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RSC Advances Supporting Information

Nanoindentation and Wear behavior of thermally stable biocompatible polysulfone-alumina nanocomposites

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RESULTS AND DISCUSSION

Methods and measurements

Fig. S1 shows FTIR spectra of bare alumina and modified alumina grafted with short PSU chains (PSU2.4k) and large PSU chains (PSU16k).

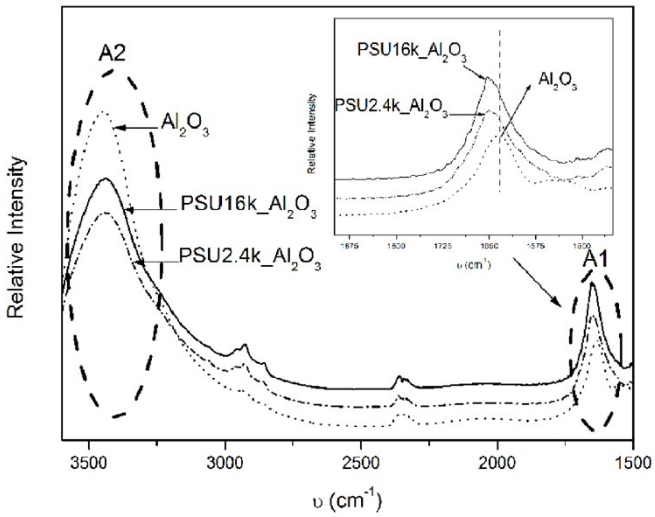

Fig.S1 FTIR spectra of bare alumina, PSU2.4k and PSU 16k grafted alumina nanoparticle

The band assigned to imine -C=N stretching (1652 cm^{-1}) overlaps with bare alumina surface –OH bending at 1634 cm^{-1}. Therefore, to proof the presence of imine groups the intensity of the two characteristic –OH bands at 3450 cm^{-1} (stretching)(A2) and 1634 cm^{-1} (bending)(A1) was compared: I_{1634}/I_{3450} was 0.27 for bare alumina while I_{1652}/I_{3450} increased to 0.47 and 0.51 for PSU16k and PSU2.4k respectively. This finding confirms the presence of imine groups on the surface of alumina.

Fabrication of nanocomposites

Fig. S2 displays a comparison of the neat PSU and a nanocomposite with 2 wt% of modified-nanoparticles. This figure shows the similar transparency when comparing the neat PSU and nanocomposite, demonstrating the successful dispersion of nanofillers without sacrificing the transparency necessary for this type of applications.

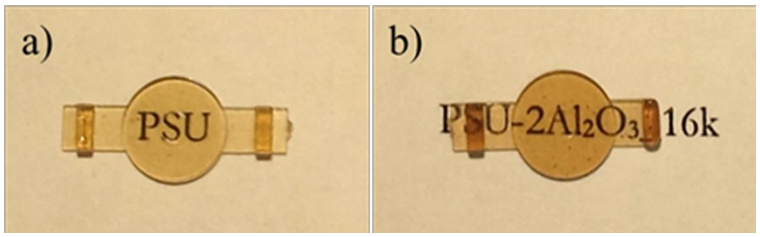

Fig. S2 Specimens' transparency comparison a) neat PSU, b) nanocomposite PSU/PSU16k_2Al_2O_3

Surface modification of nanoparticles

Fig. S3 presents a comparison of the Raman spectra analyzed for the bare, VTMS-modified and PSU-modified nanoparticles. This comparison allowed the detection of bands at 1272 cm^{-1}, 1410 cm^{-1} and 1607 cm^{-1} in VTMS-modified nanoparticles, and 1607 cm^{-1} in VTMS-modified nanoparticles, confirming the presence of C=C double bonds on nanoparticle surface.[1]

In the case of the PSU-modified nanoparticles, the 1272 cm^{-1} and the 1410 cm^{-1}signals are not very noticeable, probably due to the masking of this signal with the bands related to the presence of PSU. The signal 1607 cm^{-1} is masked with the signal of the PSU signals attributed to the benzene rings.

It needs to point out that the PSU signals observed were attributed to the presence of grafted PSU molecules on the surface of the nanoparticles which were washed several times with dimethylacetamide until characteristics signal of unreacted PSU by FTIR was not detected in the supernatant. This washing process was carried out to make sure the PSU not grafted to the nanoparticles were removed before the measurement. This indicates the combined presence of the inserts and the PSU molecules, agreeing with the results from the XPS analysis previously showed.

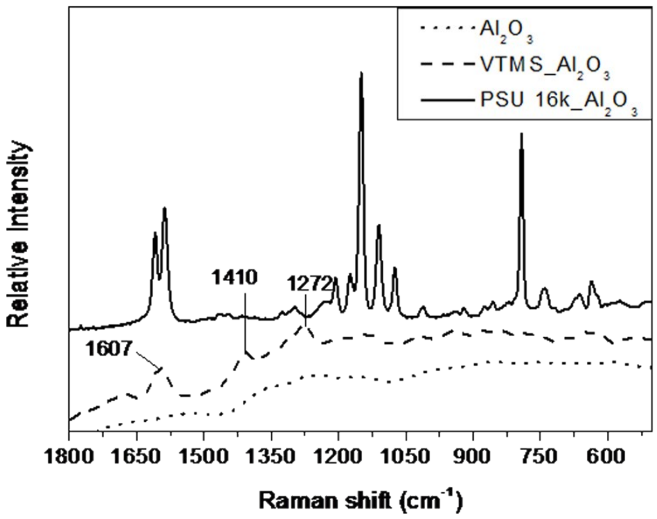

Fig. S3 FT-Raman spectra a) Al_2O_3 (dashed line), b) Al_2O_3-VTMS (dotted line) and c) PSU16k_Al_2O_3 (continuous line)

