Supplementary Materials

Simultaneous effect of carboxyl group-containing hyperbranched polymer on the glass fiber-reinforced polyamide 6/hollow glass microsphere syntactic foams

Jincheol Kim[1, †], Jaewon Lee[1, †], Sosan Hwang[1], Kyungjun Park[1], Sanghyun Hong[2], Seojin Lee[2], Sang Eun Shim[1,*], and Yingjie Qian[1,*]

[1] Department of Chemistry and Chemical Engineering, Education and Research Center for Smart Energy and Materials, Inha University, Incheon 22212, Republic of Korea

[2] H&A R&D Center, LG Electronics., LTD, 51 Gasan digital 1-ro, Geumcheon-gu, Seoul, 153802, Korea

[†] These authors contributed equally to this work.

[*]*Corresponding author. E-mail address*: seshim@inha.ac.kr for SE Shim, yjqian@inha.ac.kr for Y Qian

Table S1. DSC data for syntactic foams and a glass fiber reinforced PA 6 composite under non-isothermal crystallization.

Sample code	T_m (℃)	ΔH_f (J/g)	X_c (%)	T_c (℃)	T_{onset} (℃)	ΔH_c (J/g)	ΔH_c^* (J/g)
PA 6	221.3	47.95	19.98	192.5	196.3	55.46	55.46
PA 6/HGM 5	221.5	45.92	20.36	191.7	195.8	51.11	54.39
PA 6/HGM 20	222.1	41.94	21.63	190.3	195.0	46.24	57.23
PA 6/GF 5	221.4	47.77	21.23	192.3	196.2	54.25	57.86

Table S2. Crystallization kinetic analysis of non-isothermal crystallization data for syntactic foams and a glass fiber reinforced composite.

Sample code	n	Z_t	Z_c	$t_{1/2}$ (min)	Adj. R-Square
PA 6	3.5	1.981	1.071	0.74	0.9996
PA 6/HGM 5	3.4	1.904	1.066	0.74	0.9998
PA 6/HGM 20	3.4	1.365	1.032	0.82	0.9999
PA 6/GF 5	3.6	1.871	1.065	0.76	0.9997

Table S3. Comparison of the mechanical properties of neat PA 6, syntactic foams, and a glass fiber reinforced PA 6 composite.

Sample code	Specific gravity	Tensile strength (MPa)	Elongation (%)	Flexural modulus (MPa)	Flexural strength (MPa)
PA 6	1.125	80.2 ± 2.6	13.6 ± 13.8	2843 ± 73	35.3 ± 0.9
PA 6/HGM 5	1.063	67.8 ± 1.3	8.4 ± 6.1	3023 ± 68	37.5 ± 0.8
PA 6/HGM 10	1.018	62.9 ± 1.2	3.3 ± 0.8	3215 ± 28	39.9 ± 0.3
PA 6/HGM 15	0.983	52.8 ± 1.5	2.1 ± 1.8	3360 ± 23	41.7 ± 0.3
PA 6/HGM 20	0.940	47.6 ± 2.3	1.6 ± 0.4	3343 ± 46	41.5 ± 0.6
PA 6/GF 5	1.167	90.4 ± 4.1	3.2 ± 1.6	3371 ± 74	41.8 ± 0.9

