

Electronic Supplementary Information

Image analysis of the optical micrographs

The optical micrographs (Olympus BX51, Tokyo, Japan) of the blend films have been analyzed to estimate the area fractions of the PCL and PEO phases and the characteristic sizes of their domains. The micrographs have been converted first to binary images by manually evidencing the different polymeric regions of the samples. The binary images obtained in this way have been subsequently analyzed using the public domain ImageJ[®] software.

As an example, original optical micrographs of the PEO30 sample are compared in Figure S1 with the images processed after binary conversion of the domains. The low-magnification images

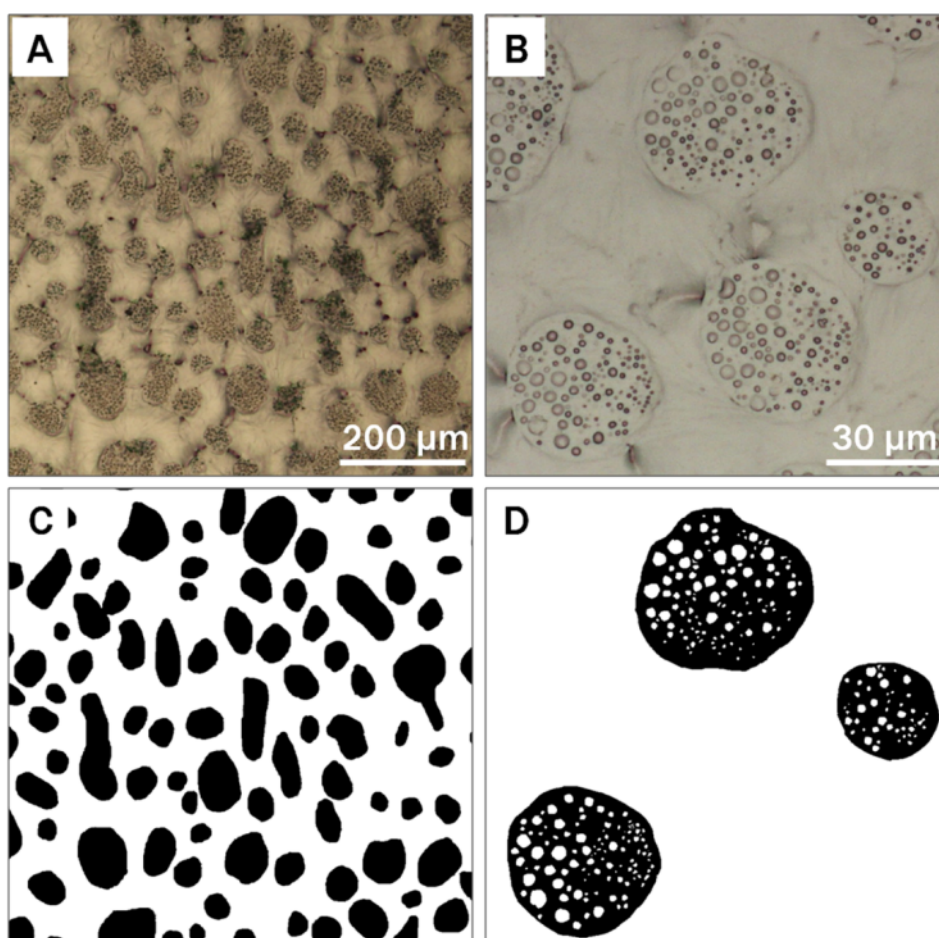


FIGURE S1 - Original POM micrographs (A, B) and corresponding binary images obtained after manual conversion of the phase domains (C, D).

have been analyzed to determine the fraction areas occupied by the PCL- and PEO-rich phases and the size (diameter) of the dispersed domains. The high-magnification images have instead been used to estimate the fraction area of the small-scale PCL entities contained in the PEO-rich regions, as well as the PEO entities enclosed in the PCL-rich domains.

Surface topography of the filled blend samples

Representative micrographs of the surfaces of the filled blend films, obtained by confocal microscopy, are reported in Figure S2 (NPs content 3 wt%) and S3 (NPs content 5 wt%). As highlighted in Section 3.2, the incorporation of NPs leads to the formation of a “relief structure”: the films are thicker than their unfilled counterparts, the PCL-rich domains having smaller size but greater height and numerical density.

