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Relationship between photofixed condensate, effluent and bulk composition of several common RTV materials

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Raman spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy are employed to analyze the bulk compositions of five kinds of Room Temperature Vulcanized (RTV) silicones (CV2568, RTV566, DC93-500, SCV2590 and SCV2590-2) that are commonly employed in orbiting spacecraft. It is found that polydimethylsiloxane (PDMS), silicon dioxide, Tetra-n-propylsilicate (NPS), silicic acid, tetraethyl orthosilicate, and trimethylsilanol are contained in all of them. The outgassing products from those silicones are characterized by FTIR. By comparing the position of the peaks, it is found that the outgassing products of each material are PDMS and NPS which are consistent with the compositions of samples determined with Raman and FTIR respectively. These results indicate that the composition analysis of bulk or thin film silicones with Raman and FTIR could be used as the guideline to predict the outgassing products of silicones. This in turn can lead to a more global approach for determining photofixing issues associated with outgassing. In support of this, the photofixed films from pure PDMS, NPS, and their mixtures were analyzed by spectroscopic ellipsometry and their optical constants were determined.

I. Introduction

In general, silicones are heat-resistant and rubber-like, and they are commonly used in aerospace as sealants and adhesives where they are exposed to harsh environments. However, Room Temperature Vulcanized (RTV) silicones contain volatile contaminant materials (VCM) and when exposed to sunlight in orbit these materials outgas and can redeposit/photofix on spacecraft surfaces [1]. Atomic oxygen can also oxidize silicone polymers and silicone contamination to produce non-volatile silica deposits [2-4]. Contamination on optical instrument and other critical satellite surfaces is one of the major factors in determining the lifetime of spacecraft. [5] However the ASTM standards for qualifying RTV's for aerospace use are based on total mass loss, not on the effect of the mass lost on the system.[6-7] In view of this some groups have studied the optical properties of photofixed VCMs for a range of RTV materials and some work has been performed on identifying the outgassing species as well. [8-14] Rather than quantify the optical properties of the photofixed films generated by each RTV, the approach taken here is to relate

the RTV bulk compositions, which can be readily determined, to the outgassing species, where these results can be used to generate a set of simulator materials that produces the outgassing species of a wide range of RTV's. The optical properties of the photofixed films resulting from the outgassing of the simulator materials may be useful for setting boundaries on the optical properties of photofixed films produced from a broad range of RTV materials.

II. Sample Preparation and Experimental Apparatus

The commonly used aerospace silicones CV2568, SCV2590 and SCV2590-2, from Nusil Silicone Technology, RTV566 from Momentive, and DC93-500 from Dow Corning were chosen for this research. The CV2568 and RTV566 are red, DC93-500 and SCV2590 are clear, and SCV2590-2 is black. All of them are ultra-low outgassing space-grade encapsulants, and have wide applications requiring low outgassing and minimal volatile condensation under extreme operating conditions to avoid condensation on sensitive devices.

Raman spectroscopy and FTIR spectroscopy were employed to study the bulk composition while FTIR spectroscopy was also employed for the outgassing study. All the bulk samples were prepared and cured per the product profiles from each company for bulk Raman measurement; for FTIR measurement, a small amount of each mixture was smeared on a silicon wafer, and the silicon wafer was spun at a speed of 3500 revolutions per minute (rpm) for 30 seconds to form the thin films. In order to perform the outgassing study the bulk samples were cut into small pieces, placed into an FTIR quartz cell with KBr windows. A flexible silicone rubber heater was attached to the exterior of the cell and it could heat the cell from room temperature to 100 °C in about 15 minutes, causing the RTV to outgas. The detailed procedures on measuring the outgassing products with FTIR are described in Table. 1.

