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Polydimethylsiloxane/Additive Systems for Thermal and Ultraviolet Stability in Geostationary Environment

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The development of radiation resistant materials is an ongoing challenge for space industry. High-energy irradiation (ultraviolet, electrons, neutrons, protons) induce damage to materials and electronic components in spacecrafts. Silicone resins are often used and play a key role as coatings and adhesive materials for satellites. Polydimethylsiloxanes show material exhaustion after long-term exposure to ultraviolet irradiation. Consequently, solutions are required to increase their thermo- and photostability under solar irradiation. Three different families of additives, namely ultraviolet absorbers, hindered amine light stabilizers, and a carbazole derivative are investigated. Those ultraviolet stabilizers were mixed with polydimethylsiloxane, then a cross-linking process was run by hydrosilylation. When ultraviolet absorbers could not be used due to a miscibility problem, addition of 0.5 wt % of bis (2,2,6,6-tetramethylpiperidin-4-yl)decanedioate (hindered amine light stabilizer 1) was shown to increase the thermal stability, measured by thermogravimetric analysis, from 360 to 395°C (Td_{5%}). Using visible near-infrared spectroscopy and after 450 equivalent solar hours of ultraviolet irradiation, an average increase of 2.6% in the ultraviolet stability was also obtained in the wavelength range from 250 to 400 nm. A polydimethylsiloxane/dibromocarbazole 1.0 wt % did not improve the ultraviolet stability but exhibited a strong increase (about 100°C) of the degradation temperature of the polydimethylsiloxane.

I. Introduction

THE space environment around the Earth is exceptionally complex and has a significant impact on the lifetime and performance of any orbiting satellite. Space irradiation is an important research area in aerospace industry. High-energy particles induce damage to materials

and electronic components in spacecrafts [1–3]. Silicone resins are often used and play a key role as coatings for space materials due to their high chain mobility and flexibility. For example, polydimethylsiloxane (PDMS) is a silicone polymer known to possess a high thermal stability and good resistance to oxidation and hydrolysis. The low glass transition temperature of polysiloxane resins makes them attractive for a wide variety of common applications such as adhesives and fabric finishing agents, but they are also increasingly considered in high-value aerospace applications, in particular as varnishing or encapsulating [4,5]. For these specific applications, PDMS resins have to be qualified in optical, thermal, and outgassing properties [6]. To consider their use as thermal control coating, it is necessary to improve their thermal and photostability in harsh environment.

The degradation mechanisms of PDMS under space conditions were described by several groups [7–11]. Their degradation under UV irradiation depends on the UV wavelength range and the dioxygen presence. Characteristic bonds of PDMS (Si-H, Si-C, Si-O, and C-H) are subject to homolytic cleavage and formation of free radicals. These highly reactive radicals can undergo various reactions such as recombination, disproportionation, and hydrogen abstraction. It is proposed that photon absorption by unsaturated bonds formed in the material leads to further photochemical reactions and eventually to the degradation of the PDMS resin by causing several inter- and/or intramolecular rearrangements [12,13]. Consequently, improved UV stability might be accomplished by limiting the formation of uncontrolled species, which bring important degradations. There are mainly two strategies to limit the material degradation against solar irradiation: the use of additives or protective coatings. In the last few years, several methods were investigated to restrict the damage caused by UV irradiation, namely the use of additives such as silsesquioxanes [14] and inorganic [15] or organic copolymers [16]. To protect the PDMS films, some researchers have also envisaged the deposition of ZnO or ZnO-doped quantum dots in the form of multilayers to obtain a UV-blocking material [17,18]. Another drawback of PDMS results from the insufficient thermal

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stability of the polymer when used as thermal control coating [19]. This thermal stability could be improved by incorporating silica nanoparticles within the matrix or cross-linking the matrix with polymethylmethoxysiloxane [20,21]. Loading levels between 10 and 50% are necessary to obtain significant effects on the PDMS properties, but it is accompanied with a loss of transparency.