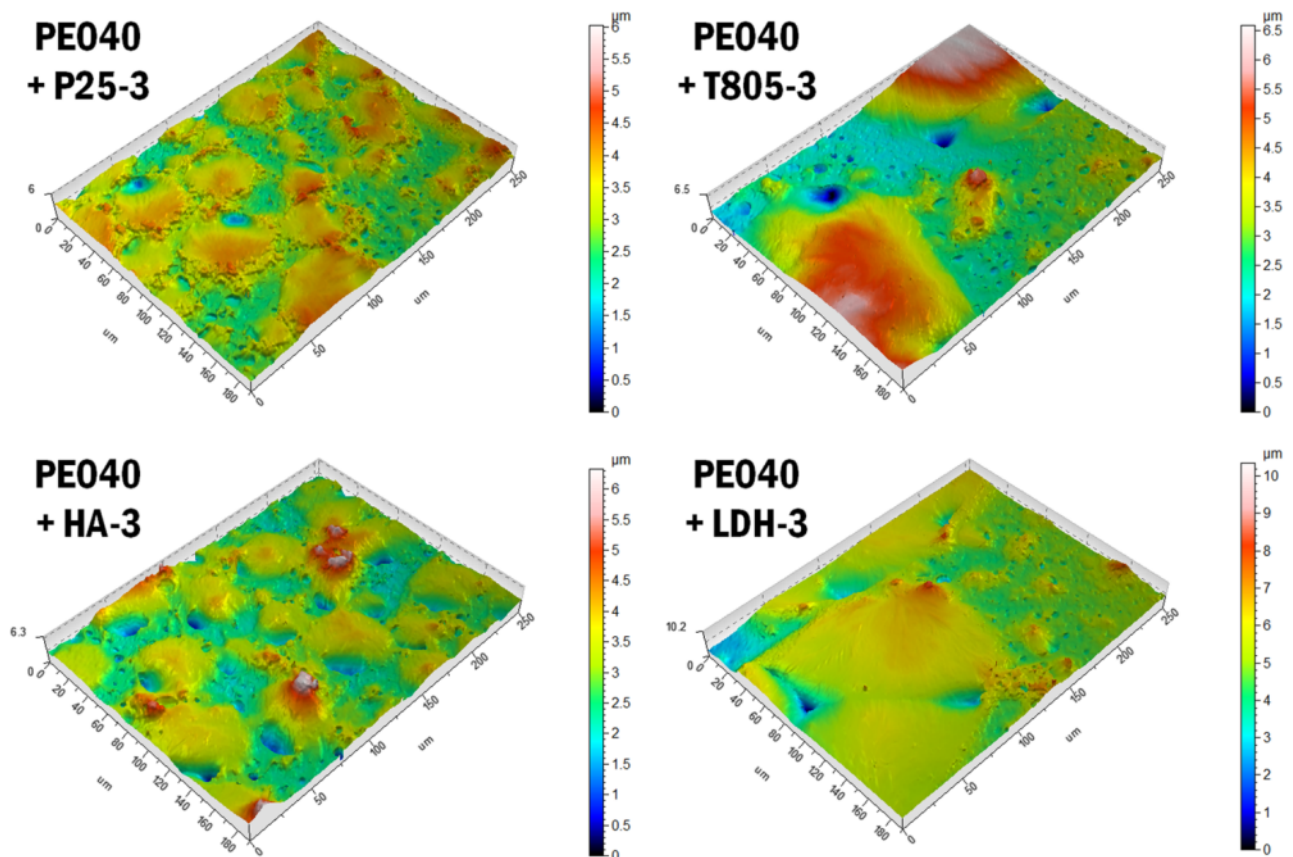


FIGURE S2 - Surface topography of films of PCL/PEO blends with 3 wt% NPs concentration.