Table. 1 Experimental Procedure for Outgassing Measurement via FTIR

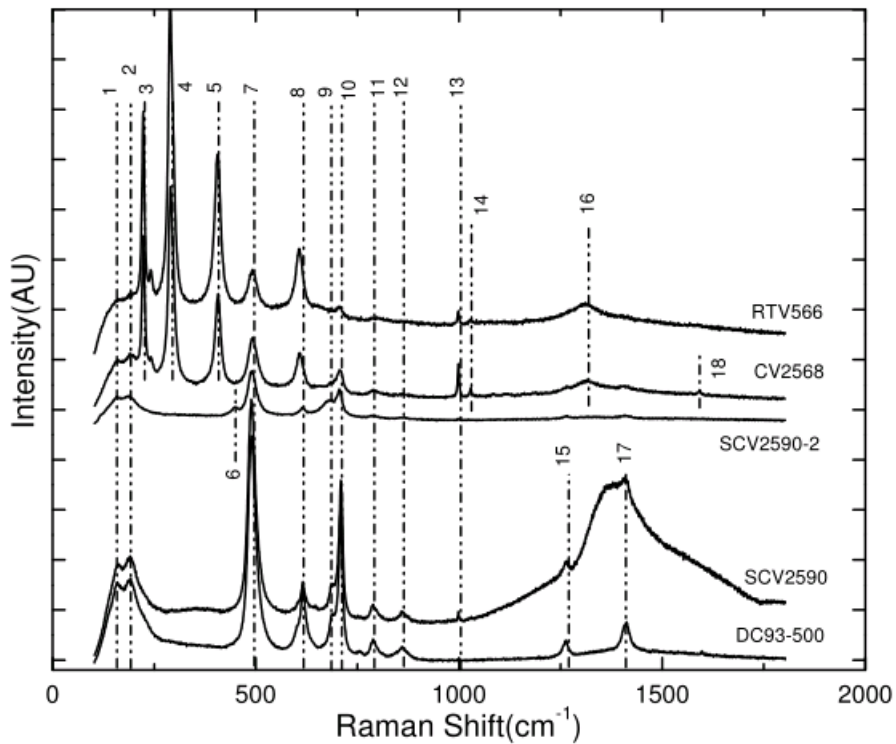
Background measurement	Gas sample measurement
1. Place cell in the FTIR chamber	1. Heat sample at 100 °C for 30 min, at
2. Flow pure dry N ₂ through the cell at rate of 30 ml/min for 20 min	the same time, keep flowing N ₂ through the cell at 5 ml/min
3. Run FTIR to get background spectrum	2. Heat sample for another 60 min
	3. Run FTIR to get absorption spectrum

The photofixed films were deposited by placing the source material in a shuttered effusion cell in a cryo-pumped vacuum chamber, base pressure less than 10⁻⁶ Torr. The cell temperature was set at the desired level, 50 °C, and the shutter was opened. The outgassing flux was made incident on a silicon substrate along with the vacuum ultraviolet

(VUV) light from a Xe continuum lamp.[15] The lamp does a good job of simulating the VUV portion (wavelength below 200nm) of the Air Mass zero (AM0) solar spectrum. After the desired time period the shutter is closed, the cell turned off but the light remained on to continue to photofix any outgassing flux that may arrive at the substrate until the cell cools to below 30 °C. The sample is removed from the system, where the photofixed film's optical properties are determined by spectroscopic ellipsometry.

III. Results and Discussion

The Raman spectra were collected with a fiber optic probe using 785 nm excitation, and they are shown in Figure 1. The peaks are all labeled with numbers, and they are matched by referring to the literature related to Raman spectra [16-20].



NPS and H_4SiO_4 : 1, 2, and 18; Fe_2O_3 : 3, 4, 5, 14, and 16; FeO: 6; PDMS: 7, 10, 12, and 15;

$(CH_3)_3SiOH$: 8; PDMS and NPS: 9; SiO_2 : 11; $C_8H_{20}O_4Si$: 13 and 17

Fig. 1 Raman spectra of silicone samples: RTV566, CV2568, SCV2590-2, SCV2590, and DC93-500 bulk

