Electronic Supplementary Material (ESI) for RSC Advances.

Urea formaldehyde (UF) microcapsules loaded with corrosion inhibitor for enhancing the anti-corrosive property of acrylic-based multi-functional PU coatings

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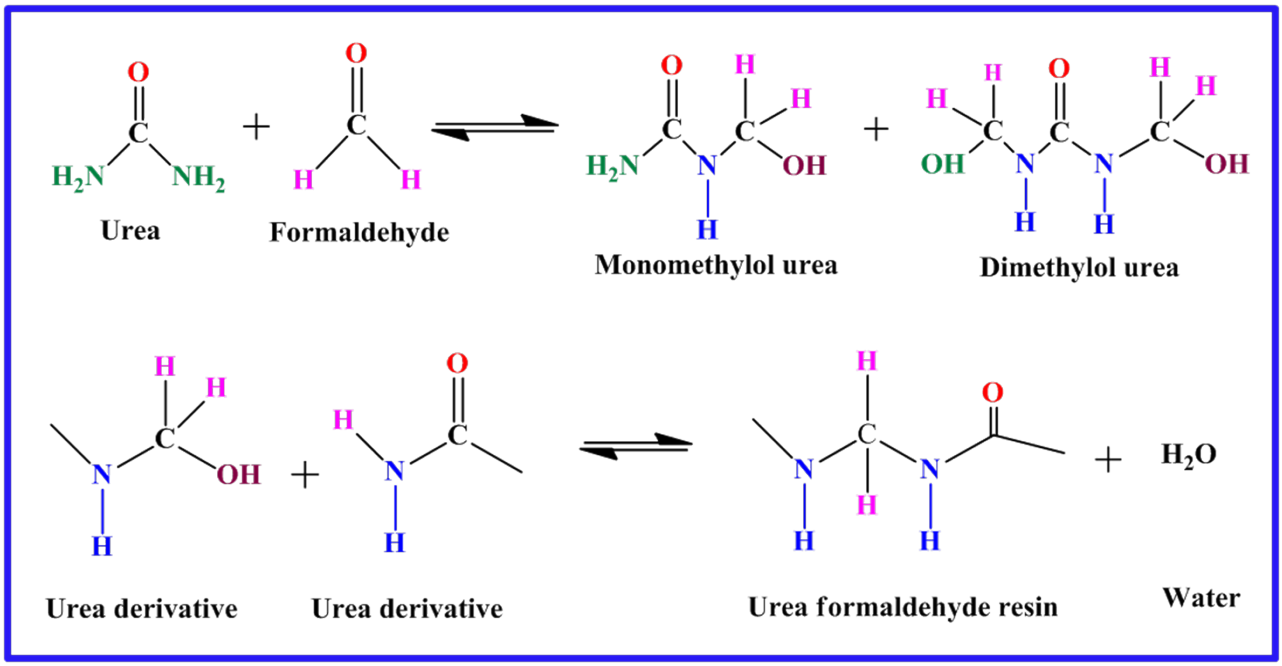
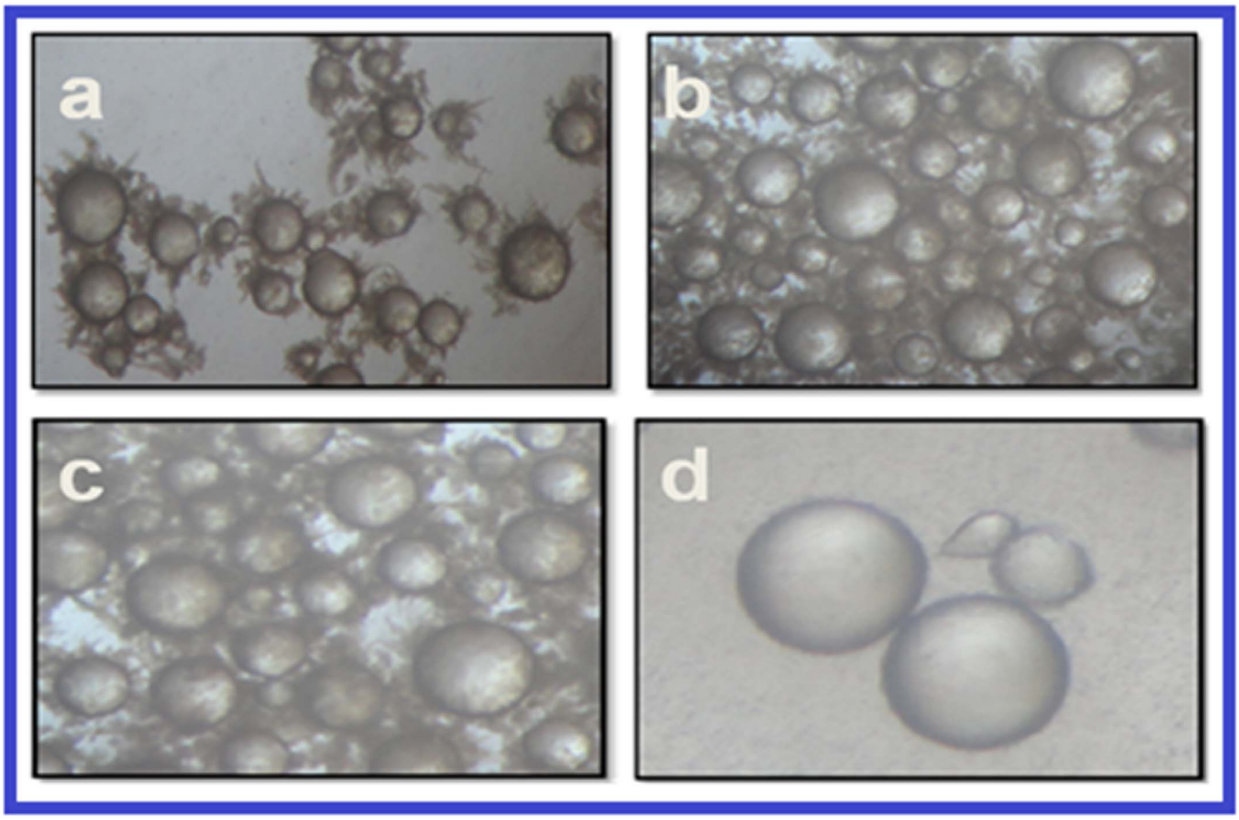
Supporting information



