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The Synthesis and Applications of Cr-Doped GLYMO and GLYMO/DAMO Surface Coating Systems for Absorbing UV-light by Sol-Gel Process

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A new glass coating system, containing γ-glycidoxypropyltrimethoxysilane/Cr^{3+} (system I:GLYMO/Cr^{3+}) and γ-glycidoxypropyltrimethoxysilane/N-aminoethyl-3-aminopropyltrimethoxysilane/Cr^{3+} (system II:GLYMO/DAMO/Cr^{3+}), was synthesized by the sol-gel technique for UV light absorption applications. UV-visible spectroscopy (UV-VIS) was utilized to investigate the optical properties of coating materials. Especially system II showed very low transmission in the UV wavelength regions (300–400 nm) after thermal treatment of the coated surface. The UV transmission property of surfaces did not change at 80, 100, 450 or 500 °C, but a T value as low as 0.07% was obtained between 150 and 450 °C.

Key Words: Sol-gel technique, coating, optical properties, GLYMO.

Introduction

Ordinary glass is not suitable for optical applications since it has low flexibility, high brightness and a high process temperature. In addition, it transmits an important part of the UV-light (300-400 nm), which causes damages in the human system[1]. However, the addition of polymer-based optical materials, e.g., PMMA, polystrene or organic modified silane, onto the surface eliminates these disadvantages.

Various TiO_2-M_aX_b (M_aX_b: soluble salts of transition metals such as Ni, Pb, Ta) coating compositions have already been developed as a coating system and they have been found to be very effective for decreasing the transmission property of ordinary glass between 300 and 400 nm [2,3]. Apart from these binary TiO_2-M_aX_b systems, different coating systems have also been developed by the sol-gel technique using a TiO_2-CeO composition, but the coated surfaces have shown relatively low transmission in the visible region[3]. It is known

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that the UV absorption property of coated glass is affected by heat treatment, the type and concentration of metal ions and/or organic modified silanes[4].

The sol-gel technique is a low temperature method that has been successfully utilized to prepare optical materials by incorporating different cations or molecules in a silica host[5,6]. The advantages of the sol-gel technique come from the uniformity of chemical compositions in the final product and the low contamination caused by its preparation process. The relatively low temperature allows the incorporation of large numbers of inorganic and organic additives into the material[7]. Soluble salts of transition metals have mostly been used to incorporate metal ions in the SiO_2 network[8]. Chromium has long been chosen as a coloring agent in glass, but the limited solubility of chromium oxide in glass has restricted its application. Chromium ions are very interesting for optical spectroscopy and laser physics[9]. For example, Cr^{3+} in inorganic glasses is an active medium for tunable solid-state lasers[10] and a sensitizer of Nd-lasers[11]. Therefore, chromium has been incorporated in the SiO_2 network by the sol-gel technique and several optic-spectroscopic studies have already been reported[9,12−14]. The best known organofunctional alkoxysilane is γ-glycidoxypropyltrimethoxysilane (GLYMO) and it is used as a SiO_2 source. γ-Glycidoxypropyltrimethoxysilane modified ormosils have found usage in a variety of applications and these applications have been reported by various researchers. Chu et al. found that GLYMO could be used as a binder in colloidal silica coatings, leading to increased density, higher film thickness, and improved adhesion to polymer substrates[15]. Schmidt found that inorganic-organic nanocomposites prepared from epoxy-functionalized silanes act as hard coatings on polymers, and scratch-abrasion resistant coatings can be obtained on glass[16]. Que and Hu have synthesized highly transparent, dense and pore-free films from hybrid materials containing γ-glycidoxypropyltrimethoxysilane/titania and methyltrimethoxysilane for optical waveguides[17]. Furthermore, TiO_2-CeO_2 and TiO_2-PbO systems have been prepared by Kundu and Mukherjee[4] for the deposition of coatings on ordinary glass by the sol-gel technique to absorb UV radiation and achieve maximum transmission in the visible wavelength region.