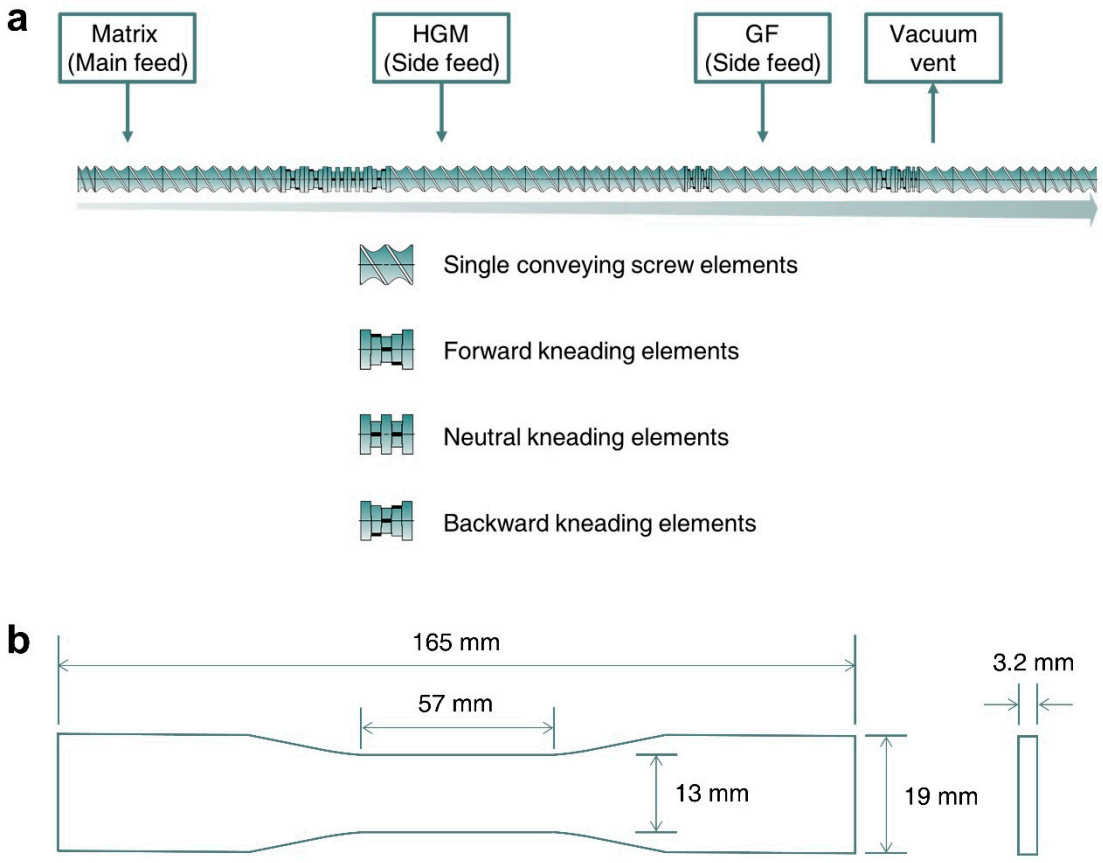
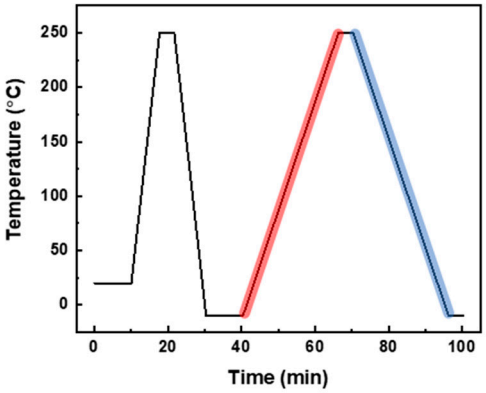


Figure S1. (a) Twin-screw configuration representing extrusion process starting from left to right. HGMs and GFs are side-fed in the middle. (b) Tensile test specimen dimension in accordance with ASTM D638 Type I standard. Gauge length of the specimen is 50 mm



#SEG. 1	Isothermal at 20℃ for 10 min
#SEG. 2	Heating at 30 ℃/min from 20 ℃ to 250 ℃
#SEG. 3	Isothermal at 250℃ for 4 min
#SEG. 4	Cooling at 30 ℃/min from 250 ℃ to -10 ℃
#SEG. 5	Isothermal at -10℃ for 10 min
#SEG. 6	Heating at 10 ℃/min from -10 ℃ to 250 ℃
#SEG. 7	Isothermal at 250℃ for 4 min
#SEG. 8	Cooling at 10 ℃/min from 250 ℃ to -10 ℃
#SEG. 9	Isothermal at -10℃ for 4 min

Figure S2. DSC profile to figure out the effect of HBP contents within RSF samples on non-isothermal crystallization behavior. Data was collected through Segment 6 on heating cycle to measure and calculate T_m, ΔH_f, and X_c. Segment 8 was implemented on cooling cycle to measure and calculate T_c, T_{onset}, ΔH_c, and ΔH_c^*.