Supporting Figure S1 Schematic representation of the reaction for UF microcapsule preparation.

Optical microscope

Initially, encapsulation of the inhibitors (2-MBT and 2-MBI) within UF microcapsules was verified via optical microscope. Images taken during inhibitor encapsulation are noted in Supporting Figure S2. These observations show that most microcapsules were spherical, with a few being ovel in shape.

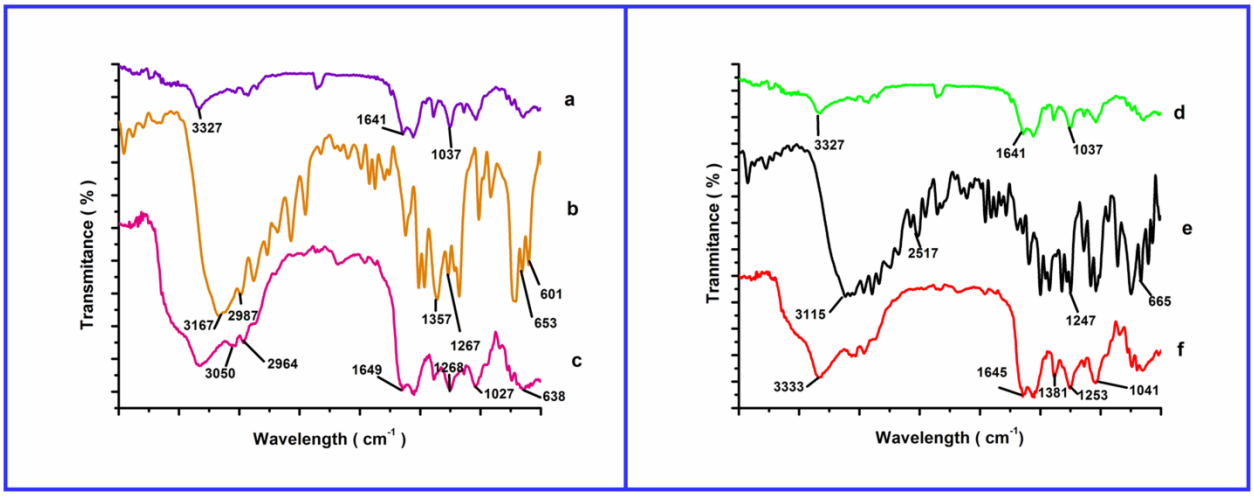


Supporting Figure S2 Optical microscopic images of microcapsules with 2-MBI (a and b); 2-MBT (c and d).

