

· 研究简报 ·

聚苯乙烯、聚甲基丙烯酸甲酯对聚氯乙烯/ 氯化聚乙烯共混体流变性的影响*

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关键词 塑料改性、流变性、聚氯乙烯、氯化聚乙烯、刚性粒子

我们的研究表明^[1,2], 刚性聚合物能显著增韧聚氯乙烯(PVC)/氯化聚乙烯(CPE)共混体, 且强度和模量基本不变或得到提高, 具有不同于弹性体增韧塑料的规律和特征. 本文研究刚性聚合物(PS, PMMA)对PVC/CPE、PVC/CPE/CaCO₃共混体流变性的影响, 并与CPE改性PVC、CaCO₃改性PVC/CPE共混体的流变性相比较. 结果表明, 刚性聚合物能改善共混体的流变性和挤出行为, 具有其独特的优点.

原材料

聚氯乙烯(PVC): S-1000, 齐鲁石化公司氯碱厂产品; 氯化聚乙烯(CPE): 含氯量35%, 潍坊化工厂产品; 聚苯乙烯(PS): 144C型, 西德BASF公司产品; 聚甲基丙烯酸甲酯(PMMA): 粒料, 上海珊瑚化工厂产品; 活性碳酸钙(CaCO₃): 超细级, 烟台义鸿华侨有限公司产品. 其它助剂均为工业品.

共混体的制备和测试

共混组分混合均匀后于170℃电热开炼机上混炼10 min. 并薄通三次下片. 破碎待用.

流变曲线由XLY-II型毛细管流度仪测定($L/D = 20/1$, 温度170℃, 吉林大学科教仪器厂生产); 挤出用联邦德国产PLE-331型Brabender塑化仪上配套挤出机进行(管状口模外径1 cm).

$$\text{挤出物膨胀率} = \frac{\text{挤出物充分松弛的外径} - \text{管状口模外径}}{\text{管状口模外径}} \times 100$$

PS、PMMA对PVC/CPE共混体流变性的影响

实验结果表明, PVC中加入CPE使共混体表现粘度上升, 流动的牛顿性较差(对比图1-a的1和5线); CPE虽使共混体的粘流活化能下降, 但共混体挤出物表面光滑性变差和膨胀率加大(表1和图2). 亦即CPE使共混体的流变性和挤出性变差, 这

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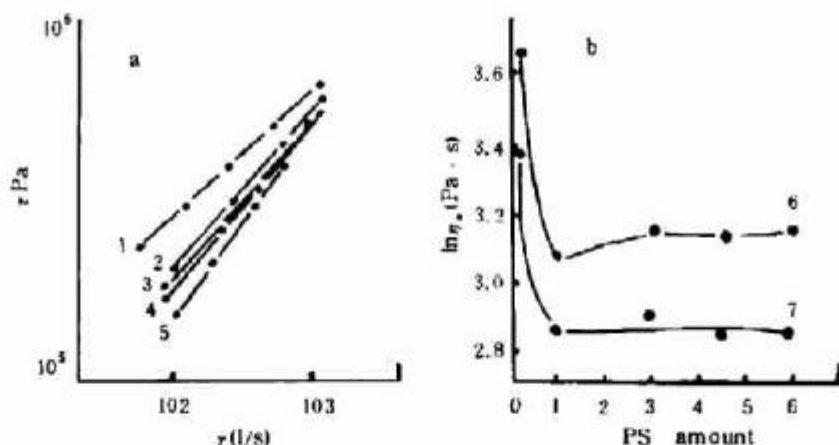


Fig.1 Shear stress (τ) vs. shear rate ($\dot{\gamma}$) and viscosity vs. PS amount for PVC/CPE/PS systems (PVC/CPE=100/15) PS amount: 1-0, 2-3, 3-4.5, 4-6, 5-pure PVC

是由于CPE的分子链较柔顺和较长所致。

由图1可见, 共混小比例的PS就可使PVC/CPE共混体的表观粘度下降, 牛顿流动性有所增强; PS的加入不影响粘流活化能和挤出膨胀率(表1), 但使挤出物外观有所改善(图2)。改变PS用量对PVC/CPE共混体的表观粘度等流变性影响不大(图1-b)。PMMA对共混体流变性和挤出性的影响与PS的影响相似(图3、表1和图2)。这种现象可能是刚性聚合物改变了熔体的超分子结构, 使熔体的流动性质有了质的改变所致^[3]; 或是刚性聚合物与基体混溶性差(尤其是PS), 在流动中起着类似润滑剂的作用。

