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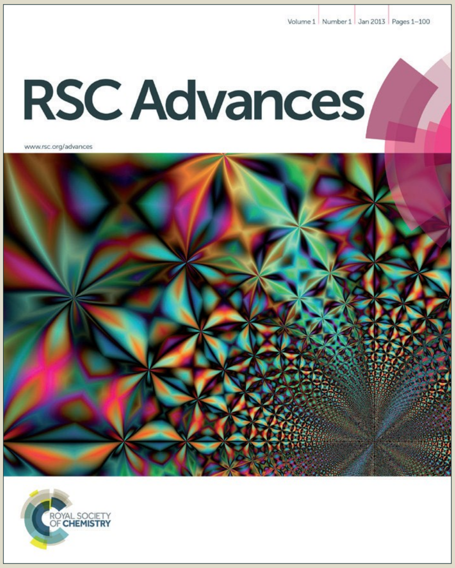

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Fluorescent citric acid-modified silicone materials†

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Novel transparent and flexible silicone materials with fluorescent properties were developed. Fluorescent derivative of 2-pyridone was incorporated into silicone matrix via condensation of citric acid with α,β-diamine groups. Obtained materials were characterized according to FT-IR spectra, contact angle and fluorescence properties. Possible applications as sensors and silicone material's markers were proposed.

Nowadays, researchers are looking for original dyes that may contribute to the development of various fluorescence techniques and expand the area of their applications e.g. in bio-imaging,[1,2] solar cells[3] and polymer probing[4]. Recently our group have discovered new type of fluorescent compounds in condensation mixture of citric acid (CA) and specific β-amines.[1,5] It was found that by the presence of three carboxyl groups and one hydroxyl group, CA is one of the most effective substrates for synthesis of materials with fluorescent properties. First reports about citric acid-based fluorescent compounds can be found in papers from 19th century. Fluorescent moiety i.e. citrazinic acid was obtained through condensation of CA with ammonia.[6] The next step of investigations in the field of fluorescent citric acid based materials was achieved almost a hundred years later by Olthoff et al. They found that CA is able to form fluorescent derivatives of 2-pyridone in reaction with D-penicillamine.[7] Similar reaction was reported for the detection of CA in human blood by *o*-aminothiophenol.[8] In recent years renewed interest in this field can be observed. Low-temperature pyrolysis of citric acid and specific β-amines lead to formation of fluorescent carbon dots (CDs).[9] A number of papers reported the synthesis of fluorescent nanoparticles using various readily available natural resources e.g. orange juice[10], edible chicken eggs[11], bamboo leaves[12] or pomelo peels[13]. More defined organic precursors as glucose, chitosan and ethylenediaminetetraacetic acid salts have also demonstrated a great potential for preparation of CDs. Among all, CA has been used predominantly. Fluorescent materials based on carbon such as CDs derived from CA possess some interesting properties such as biocompatible and non-toxic nature, chemical inertness, high photostability and straightforward one-step synthesis.[14, 15] Above properties makes them potential candidates to be applied in molecular imaging[16], solar cells[17], pH sensors[18] or ions detection[15]. Relatively high fluorescence quantum yield (QY) of CDs up to 80 % is close to traditional fluorescent dyes.[19] Fluorophores obtained through condensation of CA with α,β-diamines, α,β-amino thiols and α,β-amino alcohols and attached on the surface of CDs have recently been proved to have great impact on their QY.[5, 20, 21] These type of molecules were also successfully applied in fabrication of biodegradable photoluminescent polymers (BPLP).[1] BPLPs exhibit cytocompatibility, minimal chronic inflammatory responses *in vivo*, controlled degradability and good photostability.[2] Identification of the origin of their luminescence was possible by isolation of fluorescent agent from the hydrolysate of BPLP. It was found that derivative of 2-pyridone i.e. 5-oxo-2,3-dihydro-5H-[1,3]thiazolo-[3,2-a]pyridine-3,7-dicarboxylic acid is responsible for luminescence phenomena of BPLPs.[1] Other group of polymers in case of which 2-pyridone based fluorescent dyes probably have crucial influence on fluorescent properties are organosilane functionalized CDs[22, 23] or fluorescent mesoporous silica[24]. These types of silica CDs are capable of being functionalized with biomaterials via the silica layer which in combination with biocompatibility allows to exploit them in biomedical applications.[22] Fluorescence QY of these types of silica nanoparticles reached about 50 %. Furthermore, to apply the eco-friendly CDs in practical applications, some research groups tried to embed them in various matrixes. It was reported the trials of preparation fluorescent silica macroporous monolith[25], silicate glass and films[22, 26], ionogels[27] and diverse polymeric materials e.g. cellulose[28], polyvinyl alcohol or poly *N,N'*-dimethylacrylamide.[19, 29] Fluorescent