FT-IR analysis

FT-IR spectra of 2-MBI, 2-MBT, and UF microcapsules with active cores are shown in Supporting Figure S3. The spectrum in (b) shows a 3197-cm^{-1} absorption band for -N-H stretching and a band at 2987 cm^{-1} for Ar-CH stretching of 2-MBI. For -C-N streching, bands

were obtained at 1357 and 1267 cm^{-1}, while -C-S stretching absorption bands appeared at 601 and 653 cm^{-1}. In spectrum (c), the -N-H streching bands of a UF shell were noted at 3707 and 3050 cm^{-1}, whereas the absorption band for -CO-NH was obtained at 1649 cm^{-1}. Stretching for -C-O-C- was observed at 1027 cm^{-1}. The aromatic -C-H stretching band of 2-MBI was observed at 2964 cm^{-1}. Stretching for -C-N and -C-S present in 2-MBI were found at 1258 and 638 cm^{-1}, respectively. The data shows that the characteristic frequencies of 2-MBI were present in the FT-IR spectra of UF microcapsules containing 2-MBI as a corrosion inhibitor. Thus, FT-IR analysis clearly indicated that unaltered 2-MBI was present in polymeric UF microcapsules.



Supporting Figure S3 FT-IR spectra of (a and d) UF shell (b) core 2-MBI, (c) microcapsules containing 2-MBI, (e) core 2-MBT, (f) microcapsules containing 2-MBI.

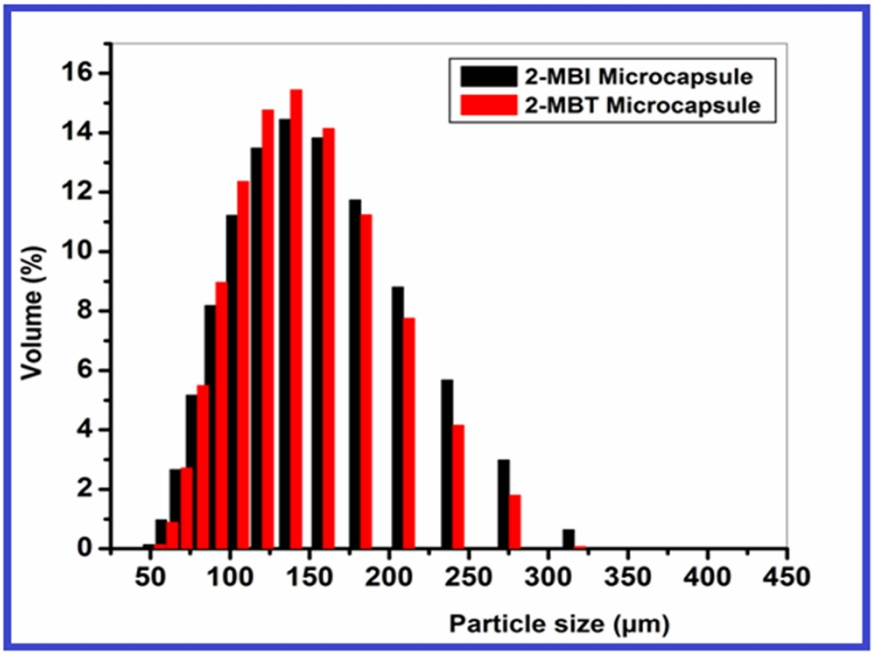
The spectrum in (e) represents the corrosion inhibitor core moiety 2-MBT, which demonstrated an absorption band at 3115 cm^{-1} for Ar-CH stretching and at 1247 cm^{-1} for aromatic -C-C stretching. In addition, -C-S and -S-H stretching vibrations were obtained at 665 and 2517 cm^{-1}, respectively. The spectrum in (f) denotes the UF microcapsules containing corrosion inhibitor 2-MBT, which yielded spectral values for –NH and -OH stretching in a merged band of 3333 cm^{-1} and a -NH-CO-NH absorption band at 1645 cm^{-1}. Streching for -CO-

NH- appeared at 1041 cm^{-1}. The -C-C stretching and -C-S stretching vibration bands were observed at 1253 and 653 cm^{-1}, respectively. The -C=N stretching band was seen at 1381 cm^{-1}. From the FT-IR spectra in (e) and (f), it was concluded that 2-MBT was encapsulated in the UF shell with structural integrity.