In this work, primrose yellow and dark yellow coating solutions were synthesized by adding Cr^{3+} ion to prehydrolyzed GLYMO and GLYMO/DAMO mixtures, and they were incorporated onto microscope slide glass surfaces by dip coating. The effects of Cr^{3+}, DAMO concentrations and thermal treatment temperature on the UV light absorption properties of coated glass surfaces were investigated using UV/VIS spectroscopy.

Experimental

Chemicals

$\gamma-$ Glycidoxypropyltrimethoxysilane (GLYMO, Fluka), [3-(2-ethylaminoethyl)amino)-propyl]trimethoxysilane (DAMO, Aldrich), and chromium(III) chloride hexahydrate (Merck) were used as received. n-Propyl alcohol (Riedel) was used as solvent after drying over molecular sieves (Fluka, 3ÅXL8) for 1 day. Microscope slide glasses (2.5 x 7.5 cm) were cleaned with acetone and dried at 80 °C before coating.

Apparatus

The optical properties of coated and heat treated (at between 80 °C and 500 °C) microscope slide glass surfaces were investigated using a Shimadzu 1601 model UV/VIS spectrophotometer at wavelength regions between 200 and 800 nm.

Procedure

The procedure for the synthesis of surface coating solutions is shown in Figure 1.

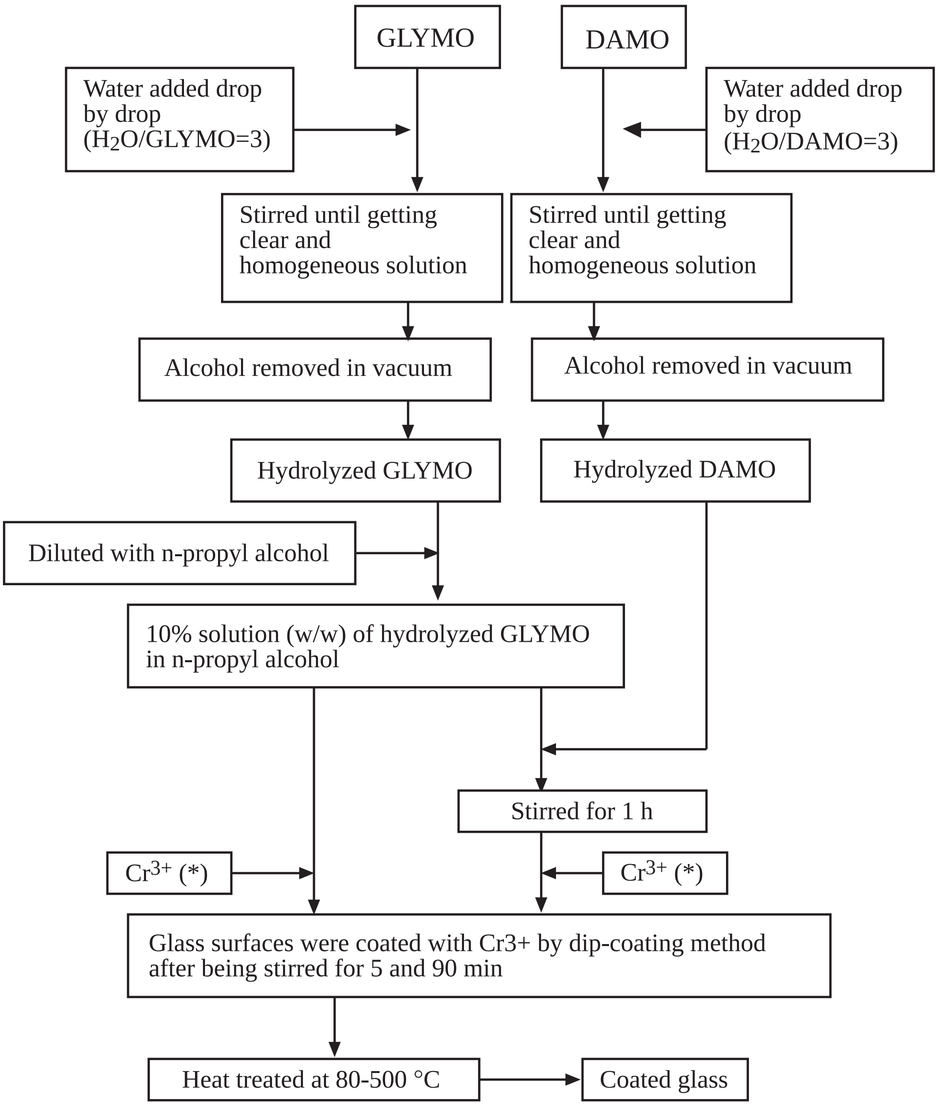

Figure 1. The procedure for the synthesis of surface coating solutions and coating glass surface.

