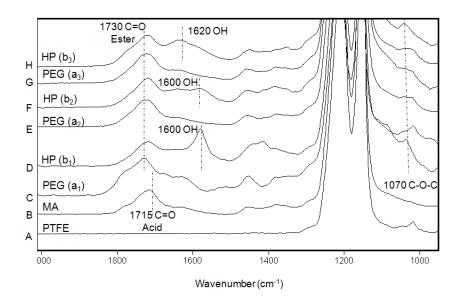
Supporting Documents

To confirm covalent attachment of the PEG and HP layers, ATR FT-IR spectroscopy was utilized as illustrated in Figure S-1-a and b. As seen in Figure S-1-a, the first MA layer is obtained by COOH-PTFE showing the band at 1715 cm⁻¹ due to C=O of COOH groups. The reactions of COOH functionalized PTFE with OH-PEG lead to ester formation (C=O). The alternating layers of HP and OH-PEG also produce ester linkages. The ATR FT-IR spectrum of the first PEG layer (a_1) shows the band at 1730 cm⁻¹ due to ester linkages between the COOH-PTFE and OH-PEG. The band at 1070 cm⁻¹ ¹ due to C-O-C of PEG was also detected. The first heparin layer (b₁) was attached in the next step which is manifested by the presence of the band at 1730 cm⁻¹ due to ester linkages that result from the reactions of COOH of HP and OH of PEG as well as the band at 1600 cm⁻¹ due to the OH bending modes of heparin. These results confirm the covalent attachment of OH-PEG and HP layers on the COOH-PTFE surface. Since the ester band formation of second $(a_2 \text{ and } b_2)$ and third layers $(a_3 \text{ and } b_3)$ is identical to those produced in the first layer (a_1 and b_1), higher intensities of the bands at 1730 cm⁻¹ due to ester linkages between PEG and HP layers and at 1620 and 1600 cm⁻¹ due to OH bending vibration of heparin are also detected, confirming the covalent attachment of OH-PEG and HP layers to COOH-PTFE surface.

An alternative path of reactions to produce CAM was to utilize NH_2 -PEG, where reactions of COOH-PTFE and NH_2 -PEG lead to amide formation (C=O-NH), also producing the alternating layers of HP and NH_2 -PEG amide linkages. ATR FT-IR spectra shown in Figure S-2-b illustrate the presence of the band at 1715 cm⁻¹ due to C=O of COOH entities in the first COOH-PTFE layer (MA) resulting from the microwave plasma reactions and at 1650 cm⁻¹ due to amide linkages produced from the reactions of COOH-PTFE and NH₂-PEG (a₁') and again the band at 1080 cm⁻¹ due to C-O-C of PEG was detected. The next reacted layer is heparin (b₁'), which is also manifested by the bands at 1630 cm⁻¹ due to NH₂ linkages resulting from the reactions of COOH of HP and NH₂ of PEG and the 1600 cm⁻¹ band attributed to OH bending vibrations of heparin, confirming covalent attachment of NH₂-PEG and HP layers. Again, as subsequent layers are reacted, the band intensities increase, indicating that the multiple layers of NH₂-PEG and HP were covalently attached to the COOH-PTFE surfaces.



a

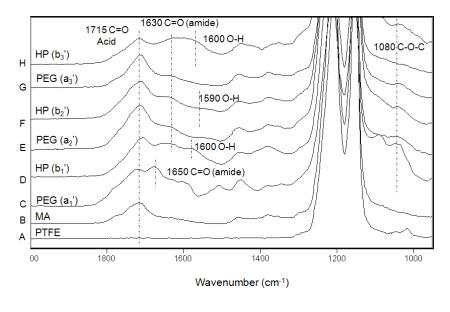




Figure S-1. ATR FT-IR spectra in the 1900-1000 cm⁻¹ region of each CAM layer; (a) ester linkages of OH-PEG: Trace A- PTFE, Trace B- MA, Trace C- PEG (a₁), Trace D-HP (b₁), Trace E- PEG (a₂), Trace F- HP (b₂), Trace G- PEG (a₃), Trace H- HP (b₃); and (b) amide linkages of NH₂-PEG: Trace A- PTFE, Trace B- MA, Trace C- PEG (a₁'), Trace D- HP (b₁'), Trace E- PEG (a₂'), Trace F- HP (b₂'), Trace G- PEG (a₃'), Trace H- HP (b₃').