Spectra (a) and (d) represent empty UF polymeric shells. The empty UF shell having a 3341 cm^{-1} peak denotes –NH and-OH stretching. The stretching frequency at 1641 cm^{-1} represents the NH-CO-NH abosorption band, and a 1037 cm^{-1} stretching frequency was noted for –CO-NH. However, these spectra contained no absorption peaks for the -S-H moiety, which is specific to the core materials. The data obtained from these FT-IR spectra clearly show that the MBI and MBT corrosion inhibitors were present in the UF microcapsules.

Particle size distribution of microcapsules

Particle size analysis of microcapsules was carried out to study particle size distributions and average particle sizes of the prepared microcapsules. All parameters were held constant during preparation of UF microcapsules except the corrosion inhibitor in order to study the effect of inhibitor on microcapsule distribution and size. Supporting Figure S4 shows a particle size histogram of microcapsules containing 2-MBI and 2-MBT corrosion inhibitors contained in UF microcapsules. The particle size graph denotes the average particle size of microcapsules as 149 μm for 2-MBI and 143 μm for 2-MBT microcapsules. Furthermore, the histogram also shows similar particle size distributions for both microcapsules. Thus, particle size analysis demonstrated that size distribution and average particle size were independent of inhibitor for the set of experiments designed to prepare UF microcapsules.



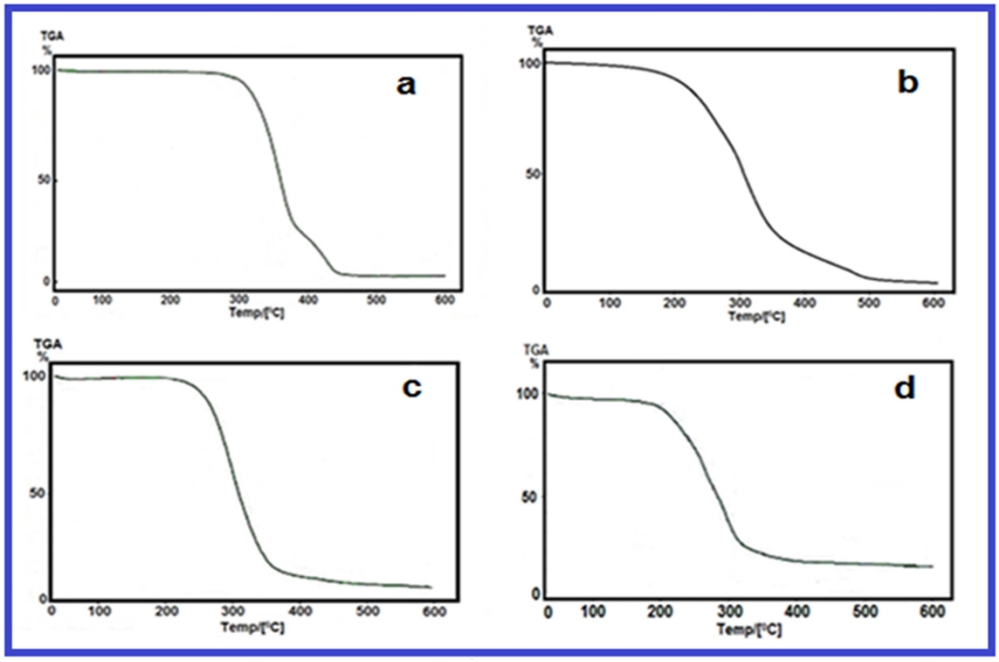
Supporting Figure S4 Particle size histogram of microcapsules containing 2-MBI or 2-MBT.

Thermogravimetric analysis

All TGA curves of pristine 2-MBI and 2-MBT with encapsulated conditions are given in Supporting Figure S5. The TGA curves show a slight weight loss up to 200 ^{0}C due to the presence of a trace amount of moisture in the microcapsules. The TGA curve for a pure core (2-MBI) showed weight loss in the temperature range of 300 to 359 ^{0}C with complete degradation of the remaining residue up to 600 ^{0}C. However, the TGA curve of its encapsulated form showed a second degradation from 200 to 255 ^{0}C of the UF polymeric shells of microcapsules.[1] The third weight loss was observed from 300 to 363 ^{0}C, corresponding to thermal degradation of 2-MBI, which confimed the presence of corrosion inhibitor in the prepared UF microcapsules.