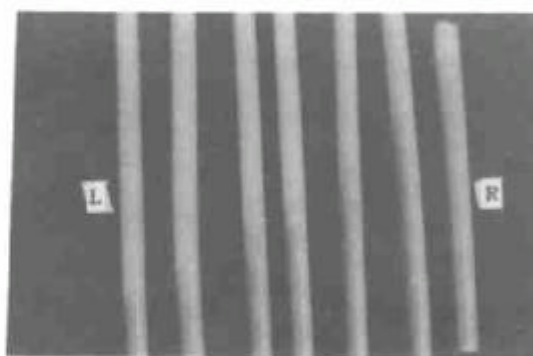


Fig.2 Photographs of extrusion appearance (from left to right: PVC, PVC/CPE, PVC/CPE/CaCO₃, PVC/CPE/CaCO₃/PS, PVC/CPE/CaCO₃/PMMA, PVC/CPE/PS, PVC/CPE/PMMA, blending ratio same as table 1)

Tab.1 Fluid activation energy (E_a) and die swelling ratio (B)

blends	PVC	PVC/CPE 100/15	PVC/CPE/CaCO ₃ 100/15/20	PVC/CPE/CaCO ₃ /PS 100/15/20/3
E_a^* (KJ/mol)	154	102	126	99
B (%)	16	25	10	11
blends	PVC/CPE/CaCO ₃ /PMMA 100/15/20/3		PVC/CPE/PS 100/15/3	PVC/CPE/PMMA 100/15/3
E_a^* (KJ/mol)	97		101	103
B (%)	9		25	26

* $\tau_w = 5 \times 10^5$ Pa, Temp. 150—180 °C

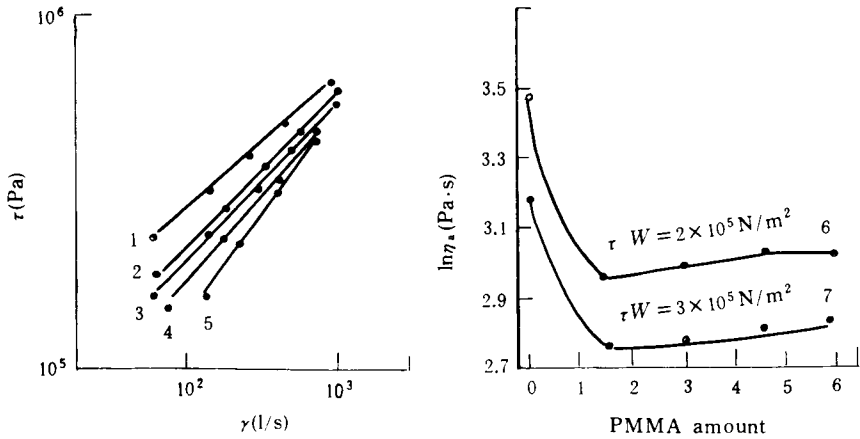


Fig.3 τ vs. γ and η_a vs. PMMA amount for PVC/CPE/PMMA systems
(PVC/CPE=100/15, PMMA amount: 1-0, 2-4.5, 3-3, 4-1.5, 5-pure PVC)

CaCO₃ 对 PVC/CPE 共混体流变性的影响

填充 CaCO₃ 使共混体的表观粘度和牛顿流动性上升 (图 4); 粘流活化能也有所增加 (表 1). 但能明显地改善挤出物外观和降低挤出物的膨胀率 (图 2 和表 1).

