UV-absorption and thermal properties of Pb-doped glymo/damo-derived coating materials prepared by sol–gel process

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Organically modified silanes referred to as ORMOSILS are new type of organic–inorganic hybrids, in which the inorganic backbone can be formed by a low-temperature process and organic groups can be modified easily by sol–gel process. These hybrid materials were proposed more than 20 years ago by Philips and Schmidt [1] and have been intensively developed during the last few years, especially for optical applications [2–5]. Ordinary glass transmits an important part of UV light (such as UVB at 280–320 nm and UVA at 320–400 nm) which is dangerous to man [6]. Transition-metal salts added to starting solution provide an inorganic network containing metal ions and entrapment of these ions are very effective for decreasing the transmission property of the glass in these wavelength regions [7, 8]. In this work, a new glass coating composition containing γ-glycidyloxypropyltrimethoxysilane (GLYMO)/3-(2-aminoethylamino)propyltrimethoxysilane (DAMO)/lead(II)nitrate was prepared by sol–gel process. After coating an ordinary glass with this coating system, lower transmissions were obtained in the UV regions. GLYMO/Pb (1/0.1 and 1/0.01 mol/mol) compositions were also examined, but gelation occurred after addition 0.1 mol of Pb into GLYMO solution. When Pb^{2+} was decreased to 0.01 mol, gelation was not observed, but UV adsorption of this coating was not different from uncoated glass until thermal treatment up to 350 °C. Therefore, GLYMO/DAMO/Pb composition was selected as coating material for glasses and the coated glasses were thermally treated up to 500 °C. GLYMO, DAMO and lead nitrate were used as they were received. The coating compositions were prepared from hydrolyzed GLYMO (H_2O/GLYMO:3, mol/mol), DAMO (H_2O/DAMO:3, mol/mol) and lead nitrate solution (GLYMO:DAMO:Pb: 1:1:0.1, 1:1:0.01, 1:0.5:0.1 and 1:0.5:0.01, mol/mol) and they are referred hereafter as $GDP_{0.1}$ and $GDP_{0.01}$, $GD_{0.5}P_{0.1}$ and $GD_{0.5}P_{0.01}$. GLYMO and DAMO were hydrolyzed without using any solvent and catalyst by adding 3 mol of water per mole of each silane. The mixture was stirred at ambient temperature; a clear and homogeneous solution was formed. Alcohol formed by the reaction of hydroxyl group of water and the methoxy group of GLYMO or DAMO was removed under vacuum. Hydrolyzed DAMO was more viscous than hydrolyzed GLYMO. Hydrolyzed GLYMO and DAMO were diluted with dried *n*-propanole (10%, w/w), separately. The diluted GLYMO solution was divided into four portions. The hydrolyzed DAMO was added into the each portion at 1:1 and 1:0.5 ratios per mole of GLYMO. They were stirred for 2 h and then $Pb(NO_3)_2$ solution was added to these mixtures to prepare GD_xP_y (x: 0.5 or 1; y: 0.1 or 0.01) coating compositions. After further stirring for 2 h at room temperature surfaces of glasses were coated by dip coating technique. The coated glasses were treated at 80, 100, 200, 250, 300, 400 and 500 °C for 1 h in air atmosphere. Thermal characteristics of hybrid materials were determined using a Schimadzu System-50 model thermal analyzer. UV-light transmittance of coated and uncoated surfaces was measured by a Jenway 6105 model UV/VIS spectrophotometer. Surface morphologies were monitored by a LEO EVO 40 model scanning electron microscope (SEM).

All coatings were colorless under 150 °C. They turned to light yellow color at 150–200 °C, to dark yellow at 200–250 °C and they became light brown at 250–300 °C. A dark brown color was observed at 300–400 °C. After 400 °C, coatings were transparent and colorless.

Briefly, UV light absorption increased with the addition of DAMO and Pb^{2+} into the hydrolyzed GLYMO solution. For example, optical transmission of the glass coated with $GD_{0.5}P_{0.01}$ showed a big difference from the glass coated with $GD_{0.5}P_{0.1}$. Fig. 1a and b show optical transmittance spectra of the glasses coated with

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$GD_{0.5}P_{0.1}$ and $GD_{0.5}P_{0.01}$, which were treated at 200–400 °C.