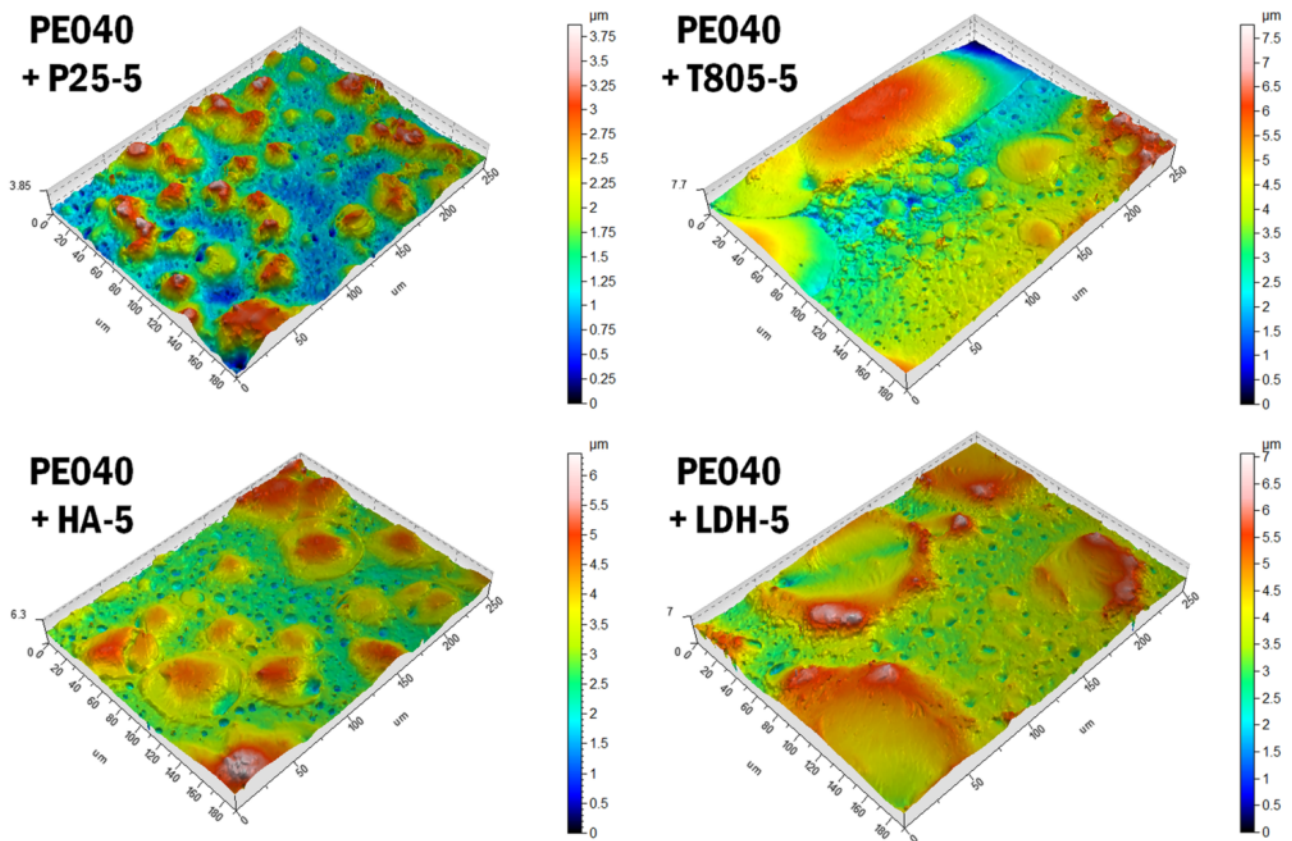


FIGURE S3 - Surface topography of films of PCL/PEO blends with 5 wt% NPs concentration.

Dynamics of titanium dioxide NPs during solvent casting

The evolution of the phase separation process of polymer solutions containing bare (P25) and silanized (T805) titanium dioxide nanoparticles is shown in the videos (sequences of optical micrographs) reported in the present section. The solvent has been let evaporate under exposure to the light of the optical microscope instead that at controlled temperature on a heater. In spite of the different casting conditions, the presented images provide valuable indications about the dynamics of assembly of the NPs. Hydrophilic P25 NPs, which are well dispersed in the starting solution, are able to flocculate in the suspending medium, eventually forming a fractal space-spanning network and promoting the formation of smaller PCL domains in comparison with the unfilled system. Conversely, hydrophobic T805 NPs form large agglomerates which further grow during solvent evaporation and eventually sediment on the substrate, obstructing the evolution of the fluid phases and promoting a coarse final morphology. The different characteristic sizes of P25 flocs and T805

aggregates are clearly appreciable taking into account the different lengths of the scale bars of the presented micrographs (30 and 100 μm for the systems containing P25 and T805, respectively).