All of them contain Poly(dimethylsiloxane) (PDMS), SiO_2 , Tetra-n-propylsilicate (NPS), H_4SiO_4 , $C_8H_{20}SiO_4$ (TEOS) and trimethylsilanol ($(CH_3)_3SiOH$). It is found that the Raman spectra of CV2568 and RTV566 are very

similar to each other, while the Raman spectrum of SCV2590 is almost the same as that of DC93-500. For SCV2590 and DC93-500, the only difference occurs where the Raman shift is between 1200 and 1800 cm^{-1} , for CV2568 and RTV566, the tiny difference is the Raman shift between 1200 and 1500 cm^{-1} , and this may be caused by the amorphous nature of the material. The Raman spectrum of SCV2590-2 is similar to DC93-500 and SCV2590. Comparing the Raman peaks in SCV2590-2 with DC93-500 and SCV2590, those do not match are from the characteristic Raman peaks of FeO [21] which gives SCV2590-2 its black color, while additional peaks in CV2568 and RTV566 are from the characteristic Raman peaks of Fe_2O_3 [21] which make CV2568 and RTV566 red.

The FTIR instrument was operated in the absorption mode, and the spectral range was from 4000 to 400 cm^{-1} . The resolution was set to 4 cm^{-1} . The FTIR spectra of the five silicones are shown in Figure 2. By comparing the position of the peaks, it was found that the peaks located around 701, 795, 1016, 1265, 1411, and 2963 cm^{-1} were from PDMS, the peak near 869 cm^{-1} was from NPS, the peak around 1081 cm^{-1} was from both $(\text{CH}_3)_3\text{SiOH}$ and H_4SiO_4 , and the other one around 2910 cm^{-1} was from $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$.

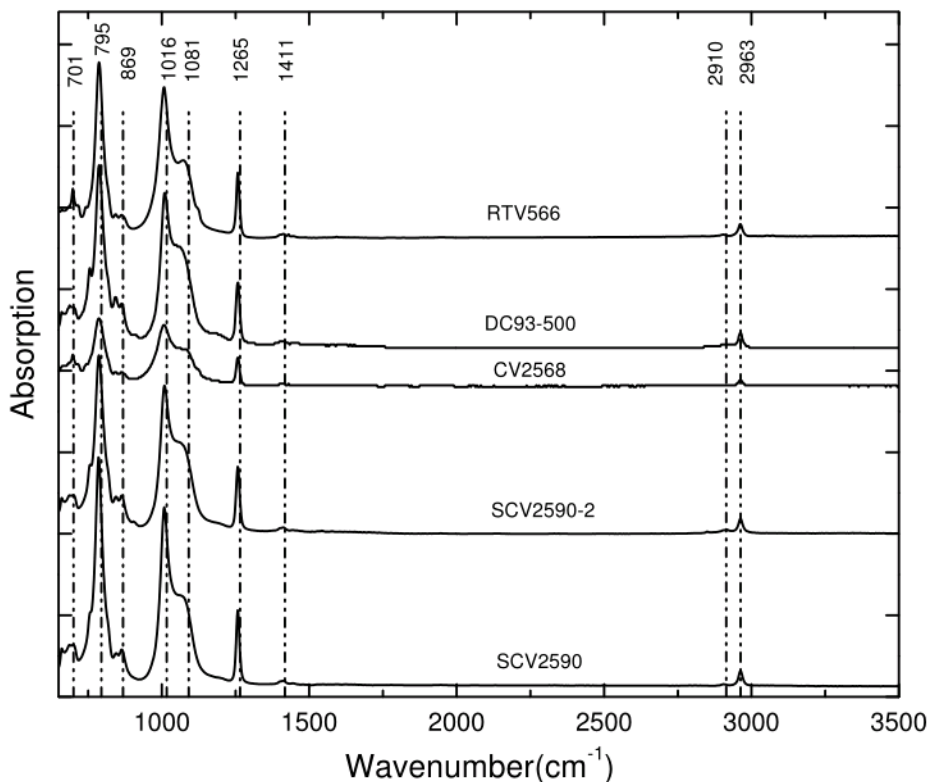


Fig. 2 FTIR spectra of silicone samples: RTV566, DC93-500, CV2568, SCV2590-2, and SCV2590 film

The experimental spectra were matched with library data contained in Essential FTIR [22] from Operant LLC. The FTIR spectra of all studied materials are very similar to that of PDMS, and the matching scores for each of them are listed in Table. 2.

