Ionic Conduction in Sol-Gel Overcoats for Organic Photoreceptors

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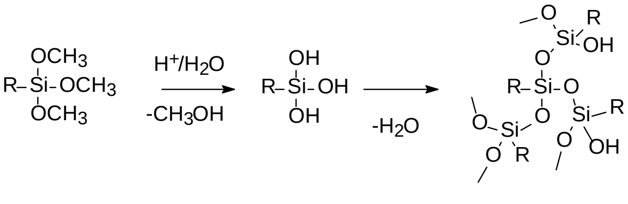
Abstract

Silsesquioxanes are a class of silicone polymers that are useful as abrasion resistant overcoats for organic photoreceptors. We have manipulated the electrical properties of this sol-gel matrix by incorporating a solid electrolyte. Solid electrolytes, also referred to as solid ionic conductors, are materials in which electrical conductivity is provided by the motion of ions. We chose (3-glycidoxypropyl)trimethoxysilane (GPS) as the most suitable commercially available monomer to form the polymer matrix for lithium iodide migration. This epoxysilane contains two ether oxygen atoms for coordination to low lattice energy salts. A good correlation was observed between the level of GPS and the electrical properties of the coating, with increasing concentration of GPS in the silsesquioxane resulting in decreased resistivity. The silsesquioxane is a hard material and the resistivity remained relatively high, between 10^{10}-10^{13} ohm-cm. However, this is a desirable resistivity for maintaining image quality with an overcoated photoreceptor.

Introduction

Silsesquioxanes are a class of silicone polymers that are useful as abrasion resistant overcoats for organic polymers.[1] In general, these overcoats are between 1.0 and 10 microns thick and are coated from aqueous alcohols. They are usually prepared by the hydrolysis and condensation of methyltrimethoxysilane (Scheme 1, R=-CH_3) to form sol-gels.[2] Previous workers have modified the silsesquioxanes by adding charge carriers such as ammonium salts. These modified materials are useful as abrasion resistant overcoats for organic photoreceptors.[3,4]



Scheme 1

We have previously reported improvements in silsesquioxane overcoats for organic photoreceptors. Propyltrimethoxysilane was introduced to make a more flexible sol-gel, and glycidoxypropyl substituted silane was used to complex with lithium iodide to lower the resistivity.[5] Aminosilanes are used as catalysts to cure the silsesquioxane. Characterizations included crosslinking, hardness, brittleness, scratch resistance, surface conductivity, bulk conductivity, and chemical permeability.

Here we discuss two series of silsesquioxanes where increasing levels of (3-gylcidoxypropyl)trimethoxysilane (GPS) was added to reduce the resistivity. The effect of a resistive sol-gel when used as a photoreceptor overcoat is that a residual potential is observed on corona charging followed by light exposure. We have used the magnitude of the residual potential as a means of monitoring the sol-gel resistivity. One series was made from 85-90 wt % methyltrimethoxysilane (MTMS) and was coated on a negatively charging film. The other series had 60 wt % propyltrimethoxysilane (PrTMS) and was overcoated on a positively charging film.

Background

Early patents, primarily from Schank at Xerox, describe the application of crosslinked siloxanol and colloidal silica to form silsesquioxane overcoated photoreceptors.[6] These abrasion resistant layers had been developed by Dow Corning and General Electric to protect polyester and polycarbonate lenses from scratching.[7] Subsequent work at Xerox showed that ammonium salts bound to the silsesquioxane matrix provided a means to control the conductivity of the overcoat.[8] This was followed by the introduction of substituted silanes bearing electronegative moieties as conductive substituents.[9] The increased conductivity allowed the use of thicker silsesquioxane layers without the build up of residual charge on the photoreceptor in the electrophotographic process.

We found it difficult to adjust the charge in a silsesquioxane matrix by adding ammonium salts because they also act as catalysts for the condensation of silanols. The addition of ammonium salts not only increased the conductivity of the overcoat, but also increased the cure of the material. There is a strong relationship between the material properties of the silsesquioxane layer such as brittleness and the amount of cure. Therefore, we sought to develop a silsesquioxane where the conductivity and the cure could be controlled independently. This was accomplished with a silsesquioxane where the conductivity is based on solid electrolyte chemistry.

