SYNTHESIS OF TITANATE COUPLING AGENTS AND THEIR APPLICATION IN MICA-FILLED POLYPROPYLENE

BY

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DEDICATED TO

MY MOTHER

CERTIFICATE

This is to certify that the thesis entitled "SYNTHESIS OF TITANATE COUPLING AGENTS AND THEIR APPLICATION IN MICA-FILLED POLYPROPYLENE" being submitted by Mr. Rajiv Kishore Jha, to the Indian Institute of Technology, Delhi, for the award of degree of DOCTOR OF PHILOSOPHY in the Department of Chemistry, is a record of bonafide research work carried out by him. Mr. Rajiv Kishore Jha has worked under our guidance and supervision, and has fulfilled the requirements for the submission of the thesis.

The results contained in the thesis have not been submitted in part or in full, to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

A series of new titanate coupling agents were synthesized for use in mica-filled polypropylene system. The coupling agents are of the general formula $Ti(acac)_2(OOCR)_2$ (where, acac is acetylacetonate anion and R = $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$ or $C_{17}H_{35}$). These were characterized by elemental analysis, molecular weight and conductance measurements, and infrared and ^{1}H-nmr spectroscopy. The coupling agents are monomeric and non-electrolytic in nature. A cis - octahedral structure has been proposed for these coupling agents. The thermogravimetric results indicate a single step weight loss for all the complexes leading to the formation of TiO_2.

Two of the new titanates namely, bis (acetylacetonato) distearato titanate (IV) and bis (acetylacetonato) dipalmitato titanate (IV) were used as coupling agent for mica-filled polypropylene system and their performance was compared with two commercial titanate coupling agents, neoalkoxy tri(dioctylpyrophosphato) titanate (LICA 38) and neoalkoxy trineodeconato titanate (LICA 01) (Kenrich Petrochemicals, Inc., U.S.A.).

Mica-filled polypropylene samples with varying mica loading (10-50 percent) were prepared by dry blending with polypropylene powder (melt flow index 10) and mica (muscovite, 10 μm). In another set of experiments, mica coated with titanate coupling agents (0.5-1.0 percent on

weight of mica) was also used as filler. The dry blended samples were extruded on a twin screw extruder and then injection molded. Various properties of the mica-filled polypropylene samples studied included, rheological, mechanical, structural, thermal and electrical.

The rheological behavior of the unfilled and mica-filled polypropylene indicated an increase in melt viscosity and a decrease in melt elasticity when mica was incorporated into polypropylene. When mica was precoated with the titanate coupling agents (0.5-1.0 percent on weight of mica) a drop in melt viscosity and an improvement in melt elasticity was observed. The drop in melt viscosity and improvement in melt elasticity was found to be a function of coupling agent concentration (0.5 - 1.0 percent).

Incorporation of mica into polypropylene resulted in a decrease in both yield stress and yield strain. The initial modulus, however, increased with increasing mica loading. The decrease in yield strain followed a linear pattern with increasing mica loading whereas the yield stress registered a pronounced decrease at higher mica loading (> 40 percent). When mica was coated with the titanate coupling agents, the yield stress and yield strain values increased as compared to uncoated mica-filled polypropylene samples. However, the initial modulus decreased. The flexural strength and impact strength showed an increasing trend at lower mica loadings (20 to 30

percent) but decreased at higher mica loadings. Titanate coating of mica resulted in an improvement in flexural strength and impact strength as compared to uncoated mica-filled polypropylene. The yield stress and flexural strength of mica-filled polypropylene samples showed maximum improvement at coupling agent concentration 0.7 percent (on weight of mica), irrespective of the chemical nature of the coupling agents used in the present investigation. Incorporation of mica also resulted in an improvement in heat distortion temperature which decreased when mica was coated with titanate coupling agents.

An improvement in thermal stability and decrease in the rate of degradation was observed when polypropylene was filled with mica. The order of reaction and activation energy of degradation also increased with the incorporation of mica. However, when mica was coated with the titanate coupling agents (0.7 percent) an increase in the rate of degradation was observed.

By differential thermal analysis, the effect of uncoated and titanate coated mica on the melting and crystallization behavior of polypropylene was studied. For mica-filled polypropylene, the melting peak temperature (T_m) shifted to a lower temperature whereas the crystallization peak temperature (T_p) shifted to a higher temperature as compared to the unfilled polypropylene. A decrease in the degree of supercooling, $\angle\Delta T(= T_m - T_p)$ was also observed which

indicated that mica acts as a nucleating agent in the crystallization of polypropylene. Titanate coated mica-filled polypropylene, however, recorded a decrease in T_p and an increase in T_m. The ΔT values increased as compared to those found for uncoated mica-filled polypropylene, thereby suggesting that titanate coupling agents retard the nucleation action of mica. X-ray diffraction studies indicate that the unit cell dimensions of polypropylene is not disturbed due to the presence of mica or titanate coupling agents.

Incorporation of mica into polypropylene resulted in an increase in dielectric constant, dissipation factor and dielectric strength. However, titanate coated mica-filled polypropylene samples registered a decrease in these values as compared to uncoated mica-filled polypropylene samples.

From the results obtained in various studies mentioned above, it was apparent that the titanates synthesized in the present investigation did act as effective coupling agents in mica-filled polypropylene system. The coupling agent, neoalkoxy tri (dioctyl pyrophosphato) titanate showed best performance while the performance of bis (acetylacetonato) distearato titanate was better than that of neoalkoxy trineodeconato titanate (commercial titanate coupling agent).