Supplementary Information

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Table S1 Elemental analysis and portion of extractables (48 h, MeOH) of composite **P2** repeated for nine times; Remainder% = 100 % − C% − N% − H%.

Sample	Extractables	Quantitative elemental analysis			
	(48 h MeOH)	C%	H%	N%	Remainder%
P2 (1)	15 %	61.0	9.53	11.7	17.8
P2 (2)	13 %	61.0	9.56	11.8	17.6
P2 (3)	14 %	61.4	9.62	11.9	17.1
P2 (4)	16 %	61.2	9.60	11.8	17.4
P2 (5)	14 %	60.9	9.44	11.7	18.0
P2 (6)	17 %	61.2	9.55	11.7	17.6
P2 (7)	–	61.8	9.67	11.9	16.6
P2 (8)	–	61.6	9.61	11.8	17.0
P2 (9)	–	60.2	9.39	11.6	18.8
	calculated	61.7 %	9.62 %	12.0 %	16.7 %

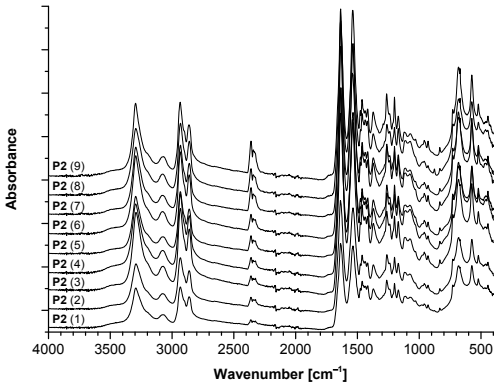


Fig. S1 ATR-FTIR spectra of composite **P2** (extracted samples) showing repetition of synthesis procedure for nine times.

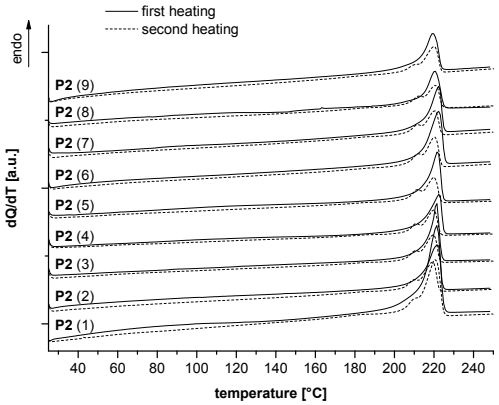


Fig. S2 DSC traces of composite **P2**, repetition of synthesis procedure for nine times; cyclic measurements, extracted samples (48 h, MeOH).

Table S2 Data acquisition details for the single X–ray diffraction analyses of **Si(*ε*-CL)$_4$ 1** and **Si(CHO)$_4$ 2**.

parameter	Value	
	Si(*ε*-CL)$_4$ 1	**Si(CHO)$_4$ 2**
CCDC	1058156	1058182
empiric formula	$C_{24}H_{40}N_4O_4Si$	$C_{24}H_{40}N_4O_4Si$
molecular weight	476.69	476.69
temperature	110 K	110 K
wavelength	0.71073 Å	0.71073 Å
crystal system, space group	orthorhombic, P n a 21	Tetragonal, I-42d
dimension of unit cell	a = 18.1083(7) Å; α = 90 deg.	a = 13.9688(3) Å; α = 90 deg.
	b = 17.6737(9) Å; β = 90 deg.	b = 13.9688(3) Å; β = 90 deg.
	c = 7.6710(3) Å; γ = 90 deg.	c = 13.3347(4) Å; γ = 90 deg.
volume	2455.03(18) Å^3	2601.97(11) Å^3
Calculated density	1.290 mg/cm^3	1.217 g/cm^3
Absorption coefficient	0.133 mm^{-1}	0.126 mm^{-1}
F(000)	1032	1032
Crystal size	0.4 x 0.4 x 0.2 mm	0.5 x 0.5 x 0.4 mm
Theta–angle for data acquisition	2.895 to 25.495	3.60 to 25.00
Limiting indices	−21≤h≤21, −20≤k≤21, −9≤l≤8	−15≤h≤16, −16≤k≤16, −15≤l≤15
Reflections collected/unique	10195 / 4209 [R(int) = 0.0477]	3191 / 1107 [R(int) = 0.0215]
Completeness of theta = 25.500	99.6 %	99.2 %
Absorption correction	Semi–empirical from equivalents	Semi–empirical from equivalents
Max. and min. transmission	1.00000 and 0.55157	1.00000 and 0.88537
Refinement method	Full–matrix least squares on F^2	Full–matrix least squares on F^2
Data/restraints/parameters	4209 / 1 / 298	1107 / 0 / 75
Goodness–of–fit	1.044	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.1307	R1 = 0.0263, wR2 = 0.0621
R indices (all data)	R1 = 0.0705, wR2 = 0.1384	R1 = 0.0282, wR2 = 0.0632
Absolute structure parameter	−0.05 (12)	−0.22 (16)
Largest diff. peak and hole	0.683 and –0.262 e.A^{-3}	0.131 and –0.172 e.A^{-3}