Hydrolytic stability of the CAM surfaces containing OH- and NH₂-PEG was determined by exposing each specimen to boiling water for 20 min while stirring. The IR analysis shown in Figure S-2-a-c show that the C=O bands at 1730 and 1630 cm⁻¹ due to ester and amide linkages before and after boiling are undistinguishable, thus indicating stability of the CAM layers.

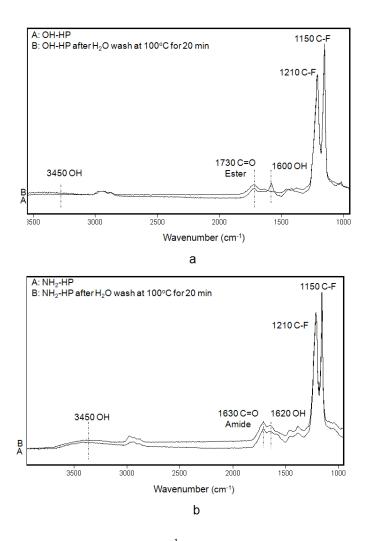


Figure S2. ATR FT-IR in the 4000-1000 cm⁻¹ region of the CAM surfaces before and after H_2O wash at 100 °C for 20 min of (a) OH-HP and (b) NH₂-HP.

In an effort to control hemocompatibility performance of heparinized materials, uniformity of PEG and HP modified surface is important. This is primarily related to the fact that the presences of unevenly areas of HP allow unwanted platelet adherence and aggregation. As illustrated in Figure S-3, the SEM images of the unmodified PTFE exhibits a certain degree roughness. After plasma modification (MA-PTFE) and CAM process (OH-HP and NH₂-HP) the surfaces become smoother.

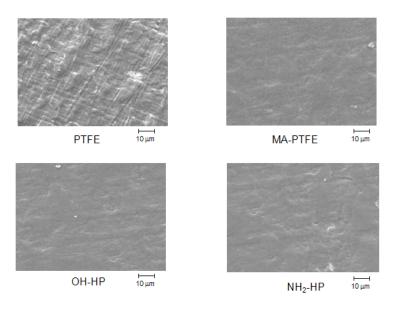


Figure S3. SEM images of PTFE, MA-PTFE, OH-HP, and NH₂-HP surfaces.

The smoothness alone indicated good surface coverage, but does not prove complete coverage. Therefore, IRIRI were conducted. Figure S-4 illustrate IRIRI images and IR spectra of the surface containing (a) OH-PEG, (b) NH₂-PEG, (c) OH-HP, and (d) NH₂-HP recorded from random areas of the surface. As seen from the spectra, the layer formed on the surface shows chemically homogenous distribution of these species by tuning to the bands characteristic of C-O-C (PEG), and O-H (HP).

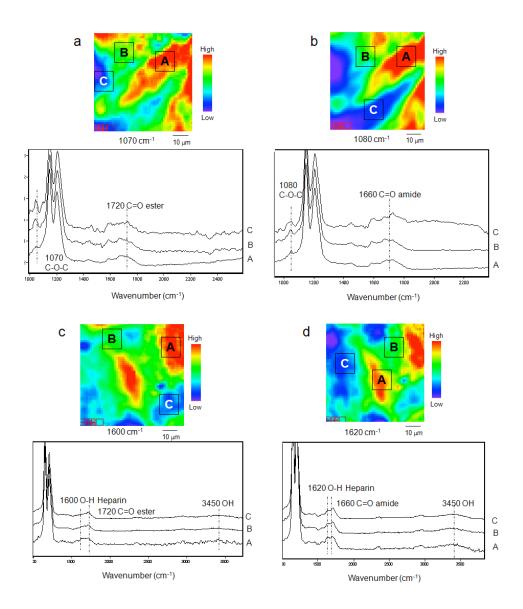


Figure S4. IRIR images and IR spectra recorded from random areas A, B, and C of (a) OH-PEG, (b) NH₂-PEG, (c) OH-HP, and (d) NH₂-HP surfaces.