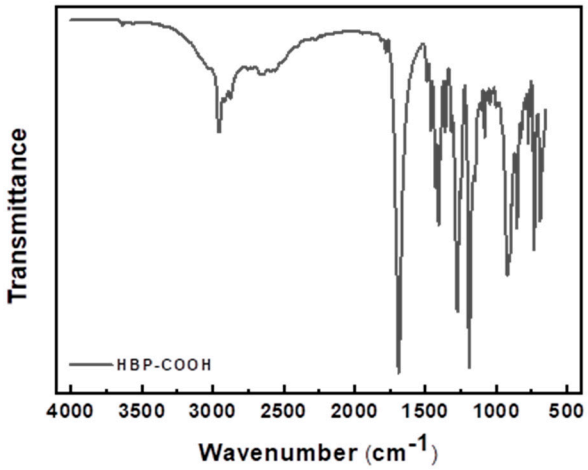


Figure S3. FT-IR spectra of HBP. OH stretching in the carboxyl group is 2952 cm^{-1} and aliphatic O-H bending is 1427cm^{-1}. Aliphatic ester group of C-O stretching is 1191 cm^{-1} and aliphatic ether group of C-O stretching is 1149 cm^{-1}.

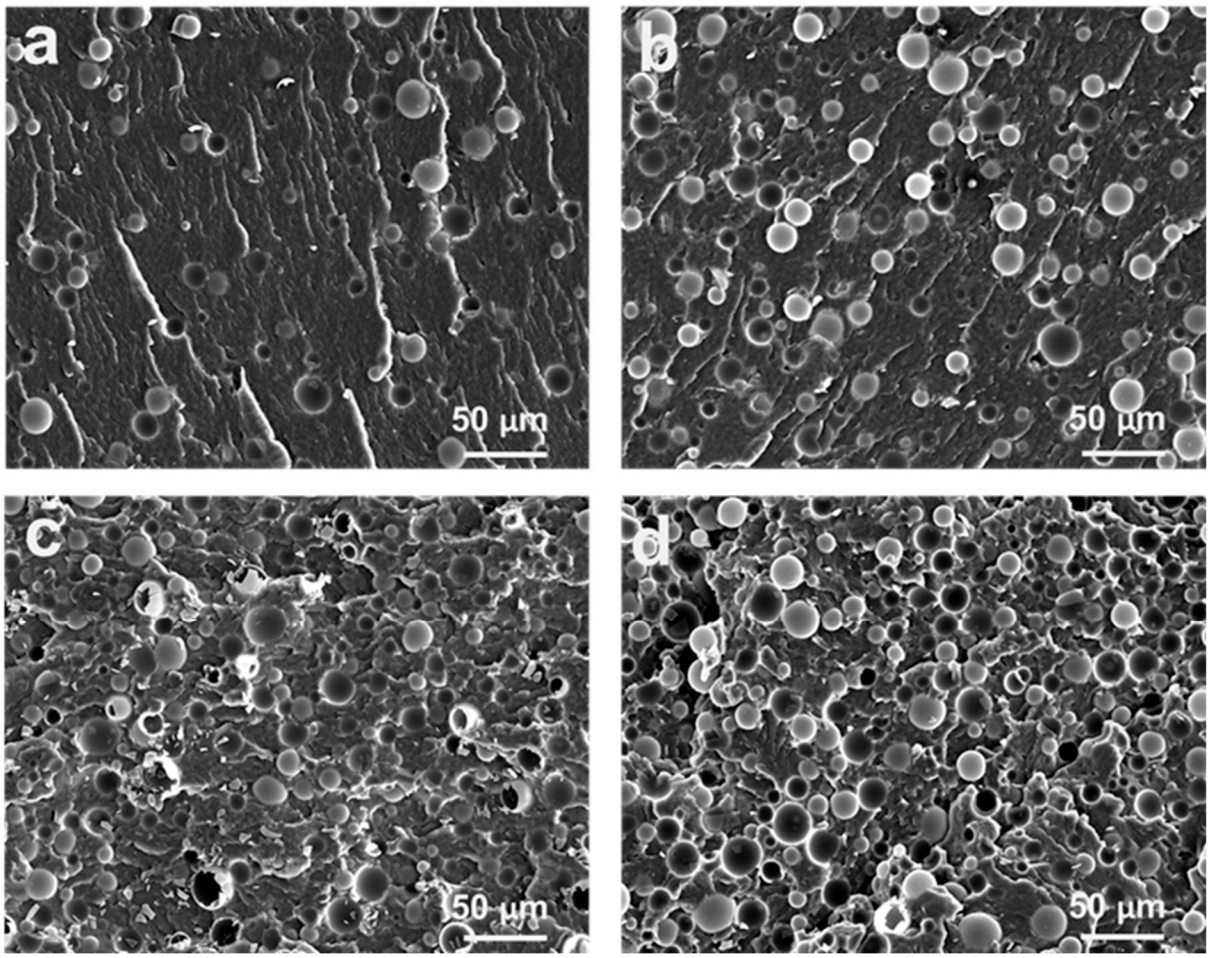