Table S3 Measured bond lengths and angles in **Si(*ε*-CL)$_4$ 1.**

bond lengths in Å

Si(1)–N(1)	1.759(4)	Si(1)–N(2)	1.755(4)	Si(1)–N(3)	1.758(4)
Si(1)–N(4)	1.760(4)	C(1)–O(1)	1.238(5)	C(1)–N(1)	1.374(5)
C(1)–C(2)	1.507(6)	C(2)–C(3)	1.541(6)	C(3)–C(4)	1.519(6)
C(4)–C(5)	1.540(6)	C(5)–C(6)	1.517(6)	C(6)–N(1)	1.517(6)
C(7)–O(2)	1.227(5)	C(7)–O(2)	1.368(6)	C(7)–C(8)	1.512(6)
C(8)–C(9)	1.534(6)	C(9)–C(10)	1.525(6)	C(10)–C(11)	1.508(7)
C(11)–C(12)	1.521(6)	C(12)–N(2)	1.475(5)	C(13)–O(3)	1.229(5)
C(13)–N(3)	1.373(6)	C(13)–C(14)	1.501(6)	C(14)–C(15)	1.527(6)
C(15)–C(16)	1.517(6)	C(16)–C(17)	1.523(6)	C(17)–C(18)	1.516(6)
C(18)–N(3)	1.475(5)	C(19)–O(4)	1.231(5)	C(19)–N(4)	1.362(6)
C(19)–C(20)	1.505(6)	C(20)–C(21)	1.547(6)	C(21)–C(22)	1.523(6)
C(22)–C(23)	1.522(7)	C(23)–C(24)	1.508(6)	C(24)–N(4)	1.475(5)

bond angels in °

O(1)–C(1)–N(1)	119.3(4)	O(1)–C(1)–C(2)	121.3(4)	N(1)–C(1)–C(2)	119.3(4)
C(1)–C(2)–C(3)	113.2(4)	C(4)–C(3)–C(2)	113.8(4)	C(3)–C(4)–C(5)	114.7(4)
C(6)–C(5)–C(4)	114.5(4)	N(1)–C(6)–C(5)	115.8(4)	O(2)–C(7)–N(2)	120.2(4)
O(2)–C(7)–C(8)	120.5(4)	N(2)–C(7)–C(8)	119.2(4)	C(7)–C(8)–C(9)	112.7(4)
C(10)–C(9)–C(8)	114.6(4)	C(11)–C(10)–C(9)	115.9(4)	C(10)–C(11)–C(12)	115.0(4)
N(2)–C(12)–C(11)	114.3(4)	O(3)–C(13)–N(3)	119.3(4)	O(3)–C(13)–C(14)	121.3(4)
N(3)–C(13)–C(14)	119.3(4)	C(13)–C(14)–C(15)	114.1(4)	C(16)–C(15)–C(14)	114.6(4)
C(15)–C(16)–C(17)	115.7(4)	C(18)–C(17)–C(16)	114.6(4)	N(3)–C(18)–C(17)	115.3(3)
O(4)–C(19)–N(4)	119.5(4)	O(4)–C(19)–C(20)	120.8(4)	N(4)–C(19)–C(20)	119.6(4)
C(19)–C(20)–C(21)	112.5(4)	C(22)–C(21)–C(20)	113.5(4)	C(23)–C(22)–C(21)	114.6(4)
C(24)–C(23)–C(22)	115.8(4)	N(4)–C(24)–C(23)	114.9(4)	C(1)–N(1)–C(6)	120.9(4)
C(1)–N(1)–Si(1)	114.8(3)	C(6)–N(1)–Si(1)	122.9(3)	C(7)–N(2)–C(12)	120.7(4)
C(7)–N(2)–Si(1)	114.6(3)	C(12)–N(2)–Si(1)	123.3(3)	C(13)–N(3)–C(18)	120.9(4)
C(13)–N(3)–Si(1)	114.9(3)	C(18)–N(3)–Si(1)	123.3(3)	C(19)–N(4)–C(24)	120.5(4)
C(19)–N(4)–Si(1)	114.9(3)	C(24)–N(4)–Si(1)	123.4(3)	N(2)–Si(1)–N(3)	109.92(16)
N(2)–Si(1)–N(1)	110.08(18)	N(3)–Si(1)–N(1)	108.24(19)	N(2)–Si(1)–N(4)	107.84(19)
N(3)–Si(1)–N(4)	110.28(17)	N(1)–Si(1)–N(4)	110.49(16)		