(*): 5 and 10 ppm (5 mL) solutions of Cr^{3+} ions prepared from $CrCl_3.6H_2O$ were added into hydrolyzed silane solutions.

The coating systems I and II were synthesized as shown in Figure 1. Gelation occurred after 60 min for system IIb(5), while system I and system IIb(10) stayed as a homogeneous and transparent solution after this period. UV measurements showed that a change in Cr^{+3} concentration does not have an important effect on the UV-light absorption of coating system I. Therefore, only the 10 ppm Cr^{+3} concentration was studied during the experiments.

Coating system II was prepared as 2 separate systems by keeping GLYMO and Cr^{+3} concentration constant and changing DAMO concentration in system I. Coating system IIa consisted of a GLYMO/DAMO/Cr^{+3} mixture in 1/0.5/5 ppm and 1/0.5/10 ppm concentrations, while system II b were contained GLYMO/

DAMO/Cr^{+3} mixtures in 1/1/5 ppm and 1/1/10 ppm ratios. These systems labeled as system IIa(5), system IIa(10), system IIb(5) and system IIb(10), respectively. Since the gelation occurred after 60 min while preparing the system IIb(5) coating solution, the experiments were carried out with system IIb(5) after 5 min agitation time.

Results and Discussion

Figures 2a and b show the UV-transmission of the coating system prepared by the addition of Cr^{+3} (10 ppm, 5 mL) into GLYMO solution after 5 min and 90 min agitation periods, respectively.