Localization of NPs in the blend films with filler content 3 wt%

Figure S4 contains representative SEM micrographs of blend films with 3 wt% of filler concentration, showing the spectra of the elemental analysis taken along (yellow) lines that cross both PCL- and PEO-rich regions. These filler distributions essentially retrace those inferred from

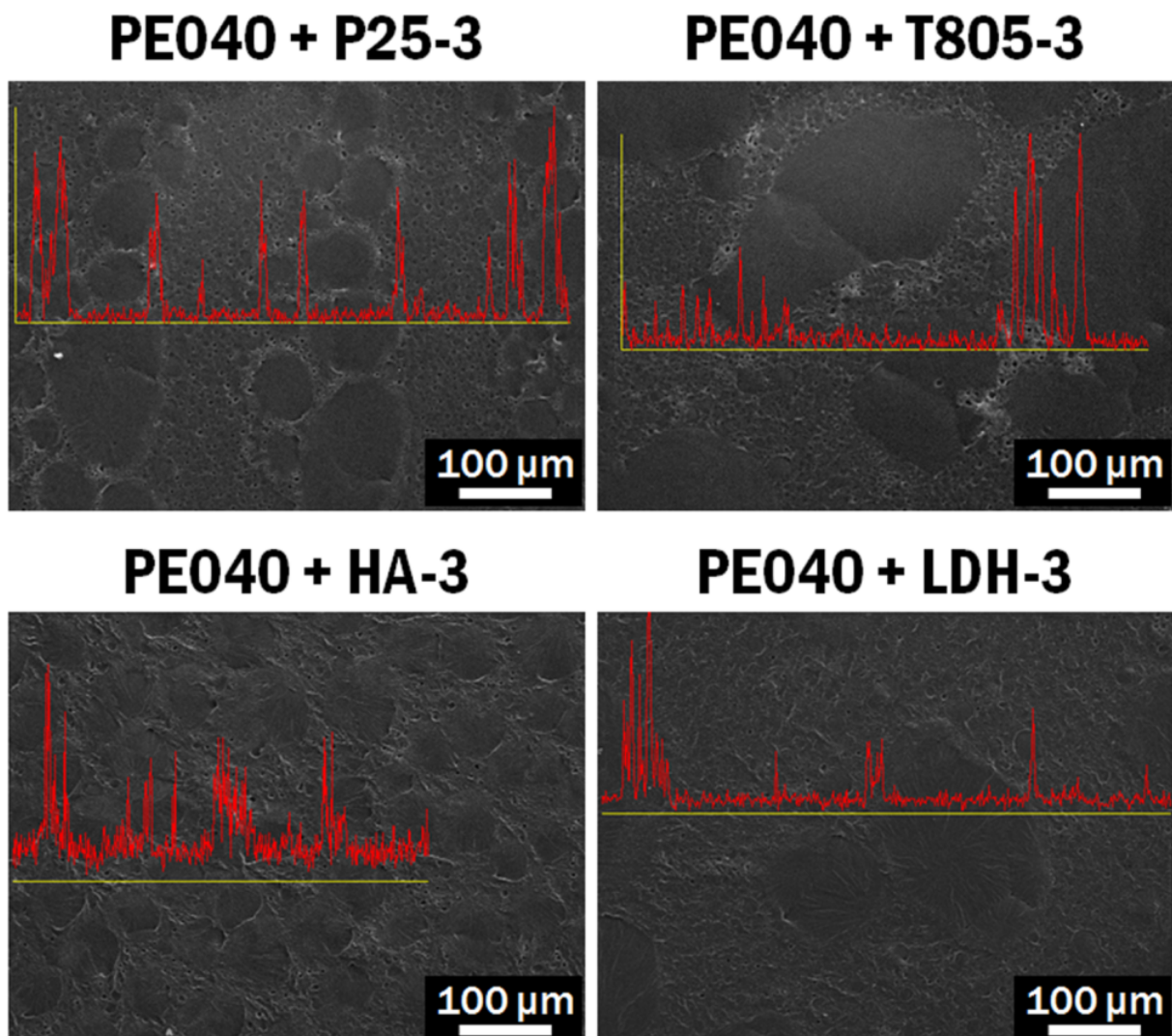


FIGURE S4 – SEM micrographs and spectra of the elementary mappings (titanium for P25 and T805, phosphorus for HA, magnesium for LDH) for the PCL/PEO blends filled with 3 wt% of NPs.

the elemental EDX mappings reported in Figure 11 of the manuscript. Considering the yellow lines as the baselines for the elemental spectra, for P25 peaks are prevalently detected in correspondence of the PEO-rich channels between PCL domains. T805 is instead present in the form of aggregates inside the PEO continuous phase. Some ground noise characterizes the spectra of HA, which is diffusely distributed in the blends; the presence of some peaks in the zones between the PCL- and PEO-rich domains reveals a slight tendency of those fillers to gather at that interphase. Such preferential distribution is even more pronounced for LDH.