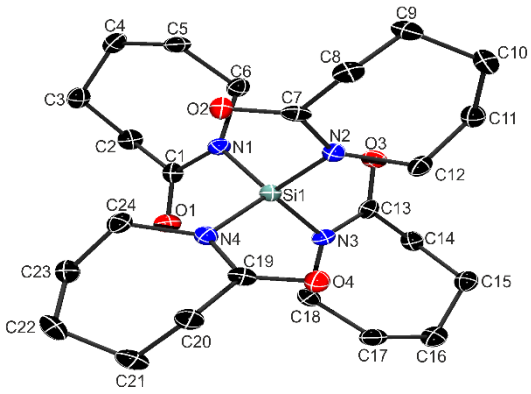
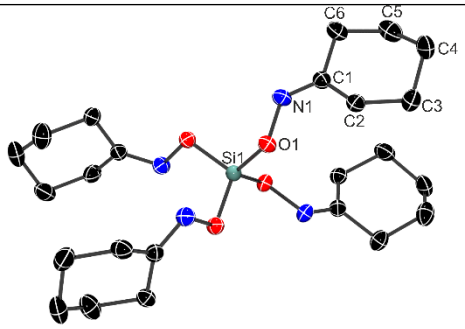


Table S4 Measured bond lengths and angles in **Si(CHO)$_4$ 2.**

	bond lengths in Å		bond angels in °
Si(1)–O(1)	1.6353(10)	(1)#1–Si(1)–O(1)#2	108.93(3)
O(1)–N(2)	1.4596(15)	O(1)#1–Si(1)–O(1)#3	110.56(7)
N(2)–C(1)	1.275(2)	O(1)#2–Si(1)–O(1)#3	108.93(3)
C(6)–C(1)	1.498(2)	O(1)#1–Si(1)–O(1)	108.93(3)
C(6)–C(5)	1.533(2)	O(1)#2–Si(1)–O(1)	110.56(7)
C(6)–H(6A)	0.9700	O(1)#3–Si(1)–O(1)	108.93(3)
C(6)–H(6B)	0.9700	N(2)–O(1)–Si(1)	107.59(8)
C(2)–C(1)	1.504(2)	C(1)–N(2)–O(1)	111.64(12)
C(2)–C(3)	1.521(2)	C(1)–C(6)–C(5)	110.78(14)
C(2)–H(2A)	0.9700	C(1)–C(6)–H(6A)	109.5
C(2)–H(2B)	0.9700	C(5)–C(6)–H(6A)	109.5
C(4)–C(3)	1.523(3)	C(1)–C(6)–H(6B)	109.5
C(4)–C(5)	1.523(3)	C(5)–C(6)–H(6B)	109.5
C(4)–H(4A)	0.9700	H(6A)–C(6)–H(6B)	108.1
C(4)–H(4B)	0.9700	C(1)–C(2)–C(3)	111.70(14)
C(3)–H(3A)	0.9700	C(1)–C(2)–H(2A)	109.3
C(3)–H(3B)	0.9700	C(3)–C(2)–H(2A)	109.3
C(5)–H(5A)	0.9700	C(1)–C(2)–H(2B)	109.3
C(5)–H(5B)	0.9700	C(3)–C(2)–H(2B)	109.3
		H(2A)–C(2)–H(2B)	107.9
		N(2)–C(1)–C(6)	127.79(13)
		N(2)–C(1)–C(2)	115.17(13)
		C(6)–C(1)–C(2)	117.04(12)
		C(3)–C(4)–C(5)	110.58(15)
		C(3)–C(4)–H(4A)	109.5
		C(5)–C(4)–H(4A)	109.5
		C(3)–C(4)–H(4B)	109.5
		C(5)–C(4)–H(4B)	109.5
		H(4A)–C(4)–H(4B)	108.1
		C(4)–C(3)–C(2)	110.23(14)
		C(4)–C(3)–H(3A)	109.6
		C(2)–C(3)–H(3A)	109.6
		C(4)–C(3)–H(3B)	109.6
		C(2)–C(3)–H(3B)	109.6
		H(3A)–C(3)–H(3B)	108.1
		C(4)–C(5)–C(6)	111.51(14)
		C(4)–C(5)–H(5A)	109.3
		C(6)–C(5)–H(5A)	109.3
		C(4)–C(5)–H(5B)	109.3
		C(6)–C(5)–H(5B)	109.3
		H(5A)–C(5)–H(5B)	108.0



