The electrophoretic deposition (EPD) is an attractive approach for development of Polyether ether ketone (PEEK) and 45S5 bio-active glass (BG®) composite coatings for biomedical applications. However, in order to establish the influence of the EPD parameters on the properties of the deposited coatings, a deeper investigation of the fundamental PEEK/BG co-EPD kinetics is required. Previous studies have reported hit and trial approach in order to optimize key EPD parameters, which is material and time consuming. Therefore, in this study, design of experiment approach was utilized to reach the optimized parameters economically. Accordingly, the PEEK/BG-EPD kinetics was established as a function of deposition time and voltage, accompanied by microscopic characterization of the deposited films. The experimental results showed that the deposition follows a linear growth law, in good agreement with the predictions of Hamaker’s law. The green coatings produced from the optimized set of parameters were sintered, in order to achieve substantial adhesion to the metallic substrate. Moreover, Chitosan/BG/Lawson composite was also deposited electrophoretically by optimized set of parameters on the sintered PEEK/BG composite coatings. Produced multilayer coatings attain multifunctional attributes; such as mechanical integrity and bioactivity from first layer, whereas, biodegradable chitosan in top layer provided an effective platform to trigger the release of antibacterial drug (Lawson). The morphology of multilayer coatings was examined by using scanning electron microscopy (SEM), elemental and compositional analysis was performed qualitatively with energy-dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD), respectively. Fourier transformed infrared spectroscopy (FTIR) was employed in order to identify the chemical structure of multilayer coatings. Moreover, wettability of the multilayer coatings was analyzed by static water contact angle measurements. Finally, in vitro bioactivity was assessed by immersing the multilayer coatings in simulated body fluid for 3, 7 and 14 days. The developed multilayer coatings were fairly homogenous, micro-porous and moderately hydrophobic. Furthermore, multilayer coatings were covered completely with apatite like layer after 3 days of immersion in SBF.