Table. 2 Matching scores of five silicones with PDMS data in library

Materials	CV2568	RTV566	DC93-500	SCV2590	SCV2590-2
Matching ratio	97.37%	98.51%	92.97%	93.50%	93.19%

As it is shown above, the FTIR spectra of the five silicone polymers are not exactly the same as that of PDMS in the library, otherwise the matching score would be 100%. The unmatched peak around 2904.6 cm^{-1} matches the characteristic peak in $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ (TEOS) [20], peak located around 1090 cm^{-1} matches the characteristic one in H_4SiO_4 [23] and $(\text{CH}_3)_3\text{SiOH}$ [24], peak located around 850 cm^{-1} matches the characteristic one in NPS [25].

FTIR spectra of outgassing products from all the silicones are presented in Figure 3. By comparing the position of the peaks, it was found that the large peaks in FTIR spectrum of outgassing materials in Figure 3 could match those of PDMS and NPS. The peaks at 758, 823, 1031, and 2862 cm^{-1} were from NPS, the one at 887 cm^{-1} was from PDMS, and the other ones located around 1089, 1262, and 2966 cm^{-1} were from both PDMS and NPS.

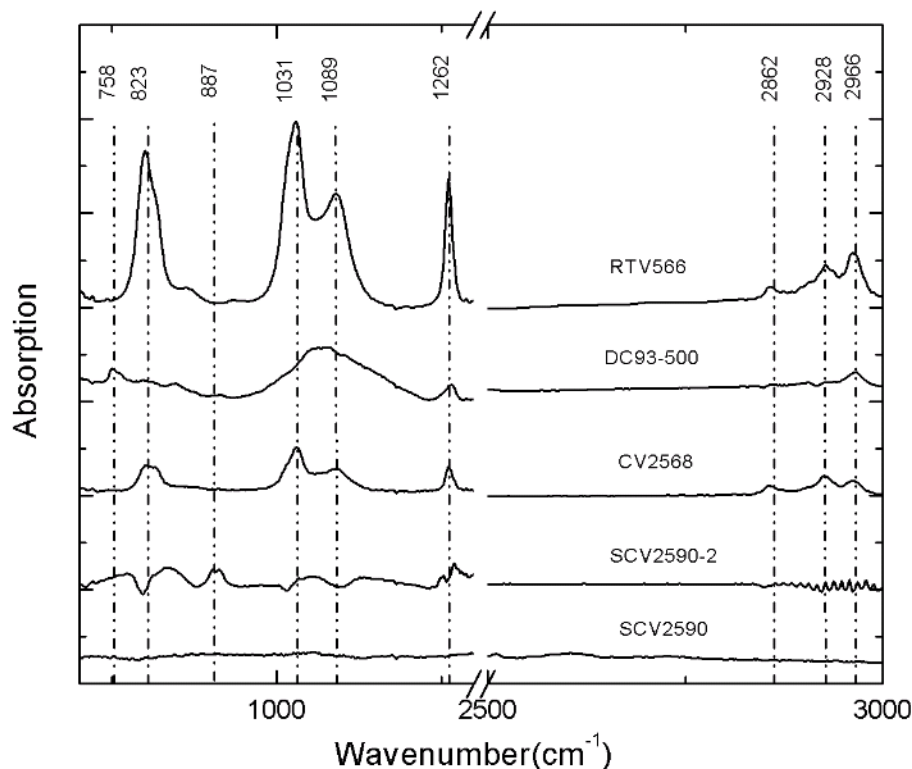
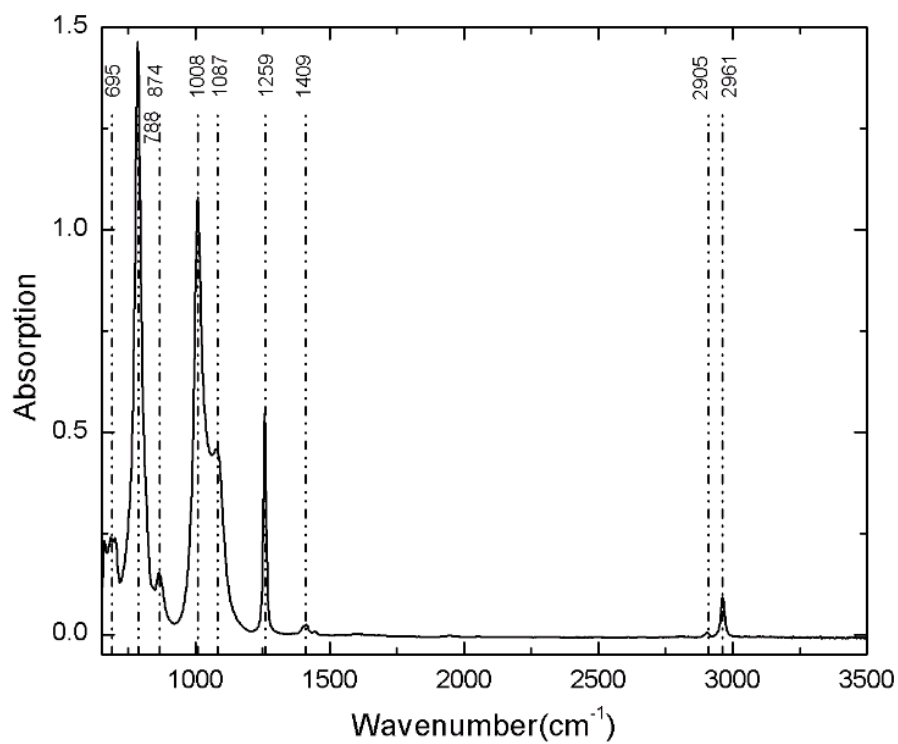
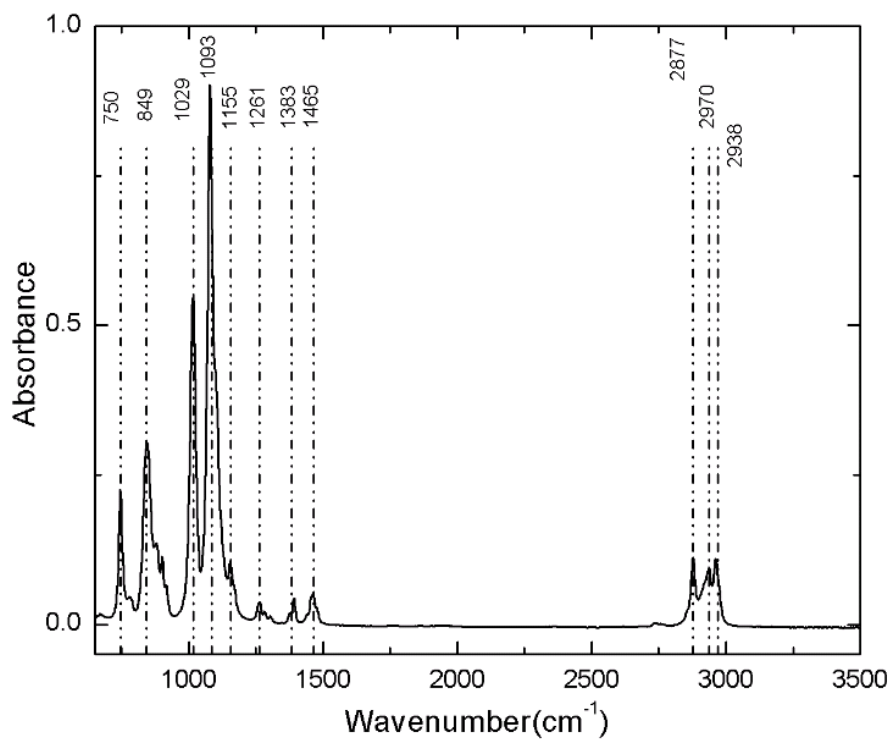


Fig. 3 FTIR spectra of outgassing products from: RTV566, DC93-500, CV2568, SCV2590-2, and SCV2590

Figure 4 shows the FTIR spectra of pure liquid PDMS (a) and NPS (b).