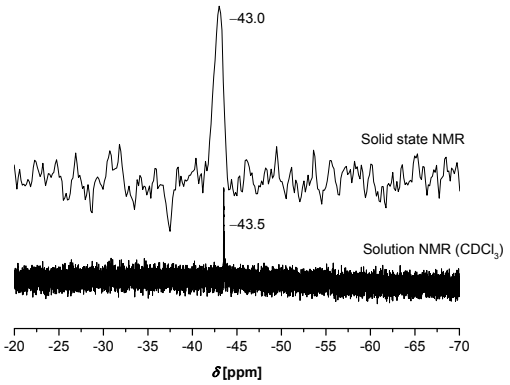


Fig. S3 solid state and solution NMR spectra of monomer **1**

Table S5 Polymerization reactions with $Si(CHO)_4$ as twin monomer with molar ratios of reactants, reaction conditions and observations.

catalyst	Molar ratios of reactants			Reaction conditions	Result	Extractables (EtOH)
	ε-ACA	$Si(CHO)_4$	ε-CL			
–	9	1	–	2.5 h, 100 °C	No reaction	–
–	4	1	0	2.5 h, 220 °C	PA6, ε-CL, CHO and cyclohexanone detectable	36 %
50 µL HCl	–	1	42	4 h, 230 °C	PA6 and ε-CL detectable 15 % in water insoluble residue	–
50 µL HCl	42	1	–	4 h, 230 °C	PA6, ε-CL and CHO detectable	23 %
50 µL CF_3COOH	–	1	42	4 h, 230 °C	No reaction	–
50 µL HCl	8	1	–	1 h, 230 °C	PA6, ε-CL and CHO detectable	39 %
10 µL H_2SO_4	6.5	1	–	30 min 200 °C, 10 min 220 °C	PA6, ε-CL and CHO detectable	–

CHO – cyclohexanone oxime; ε-CL - ε-caprolactam

At high temperatures above 220 °C under usage of ε-ACA PA6 as well as ε-CL formation is detected, but both products were formed by ε-Aminocaproic acid monomers. Therefore high extractables from hydrolysed $Si(CHO)_4$ respectively formation of cyclohexanone oxime (CHO) were observed.

Table S6 Experimental conditions and molar ratios of the tests under usage of water in comparison to the reference experiment with ε–ACA as water source.

sample	Molar ratios of reactants				Reaction conditions	Picture	Extractables (48 h, MeOH)	Observation
	H_2O	ε-ACA	$Si(ε\text{-}CL)_4$	ε-CL				
Reference PA6, ε-ACA as water source	–	1	–	4.4	3 h, 230 °C, 8 bar		10.0 %	PA6
PA6, use of water	1	–	–	11.8	4 h, 230 °C, 2 bar		19.0 %	PA6, discoloration
PA6/SiO_2 hybrid material, use of water	6.6	–	1	21.1	Precondensation of ε-CL + H_2O; 2 h, 230 °C; 2.5 bar Further reaction with **$Si(ε\text{-}CL)_4$**, 2 h, 230 °C		25.4 %	PA6, high extractables, discoloration
PA6/SiO_2/$MeSiO_{1.5}$ hybrid material, use of water	4.4	1.2	1.9	41	Addition of a second silicon monomer (1 equivalent); Premelting of ε-CL and silicon monomers, 1 h, 230 °C; Addition of ε-ACA/H_2O mixture, 3 h, 220 °C, 1 bar		99.1 %	No reaction, high extractables, discoloration
PA6/SiO_2 hybrid material, use of water	4	–	1	22	3.5 h, 230 °C, 8 bar		–	No polymeric material obtained, IR: weak Amid II-signal at 1543 cm^{-1}

Table S7 Molar ratios of reactants and portion of extractables of polymerization procedures under variation of the order of reactant addition respectively prepolymerization temperatures.

Molar ratios of reactants			Reaction conditions and order of reactant addition	Extractables (8 h H_2O, 8 h EtOH)
ε-ACA	Si(*ε*-CL)$_4$	*ε*-CL		
4.0	1	21.1	*ε*-CL+*ε*-ACA 1.5 h, 180 °C → 140 °C → Si(*ε*-CL)$_4$ 2.5 h, 220 °C, 7.5 bar	12.6 %
4.1	1	21.1	*ε*-CL+*ε*-ACA 1 h, 220 °C → 180 °C → Si(*ε*-CL)$_4$ 1 h, 180 °C, 8 bar → 2 h, 220 °C, 8 bar	0.7 %
4.0	1	21.0	*ε*-CL+*ε*-ACA 1 h, 220 °C → Si(*ε*-CL)$_4$ 3 h, 230 °C	6.1 %
4.0	1	11.3 +9.9	*ε*-CL+*ε*-ACA, 2 h, 200 °C, 10 bar; *ε*–CL+Si(*ε*-CL)$_4$, 1 h, 110 °C → 3 h, 220 °C	31.3 %
4.0	1	21.1	*ε*-CL+*ε*-ACA+Si(*ε*-CL)$_4$ 3 h, 230 °C	6.6 %