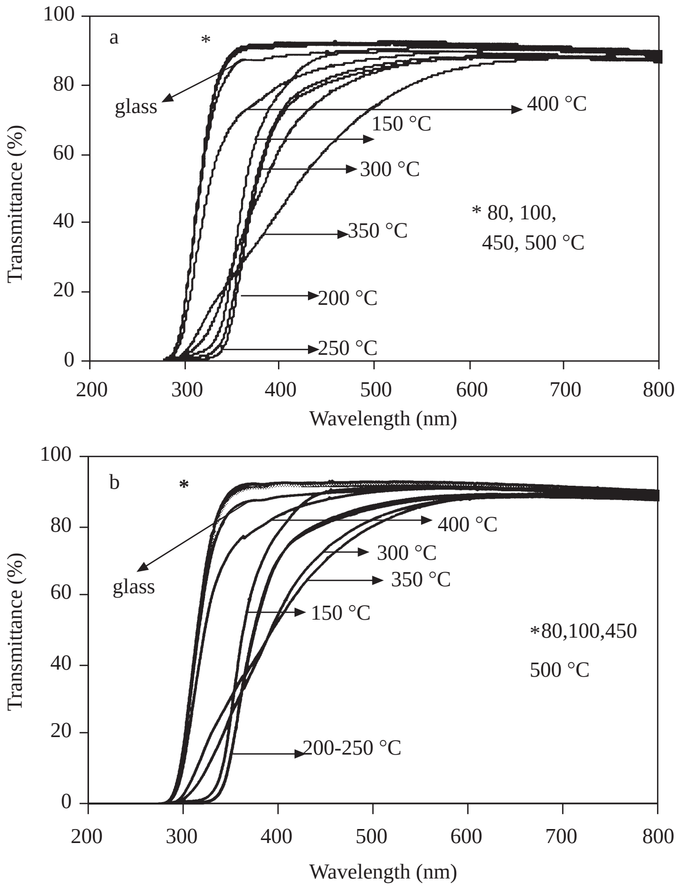

Figure 2. UV transmission of coating system prepared by addition of Cr^{+3} (10 ppm, 5 mL) a) after 5 min agitation b) 90 min agitation.

The results show that agitation time has no significant effect on the UV-light absorption of coating systems, either. A 22.5% decrease in UV transmission (between 375 and 400 nm) was obtained after 90 min agitation and thermal treatment at 350 °C. At 80, 100, 450 and 500 °C, the UV absorption of the coated glass was similar to that of uncoated glass.

Since the glass surface is coated with a transparent thin film and Cr^{+3} ion is in its main oxidation state, UV transmission is high at low temperatures (e.g., 80 and 100 °C). Above 450 °C, the percentage of Si-O-Si bonds in the structure increases and UV-light absorption decreases with separation of the organic group in the network. Colorless surfaces, which were observed between 200 and 400 ^{o}C, may be caused by the oxidation of Cr^{+3} to Cr^{+6} (or Cr^{+5}). Above this temperature, Cr^{3+} ion returns to its main oxidation state (Cr^{+3}) and charge transfer does not occur at this temperature. The colorless coating obtained at this temperature supports this observation. Agitation time has no effect in this temperature range. Only a 2-4% decrease in UV-light transmission is observed after 90 min agitation between 250 and 300 °C. The transmission increases systematically from 250 to 350 °C. The lowest transmission is obtained for the samples thermally treated at 350 °C (T% = 34). However, this coating shows low transmission in both UV and VIS regions. The samples thermally treated at 200 and 250 °C have considerably low transmission in the UV region and they show maximum transmission in the visible region. Therefore, they seem to be the best coating material for UV-light absorption applications. We think that the observed yellow color and high UV-light absorption under 420 nm is due to the Cr^{+3} complex in an octahedral environment. This complex exhibits 2 nicely localized absorption peaks corresponding to $^4A_{2g}$-$^4T_{2g}$ and $^4A_{2g}$-$^4T_{1g}$ transitions. In this geometry, the first allowed band seems to appear as a result of $^4A_{2g}$-$^4T_{2g}$ transition but the term $^4T_{1g}$ is lying close to $^4T_{2g}$, which leads to a shuffling between $^4T_{1g}$ and T_{2g}. The change in the coating's color and high UV-light absorption after 250 °C may also arise from a change in the oxidation state of Cr ion from +3 to +6 (or Cr^{+5}). Cr^{+6} (or Cr^{+5}) turns into Cr^{+3} after 400 °C and the coating becomes colorless again. This leads to a decrease in UV-light absorption.

Figures 3a and b show the UV-light transmission of the glass coated with system IIa(5) after 5 min and 90 min agitation, respectively.