(a) PDMS



(b) NPS

Fig. 4 FTIR spectra of pure liquid PDMS and NPS

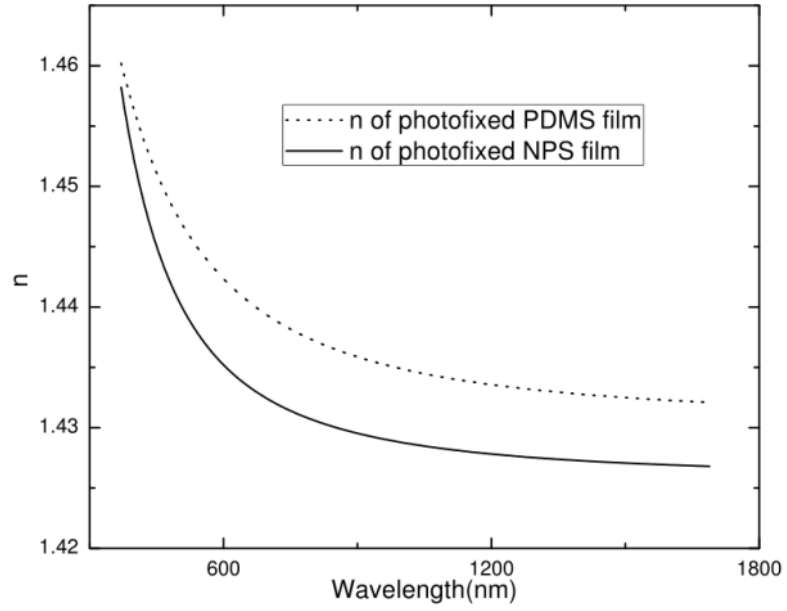
In Figure 4, the peaks for liquid PDMS are at 695, 788, 874, 1008, 1087, 1259, 1409, 2905, and 2961 cm^{-1} , the ones for NPS are at 750, 849, 1029, 1093, 1155, 1261, 1383, 1465, 2877, 2938, and 2970 cm^{-1} .

Comparing the FTIR spectra of outgassing products with those of pure liquid PDMS and NPS, it is found that the large peak located around 1008 cm^{-1} in the liquid PDMS and the large peak located around 1155 cm^{-1} in the liquid NPS do not show in the FTIR spectra of the outgassing products. The 1008 cm^{-1} peak is possibly from the Si-O-Si (angle $< 144^\circ$) bond [26-27] in the liquid PDMS and it also showed in the FTIR spectra of the five studied silicone materials, the 1155 cm^{-1} peak is possibly from the Si-O (cage like) bond [28-30] or the C-O-C bond [31], these bonds may be broken during the outgassing process, and this might be the reason why they do not appear.

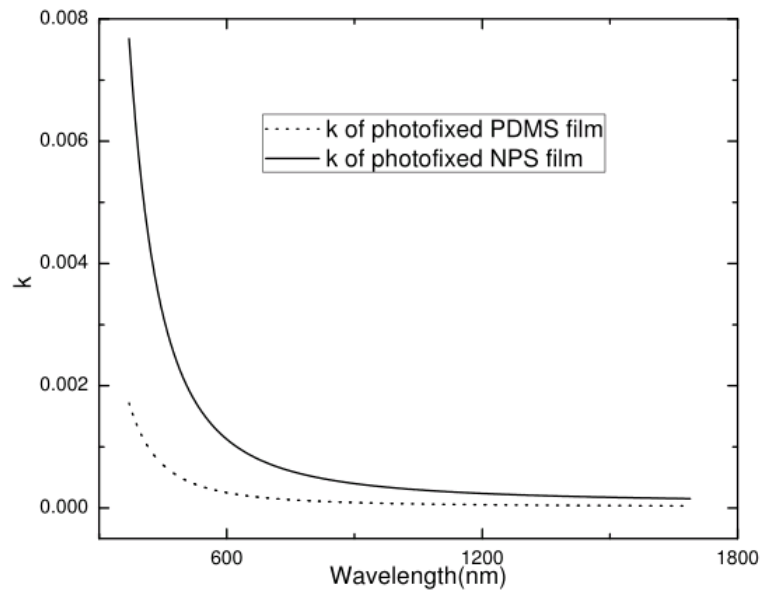
An FTIR analysis of the outgassing products of the five materials clearly shows each material outgasses both PDMS and NPS, where no other products have been detected. This does not imply that no other products are outgassed. They may be below the detectable limit of the system or are not IR active. The issue now becomes whether or not PDMS, NPS and their mixtures can be used to simulate the optical properties of the photofixed outgassed material from the RTV's. If so, this would indicate any additional undetected outgassing components from the RTV's do not contribute significantly to the photofixed material.