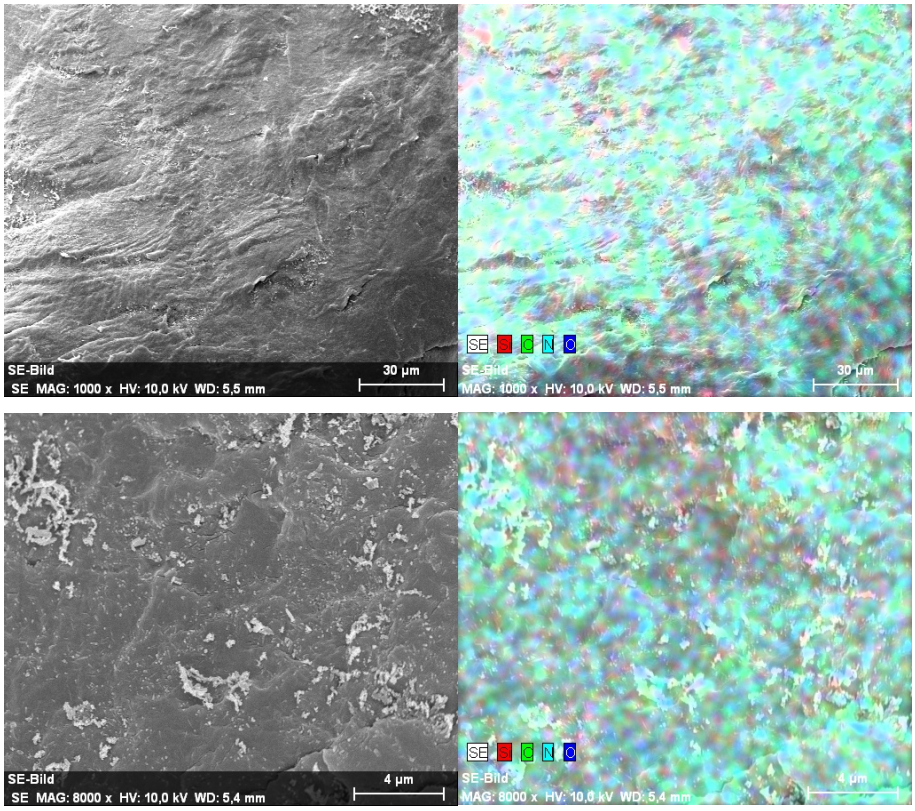


Fig. S4 Electron microscopic images and EDX patterns of composite **P1_1** with 1 wt% of SiO_2 in different magnifications; EDX showing the distribution of the elements silicon, carbon, nitrogen and oxygen.