In Fig. 1a, UV light transmission begins to decrease with increasing temperature. It was observed that the transmittance was 75, 70 and 52% at 80, 100 and 200 °C, and 43% at 250, 300, 350, 400, 450 and 500 °C at 350 nm, respectively. When 400 nm wavelength was considered, optical transmittance of the coated glass was as 80, 77 and 67% at 80, 100 and 200 °C respectively, and was 60% at 250, 300, 350, 400, 450 and 500 °C. The UV-absorption edge gradually shifted towards higher wavelength (red shift) with increasing Pb-concentration. The maximum optical transmittance was found as 80% at 400, 454, 520, 560, 580 and 600 nm. The UV light transmittance of this film changed from 42 to 59% when the wavelength changed from 350 to 400 nm. Thus, it can be suggested that these coated glasses are suitable for absorption of the UV light. Fig. 1b shows the changes in the optical transmittance of glass coated with $GD_{0.5}P_{0.01}$ sols. Results indicated that heat treatment gives rise to small changes in transmittance, whereas increase in Pb^{2+} concentration causes a decrease (Fig. 1a). The red shift in the UV-absorption edge of the glass coated with Pb-doped coating composition may be the result of the absorption of UV light by Pb^{4+}. Better results were observed when DAMO concentration was increased from 0.5 to 1.0 and Pb^{2+} concentration was decreased from 0.1 to 0.01 in the ratio (Fig. 2a and b).

The glasses coated with $GDP_{0.1}$ and treated at 200 °C showed almost no transmission property (Fig. 2a). Transmittance was 2 and 10% at 370 and 400 nm, respectively. The maximum transmittance of 80% was observed at 550 nm. This may be attributed to the electron transition between Pb^{2+} and Pb^{4+}. Electron transitions can also occur between unpaired electrons on N atoms of amine groups of DAMO. The UV light transmission values of the glass coated with $GDP_{0.1}$ at 100 °C were 350/18, 400/47, 450/75 and 500/85 [λ (nm)/T(%)]. The same results were obtained for the glasses coated with $GDP_{0.01}$ (Fig. 2b). Cracks started to form on the coating prepared from $GDP_{0.1}$ after 250 °C. It was found that $GDP_{0.01}$ coated glass surfaces have more heat-resistance and they are more transparent than $GDP_{0.1}$ coated surfaces, suggesting that it is possible to develop a coated glass by using $GDP_{0.01}$ with a maximum transmission of about 80% at 550 nm.

Fig. 3a and b show SEM photomicrographs of $GDP_{0.01}$ coated glass surface and treated at 100 and 200 °C, respectively.

The SEM photomicrographs show that the surface of the $GDP_{0.01}$ coated glass heated at 100 °C (Fig. 3a) is very porous and the surface becomes uniform by increasing the temperature to 200 °C (Fig. 3b). This difference may be due to the homogenous dispersion of organic and inorganic matrix in each other.

Thermal stability of $GDP_{0.1}$, $GDP_{0.01}$, $GD_{0.5}P_{0.1}$ and $GD_{0.5}P_{0.01}$ hybrid coating materials was determined using TGA and DTA analysis (Figs. 4 and 5).

TABLE I Weight loss stages of solid samples depending on temperature

Sample	Temperature (°C)	Weight loss (%)	Total weight loss (%)
$GD_{0.5}P_{0.01}$	Before 360	8	57
	350–480	25	
	480–510	7	
	510–900	17	
$GD_{0.5}P_{0.1}$	Before 220	3	56
	210–300	7	
	300–370	12	
	370–640	18	
	640–910	16	
$GDP_{0.01}$	Before 300	7	70
	300–450	22	
	450–476	8	
	476–510	11	
	510–19	7	
	519–905	15	
$GDP_{0.1}$	Before 270	6	60
	270–437	23	
	437–473	7	
	473–740	24	

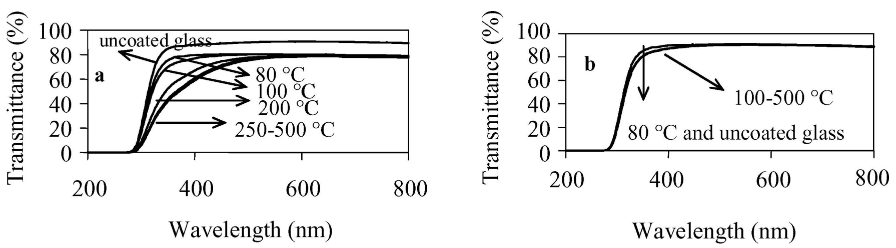

Figure 1 UV transmission spectra of the coated glass slides with $GD_{0.5}P_{0.1}$ (a), and $GD_{0.5}P_{0.01}$ (b) heat treated at 80–500 °C.