Fig. S4. shows a schematic representation of the PSU-grafted γ-alumina nanoparticles and the possible interactions of the different molecular weight PSU molecules when approaching the nanoparticle. Differences in the grafting densities are possibly attributed to the easier arrangement around the particles due to larger empty space in between short polymer molecules (i.e. PSU 2.4k) because of their shorter length when compared to the longer molecules (i.e. PSU 16k). In the last case, longer molecules already grafted onto the particle could be hindering the approximation of other PSU molecules to the surface of the nanoparticles. This can be explained as follow: certain quantity of long polymer molecules is allowed to interact with the particles until certain point. After this point, other polymer molecules that

try to approach the nanoparticles will experience interactions with the polymer molecules already grafted to the surface of the nanoparticles, which will restrict the approach of these "new" polymer molecules to the nanoparticles, this is mainly attributed to the longer length of the PSU16k when compare with the PSU2.4k molecules (See Fig. S4). Both values agreed with the rate estimated by Yamamoto[2], which, in this type of graft called "Grafting to, ranges between 0.001 to 0.05 chains/nm^2.

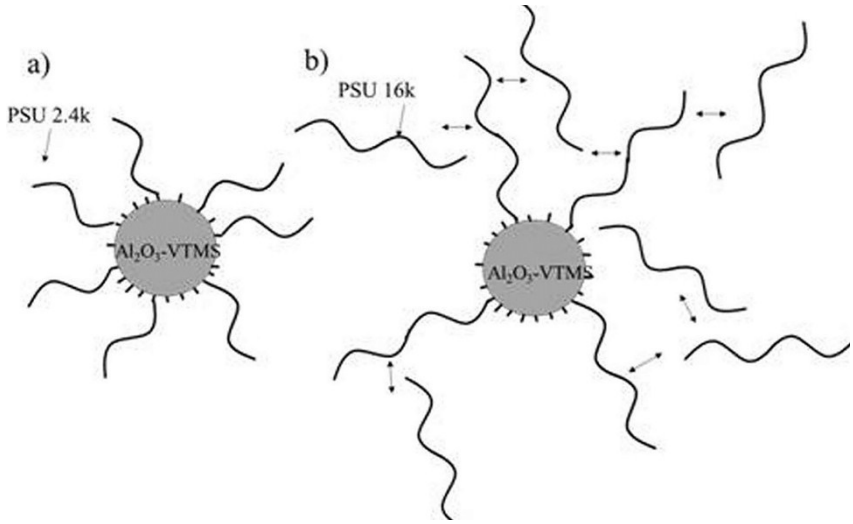

Fig. S4 Schematic representation of the PSU-grafted γ-alumina nanoparticles and the possible interactions of the different molecular weight PSU molecules when approaching the nanoparticle (double arrows): a) PSU2.4k_Al_2O_3 and b) PSU16k_Al_2O_3

Thermal stability of nanocomposites

Table S1 shows the temperature at maximum rate for the thermal degradation of the different nanocomposites prepared, T_{max}. This temperature is taken from the minimum of each derivate of the thermogravimetric curves.

Table S1 Temperature at maximum degradation (T_{max}) of PSU and nanocomposites

System	T_{max} (ºC)
PSU	533
PSU/2Al_2O_3	535
PSU/5Al_2O_3	532
PSU/10Al_2O_3	525
PSU/PSU2.4k_2Al_2O_3	537
PSU/PSU2.4k_5Al_2O_3	535
PSU/PSU2.4k_10Al_2O_3	532
PSU/PSU16k_2Al_2O_3	538
PSU/PSU16k_5Al_2O_3	536
PSU/PSU16k_10Al_2O_3	532

Friction and wear properties

Subsequently, the wear rates (WR) were calculated, estimating the weight lost (*m*) of each nanocomposite after the test (WV corresponds to the volume of material lost), using the following equations $WV = m/\rho[mm^3]$.[3,4]

$$WR = \frac{WV}{d.F}\left[\frac{mm^3}{m.N}\right] \quad (1)$$

Where ρ is the density of the nanocomposite ($\rho = \emptyset_{VAl_2O_3}\rho_{Al_2O_3} + \left(1 - \emptyset_{VAl_2O_3}\right)\rho_{PSU}$), *d* and *F* are stroke and normal force, respectively.

Table S2 Wear test results of PSU and nanocomposites

System	WV[a]	WR[b]	ΔWR[c]
PSU	1.048	42	-
PSU/2Al_2O_3	1.114	44	5
PSU/5Al_2O_3	1.113	44	5
PSU/10Al_2O_3	1.149	46	10
PSU/PSU2.4k_2Al_2O_3	0.899	36	-14
PSU/PSU2.4k_5Al_2O_3	0.980	38	-10
PSU/PSU2.4k_10Al_2O_3	0.946	38	-10
PSU/PSU16k_2Al_2O_3	1.018	40	-5
PSU/PSU16k_5Al_2O_3	1.012	40	-5
PSU/PSU16k_10Al_2O_3	0.976	40	-5

[a]WV: Wear volume (mm^3)
[b]WR: Wear rate ($10^{-4}mm^3/mN$)
[c]ΔWR: Increment of wear rate (%)

References

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