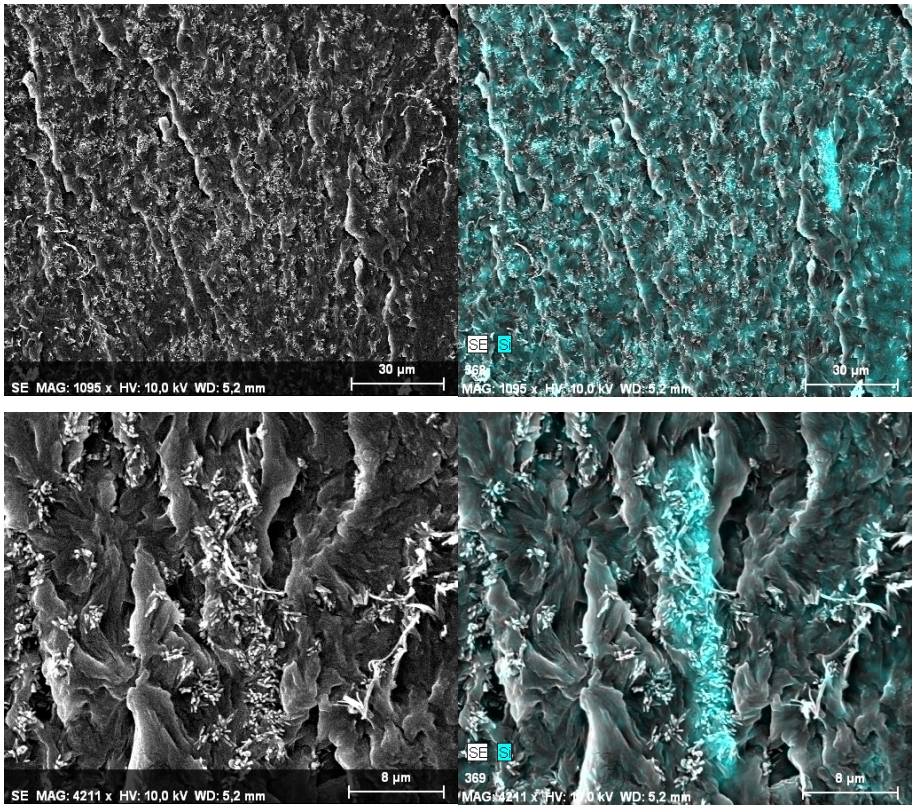


Fig. S5 Electron microscopic images and EDX patterns of composite **P1_2** with 1 wt% of SiO_2 in different magnifications; EDX showing the distribution of the element silicon.

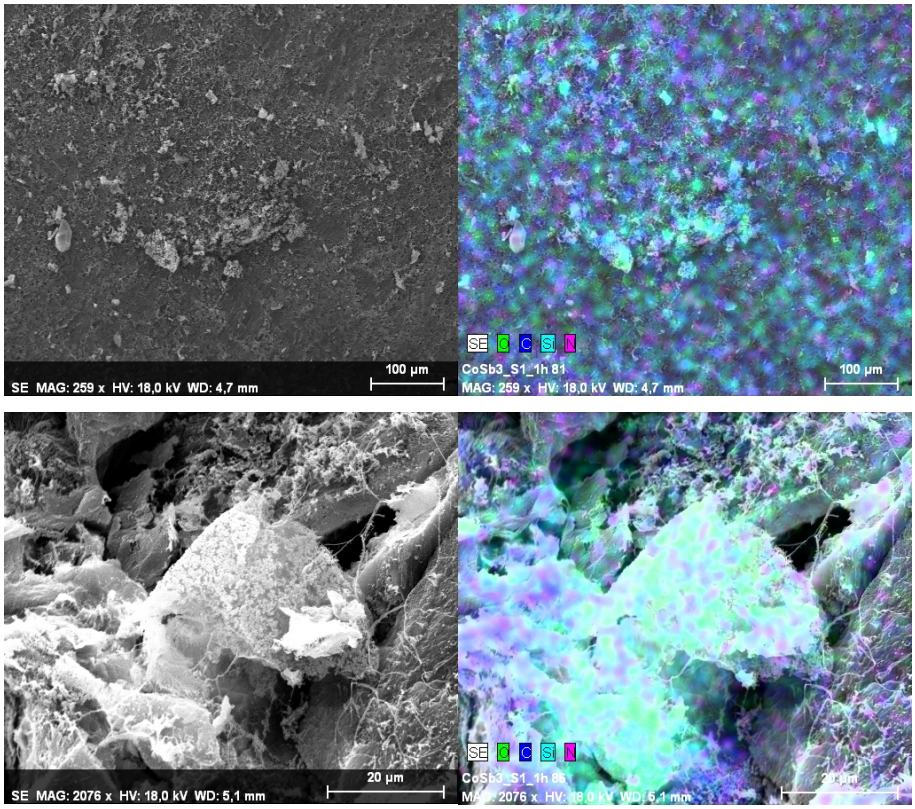


Fig. S6 Electron microscopic images and EDX patterns of composite **P1_3** with 1 wt% of SiO_2 in different magnifications; EDX showing the distribution of the elements silicon, carbon, nitrogen and oxygen.

