

材料化学工程与纳米技术

纳米TiO₂/P(MMA-BA-MAA)复合粒子的制备及聚合动力学

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摘要

用乳液聚合法制备了纳米TiO₂/甲基丙烯酸甲酯-丙烯酸丁酯-甲基丙烯酸共聚物 [TiO₂/P(MMA-BA-MAA)] 复合粒子。考察了乳化剂的浓度、单体的用量比对复合粒子形貌的影响。系统研究了乳化剂浓度、引发剂用量、单体用量比、共乳化剂浓度、反应温度对TiO₂/P(MMA-BA-MAA)复合粒子包覆反应动力学影响。用TEM、FTIR及TG分析等证实P(MMA-BA-MAA)包覆在TiO₂表面形成表面光滑、分散性好的球形核-壳复合粒子。根据动力学实验结果, 求出整个乳液聚合包覆反应的反应速率方程, 反应的表观活化能为163.0 kJ·mol⁻¹。推测可能的包覆反应机理应为无机纳米TiO₂表面吸附乳化剂分子形成所谓的TiO₂/surfactant胶束成核或均相凝聚成核。TG结果显示, 复合粒子的热稳定性高于相同条件下得到的共聚物的稳定性。ζ电位、接触角实验表明, 与纳米TiO₂相比, 复合粒子亲水性能下降、亲油性能提高。

关键词

TiO₂-含甲基丙烯酸共聚物 复合粒子 乳液聚合 动力学

分类号

Synthesis and kinetics study of TiO₂/P(MMA-BA-MAA) composite particles by emulsion polymerization

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Abstract

The TiO₂/methyl-methacrylate-butyl acrylate-methacrylic acid copolymer [TiO₂/P(MMA-BA-MAA)] composite particles were synthesized by emulsion polymerization. The emulsifier concentration and molar concentration ratios of monomers exhibited a great influence on the morphology of the composite particles. The effects of operation variables, such as emulsifier concentration, initiator concentration, molar concentration ratios of monomers, co-emulsifier concentration, polymerization temperature on the kinetic features were also investigated. The TEM images, FTIR spectra and TG analysis indicated that the composite particles of TiO₂/P(MMA-BA-MAA) with smooth surface, good dispersibility and spherical core-shell structure were obtained. The kinetics data showed that under the conditions studied the rate equation for the whole reaction of coating polymerization was deduced, and the apparent activation energy was 163.0 kJ·mol⁻¹, which suggested that the possible reaction mechanism could be "TiO₂/surfactant" micelle nucleation and homogeneous coagulative nucleation mechanism of the emulsion polymerization of MMA-BA-MAA. Thermal analysis showed that the thermal stability of composite particles was higher than that of copolymer particles formed under the same conditions. Compared with nano-TiO₂, the measurements of ζ-potential and contact angles of composite particles indicated that the hydrophilicity of composite particles decreased and the hydrophobicity increased.

Key words

titanium dioxide copolymer containing MAA composite particle emulsion polymerization kinetics

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