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properties of all of these materials were obtained in two-step syntheses (fabrication of CDs and blending into matrices). Despite many papers concerning citric acid based fluorescent materials were published, there haven't been any reports about flexible and transparent silicone materials with fluorescence properties until now.

Herein, we report a method of synthesis of innovative silicone materials with fluorescent properties (FSM). Our material is distinguished by flexibility, transparency and chemically bonded fluorophore. Silicone materials based on poly(dimethylsiloxane) (PDMS) and tetraethoxysilane (TEOS) are known very well and they have been in use for many years in industry and medicine.[30, 31] Our modification comprises chemical incorporation of fluorescent derivative of 2-pyridone in the surface layers of material. The formation of this molecule was accomplished in two stages. The first step was the incorporation of α,β-diamine moieties into chemical structure of silicone polymer. Thus, *N*-[3-(Trimethoxysilyl)propyl] ethylenediamine (TMS) was used as a source of α,β-diamine groups. The next step involved surface condensation of these groups with CA. The resulting fluorescent molecule constituted of 5-oxo-1,2,3,5-tetrahydroimidazo[1,2-a]pyridine-7-carboxylic acid (Fig. 1).

Two different methods of modification were developed. The first one assume chemical incorporation of TMS in total volume of material by mixing it with PDMS and TEOS (about 1% of TMS is sufficient for modification). After crosslinking of polymer at 50°C for 24 h, it was immersed in THF solution of CA and then it was heated at 100°C for 2 hours. Afterwards the fluorescent material was extensively washed with distilled water, dried and left for further analyses (Fig. S1†) (Method I). In contrast, the second method was based on incorporation of TMS into pre-crosslinked silicone matrix what was accomplished through polycondensation of PDMS and TEOS in room temperature for 24 h. Next, the material was immersed in ethanol solution of TMS and then cross-linked for another 24 h. The next steps were similar as in the first method (Fig. S2†) (Method II). Dibutyltin dilaurate was used as a catalyst of polycondensation of siloxanes in both methods. Materials manufactured according to above protocols are flexible and transparent. Modification is not visible under daylight (Fig. 2A) and can be observed only under UV light (Fig. 2B). Mechanical properties of FSM depends on PDMS molecular weight. The higher the molecular weight of PDMS the more mechanically resistant the material.

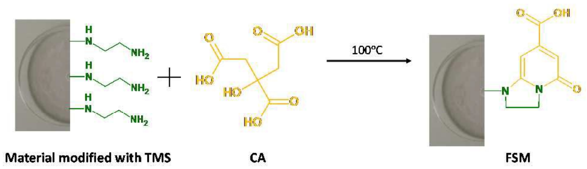

Fig. 1. Synthesis scheme of 5-oxo-1,2,3,5 tetrahydroimidazo[1,2-a]pyridine-7-carboxylic acid on surface layers of the silicone material.

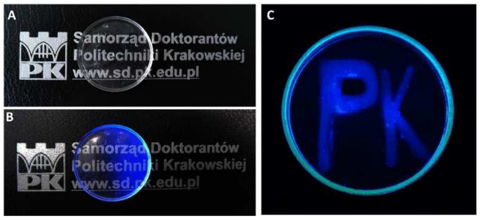

Fig. 2. Half modified silicone material (A) under daylight; (B) under UV light 365 nm. (C) Fluorescent symbols obtained on the modified silicone material.