Other additives were reported in the literature as UV stabilizers, i.e., hindered amine light stabilizers (HALSs) [22], ultraviolet absorbers (UVAs) [23], and carbazoles [24]. HALSs, derived from 2,2,6,6-tetramethyl piperidine, are efficient light stabilizers that prevent the degradation of various polymers such as polyethylene. The mechanism of UV inhibition by HALS and UVA differs due to their chemical structures. In contrast, carbazoles and their polymeric derivatives act as UV absorbers due to their aromatic structure [25]. In this work, different UV stabilizers were mixed before the cross-linking of the PDMS by hydrosilylation [26,27]. The thermal and optical properties of PDMS were studied under UV irradiation at room temperature and under vacuum.

II. Experimental Part

A. Materials

PDMS was provided by MAP as a bicomponent material: base and curing agent. The base contains predominantly vinyl-terminated PDMS and Pt catalyst (Karstedt). The curing agent is a mixture of vinyl-terminated PDMS and hydride-terminated PDMS. Reference PDMS samples were prepared by mixing the base with the curing agent in a 10:1 ratio by weight. UV stabilizers are commercially available and purchased from Sigma Aldrich: 3,6-dibromo-9H-carbazole (carbazole 1), bis(2,2,6,6-tetramethylpiperidin-4-yl)decanedioate (HALS 1), bis(2,2,6,6-tetramethyl(octyloxy)piperidin-4-yl) decanedioate (HALS 2), 2-(tert-butyl)-6-(5-chloro-2H-benzo[d][1,2,3] triazol-2-yl)-4-methylphenol (UVA 1), and (2-hydroxy-4-methoxyphenyl) (2-hydroxyphenyl)methanone (UVA 2). The additive solutions were prepared at 10 mg/ml in n-heptane, dispersed into the base, and sonicated. Afterward, the mixture was homogenized by using a mechanical dispersion. Then, the solvent was removed under vacuum for 2 h, and the mixture was added to the curing agent for 15 h at 70°C to obtain the final cross-linked materials. The prepared formulations contained 0.5 to 2.0 wt% of additives. The thickness of the prepared samples was measured with a sliding caliper and was approximately 100 μm .

B. Initial Characterizations

Preliminary characterizations were carried out to validate the industrial cross-linking process and the resulting properties of the new silicone material.

Thermogravimetric analysis (TGA) of PDMS samples (10–15 mg) was performed on a TA Instruments Q50 under nitrogen atmosphere using platinum pans. Temperature profiles ranged from 25 to 600°C with a heating rate of 10°C · min⁻¹.

Differential scanning calorimetry (DSC) measurements were carried out on a TA Instruments DSC Q100 LN2 (*t/T* modulation) by heating from -150 to 150°C with a ramp of 5°C · min⁻¹ and with samples weighted around 5 mg. The analyses were made with helium atmosphere using aluminum pans; the instrument was calibrated with indium sample.

ATA Instrument RSA3 (dynamic mechanical analysis, DMA) was used to study the thermomechanical properties of the PDMS samples under nitrogen atmosphere from 0 to 200°C at a heating rate of 5°C · min⁻¹. The measurements were performed in compression mode at a frequency of 1 Hz, an initial static force of 0.5 N, and strain sweep of 0.1%.

C. Aging and Postcharacterizations

UV irradiation was performed in a vacuum chamber coupled to a short arc xenon lamp (Oriol solar simulator, 1000 W). This equipment allows reproducing the solar irradiation distribution (250–2500 nm) close to the UV solar conditions. During the UV experiment, the pressure was maintained under 10⁻⁵ mbar, and a water-cooling

system was used to control the temperature of the sample holder (25–30°C). A black paint was recovering the vacuum chamber to inhibit the reflection of UV radiations. The experiment time was in a range 450–500 of equivalent solar hours (ESH) corresponding to six months of geostationary flight. The change of the transmittance after UV irradiation allows estimating the UV resistance. The initial materials should have a high initial transmittance (greater than 90%) in the wavelength range from 250 to 1000 nm. The change in transmittance between 250 and 400 nm was used to estimate the UV stability of the composites, due to the fact that this wavelength range corresponds to 90% of the UV doses emitted by the sun.

Ultraviolet–visible–near-infrared (UV-vis-NIR) spectroscopy analyses were performed before and after photoaging (250–1000 nm) on a Perkin Elmer Lambda 900 double beam combined with an integrating sphere of 150 mm diameter in a spectral range from 250 to 1000 nm. The spectra were obtained with a scanning speed of 400 nm/min and a resolution of 1 nm.