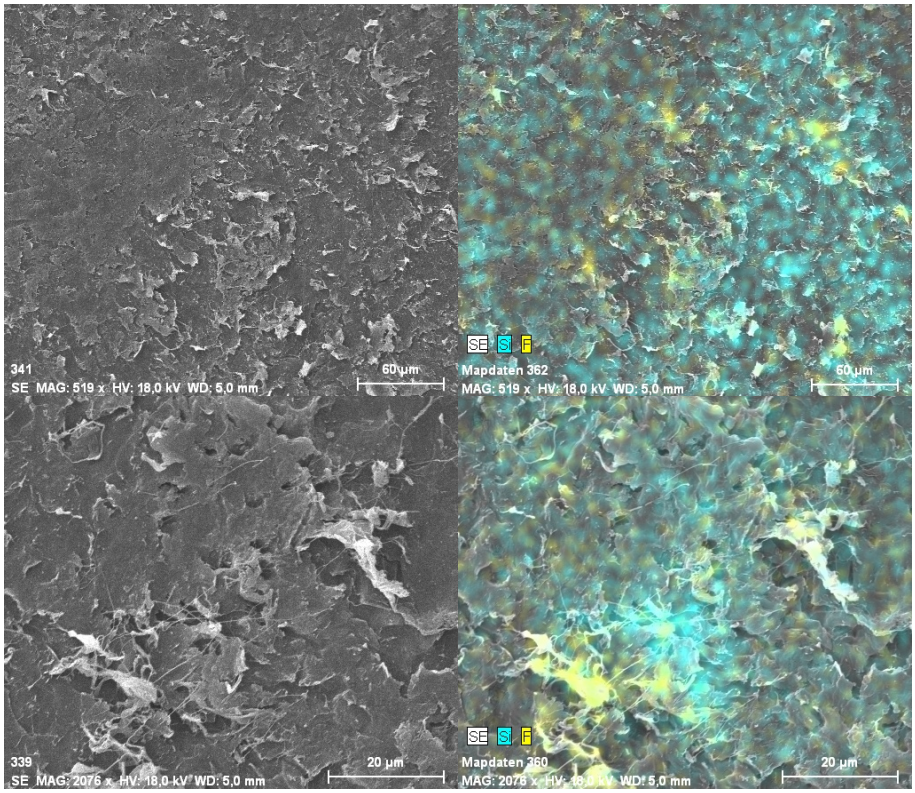


Fig. S7 Electron microscopic images and EDX patterns of composite **P2** with 2 wt% of SiO_2 in different magnifications; EDX showing the distribution of the elements silicon, carbon, nitrogen and oxygen.

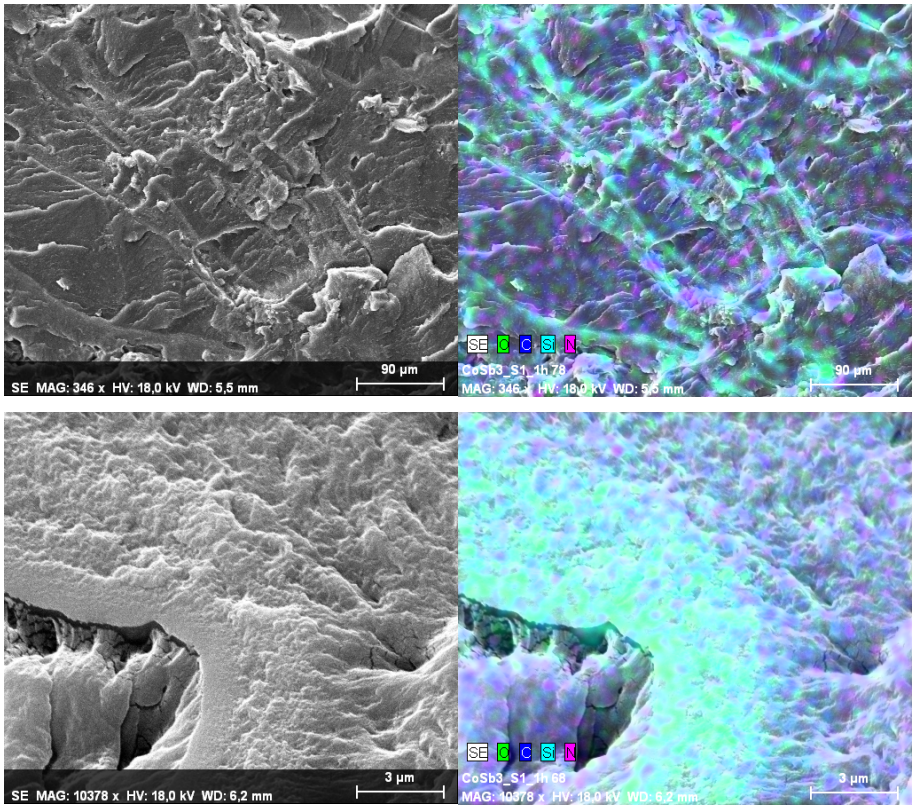


Fig.. S8 Electron microscopic images and EDX patterns of composite **P5_1** with 5 wt% of SiO_2 in different magnifications; EDX showing the distribution of the element silicon, carbon, nitrogen and oxygen.