Figure S4. SEM microphotographs of syntactic foams on fractured surfaces after tensile test: PA 6/HGM 5 (a), PA 6/HGM 10 (b), PA 6/HGM 15 (c), and PA 6/HGM 20 (d).

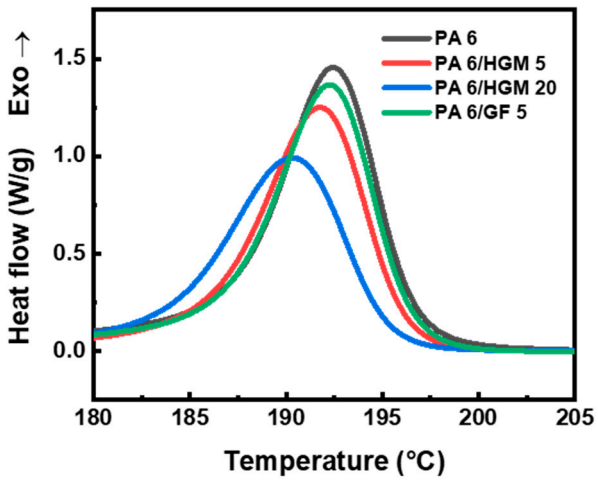


Figure S5. DSC thermograms of syntactic foams. The more the HGM was introduced, the lower the peak of crystallization temperature was found.