Furthermore, we were able to obtain fluorescent symbols on the surface of silicones by partial reaction of material prepared through method I with CA. Moreover, induction of previously prepared symbol on samples fabricated using method II by heating entire surface in the presence of CA is also possible (Fig. 2C). Recently, a series of papers have reported formation of various fluorescent polymer materials. Fluorescent properties can be obtained on the entire area of these materials through addition of CDs at the fabrication stage. The modification is sometimes accompanied by yellowing of the material which impairing the aesthetic values.[22, 27] Moreover, fluorophores are mostly blended within the polymer matrix rather than chemically bonded.[22-26, 28, 32] Thus, it was not possible to create fluorescent symbols and inscriptions because of an obstacle with introduction of the CDs at specific location over the material. Therefore, inkjet-printing technique was proposed to overcome this issue.[14, 19, 26, 33-35] However, this method can be applied only for materials which absorb CD solution and even though patterns received in this manner might be prone to leaching out, attrition and fading of the ink. Our methodology of patterning of silicones is based on chemical incorporation of ring fused 2-pyridone into specific part of material which in our opinion is more resistant to mechanical factors and environmental conditions than printed images. This makes it a really promising method of marking polymeric materials e.g. anti-counterfeit fields or optoelectronic devices.

We examined FT-IR and fluorescence emission spectra, contact angles, fluorescence stability and potential applications of FSMs. The Fourier transform infrared (FT-IR) spectra (Fig. 3) shows characteristic signals of silicone materials.[36, 37] The peaks at 1009 and 1081 cm^{-1} can be ascribed to the symmetric and asymmetric stretching vibration of Si-O-Si groups. The band at 871 cm^{-1} was assigned to stretching vibrations of Si-OH. The peaks at 1257 and 787 cm^{-1}

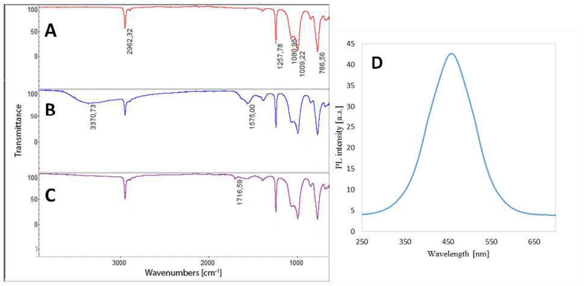

Fig. 3. FT-IR spectra of (A) unmodified silicone, (B) modified silicone with TMS, and (C) FSM. (D) Fluorescence emission spectra of FSM.

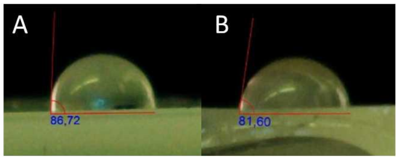

Fig. 4. Contact angle photographs of (A) unmodified silicone material and (B) FSM.

were attributed to the C-H scissoring and rocking vibrations of Si-CH_3. The band corresponding to the C-H stretching vibrations of CH_3 groups was observed at 2962 cm^{-1}. All of these signals are observed in case of unmodified samples, materials modified with TMS and FSM samples. Furthermore, the absorptions at 3370 and 1575 cm^{-1} in the spectrum of materials modified with TMS are due to asymmetric stretching and scissoring vibrations of N-H respectively, confirming the presence of NH_2 and NH groups on the surface of modified silicone material (Fig. 3B). FT-IR spectrum of fluorescent silicone material show modes of C=O stretching vibrations at 1716 cm^{-1} derived from COOH groups while signals from NH and NH_2 groups disappeared (Fig. 3C). It confirms the successful reaction of α,β-diamine groups with CA leading to fluorescent molecules (Fig. 1). The signals in the FT-IR spectra are predominated by silicone matrix since the quantity of TMS is as low as 1% mass and even lower for the fluorescence molecules. FSM samples excited with 365 nm light emit strong, blue luminescence at 460 nm (Fig. 3D) which is in agreement with the data reported for other fluorescent derivatives of 2-pirydone.[5, 19]

Contact angle measurements showed that the surface of FSM is more hydrophilic compared to unmodified silicone due to the presence of carboxylic groups of the dye at the surface of the material (Fig. 4). However, these differences are rather minor what promotes the employment of our modification in current applications of PDMS/TEOS based materials.