To estimate the degradation of the materials all over the solar spectrum and for different wavelength ranges, the following formulas of solar transmittance were used [28,29]:

$$T_s = \frac{\int_{250}^{1000} T_s(\lambda) \cdot I_s \cdot d(\lambda)}{\int_{250}^{1000} I_s \cdot d(\lambda)} \quad (1a)$$

$$T_i = \frac{\int_{250}^{1000} T_i(\lambda) \cdot I_s \cdot d(\lambda)}{\int_{250}^{1000} I_s \cdot d(\lambda)} \quad (1b)$$

$$T_f = \frac{\int_{250}^{1000} T_f(\lambda) \cdot I_s \cdot d(\lambda)}{\int_{250}^{1000} I_s \cdot d(\lambda)} \quad (1c)$$

where T_s the mean spectral transmittance of the material, I_s the spectral irradiance of the sun (watt/micrometer/meter², W/ $\mu\text{m}/\text{m}^2$), T_i is the initial mean transmittance before irradiation, and T_f is the final mean transmittance after irradiation [$d(\lambda) = 1 \text{ nm}$].

ΔT_s is the level of degradation on each wavelength range in percent:

$$\Delta T_s(\%) = T_i - T_f \quad (2)$$

and Δg is the gain in UV stability in percent:

$$\Delta g(\%) = \Delta T_s \text{ Neat PDMS} - \Delta T_s \text{ PDMS/additive} \quad (3)$$

D. Evolution of the Optical Properties During the Photoaging

Optical performance is the main parameter in the space domain that defines the quality of the UV protective coating. To investigate the optical performance, an unexposed composite coating was compared to a sample that has received 450–500 ESH. To meet the requirements of the optical properties, the maximum loading level of additives employed in the PDMS matrix was adjusted to 2.0 wt%. The photostability of the PDMS/additive was investigated by performing photoaging experiments based on a specifically designed procedure for the characterization of aerospace coatings. For these experiments, thin PDMS films (100 μm thickness) containing 0.5 to 2.0 wt% of UV additives were prepared, and the transmittance was measured before and after UV irradiation. The UV photoaging tests were conducted through two irradiation sessions. To calculate more precisely the improvement in UV stability of the films, Eq. (1a) was employed for two wavelength ranges (250–1000 nm and 250–400 nm). These calculations permit to obtain the mean transmittance of the materials on the wavelength range, which was used to compare the behavior of each composite under UV irradiation. The initial mean transmittance T_i is calculated for each film before irradiation Eq. (1b). Afterward, the final mean transmittance T_f is also calculated after irradiation [Eq. (1c)]. Equation (2) was used to obtain the level of degradation on each wavelength range. Finally, the gain in UV stability (Δg) was estimated with Eq. (3).