The TGA curve shows the thermal degradation of pure 2-MBT between 240-360 ^{0}C. In the case of its microcapsules, a second weight loss was noted from 230 to 264 ^{0}C, and a third weight loss

occurred from 265 to 350 ^{0}C. The former is associated with the decomposition of the UF polymer shell, while the latter is associated with degradation of 2-MBT, thus indicating its presence in UF microcapsules. The thermal study of cores and their microcapsules suggested that the two inhibitors had different thermal degradation temperatures. Encapsulation of each inhibitor in the UF shell was confirmed in the present study.



Supporting Figure S5 TGA curves of (a) core 2-MBI, (b) UF microcapsules containing 2-MBI corrosion inhibitor, (c) core 2-MBT, and (d) UF microcapsules containing 2-MBT corrosion inhibitor.

Corrosion study

Supporting Table S1 Corrosion parameters obtained from a Tafel polarization plot of PU coatings containing encapsulated 2-MBI corrosion inhibitor and tested against 0.5 M HCl solution.

Microcapsule Loading (%)	I_{corr} µA. cm^{-2}	E_{corr} mV	beta c(mv)	beta a(mv)	CR (myr)	% IE	θ
Uncoated	39.502	-493.46	186.2	68.7	12.794	-	
0%	30.368	-507.81	250.4	71.6	9.898	23.12288	0.231229
1%	20.364	-495.42	381.5	73.1	6.637	48.44818	0.484482
2%	20.267	-493.62	281.5	67.8	6.606	48.69374	0.486937
3%	17.508	-504.753	280.8	72	5.706	55.67819	0.556782
4%	16.634	-496.849	355.6	67	5.422	57.89074	0.578907
5%	16.177	-502.733	384.2	68.3	5.273	59.04764	0.590476

Supporting Table S2 Corrosion parameters obtained from a Tafel polarization plot of PU coatings containing encapsulated 2-MBT corrosion inhibitor and tested against 0.5 M HCl solution.

Microcapsule Loading (%)	I_{corr} µA. cm^{-2}	E_{corr} mV	beta c(mv)	beta a(mv)	CR (myr)	% IE	θ
Uncoated	39.502	-493.46	186.2	68.7	12.794	-	
0%	30.368	-507.81	250.4	71.6	9.898	23.1228799	0.2312288
1%	27.884	-506.602	340.7	82.1	9.089	29.4111691	0.29411169
2%	21.306	-501.014	288.1	76.6	6.944	46.0634905	0.4606349
3%	15.633	-510.99	311.7	65.7	5.095	60.4247886	0.60424789
4%	14.984	-500.715	347	73	4.884	62.0677434	0.62067743
5%	14.796	-500.195	410.6	71.2	4.822	62.5436687	0.62543669

Weight loss study

Supporting Table S3 Corrosion parameters obtained from a weight loss study of PU coatings containing encapsulated 2-MBI corrosion inhibitor and tested against 0.5 M HCl solution.

Microcapsule Loading (%)	CR (g cm^{-2} h^{-1})	% IE	θ
Uncoated	186.834	-	-
0%	97.0222	48.07037	0.480704
1%	86.68436	53.60353	0.536035
2%	42.46622	77.27061	0.772706
3%	34.95174	81.29262	0.812926
4%	24.19402	87.05053	0.870505
5%	20.21236	89.18165	0.891816

Supporting Table S4 Corrosion parameters obtained from a weight loss study of PU coatings containing encapsulated 2-MBT corrosion inhibitor and tested against 0.5 M HCl solution.

Microcapsule Loading (%)	CR (g cm^{-2} h^{-1})	% IE	θ
Uncoated	186.834	-	-
0%	97.0222	48.07037	0.480704
1%	56.98842	69.49783	0.694978
2%	42.49517	77.25511	0.772551
3%	31.41892	83.18351	0.831835
4%	17.07046	90.8633	0.908633
5%	10.84459	94.1956	0.941956

Supporting reference:

1. G. Wu, J. An, X. Tang, Y. Xiang and J. Yang, *Adv. Funct. Mater.,* 2014, **24,** 6751–6761.