

# Synthesis and properties of cationic core-shell fluorinated polyurethane acrylate

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**Table S1.** Typical dosage for cationic polyurethane aqueous dispersion (CWPU)

IPDI/ mol	PCDL/mol	MDEA /mmol	TMP/ mmol	BDO/ mmol	HEMA/ mol
0.07	$1.75 \times 10^{-2}$	2.9	4.4	4.4	$1.2 \times 10^{-2}$

**Table S2.** Tensile strength, Elongation at break and Young's modulus of FPUA

Samples	Tensile strength/MPa	Elongation at break/%	Young's modulus/MPa
CWPU	6.3±0.05	108.21	724.62±0.05
30/70FPUA	23.35±0.08	74.17	680.88±0.08
50/50FPUA	18.61±0.04	9.98	563.96±0.04

**Table S3.** The adhesion, impact resistance and flexibility of FPUA

Samples	Pencil hardness	Adhesion/level	Flexibility/mm	Impact resistance
CWPU	H	2	1	Undamaged
30/70 FPUA	2H	1	1	Undamaged
50/50FPUA	2H	1	1	Undamaged

**Table S4.** The  $T_g$ , modulus and crosslink density of FPUA

Samples	$T_g/^\circ\text{C}$	Modulus at 25°C/MPa	Modulus at $T_g$ +60°C/MPa	Crosslinking density/mol $\cdot\text{m}^{-3}$
50/50FPUA	113.6	150	2.6	233.4
30/70FPUA	92.9	600	5.4	508.3

**Table S5.** Atomic percentage of FPUA film surfaces before and after wearing test.

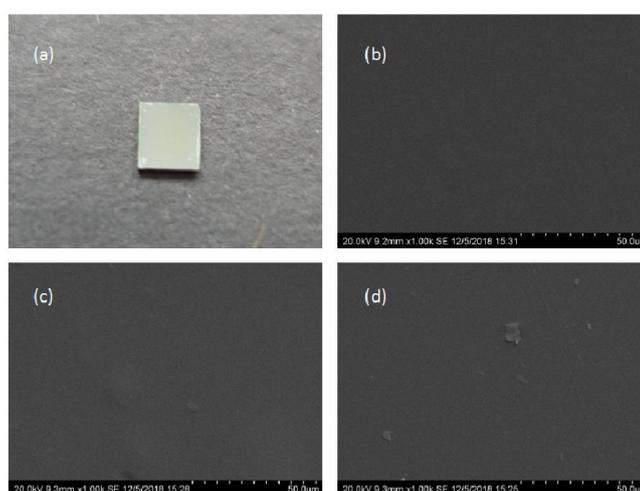
Samples*	F	O	N	C
a <sub>1</sub>	14.75%	18.32%	7.21%	59.72%
a <sub>2</sub>	2.56%	20.96%	8.87%	67.6%

b <sub>1</sub>	9.31%	21.58%	6.19%	62.92%
b <sub>2</sub>	5.47%	25.43%	6.45%	62.65%

\* (a<sub>1</sub>, a<sub>2</sub>, b<sub>1</sub>, b<sub>2</sub> represent the elemental content before and after PA/PU=50/50; PA/PU=30/70 film wearing, respectively.)

**Table S6.** The contact angle of water, diiodomethane and hexadecane droplets on the films

Test droplets	Water	Diiodomethane	Hexadecane
CWPU	68°	22°	15°
30/70FPUA	89°	66°	51°
50/50FPUA	99°	74°	55°



**Figure S1.** SEM images of the films. (a) Monocrystalline silicon coated sheet; (b) CWPU; (c) 30/70FPUA; (d) 50/50 FPUA

The SEM micrograph depiction of the CWPU, 30/70FPUA, and 50/50FPUA films, respectively, on the film surface are illustrated in Figures S1(b), (c), and (d). While both 30/70FPUA and 50/50FPUA film surfaces exhibit varying levels of minor protuberances, which are instigated by the incompatibility of fluorinated groups and the polyurethane carbon chain due to the soft and hard bimodal micro-phase segregation phenomena, the WPU film surface possesses the most smooth and planar character among the group. Fluorinated groups will migrate to the surface of film during the formation of dry films, which would accentuate the micro-phase separation phenomena. Nevertheless, the macro structure remains unaltered as a whole, notwithstanding the presence of some level of separation at the micro level.

**Table S8.** Thermal stability of FPUA films

Formulation	T <sub>max1</sub> (°C)	T <sub>max2</sub> (°C)	Y <sub>c</sub> at 600 °C (%)
50/50FPUA	337	418	4.95
30/70FPUA	339	428	1.26