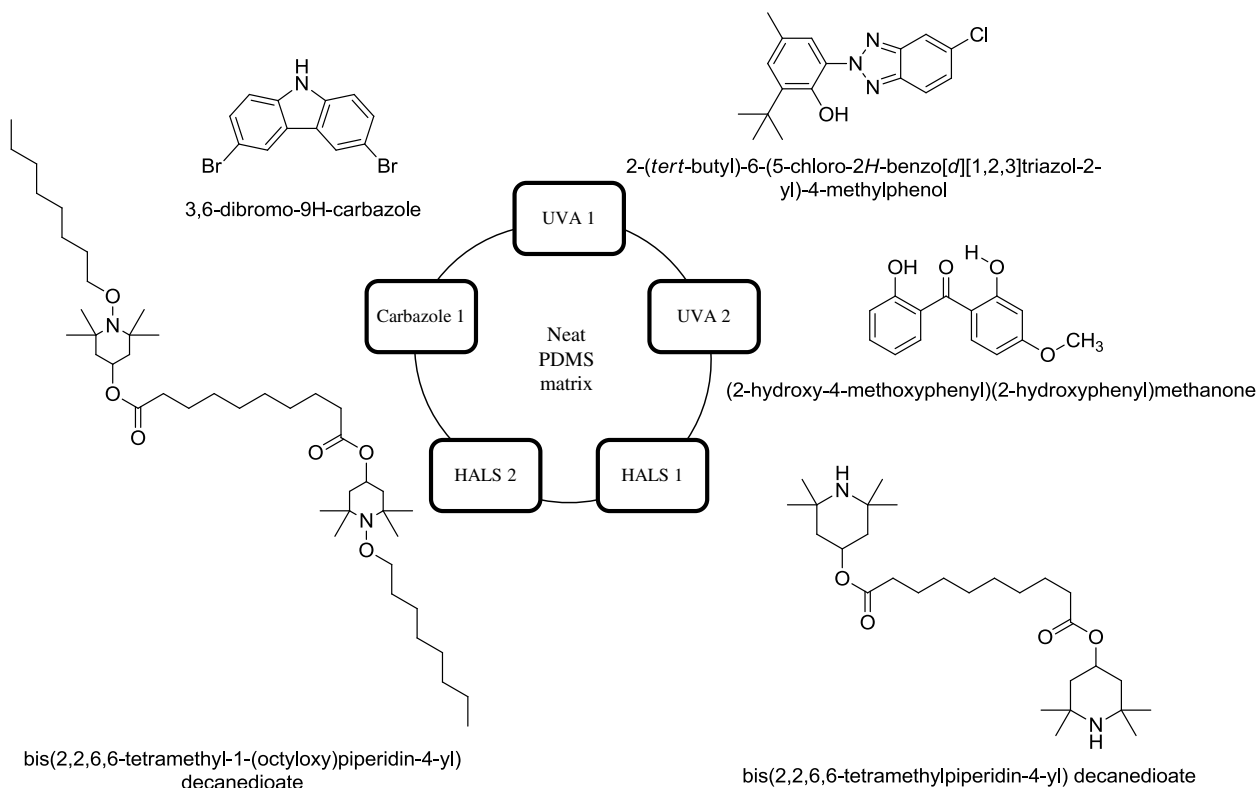


Fig. 1 Structures of studied UV stabilizers for cross-linked PDMS.

III. Results and Discussion

Cross-linked PDMS were synthesized and characterized in the presence of several UV stabilizers, which are illustrated in Fig. 1. Two different chemical structures of HALS only differing by the moiety on their piperidine unit were studied. HALS 1 possesses a hydrogen atom on the piperidine nitrogen, which can form hydrogen bonds with the oxygen atoms in the PDMS chains. In contrast, HALS 2 bears an alkoxy chain, which can act as a plasticizer of the PDMS. The efficiency of HALS is explained by a regenerative process, which was described by McCusker and Gijsman [30,31]. HALSs are made of secondary or tertiary cyclic amine units and of ester groups. After oxidation of the amine moiety, the formed nitroxide can act as radical scavenger. More important, the nitroxyl radicals can react with polymeric alkyl radicals to form alkoxy hindered amine derivatives, which are postulated to further react with alkylperoxy radicals, forming dialkylperoxides and regenerating the active nitroxyl radicals [32]. In addition, HALS can be used to enhance flame retardancy of polymeric materials. Two commercial UV stabilizers, i.e., 2,2'-dihydroxy-4-methoxybenzophenone (UVA 1) and 2-*tert*-Butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UVA 2), were also used. UVAs absorb a photon to reach an excited state. Phenolic types can undergo a rapid hydrogen transfer to a heteroatom in their first excited singlet state to form a vibrationally excited ground state species, which can lose thermal energy and transfer back the hydrogen to reform the fundamental state. This cycle is completed within nanoseconds for most UVAs [33,34]. The photon absorption by the PDMS chain is therefore expected to be decreased. Finally, carbazole-based compounds present also an interest as UV stabilizers for PDMS resins because they are well-known fluorescent labels in biology and possess an excellent UV absorption [35].

A. Hindered Amine Light Stabilizers as Polydimethylsiloxane Additives

All systems (PDMS/additive), with a variation of 0.5–2.0 wt% UV stabilizers added, were characterized by TGA, DSC, and DMA to determine their thermal properties, elastic modulus, and cross-linking process before UV irradiation. The temperature of cross-linking was

recorded by DSC analysis on the neat PDMS. The thermogram revealed an exothermic event at 80°C corresponding to the formation of a three-dimensional network. To confirm the efficiency of the curing process (15 h at 70°C), DSC analyses were performed on neat cross-linked PDMS, and no exothermic peak during the first temperature ramp was observed at 80°C. In the same way, the features of the cross-linked PDMS/additives were investigated. After the curing process, no exothermic signal was recorded in the presence of the HALS. The glass transition temperature of the PDMS was unchanged at –120°C. Elastic modulus measured by DMA was also shown to be identical for the neat and composite PDMS at about 10⁶ Pa and in the expected range of elastomeric materials [36].

