Modification of graphene oxide for polyurethane composite by combination of isocyanate and diisocyanate

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Abstract

Utilization of graphene oxide (GO) in polymer composites has attracted both academic and industrial interest because it can produce a dramatic improvement in properties at very low filler content [1, 2]. Surface modification of GO is required to obtain good dispersion of GO in polymer matrix. Moreover, suitable modification method can introduce desired function groups, and thus, GO either has strong interaction with polymer or reacts with polymer to create covalent bonding with polymer. Functionalization of GO by treatment with isocyanate, which could be carried out in mild condition, is the most common method to modify GO for polymer composite. Modification of GO with several different isocyanate compounds was first reported by Stankovich et al.[3]. However, they did not successfully introduce a high reactive functional group into GO surface. Chemical treatment of GO with diisocyanate was also reported by Zhang et al. [4]. Unfortunately, GO sheets were crosslinked to form lamellar porous structures via reaction of diisocyanate with the carboxyl and hydroxyl groups on both sides of the sheets. Here, we report on modification of GO by combination ethyl isocyanate (EI) and 4,4-methylenebis(phenyl isocyanate) (MDI) with molar ratio of 1:1. Then, composites of the modified GO and polyurethane (PU) were synthesized via in situ polymerization method. To our knowledge, this is the first report on combination of isocyanate and diisocyanate to modify GO. The modified GO readily forms a stable colloidal dispersion in all polar aprotic solvents, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), and dimethylsulfoxide (DMSO). The free isocyanate groups, which come from MDI, can react with hydroxyl groups of diols/ polyols to create strong covalent bonding between GO sheets and polyurethane. As expected, addition of very low GO content produced a dramatic improvement in mechanical properties of PU. In particular, the tensile strength and Young’s modulus significantly increased from 8.9 MPa and 2.6 MPa for pristine polyurethane to 19.3 MPa and 4.7 MPa for composite containing 0.03 wt% GO content, respectively, without losing of elongation at break. Notably, all composite films with 0.2 mm in thickness still had good transparency up to 0.1 wt% of GO content.

References

Figure 1. Scheme of modification of GO (a) and preparation of polyurethane/ graphene oxide composites (b).

Figure 2. Photographs of pristine PU and composite films.