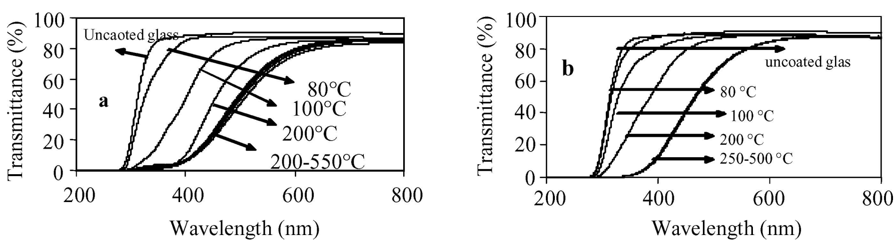

Figure 2 Transmission spectra of the coated glass slides with $GDP_{0.1}$ (a), and $GDP_{0.01}$ (b), heat-treated at 80–500 °C.

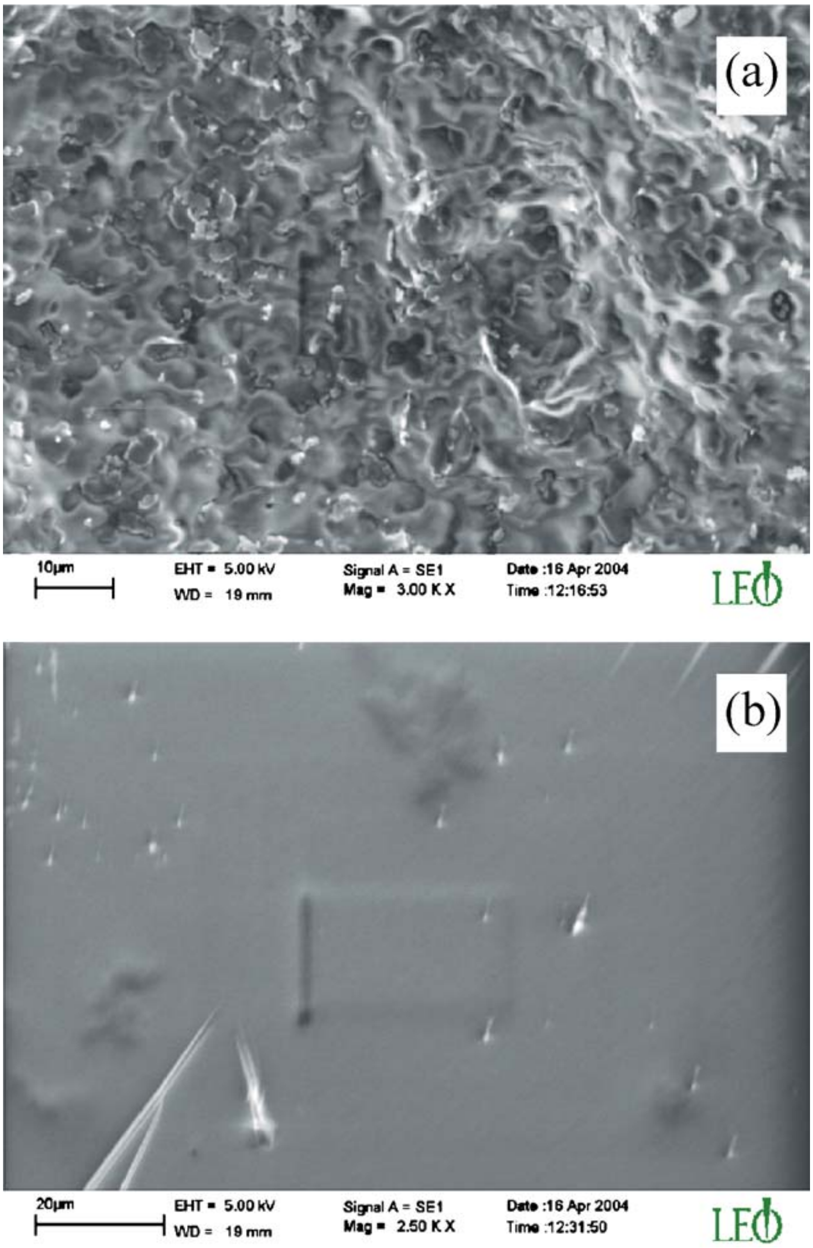

Figure 3 SEM photomicrographs of thermally treated coating materials at 100 °C (a) and 200 °C (b).

Before the thermal analysis, powders of hybrid coating material were prepared. For this purpose, the coating solution was poured into a Petri dish and dried at 80–100 °C in a sterilizer, with a heating rate of 5 °C/min for a day. As seen from Fig. 4, there are four stages of weight loss for $GDP_{0.1}$ and $GD_{0.5}P_{0.01}$, while there are five and six stages of weight loss for $GDP_{0.01}$ and $GD_{0.5}P_{0.1}$, respectively. These stages are briefly listed in Table I.

