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Nanocoatings based on graphene related materials for gas barrier and heat shielding applications

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The Layer by Layer (LbL) assembly was chosen to deposit graphene related material (GRM) based coatings capable of conferring gas barrier or flame retardancy to polymers. The term GRMs indicate every 2D material with high aspect ratio formed by graphene sheets stacked together by low interactions. Graphite nanoplatelets (GNP) and graphite oxide nanoplatelets (GO), which consist in GNP with oxygen functionalization, are used more specifically for particles with thickness in the range of nanometers and variable lateral size. The recent literature shows that GO can be employed in the water-based deposition of gas barrier coatings. However, the intrinsic defectiveness and the high water sensitivity of this material, makes GO unsuitable for packaging applications that require very low oxygen transmission rates at high humidity. GNP may overcome this problem but their suspension in water is a challenge due to the low affinity of GNP towards water. In this thesis, different liquid exfoliation strategies for the production of water-based GNP suspensions were evaluated encompassing the use of a polyaromatic surfactant and polyelectrolytes as GNP dispersing/stabilizing agents. In a first attempt, GNP were tip-sonicated in presence of a perylene bis-imides derivative but, the obtained suspension was not sufficiently stable due to the self-stacking of employed molecules. In contrast, the presence of either positively or negatively charged polyelectrolytes yielded highly stable (up to 4-5 months) GNP suspensions. The so produced suspensions were employed in a LbL assembly, yielding thin coatings where GNPs are preferentially oriented parallel to the substrate surface and embedded within a polyelectrolyte assembly. The resulting “brick and mortar” morphology is able to increase the tortuosity path of permeating molecules thus enhancing the gas barrier properties of PET films and achieving below detection limits oxygen transmission rates. These results outclass other GNP-based systems reported in the literature with the additional advantage of being thinner. Similar coating structures were employed for flame retardant purposes exploiting the high aspect ratio of GNP in order to prepare coatings able to act as a barrier to the release of volatiles released by the decomposition of substrates during combustion. To this aim, GO nanoplatelets were LbL assembled on open cell polyurethane foams (PU) employing either Chitosan (CHIT) or polydiallylammoniumchloride (PDAC) as positive polyelectrolytes. The GO/polycations LbL depositions were able to penetrate inside the foam and homogenously coat every surface available with a nanostructured coating where GO nanoplatelets are embedded within a continuous polyelectrolyte matrix in a brick and mortar-like fashion. Both systems showed the suppression of melt-dripping phenomenon and retention of sample geometry during flammability tests. The effect of nanoplatelets aspect ratio was investigated in CHIT/GO assemblies showing that similar flame retardant performances can be obtained by depositing thinner and smaller nanoparticles, demonstrating the importance of the number of interfaces, with the advantage of reduced coating add-on. The effect of modified ionic strength was evaluated in PDAC/GO assemblies by the addition of a phosphate salt, which allows depositing thicker coatings. Samples prepared at modified ionic strength showed self-extinguishment in flammability test and no ignition at all when exposed to heat flux typical of developing fires (35 kW/m^2). This is ascribed to the barrier effect of GO towards volatiles obtained from PU pyrolysis. To further improve the efficiency and performance of these GRM-based coatings, a new one-step approach, where the assembly of GRM is forced by the solvent removal, was developed. Microfluidized GNP water-based suspensions were employed, evaluating different grade of exfoliation. The one-step deposited coating yielded morphologies similar to LbL assembled coatings. Combustion behaviour was not affected by GNP dimensions; however, the addition of a phosphate salt to the GNP suspensions deposited on the foams allow to reach self-extinguishment. Concluding, GNP have a beneficial effect on the overall flame retardancy but a phosphate salt is needed for reaching superior performances.