Furthermore, we found that our materials can be exploit as iron ions, chromates and ascorbic acid sensors. FSM immersed in water and Fe^{3+} solution are shown in Figure 5A. When materials were excited with 356 nm UV light fluorescence quenching in Fe^{3+} solution could be observed (Fig. 5A II). We found that linear relationship between fluorescence emission intensity and concentration of iron ions exist. The higher the Fe^{3+} concentration the less fluorescence emission of material can be observed until complete quenching at ~0,57 mg/ml of iron (Fig. 5B). As shown in Figure 5D I the linear range is 0,0011-0,0709 mg/ml of Fe^{3+}, in which the fluorescence intensity vs the Fe^{3+} concentration plot can be curve-fitted into (I_0/I)= 57,65x +1,175 with a correlation coefficient R^2 of 0,986. Above Fe3+ detection range is similar to that reported in the literature for CD based Fe3+ sensor but can be easily recovered unlike CD-based sensor.[38] Moreover, "turn off" fluorescence of silicone material in water solutions of $Cr_2O_7^{2-}$ is also observed (Fig. 5C). The total fluorescence quench occurs at ~0,11 mg/ml of chromates solution. A good linear relationship of fluorescence intensity and $Cr_2O_7^{2-}$ concentration is observed from 0,0035 to 0,0564 mg/ml (Figure 5D II), according to (I_0/I)= 44,43x+1,245 with a correlation coefficient R^2 of 0,992. Concentrations of chromates which can be detected using FSM are much higher compared to CD based sensors (from $0,108·10^{-5}$ to 0,0054 mg/ml Cr2O7).[39] Detection of iron ions and chromates is based on the inner filter effect[39]. The absorption bands of Fe^{3+} and