Solid electrolytes have been prepared by modifying GPS with ethylene oxide moieties.[10] Ionic conduction is facilitated by competitive cation binding with ether oxygens. This results in increased ion diffusion and increased conductivities, $\sigma < 10^{-7}$ ohm^{-1} cm^{-1}. The sol-gel reaction, of hydrolysis and condensation of the alkoxysilane, results in an inorganic-organic copolymer. These ORMOCERs (ORganically MOdified CERamics) have been proposed as mini-batteries, rechargeable systems and electrochromic windows. Another ORMOCER uses aminosilane to form conductive electrodes where the cation is the protonated amino group and the anion moves through the matrix to carry the charge.[11]

We combined alkylsilanes to control the mechanical properties of the coating, glycidoxysilanes to complex low lattice energy salts such as lithium iodide to control conductivity, and aminosilane to control the level of cure of the material. The mechanism for the transport of a salt through a hard, high T_g matrix of the silsesquioxane is not clear. Solid electrolytes of amorphous polymers are usually based on segmental motion of a flexible matrix. The high field across the photoreceptor may be responsible for the ion migration in the overcoat.

Previous workers had used similar sol-gel chemistry to form photoreceptor overcoats, but did not add salt or any other catalyst that could dissociate in the polymer network to carry the charge.[12] The absence of salt minimized image spread at high humidity, but limited the protective layer to less than two microns.

Experimental

Two series of sol-gels were prepared with varying levels of GPS. One had GPS increasing from 10 to 12.5 to 15 wt %, with a corresponding decrease in the MTMS content. 3-Aminopropyltrimethoxysilane (APTMS) was added to the "methyl" sol-gels at 4.0 wt % to achieve a consistent cure. Two levels of LiI were examined as the mobile charge carrier at 1.5 (Table 1) and 0.75 wt % (Table 2). The "propyl" sol-gel consisted of 60 wt % PrTMS, a GPS concentration range of 5 to 10 to 20 wt %, with a corresponding decrease in methylsilane MTMS (Table 3), 7.5 wt % of aminosilane APTMS, and 0.75 wt % LiI. Synthesis of the silsesquioxanes was carried out by mixing the alkoxysilanes, followed by the dropwise addition of glacial acetic acid. Water was added dropwise at a level of 2 equivalents per alkoxysilane. The reaction was stirred for two days, and then diluted with an approximate equivalent amount of ethanol. The reactions were stirred for an additional 2 weeks before adding addenda: 1 wt % of low molecular weight poly(dimethylsiloxane) (PDMS) to act as a lubricant, lithium iodide, and 10 wt % of bis[N-ethyl-N-(2-hydroxyethyl)anilino]diphenylmethane as an acid scavenger.

The photoreceptor is first overcoated with a thin (0.1-0.5 micron) primer layer, such as poly(methacrylate-co-methylmethacrylate-co-methacrylic acid). Overcoat web coating was typically carried out at 10 ft/min with ramped heating (90 °C average). Post curing was at approximately 80 °C for 24 h. The thickness of the overcoat ranged between 1-5 microns.

The bulk conductivity of the overcoats was evaluated by measuring the residual potential after photodischarge of the corona charge photoreceptor using two different techniques. Low intensity continuous exposure (LICE) characterization employs a corona to charge a photoreceptor sample that is then exposed to 1 erg/cm^2 sec of light at the wavelength of interest through a "transparent" electrostatic probe. The surface potential is continuously recorded before, during, and after exposure. Measurements at different relative humidity (RH) were carried out after the films were equilibrated for approximately 5 min.

Overcoated films were also evaluated for residual voltage after 2000 electrophotographic cycles at 50 °C and 15% (RH). This regeneration sensitometry characterization is an electrical only test carried out on a belt drive apparatus fitted with a DC gridded corona charger, voltmeters, erase lamp, and a 160 µsec Xenon flash lamp for exposing the film.

