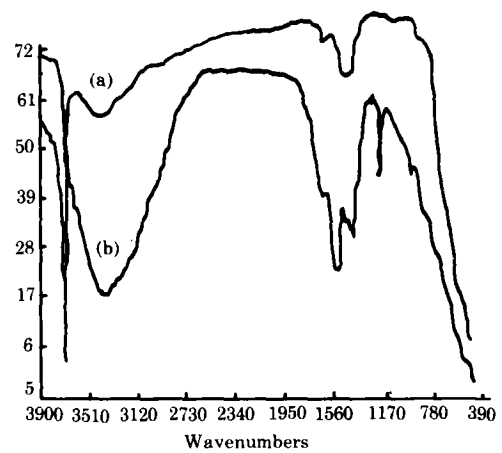

Fig.4 IR spectra of MgO (a) and its grafts (b)

IR absorption spectra of pure Al_2O_3 and MgO and their grafted samples are shown in Fig.3 and 4, respectively. The differences between the absorption before and after grafting indicate that the grafting reactions have been carried out. Comparisons of the photographs taken by SEM between Al_2O_3 and MgO and their grafted samples confirm that grafting reactions have occurred.

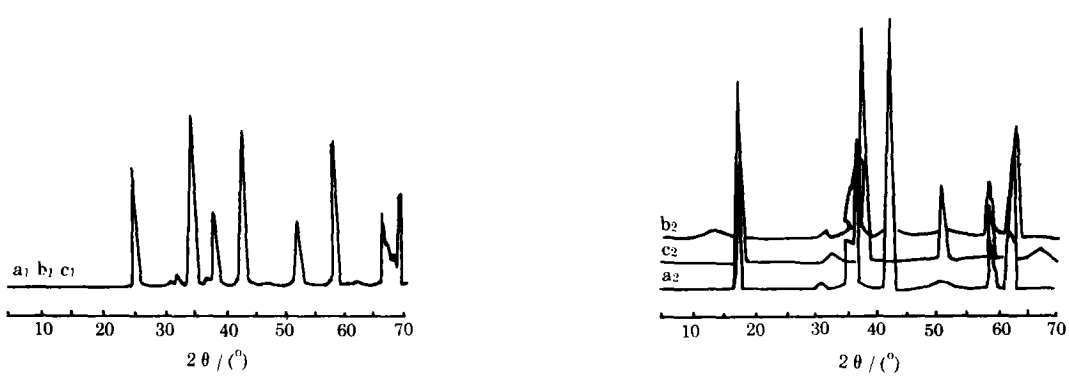

Fig.5 X-diffraction pictures of samples

a_1: Al_2O_3, b_1: Blend of Al_2O_3 and PMAA (40 %), c_1: Al_2O_3-g-MAA;

a_2: MgO, b_2: Blend of MgO and PMAA (40 %), c_2: MgO-g-MAA

The X-diffraction tests (see Fig.5) shows that before and after irradiation the crystal peaks of Al_2O_3 have not changed, which indicates that the grafting of MAA reaction occurs only at the surface. On the other hand, the grafting reaction

penetrates the surface of MgO.

3.2 ESR study of radiation grafting

The sample of Al_2O_3 before irradiation did not give any ESR signal, which shows that Al_2O_3 has no paramagnetic crystal defects or impurities. But after irradiation the ESR signals will appear. The electron spin concentration changed with dose as shown in Fig.6. The calculated values of N_x are presented in Table 1.

These results explain that after irradiation an active centre of spin in Al_2O_3 has been created, which can initiate the grafting reaction.

The sample before irradiation of MgO give a weak ESR signal, which shows that there are paramagnetic crystal defects (or impurities). After irradiation the ESR signal has greatly enhanced as shown in Fig.7. The values of N_x are calculated in Table 2.

We can see that the value of N_x increases with dose.

In the irradiated metal oxides the important radiation defects are the colour centres of electron or vacancy. The electron's colour centres are F^+ and F centres.