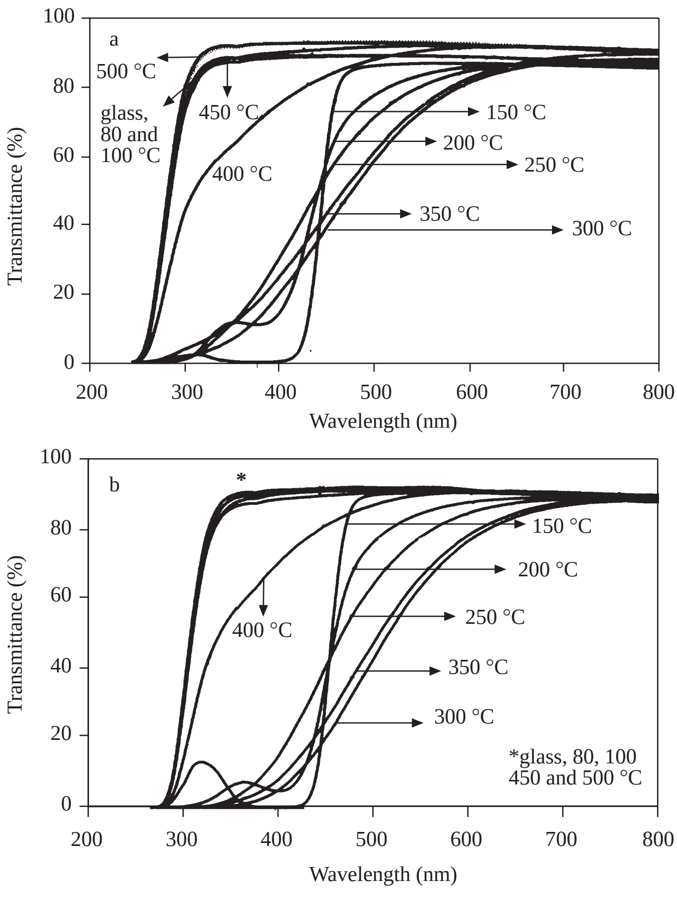

Figure 3. UV-light transmission of the glass coated with system IIa(5) after 5 min (a) and 90 min (b) agitation.

The results indicate that no significant changes are observed using long agitation at 80, 100, 400 or 500 °C and these surfaces have the same UV-light transmission as the uncoated glass surface at all wavelengths. At 80 and 100 °C, UV-light transmission is 87% after 5 min agitation and it reaches 91% after 90 min (at 400 nm). Between 150 and 400 °C, agitation time seems to affect the UV-light absorption of the coated surfaces. The transmission is 1.84% at 325 nm for 5 min and it reaches 13% for 90 min agitation. Transmission takes relatively low values at 375 and 400 nm and they are 0.43% and 0.15% for 5 min agitation, respectively. For 90 min agitation, they are equal to 0.5% and 0.07% at corresponding wavelengths. Transmission increases again with the increase in wavelength from 475 to 500 nm and it remains constant after this point. At 500 nm, transmission takes 84% and 90% values for these agitation periods, respectively.

In the UV region, transmission of the coated glasses, which are thermally treated at 200, 250, 300 and 350 °C, is considerably small compared to the surfaces thermally treated at 150 °C for both agitation times. Coating materials with minimum transmission in the UV region and maximum transmission in the visible region can be obtained by the addition of DAMO to system I [system IIa(5)] after thermal treatment at 150 °C. If 200 and 250 °C are considered, system IIa(5) is more convenient for UV absorption applications. Maximum absorption is observed between 300 and 400 nm and reaches a minimum value after 425 nm.

Maximum absorption between 300 and 400 nm and minimum absorption after 425 nm may be due to 3 reasons: 1. Cr^{+3} ion is arranged in an octahedral geometry and allowed transition for Cr^{+3} ion can be $^4A_{2g}$-$^4T_{2g}$ or $^4A_{2g}$- $^4T_{1g}^{24}$, 2. Change in the oxidation state of Cr ion from +3 to +6 (or +5) and 3. n→ $\sigma*$ transition of unpaired electrons on amine groups. Transmission reaches a maximum in all wavelengths after 400 °C. This arises from the formation of an inorganic network (Si-O-Si) by the removal of organic residues. Since the oxidation state of Cr changes from +6 to +3, the yellow coating becomes colorless and transparent again after 450 °C.

Figure 4 shows the UV/VIS-light transmission of the glass coated with sytem IIa(10) after 5 min (a) and 90 min (b) agitation, respectively.