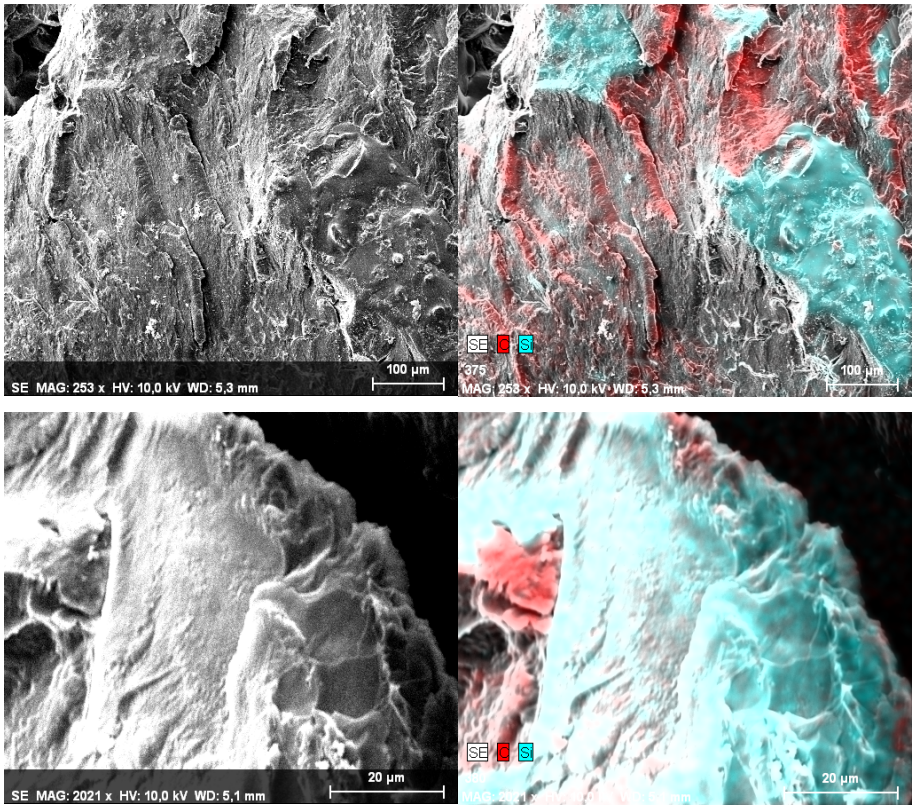


Fig. S9 Electron microscopic images and EDX patterns of composite **P5_2** with 5 wt% of SiO_2 in different magnifications; EDX showing the distribution of the element silicon and carbon.

Table S8 Results of cyclic DSC measurements of the PA6/SiO_2 composite materials.

		1. heating			crystallization			2. heating				
Sample	**SiO_2**	**Int. [J·g^{-1}]**	**Onset [°C]**	**Peak [°C]**	**Int. [J·g^{-1}]**	**Onset [°C]**	**Peak [°C]**	**Int. [J·g^{-1}]**	**Onset [°C]**	**Peak 1 [°C]**	**Peak 2 [°C]**	α^{1-3}
R	0 wt%	83.7	213.0	220.5	–65.1	190.7	185.1	82.7	211.8	–	220.5	36.0
P1_1	1 wt%	89.6	211.7	220.9	–68.2	188.7	184.2	55.3	211.2	210.8	219.7	24.3
P2	2 wt%	84.4	211.4	219.5	–64.3	190.8	187.3	84.9	210.8	211.4	219.0	37.7
P5_1	5 wt%	77.1	211.5	219.0	–56.7	187.4	179.4	67.7	211.1	–	220.0	31.0

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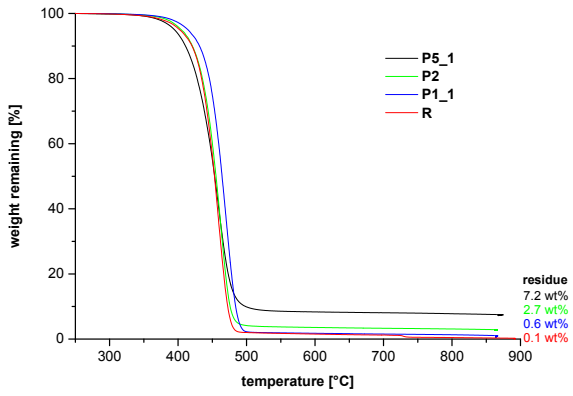

Fig. S10 TGA curves for samples with 1, 2 and 5 weight% SiO_2 (**P1_1**, **P2** and **P5_1**) in comparison to polyamide 6 (**R**).

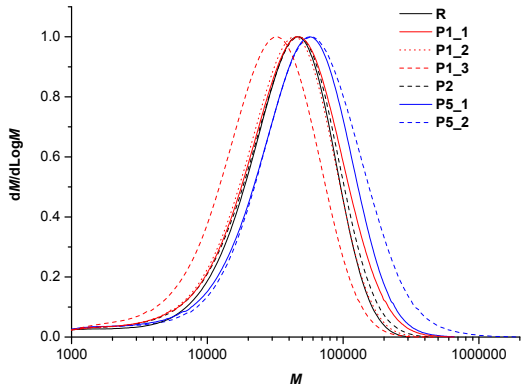

Fig. S11 SEC profiles of composite material **P1_x** with 1 weight% SiO_2, **P2** with 2 wt% of SiO_2 and **P5_x** with 5 weight% SiO_2 in comparison to the PA6 as reference; extracted samples (48 h, MeOH); normalized to peak height.