Below 350 °C, weight losses may be resulted from evaporation of water and organic solvents, and thermal decomposition of organic groups. Between 350 °C and 910 °C, weight loss is attributed to carbonization, further combustion of organic groups and condensation of Si—OH groups in Si–O–Si network. Maximum weight loss of $GD_{0.5}P_{0.01}$ is almost equal to that of $GD_{0.5}P_{0.1}$. The temperature where maximum weight loss was observed (T_{max}) for $GD_{0.5}P_{0.1}$, shifts toward high temperatures and this was caused by the higher Pb concentration in $GD_{0.5}P_{0.01}$. Maximum weight loss of

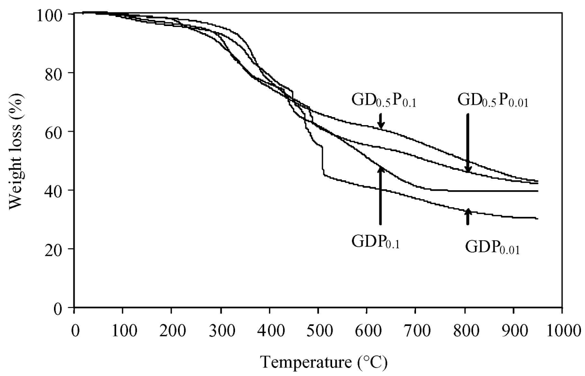

Figure 4. TGA curves of the samples $GDP_{0.1}$, $GDP_{0.01}$, $GD_{0.5}P_{0.1}$ and $GD_{0.5}P_{0.01}$.

$GDP_{0.01}$ is higher than $GDP_{0.1}$. $GDP_{0.01}$ has lower Pb concentration than $GDP_{0.1}$. Therefore, the thickness of film will be lower after heat treatment at high temperatures. The results suggest that SiO_2-PbO film may be obtained by a thermal treatment at 400 °C or 500 °C.

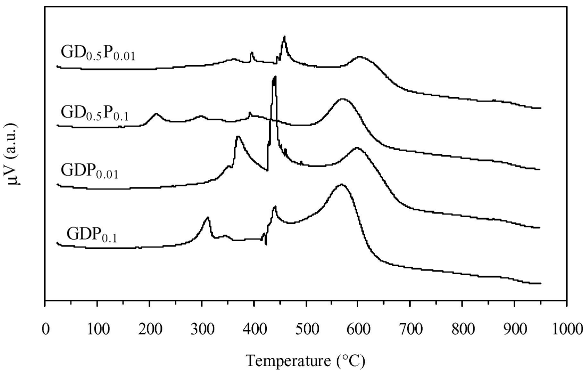

Figure 5. DTA curves of the samples $GDP_{0.1}$, $GDP_{0.01}$, $GD_{0.5}P_{0.1}$ and $GD_{0.5}P_{0.01}$.

Since the weight loss is caused from the removal of organic groups, the coating material with high DAMO content has higher weight loss values compared to the other sample. Experimental results are consistent with theoretical predictions. For $GD_{0.5}P_{0.1}$ and $GD_{0.5}P_{0.01}$, the weight loss was about 56–57%, while it was 60 and 70% for $GDP_{0.1}$ and $GDP_{0.01}$, respectively. Increase in Pb content, decreases the total weight loss upon thermal treatment. Since thermal treatment has no effect on the inorganic groups, the weight loss of $GDP_{0.1}$ is smaller than $GDP_{0.01}$. The same argument is also valid for $GD_{0.5}P_{0.1}$ and $GD_{0.5}P_{0.01}$.

DTA curves show that all the reactions, which cause formation of inorganic network, are exothermic. Sharp exothermic peaks appeared at temperatures where the maximum weight loss was observed. Exothermic peaks observed at temperatures from 220 °C to 570 °C can be attributed to evaporation of water and decomposition of organic groups. Wide exothermic peaks observed after these temperatures can be attributed to condensation of inorganic groups into Si–O–Si networks. These wide peaks appear at higher temperatures for the samples with less Pb content. This is an expected result, because these hybrids form more Si–O–Si network depending on the amount of organic groups.

In conclusion, a coating composition was developed for UV-absorption applications. UV-transmission of ordinary glass was lowered to 2 and 10% at 350 and 400 nm, respectively, by using $GDP_{0.1}$ hybrid material. Because of its surface morphology, $GDP_{0.01}$ is better than $GDP_{0.1}$. 18 and 47% transmissions were obtained at 350 and 400 nm for $GDP_{0.01}$, respectively. DAMO content is also effective on UV-absorption property. With 50% decrease in DAMO concentration, only 50–75% transmittance was obtained on the glass surface. Results showed that $GDP_{0.01}$ can be successfully utilized in UV-absorption applications.

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