When Cr^{+3} concentration increased to 10 ppm in system IIa, the same transmissions as for uncoated glass are obtained at 80, 100, 450 and 500 °C. However the transmission values change considerably between 150 and 400 °C. UV spectra show that 150 °C is the optimum treatment temperature for the most appropriate coating. Minimum UV and maximum VIS-light transmission are observed only at this temperature. However agitation time also has some effect at 150 °C. For 90 min agitation, there are 36% and 24.2% increases in UV-light transmission at 300 and 325 nm wavelengths, respectively. UV transmissions take the following values at 425, 450 and 475 nm for 5 and 90 min (5 min /90 min; % T): 6.8/1.4, 35/26.1 and 80.1/82.

After these wavelengths, the coating obtained after 90 min agitation shows 5% more transmission than after 5 min agitation. The surfaces thermally treated between 200 and 400 °C show low transmission in both UV and VIS-light regions. The wavelengths that show maximum transmission for 5 and 90 min agitation are shown in Table 1 between 150 and 400 °C.

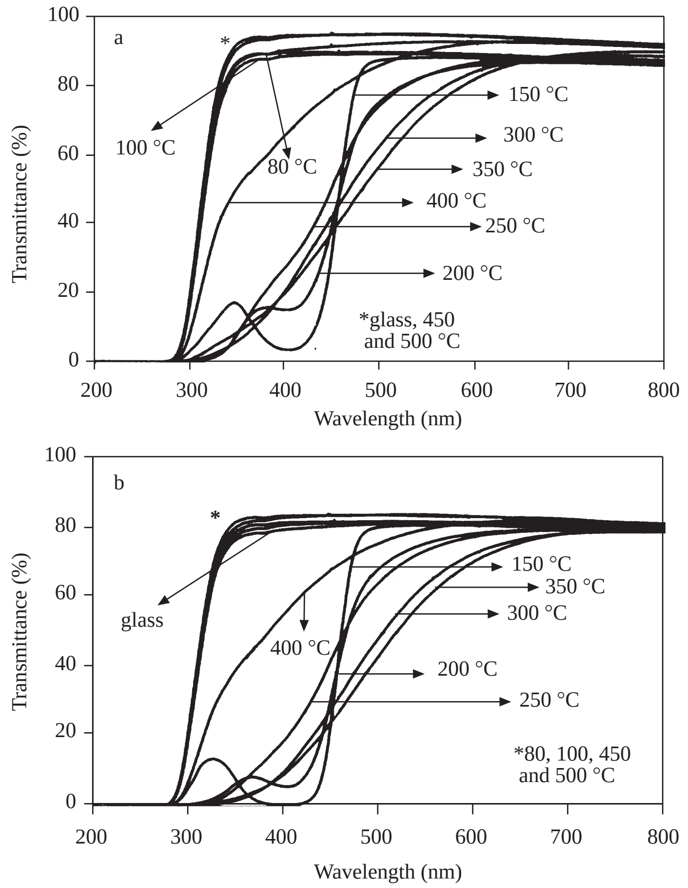

Figure 4. UV-light transmission of the glass coated with system IIa(10) after 5 min (a) and 90 min (b) agitation.

Table 1. Wavelengths that show maximum transmission for 5 and 90 min agitation between 150 and 400 °C.

Temperature (°C)	Wavelength (nm)	Transmission (%, 5 min/90 min)
150	475	80/82
200	500	74.4/75.82
250	525	78.3/77.6
300	550	75.5/71.1
350	550	71.5/66.5
400	425	77/69

According to these results, the coating material with minimum UV and maximum VIS-light transmission is obtained at 150 °C with a 10 ppm Cr^{+3} concentration. Cr^{+3} concentration is not important for 90 min agitation and the coatings obtained in both concentrations are appropriate for UV-light absorption. The color change, which is caused by previously indicated results, is observed for this coating system also.