Results and Discussion

Methylsilsesquioxanes

Abrasion resistant silsesquioxane overcoats are generally made from methylsilsesquioxanes because they give the highest degree of scratch resistance. We found that incorporating 10 to 15 wt % of GPS and 1.5 to 0.75 wt % of LiI produced a photoreceptor overcoat that was useful in electrophotographic applications. Results from measurements of the residual potential for three silsesquioxane overcoats with increasing GPS content are shown in Table 1. The silsesquioxanes were 1 micron thick on a negative charging photoreceptor. Photosensitivity measurements were made at 39%, and 5% RH using LICE. The trends in the data indicate a lower residual voltage with increasing GPS content. A dependence on RH is also evident, indicating water plays a role in the charge migration. The contribution of the aminosilane to the conductivity should be constant in each sample. The lithium iodide content was the same in each sample at 1.5 wt %.

Table 1. Residual Voltage of Methylsilsesquioxane Overcoated Film by LICE

MTMS/GPS	LICE at 39% RH (V)	LICE at 5% RH (V)
90/10	-22	-28
87.5/12.5	-20	-34
85/15	-15	-22

The capability of the abrasion resistant hard coats to dissipate charge with cycling was studied by placing the films through 2000 charge, expose, erase cycles. Three sol-gels with the same silane compositions, but with half the level of conductive salt, were prepared in the same way as those above. As shown in Table 2, all of the overcoated films had a higher residual voltage than the film with no overcoat. However, the increase was greater for the overcoats with lower levels of GPS.

Table 2. Residual Voltage of Methylsilsesquioxane Overcoated Film by Regneration Sensitometry

MTMS/GPS	Residual Sensitometry (V)
90/10	182
87.5/12.5	175
85/15	150
No overcoat	140

Propylsilsesquioxanes

A less brittle silsesquioxane overcoat was prepared by formulating a sol-gel with higher organic content. PrTMS was incorporated at 60 wt %, and the balance was made from three variations in the ratio of methyl to glycidoxysilanes (MTMS/GPS). Because these coating were less brittle and also not as scratch resistant, they were coated at 4 micron thickness. Also, the photoreceptor in this case was positive charging. Residual voltages are given in Table 3. Little difference was seen in the LICE measurements at 5 and 10 wt % GPS, but lower residual voltage was observed at 20 wt %. The resistivity of all three overcoats increases at 0% RH.

Table 3. Residual Voltage of Propylsilsesquioxane Overcoated Film by LICE

PrTMS/MTMS/GPS	LICE at 34% RH (V)	LICE at 0% RH (V)
60/35/5	53.3	63.3
60/30/10	56.7	63.3
60/20/20	6.7	30.0

The aminosilane content was higher in the sol-gels containing propylsilane PrTMS because these formulations were more difficult to cure than those above. Thus, it was necessary to almost double the aminosilane concentration for the ‘propyl’ as compared to the ‘methyl’ sol-gel. APTMS (7.5 wt %) produced a level of cure in the propylsilsesquixoane that had similar abrasion resistance to the methylsilsesquixoane. This increased quantity of amino substituents did not result in higher conductivity. The 60/35/5 and 60/30/10 samples both had high residual voltages between 53 to 63 V at ambient and low RH. Electrical properties similar to those given in Table 1 were achieved when 20 wt % of the glycidoxysilane GPS was incorporated into the overcoat. The mechanical properties were similar for the three propylsilsesquioxane. Thus, the electrical properties were adjusted by controlling the concentration of the GPS in the formulation, while the cure was controlled with the concentration of aminosilane APTMS.

Conclusions

Ionic conductivity can be introduced into a silsesquioxane abrasion resistant overcoat through the combination of a polar substituent with a low lattice energy salt, such as lithium iodide. These addenda have only a small effect on the level of cure in the overcoat when compared to aminosilanes. Thus, it is possible to control the electrical and mechanical properties of a silsesquioxane overcoat independently to allow for protection of the photoreceptor with minimal degradation of the electrophotographic image.

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Biography

Wayne Thomas Ferrar is currently an associate scientist at NexPress Solutions LLC, a Heidelberg/Eastman Kodak joint venture. Before joining NexPress earlier this year, he was a research associate with Eastman Kodak’s Office Imaging Research and Development Laboratories. He received a Doctorate in Chemistry in 1981 from Penn State University, where he studied polyphosphazenes and other polymers with Prof. Harry R. Allcock. At Kodak he continued to work on inorganic polymers, including phosphazenes, siloxanes, and sol-gels, as well as vinyl polymers and polyesters, applying them as imaging materials in photography, inkjet, and electrophotography.