Towards this end photofixed films from pure PDMS, NPS and three mixtures of PDMS and NPS (volume ratios were 20:80, 50:50, and 80:20 respectively) were generated as discussed above. Their optical constants in the 380-1700 nm wavelength range were determined by spectroscopic ellipsometry, where in all cases the data were fit to a Cauchy optical model with film thickness input measured by profilometry. Figure 5 shows the optical constants of pure PDMS and NPS photofixed films where the optical constants of the mixtures are seen in Figure 6.

Figure 5 shows that the optical constants of photofixed films from pure PDMS and NPS, while not identical, are similar in magnitude and wavelength dependence. Figure 6 shows that the optical constants of the photofixed films from mixtures of PDMS and NPS are a function of the volume ratios of PDMS and NPS. However, these data cannot be fit to simple mixtures of PDMS and NPS via the effective medium approximation (EMA). [32] This may indicate that the materials react as a result of heating and/or photofixing. In any event, these data may serve as limits for the optical constants of photofixed films from PDMS and NPS containing materials, much like the Zeiner constants.[33]

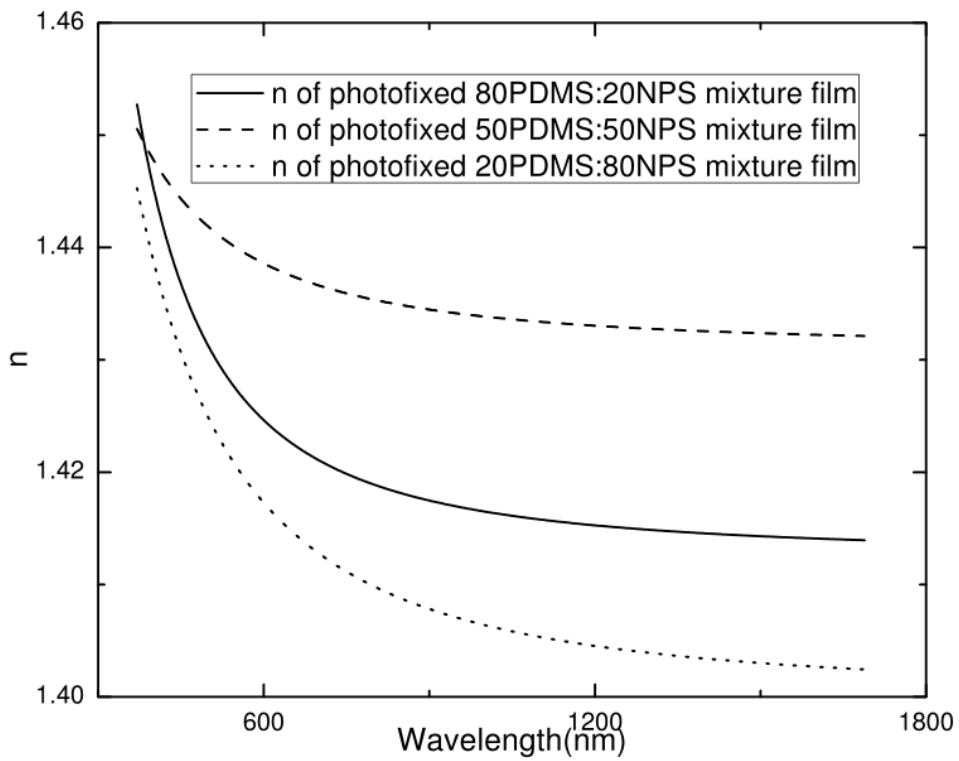


(a) n

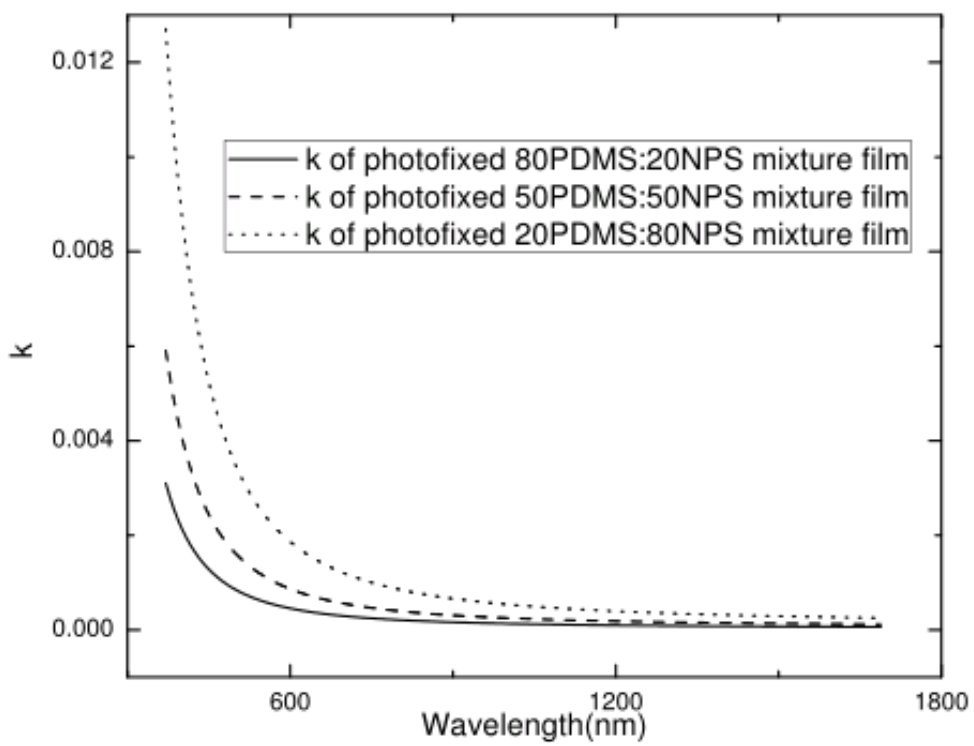


(b) k

Fig. 5 Optical constants of photofixed films from pure liquid PDMS and NPS



(a) n



(b) k

Fig. 6 Optical constants of photofixed films from mixtures of liquid PDMS and NPS

IV. Conclusion

It is found that PDMS, SiO₂, NPS, H₄SiO₄, C₈H₂₀SiO₄, and (CH₃)₃SiOH are contained in all the five studied silicones, as shown by Raman and FTIR spectroscopy data taken from bulk materials. In addition, Raman data shows the color additives Fe₂O₃ in CV2568 and RTV566, and FeO in SCV2590-2. The FTIR analysis of the outgassing products from the five materials clearly shows each material outgasses both PDMS and NPS.

The optical constants photofixed films of PDMS, NPS and their mixtures were determined in order to assess their utility to bound and/or simulate the photofixed films from the RTV's themselves. It was found that the optical constants are a function of the volume ratio of the initial material although their optical behavior in the 380- 1700 nm range does not appear to be that of simple mixtures. In addition the index of refraction pure materials and mixtures are bounded by PDMS on the high side and the 20:80 PDMS:NPS mixture on the low side, while the extinction coefficient values are bounded by the 20:80 PDMS:NPS mixture on the high side and pure NPS on the low side. A complete evaluation of this approach requires a detailed measurement of the photofixed films of the RTV's which is currently underway.

Acknowledgments

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