Figure 5 shows UV/VIS light transmission of the glass coated with system IIb(5) after 5 min agitation.

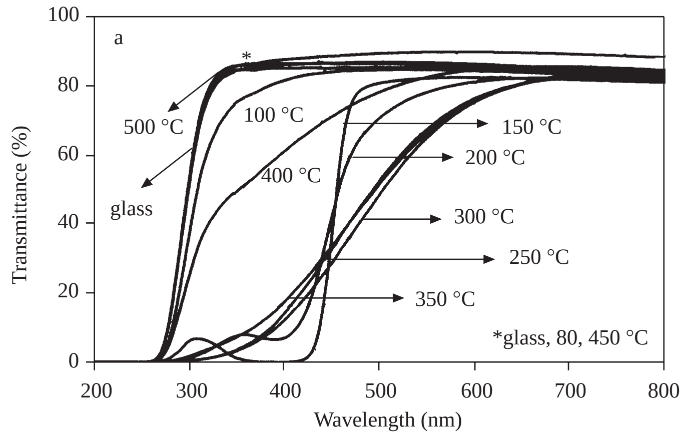

Figure 5. UV/VIS-light transmission of the glass coated with system IIb(5) after 5 min.

According to Figure 5, UV and VIS light transmissions are very low at 250, 300 and 350 °C. The maximum transmissions are observed at 550 nm and they are equal to 66%, 64% and 65% at the indicated temperatures. The surfaces, which were thermally treated at 150 and 200 °C, have better UV absorption than the surfaces thermally treated at other temperatures. Since the minimum UV and maximum VIS-light transmissions are obtained at 150 °C, this temperature can be considered optimum for system IIb(5).

It was indicated before that 90 min agitation gives better UV absorption results than 5 min agitation at 150 °C for system IIa(5). These results are summarized in Table 2 in comparison with system IIb(5).

Table 2. Transmissions of system IIa(5) and b(5) coated glasses at 150 °C.

λ (nm)	T% System IIb (5) (5 min)	T% System IIa (5) (90 min)
300	2.07	4.90
325	6.68	13.10
350	3.44	6.11
375	0.48	0.50
400	0.09	0.07
425	0.33	0.50
450	12.45	23.21
475	70.30	81.77
500	81.10	89.38
525	82.43	89.95
550	83.10	90.15
575	83.40	90.20
600	83.50	90.16

According to these results, transmission is low at almost all wavelengths for system IIb(5), which has a higher DAMO concentration. In this system, the number of amine groups around Cr^{+3} increases with increasing DAMO content. Therefore the number of unpaired electrons that cause n $\rightarrow$ σ^* transition is higher than in system IIa(5). Thus, the surfaces show considerably better UV absorption at 150 and 200 °C. The VIS-light transmission of system IIb(5) is lower than that of system IIa(5) at 150 °C, because the defects in the network increase with the increasing number of -O-C-O, -C-N-C and –Si-C bonds at this temperature.

Figure 6 shows the transmissions of the surfaces coated with system IIb(10) after 5 and 90 min agitation.