TGA analyses revealed that the amount of added HALS has an impact on the thermal stability of the material (Fig. 2). The main degradation temperature of the neat PDMS recorded at Td_{5%} = 360°C corresponds to the depolymerization of PDMS backbone through random chain scission reactions and formation of

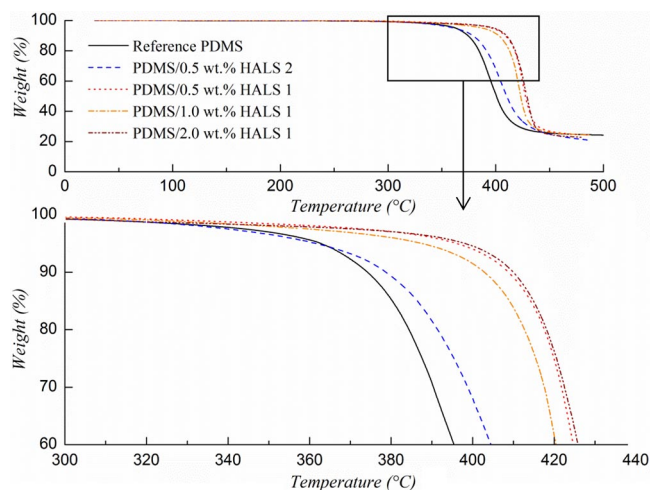


Fig. 2 Thermal degradation profile of PDMS with HALS 1 and 2 under nitrogen.

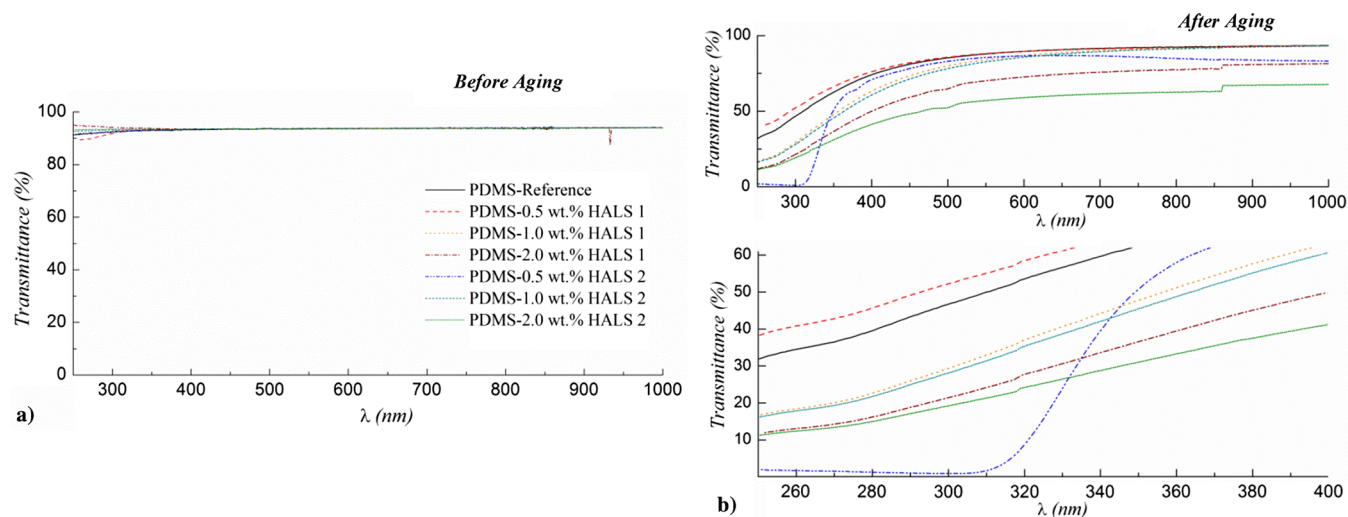


Fig. 3 UV spectra (250–1000 nm range) of PDMS films prepared with HALS 1 and 2: a) before, and b) after UV irradiation (450 ESH).

low-molar-mass cyclic siloxane species [37,38]. The degradation temperature at 5% weight loss for the silicone resin with 0.5 wt% HALS 2 was close to the initial PDMS (Fig. 2). No influence on the thermal stability was observed with higher amounts of HALS 2. In contrast, HALS 1 showed a significant effect on the thermal stability with a $T_{d5\%}$ up to 395°C.