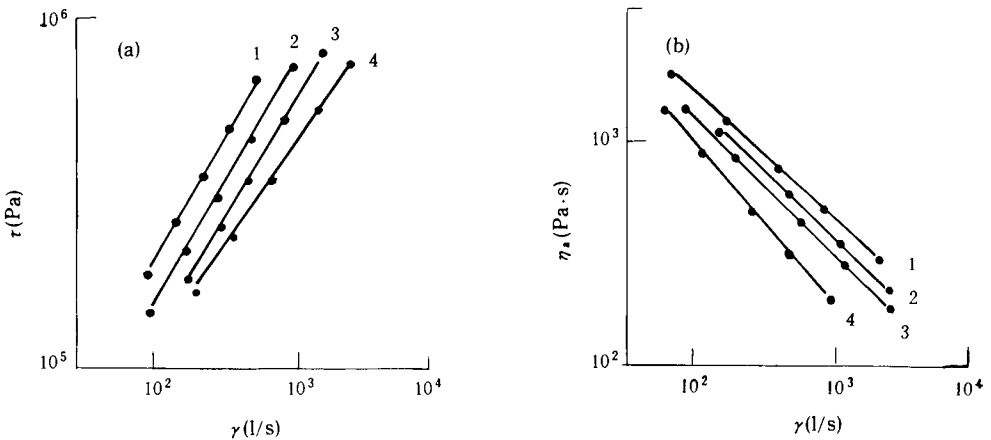


Fig.4 τ vs. γ . and η_a vs. γ for PVC/CPE/CaCO₃ systems CaCO₃ amount: 1-30, 2-20, 3-10, 4-0, PVC/CPE=100/15

PS、PMMA 对 PVC/CPE/CaCO₃ 共混体流变性影响

前述可见, 刚性聚合物和 CaCO₃ 对 PVC/CPE 共混体的流变性和挤出性影响各有优缺点. 并用结果表明, 填加少量刚性聚合物就能降低 PVC/CPE/CaCO₃ 的表观粘度; 且刚性聚合物用量大则表观粘度下降也大; 共混体的非牛顿流动性基本不变 (图 5). 由表 1 和图 2 可见, 填加刚性聚合物的 PVC/CPE/CaCO₃ 共混体仍保持着良好的挤出物外观和低的膨胀率, 亦即刚性聚合物和 CaCO₃ 对 PVC/CPE 共混体流变性和挤出行为具

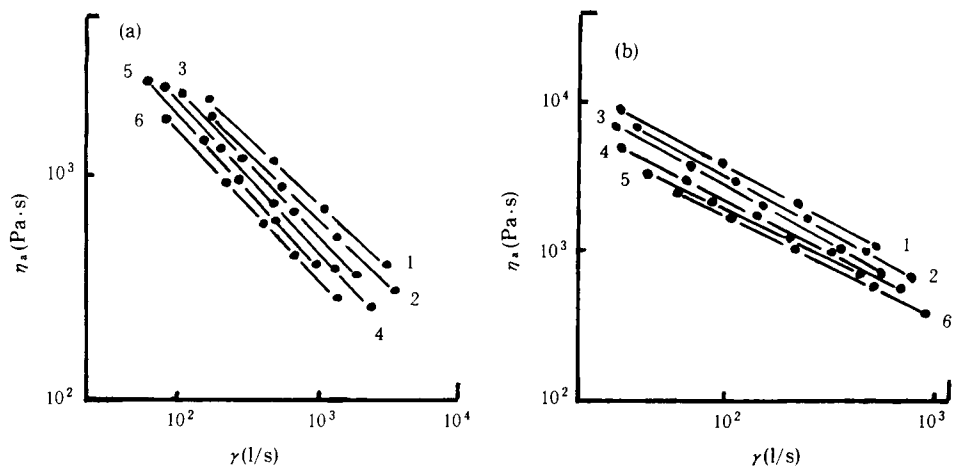


Fig.5 Viscosity vs. shear rate for PVC/CPE/CaCO₃/PS (5-a) and PVC/CPE/CaCO₃/PMMA (5-b) PVC/CPE=100/15; 1,3,4-CaCO₃ 20; 2,5,6-CaCO₃ 10; 3,5-PS (PMMA) 1.5; 4,6-PS / (PMMA) 4.5

有优缺点互补的作用,显示了这种共混改性体系的独特优点,值得进一步的研究和应用开发.

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THE EFFECTS OF PS AND PMMA ON RHEOLOGICAL BEHAVIOR OF PVC/CPE BLENDS

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ABSTRACT

PVC/CPE blend modified by rigid particles has good combined properties. In this paper, the effects of rigid particles (PMMA, PS, CaCO_3) on the rheological behavior of PVC/CPE systems were studied. The results showed that the apparent viscosity (η_a) were decreased, extrusion surface smooth and Newtonian fluidity were slightly improved by filling a little amount of rigid polymers (PS, PMMA) to PVC/CPE blends. The fluid activation energy (E_η), Newtonian fluidity, extrusion surface smooth and η_a of PVC/CPE blends were increased by filling CaCO_3 and die swelling ratio was decreased. The newtonian fluidity, E_η and η_a of PVC/CPE/ CaCO_3 blends can be decreased by filling rigid polymers, and good extrusion surface smooth and low die swelling ratio unchanged.

Key words Modified plastics, Rheological behavior, PVC/CPE blends, Rigid particle