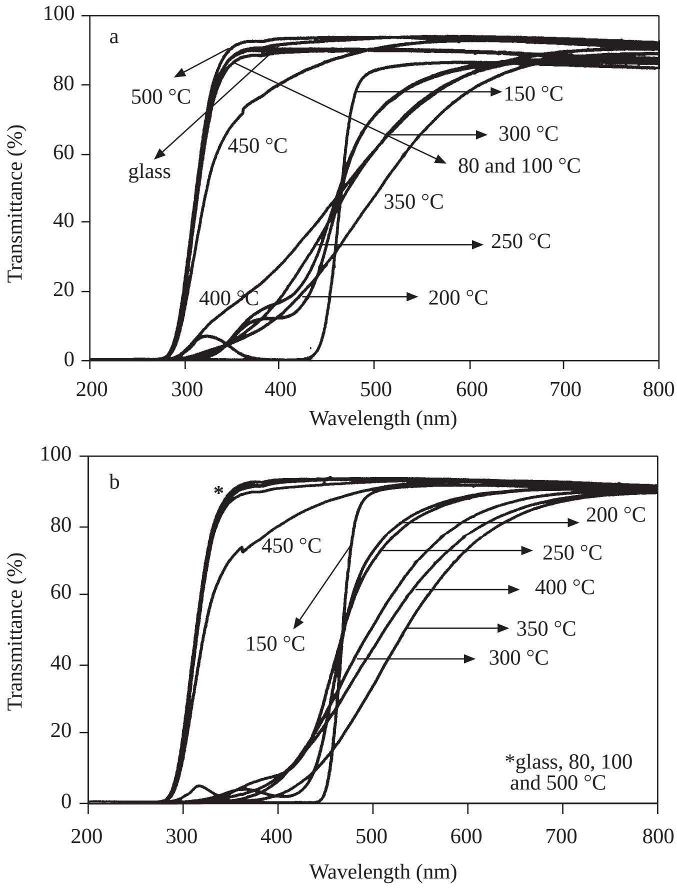

Figure 6. UV/VIS-light transmission of the glass coated with system IIb(10) after 5 min (a) and 90 min (b) agitation.

System IIb(10) is homogeneous at all agitation times and there is no gelation. The coatings are colorless and their transmission is similar to those of ordinary glass at 80, 100, 450 and 500 °C. However, the transmission of the coating changes dramatically between 150 and 450 °C. For 90 min agitation, UV transmission reaches the lowest values in this temperature range. VIS-light transmission (475 nm) is maximum only at 150 °C treatment temperature for 90 min agitation. This behavior can be seen at 200 °C, but it is small compared to that at 150 °C. If 475-550 nm is considered the most sensitive wavelength for the human eye, 150 °C treatment temperature and 90 min agitation are the most appropriate reaction conditions for UV-light absorption. Table 3 shows the observed color of the coating systems according to their treatment temperatures.

Table 3. Observed color of coating systems according to their treatment temperatures.

Temperature (°C)	Observed Color
150	Transparent
250	Light Yellow
250-400	Dark Yellow
<400	Transparent

Conclusion

In this study, functional silanes containing epoxy and amino groups were used in combination to prepare a new coating system. As a starting material, this coating system was new in the literature and its UV-light absorption property was investigated. Except for system I, all coating systems showed good absorption. All glass surfaces were stable for a long time and there was no change in adsorption with instant temperature changes. For example, the same UV-measurement results (% T) were obtained for system IIb(10) even after 8 months. The properties of the coating systems are summarized in Table 4 according to their UV- and VIS-light absorption.

Table 4. The summarized properties of coating systems according to their UV- and VIS-light absorption values (%T values were given for 300, 350, 400, 450 and 500 nm, respectively).

Coating system	Temperature (°C)	Agitation time (min)	T%
System I	200 - 250	Not important	0.14/15.58/71.3/80.60/84.51 (for 200 °C)
System IIa(5)	150	90	4.89/6.12/0.073/23.21/89.38
System IIa(10)	150	5	3.37/16.13/3.49/35.21/85.58
System IIb(5)	150-200	5	2.07/3.44/0.09/12.45/81.10 (for 150 °C)
System IIb(10)	150	90	1.66/0.29/0.04/3.54/87.17

The results show that the UV-light adsorption of coated surfaces changes with Cr and DAMO concentrations. If the Cr^{+3} ion concentration is high and the DAMO concentration is low [system IIa(5)], the absorption of the films is good. When the DAMO and Cr^{+3} ion concentrations are both high, the UV absorption of the surfaces is considerably higher [system IIb(10)]. However when the agitation time and treatment temperature are considered, system IIa(10) is the best coating system for UV absorption applications, because the treatment temperature and reaction time are low for this system.

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