UV-vis-NIR spectroscopy was then performed to observe any difference in UV stability between the neat silicone resin and the resins containing 0.5 to 2.0 wt% of HALS 1 and 2 (Fig. 3). The change in UV transmittance of the PDMS films before irradiation is presented Fig. 3a. Concerning the neat PDMS, the transmittance before irradiation is relatively constant throughout the wavelength region from 250 to 1000 nm with a transmittance of around 92%. Regardless of the additives used, the optical properties before irradiation were similar, and the initial transmittance measured was above 90%. After the UV irradiation (450–500 ESH), a loss of transmittance equal to 32% at 250 nm is observed for the neat PDMS (Fig. 3b). Its degradation is induced by the homolytic bond cleavage on the main chain leading to inter- and/or intramolecular rearrangements. These photochemical reactions explain the yellowing of the neat resin. This coloring could also be caused by the Karstedt's catalyst because, under specific UV irradiation, colloidal Pt species are formed, leading to a loss of optical transparency [39]. Regardless of the nature and the amount of HALS investigated, a higher UV degradation was observed in the wavelength ranges of 250–1000 and 250–400 nm for all materials except for the PDMS containing 0.5 wt% of HALS 1 (Fig. 3b). An average increase of 2.6% in UV stability was determined for the latter in the wavelength range from 250 to 400 nm. The radicals formed from this additive are expected to trap radicals coming from the polymer degradation. Gijsman et al. reported that the efficiency of HALSs as UV stabilizers depends on the presence of dioxygen and that high O_2 levels are beneficial [31]. The UV irradiation was performed here under high vacuum (10^{-5} mbar), meaning that only traces of dioxygen are present and that the efficiency of HALS is expected to be lower. Besides, the two studied structures only differ by the moiety on their piperidine unit. HALS 1 possesses a hydrogen atom at the piperidine nitrogen, whereas HALS 2 bears an alkoxy chain. The bond enthalpy is higher for N-H bond than N-O bond (i.e., 93 versus 55 kcal · mol⁻¹), meaning that the homolytic cleavage of the N-O bond is much easier [32]. The degradation of PDMS with HALS 2 is more pronounced and can be explained by an easier formation of radicals that contribute to the degradation instead to trap the radicals formed by the degradation of the PDMS. This hypothesis was confirmed by an increased loading of additives, whatever the structure, which leads to a pronounced degradation and as also observed for polypropylene [40].

B. Ultraviolet Absorbers and Dibromocarbazole as Polydimethylsiloxane Additives

2, 2'-Dihydroxy-4-methoxybenzophenone (UVA 1), 2-tert-Butyl-6(5-chloro-2H-benzotriazol-2-yl 4-methylphenol (UVA 2), and 3,6-dibromo-9H-carbazole were studied as UV stabilizers for PDMS resins. In contrast to the HALS additives, UVAs were specifically developed for space applications and other polymers because their UV inhibition mechanisms do not require oxygen. Unfortunately, no miscibility between those UVAs and the PDMS could be obtained, resulting in heterogeneous and not usable materials.

The cross-linking process of a silicone resin containing 1.0 wt% of 3,6-dibromo-9H-carbazole was followed by DSC. A curing process of 15 h at 70°C was again appropriate. The elastic modulus measured by DMA at 10^6 Pa was not modified by addition of the carbazole derivative. Halogens (Cl and Br) are well known to be good flame retardants and were used for decades in electrical engineering applications, textile treatments, product construction, and polyurethane foams to prevent ignition or to delay and slow the spread of fire by interrupting or disturbing the combustion process [41–43]. Bromine atoms in dibromocarbazole are also expected here to induce higher thermal stability than neat PDMS. The PDMS/dibromocarbazole thermogravimetric analysis showed a strong increase (about 100°C) of the degradation temperature as compared to the neat PDMS, with a $T_{d5\%}$ close to 460°C (Fig. 4).

