PMMA/$CaCO_3$纳米复合粒子的制备及在PVC中的应用

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关键词：纳米 $CaCO_3$，微悬浮聚合，包覆结构，改性

聚合物和无机填料之间互相作用的最佳状态就是填料均匀地分散在聚合物基体中，并且无机粒子表面有一定厚度的聚合物存在。纳米粒子粒径小，表面能高，易于团聚形成团聚体。采用原位聚合法在无机纳米粒子表面包覆聚合物引起了人们广泛的兴趣。纳米粒子被聚合物包覆，可促进其在聚合物基体中的分散，改善纳米无机粒子与聚合物间的亲合性[1]。

本研究选用平均粒径为90nm的立方形碳酸钙。采用油酸在水介质中，超声作用下对纳米碳酸钙表面修饰。然后进行微悬浮法原位PMMA接枝包覆制备PMMA/$CaCO_3$纳米复合粒子。油酸分子中的羧基可与 $CaCO_3$ 粒子表面形成羧酸盐，不饱和双键为下一步聚合物接枝提供了接枝点[2-3]。

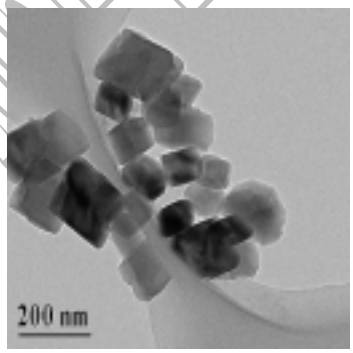

Fig. 1 The TEM morphology of $CaCO_3$ treated by oleic acid

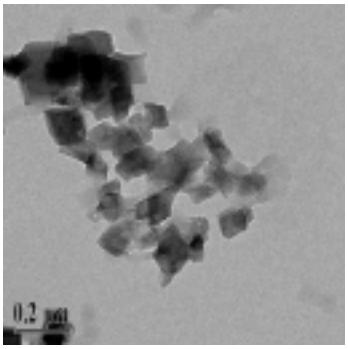

Fig. 2 The TEM morphology of PMMA/$CaCO_3$ composite particles

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通过透射电子显微镜（TEM）观察了油酸修饰碳酸钙及 $PMMA/CaCO_3$ 纳米复合粒子微观结构形态。如图 1 所示，油酸修饰碳酸钙粒子为立方型，分散状态较好且没有凝聚现象。图 2 为 $PMMA/CaCO_3$ 纳米复合粒子的 TEM 照片，图中黑色方形部分为 $CaCO_3$ 粒子，与图 1 相比,碳酸钙粒子的棱角显得不很明显,可能是由于 PMMA 包覆在其表面相，碳酸钙粒子被聚合物包覆并粘连在一起，以团聚体的形式存在。采用动态光散射仪（DLS）测定了 $CaCO_3/PMMA$ 复合粒子的粒径,图 3 为 $PMMA/CaCO_3$ 纳米复合粒子的粒径及其粒径分布曲线，从图 3 可以看出,纳米复合粒子的粒径分布较窄，平均粒径为 225.5nm。与无机纳米碳酸钙的粒径 90nm 相比，复合粒子中碳酸钙被聚合物包覆并粘连在一起，可能以复合的大粒子形式存在。

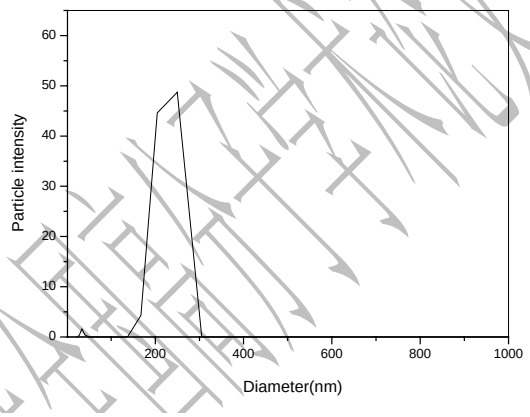

Fig.3 Particle diameter distribution of $PMMA/CaCO_3$ composite particles

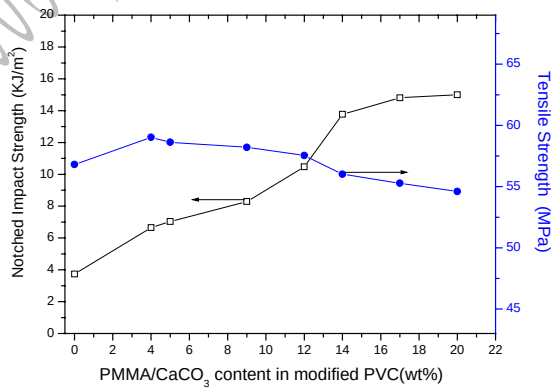

Fig.4 Influence of $PMMA/CaCO_3$ content on the mechanical properties of modified PVC

将所得 $PMMA/CaCO_3$ 纳米复合粒子与 PVC 共混制备了

PVC/PMMA/$CaCO_3$复合材料，考察了 PMMA/$CaCO_3$复合粒子用量对共混树脂力学性能的影响。图 4 所示为不同复合粒子含量与共混树脂力学性能之间的关系曲线,随着复合粒子用量的增加,PVC/ PMMA/$CaCO_3$复合材料的冲击强度呈现升高趋势，当复合粒子用量为 20wt%时，冲击强度较纯 PVC 提高 2.5 倍。共混树脂拉伸强度在复合粒子较低含量(<12wt%)时有所升高,但是当复合粒子含量过高后反而降低。

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Preparation of PMMA/$CaCO_3$ Composite Particles and Application in PVC

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PMMA/$CaCO_3$ composite particles were prepared by micro-suspension polymerization. The $CaCO_3$ was firstly treated with oleic acid (OA) which has unsaturated bond, followed by radical grafting through micro-suspension polymerization. The morphology of the $CaCO_3$ treated by the OA and PMMA/$CaCO_3$ composite particles were studied by TEM. Study results of dynamic laser scattering （DLS）demonstrated that the average diameter of the PMMA/$CaCO_3$ composite particles was 225.5nm. The influence of the content of the PMMA/$CaCO_3$ composite particles on the mechanical properties of

PVC and the PMMA/$CaCO_3$ blend was investigated. The study results show that the notched impact strength of the blend improved obviously with an increasing of the PMMA/$CaCO_3$ content, and the tensile strength has significantly unchanged. The notched impact strength of PVC and the PMMA/$CaCO_3$ blend was increased 2.5 times that of PVC when the content of the PMMA/$CaCO_3$ composite particles was 20wt% of the blend.

Keyword： nano-$CaCO_3$ ， micro-suspension polymerization ， encapsulation structure，modification