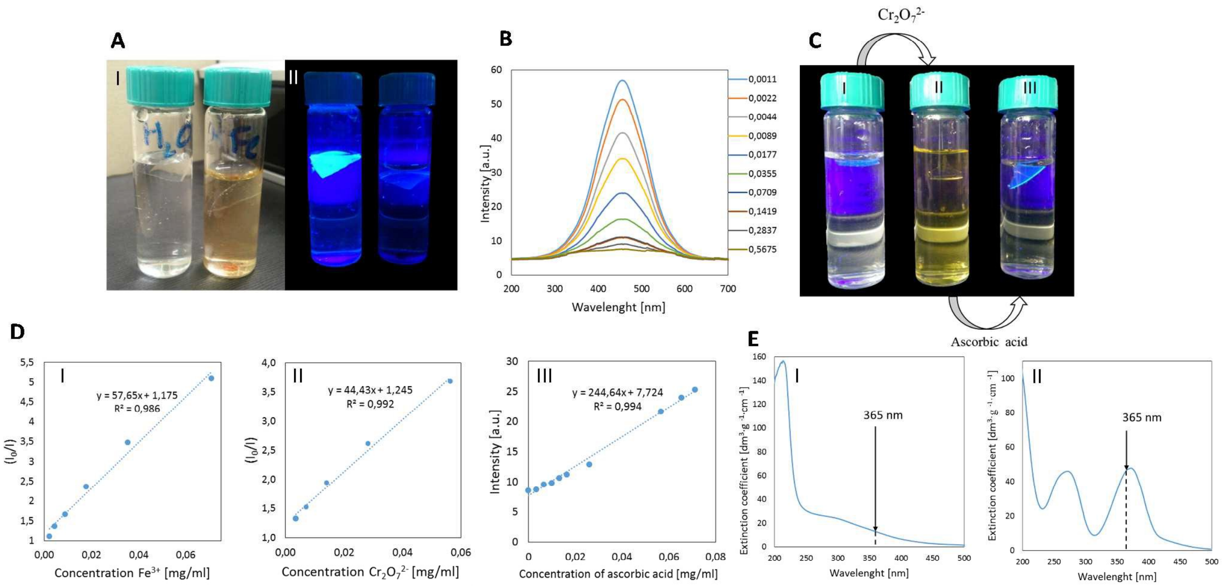

Fig. 5. (A) FSM in water (left) and Fe^{3+} solution (right) under daylight (I) and under UV light 365 nm (II); (B) Fluorescence emission spectra of FSM in various concentrations of the Fe^{3+} [mg/ml]; (C) FSM in water (I), $Cr_2O_7^{2-}$ solution (II) and $Cr_2O_7^{2-}$ solution with AA (III) under UV light 365 nm; (D) the plot of fluorescence for FSM quenched by Fe^{3+} (I) and $Cr_2O_7^{2-}$ (II) solution, the plot of the fluorescence intensity of FSM against AA concentration (III). (E) Absorption spectrum of Fe^{3+}(I) and $Cr_2O_7^{2-}$ (II) solution.

Table 1. Fluorescence emission intensity of FSM under various environmental conditions after 1 and 6 months.

Storage environment	The maximum intensity of fluorescence emission before the test	The maximum intensity of fluorescence emission	
		After 1 month	After 6 months
Water	28,915	35,484	35,672
0,1 M HCl	30,705	37,375	36,768
0,1 M KOH	30,464	25,604	25,124
Acetone	13,698	25,564	25,577
Ethanol	29,895	43,901	42,826
THF	18,003	27,389	27,973
Heptane	19,672	26,848	25,011
Detergent	26,787	45,989	44,971
Buffer pH 4	25,834	29,582	29,739
Buffer pH 9	26,152	36,279	36,982
String bag	25,061	26,841	26,179

Cr(IV) covered the excitation bands (365 nm) of FSM (Fig. 5E). This "turn off" fluorescent sensor has potential application for the detection of these metals in the environmental industry e. g. in drinking water. Furthermore, there is a possibility to "turn on" fluorescence of material immersed in Cr(VI) solution. Elimination of the inner filter effect can be carried out by reduction of Cr(VI) to Cr (III) by e. g. ascorbic acid (AA).[39] The fluorescence was enhanced gradually with increasing amount of AA. The linear response of "turning on" fluorescence with correlation coefficient R^2 of 0,994 is shown in Figure 5D III. Using FSM it is possible to detect AA in the range of 0,0033-0,0712 mg/ml which is much wider range compared to 0,0053-0,0176 mg/ml using CDs.[39] Moreover, reduction reaction of Cr(VI) in the presence of AA require bland reaction conditions so it is easy to carry out.[40] Thus our FSM can be used in detection of vitamin C.

In order to examine possible application of our modification as silicone material's markers the fluorescent stability tests were conducted. Fluorescence emission intensity measurements of materials were conducted under various environmental conditions. Then materials were exposed for 1 month to the same surroundings and fluorescence emission intensities were measured again. As shown in Table 1, most of the studied variants have not affected the fluorescence emission intensity of FSMs. Moreover, these materials exhibit comparable fluorescence intensity after 6 months which is promising to our method of modification in terms of fluorescent marking of silicone materials.

Conclusions

In summary, we developed a methodology for the synthesis of transparent and flexible silicone materials with fluorescent properties. Fluorescent derivative of 2-pirydone was chemically bonded to the silicone matrix through condensation of CA with α,β-diamine groups derived from TMS. Presented modification retains physicochemical properties of non-fluorescent materials. As few as 1 % mass of TMS is efficient to produce transparent, elastic materials with strong and resistant fluorescence properties. Thus, our idea for modification of PDMS/TEOS based materials can be an effective way to expand the area of their applications. Furthermore, incorporation of derivative of 2-pyridone in the specific location of materials seems to be really promising technique for fluorescent marking of polymeric materials. More detailed investigations on the FSM and modification of another types of materials will be subject of future publications.

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