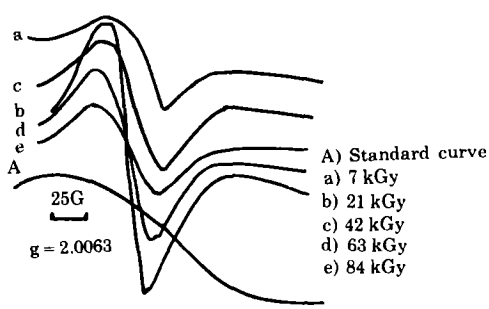

Fig.6 The relationship of spin concentration of Al_2O_3 with dose

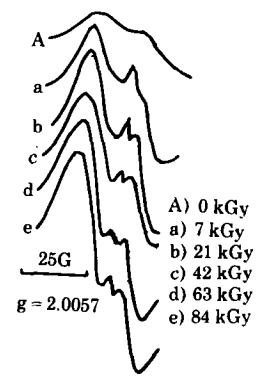

Fig.7 The relationship of spin concentration of MgO with dose

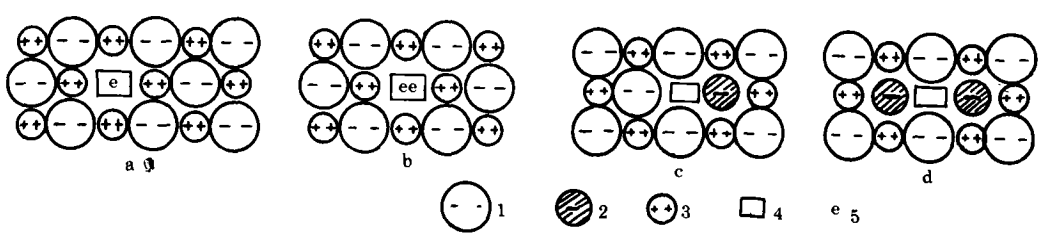

Fig.8 The crystal defects of irradiated metal oxides

a: F^+ centre, b: F centre, c: V centre, d: V centre

1: Oxygen ion, 2: Oxygen ion trapped by vacancy, 3: Metal ion, 4: Vacancy, 5: Electron

F^+ centre appears when one electron traps in an oxygen ion vacancy, which is paramagnetic, whereas when two electrons trap in one oxygen vacnacy, this gives F

centre, which is antiparamagnetic. A V^- centre is created when univalent oxygen is trapped with one anion hole, it is paramagnetic. A V centre is when two anion holes around one cation vacancy trap one univalent oxygen ion respectively, which has an antiparamagnetic property.

Table 1

The effect of dose on the value of N_x (Al_2O_3)

Dose / kGy	7	21	42	63	84
N_x / $10^{17}eg^{-1}$	1.02	1.42	1.47	1.70	1.37

Table 2

The effect of dose on the value of N_x (MgO)

Dose / kGy	7	21	42	63	84
N_x / $10^{17}eg^{-1}$	1.57	1.67	2.27	2.72	2.59

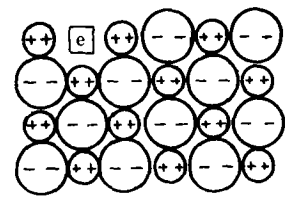

Fig.9 F_s^+ centre of irradiated polycrystal of metal oxides

Meaning of symbols in Fig.9 is as same as those in Fig.8

Table 3

The effect of temperature on value of N_x (Al_2O_3)

T / °C	N_x / $10^{17}eg^{-1}$	Note
25	2.55	
37	2.51	Reduced by 1.5 % compared with 25 °C
70	2.38	Reduced by 6.67 % compared with 25 °C

Table 4

The effect of storage time on value N_x (Al_2O_3)

Time / d	N_x / $10^{17}eg^{-1}$	Note
0	1.71	
8	1.51	Reduced by 11.7 % after 8 days
30	1.47	Reduced by 14.04 % after 30 days

Table 5

The value of N_x in irradiation of Al_2O_3 or MgO in the mixture solvents

System of samples	N_x / $10^{17}eg^{-1}$
Al_2O_3 + CH_2Cl_2 - H_2O	2.01
Al_2O_3 + $CHCl_3$ - H_2O	1.59
Al_2O_3 + CCl_4 - H_2O	1.36
MgO + CH_2Cl_2 - H_2O	1.31
MgO + $CHCl_3$ - H_2O	1.21
MgO + CCl_4 - H_2O	0.98

So we suggest that the signals appearing on the ESR spectrum can only be caused by F^+ or V^- centres, and that they may be the active points of graft initiation. In the irradiation of polycrystal oxides, the chance of forming F^+ centres at the surface increases with time. This F^+ centres at the surface (named F_s^+ centre) is quite different from that of the interior, it has good thermal stability, and plays a main role in catalysting reaction and absorption process. (Fig.8, 9).

By the tests of the value of N_x changed with temperature and stability of storage at room temperature; they show that the ESR signals slowly decrease with temperature, also with the time of storage (Table 3,4).

Under pre-irradiation and mutual irradiation methods, the grafting reactions

were activated by small molecular compounds. Three mixed solvents of CH_2Cl_2, $CHCl_3$, CCl_4 with H_2O by the ratio 2:3 were made, then Al_2O_3 or MgO were added into them under mutual irradiation respectively. The calculated value of N_x are given in Table 5.

From Table 5, it can be seen that the value of N_x increases with the hydrogen concentration in small molecules. We consider that the atoms H delivered from the radiolysis of CH_2Cl_2, $CHCl_3$ *etc* are very active. It may be with certain excited state. It may combine with V^- centre to form OH^- ($H + O^- \longrightarrow OH^-$) and then eliminate the V centre. On the other hand, F_s^+ centres easily capture the active H to form excited particles of F_s^+ (H) type and then surface vacancies of oxygen ions will be increased. Further trapping of free electrons will form new F_s^+ centres and then increase the number of active points. Therefore it could be concluded that the defects of F^+ and V^- centres in the radiation of inorganic oxides are active points for initiating grafting reactions. If the compound contains hydrogen the V^- centre will be eliminated and the F_s^+ centre will be excited, so that the graft yield will greatly enchanced. The addition of active small molecules to the grafting system and the mechanism of that enhancement of the process is an attractive area for further study.

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