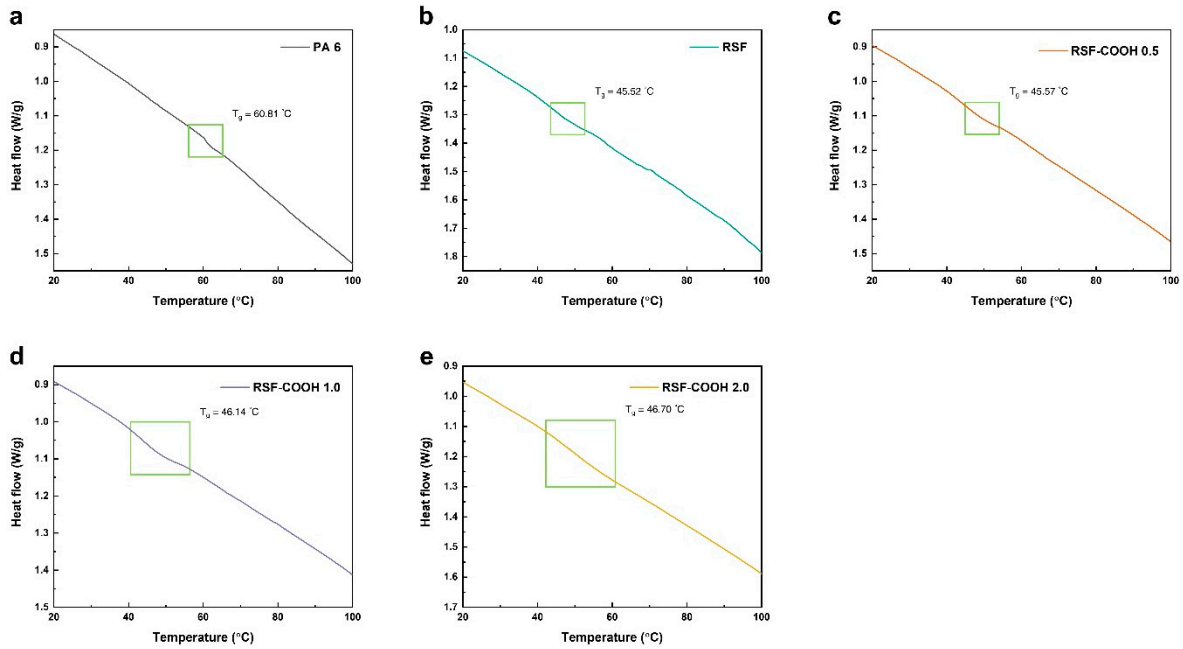


Figure S6. DSC thermograms ranging from 20 °C to 100 °C of the PA 6 (a), RSF (b), RSF-COOH 0.5 (c), RSF-COOH 1.0 (d), and RSF-COOH 2.0 (e) for the glass transition temperature (Tg) evaluation. Tg of each sample is depicted in the plots**.**

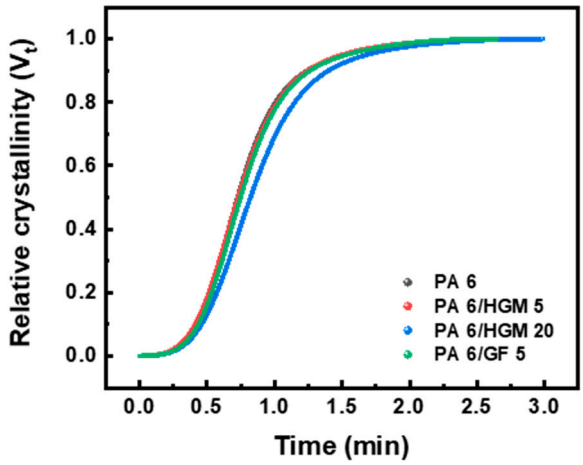


Figure S7. Plots of relative crystallinity (V_t) vs time for the non-isothermal crystallization of neat PA 6, syntactic foams with different HGM contents, and reinforced PA 6 composites.

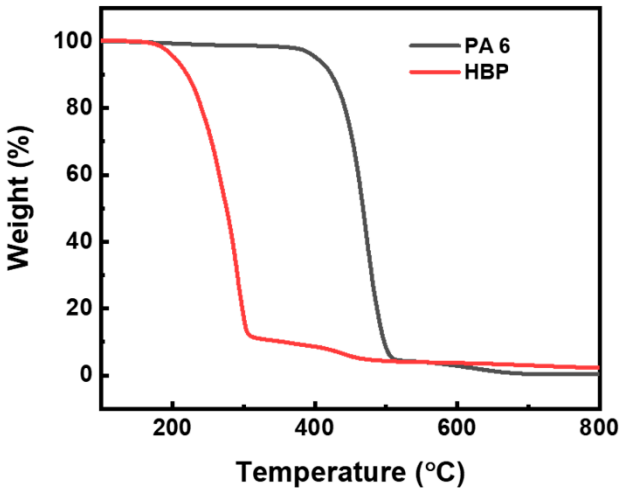


Figure S8. TGA thermograms of PA 6 and HBP.