UV-vis-NIR spectroscopy was then performed before and after UV irradiation on a PDMS prepared with 1.0 wt% of

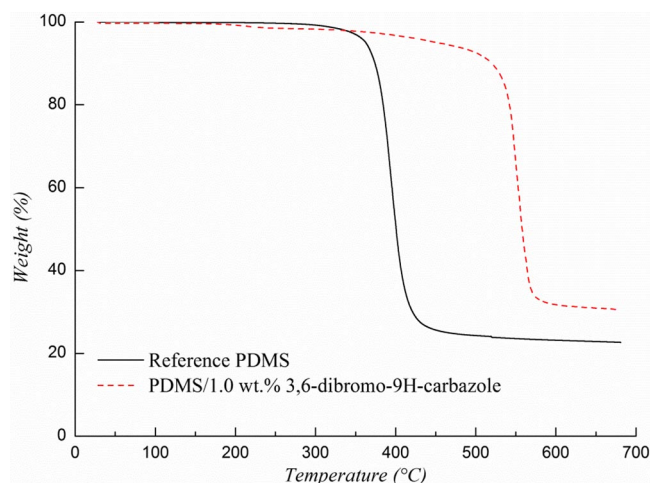


Fig. 4 Thermal degradation of PDMS with 1.0 wt% of dibromocarbazole under nitrogen atmosphere.

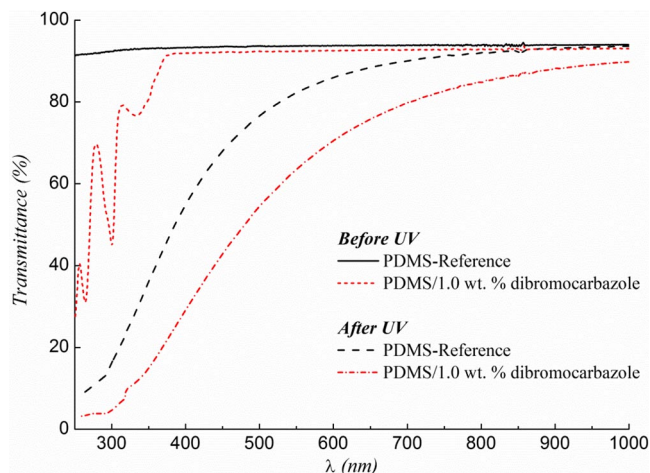


Fig. 5 UV-vis-NIR spectra of PDMS films with dibromocarbazole, before and after UV irradiation (500 ESH).

dibromocarbazole. The bond enthalpy is relatively low for C-Br ($68 \text{ kcal} \cdot \text{mol}^{-1}$), and the homolytic cleavage can occur quite easily. The change in UV transmittance of the PDMS films before irradiation is presented in Fig. 5. The transmittance of the neat PDMS before irradiation is rather constant throughout the wavelength region of 250–1000 nm with a transmittance around 90%. In contrast, the transmittance before UV irradiation for a silicone resin containing 3,6-dibromo-9H-carbazole is 30% lower for short wavelength as compared to the reference material and is explained by the light absorbance of the carbazole derivative at $\sim 280\text{-nm}$ [44].

After the UV irradiation, a loss of transmittance is observed between 250 and 400 nm, going down to 7% at 250 nm for the neat PDMS (Fig. 5) and 3% for the PDMS/1.0 wt% dibromocarbazole. The difference of transmittance between neat PDMS shown Figs. 3, 5 is due to an irradiation time difference: 450 and 500 ESH, respectively. The degradation of the silicone resin with 1.0 wt% of dibromocarbazole was not satisfying, with a calculated average decrease of 14.5%.

IV. Conclusions

Different additives (hindered amine light stabilizer (HALS), ultraviolet absorber (UVA), and dibromocarbazole) for silicone resins were investigated with the aim to enhance the thermal and UV stabilities of cross-linked polydimethylsiloxane (PDMS). The chemical compatibility between the UV stabilizers and the polymer was shown to be a key feature. HALS and dibromocarbazole yielded homogeneous materials when UVAs did not. Addition of 0.5 wt% of HALS 1 can slightly improve both the thermal stability (from 360 to 395°C) and the UV stability (up to 2.6%). Increasing the amount of this additive led to a decrease of the UV stability and a yellowing of the resin. The use of a dibromocarbazole revealed the efficiency of an aromatic/halogen structure as a thermal stabilizer of a PDMS resin.

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