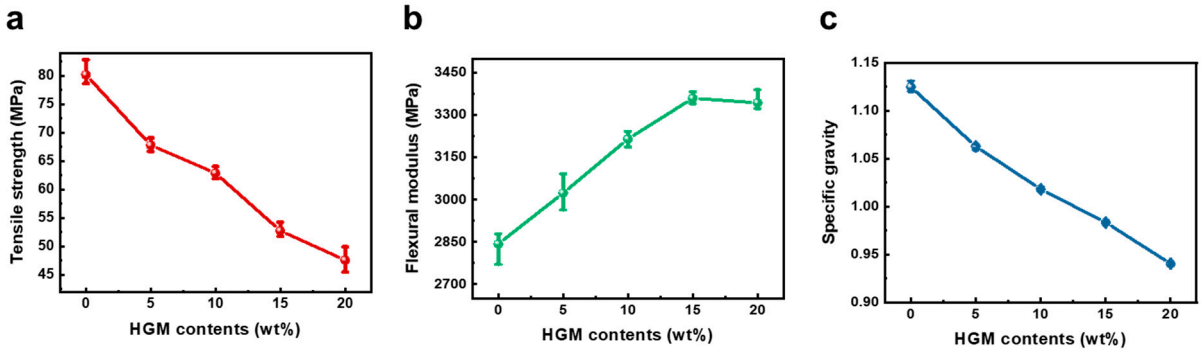


Figure S9. Tensile strength (a), flexural modulus (b), and specific gravity (c) of syntactic foams with various HGM contents.

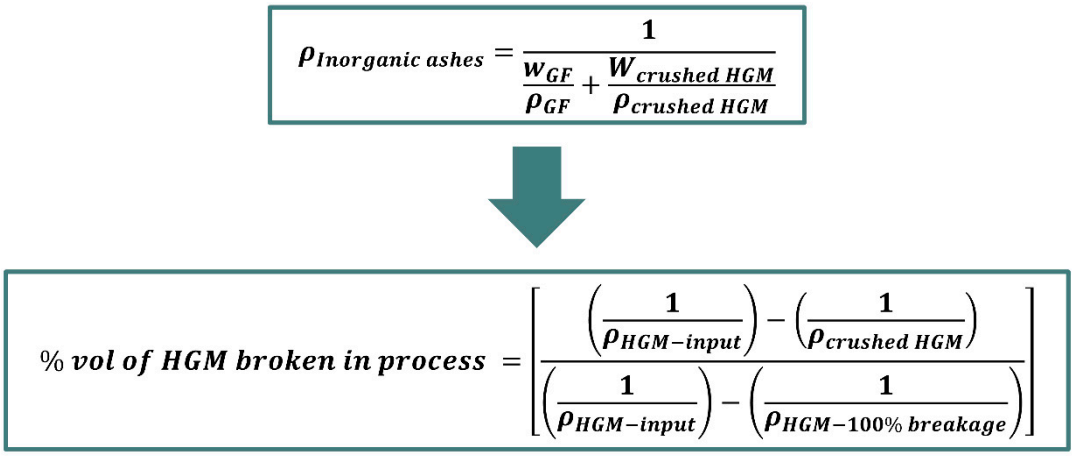


Figure S10. Equations for calculating HGM breakage. The density of HGMs reaches 2.54 g/cm^3 at 100% breakage. By exposing the pellets to 550 ℃ for 2 hrs to remove the matrix (PA 6), true densities of the residual inorganic ash consisting of HGMs and GFs were measured by gas pycnometer, which were 0.4365 and 2.4510 g/cm^3, respectively.

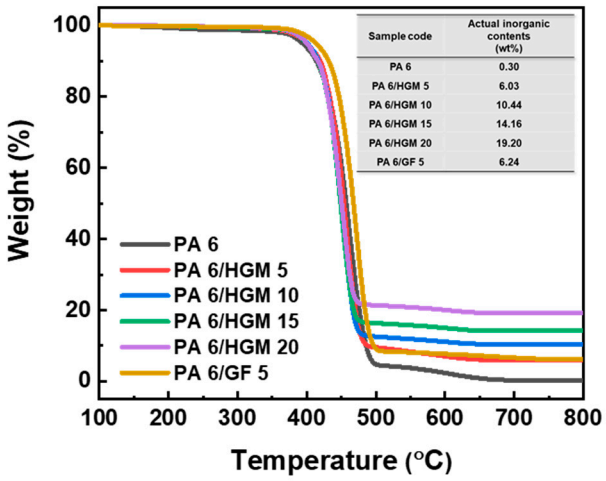


Figure S11. TGA thermograms of syntactic foams and a glass fiber reinforced PA 6 composite. Inset: actual inorganic filler contents.