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Gregory R. Yandek, Joseph M. Mabry (AFRL/RZSM);
Patrick N. Ruth (ERC)

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Air Force Research Laboratory (AFMC)
AFRL/RZSM
9 Antares Road
Edwards AFB CA 93524-7401

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AFRL/RZS
5 Pollux Drive
Edwards AFB CA 93524-70448

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14. ABSTRACT

Montmorillonite-smectite clay consists of anisotropic clay platelets, generally a nanometer in thickness by hundreds of nanometers laterally, bound together by charge balancing cations. Clay dispersion in polymer hosts has been shown to impart a number of improvements including increased barrier properties, fire resistance, reduced coefficient of thermal expansion, and superior mechanical properties all in relation to the near host polymer. The dispersion of clay in a host material occurs first by intercalation, where the host medium penetrates the galleries causing an increase in inter-plate distance, followed by exfoliation, where the clay platelets migrate away from each other disrupting long rnage order. A high degree of exfoliation can be difficult to achieve in many polymer hosts due to the polarity of the clay platelet and the inorganic nature of naturally occurring cations such as sodium. Dispersion may be facilitated by imparting organic character to the clay through a cation exchange with an organic ammonium salt, and also by introducing polar nature to the intended polymer host. Recently, it has been shown that clay with certain organic cations exhibits spontaneous room temperature and temperature-initiated exfoliation in hydroxyl- and carboxyl-terminated liquid polybutadiene rubbers (CTPB and HTPB, respectively) in the absence of shear. These observations represent a simple process to achieve sought after barrier properties in polymer materials in a relatively simple and reproducible manner. This work represents a more comprehensive examination of the attempted dispersion of a number of different grades of clay in HTPB using polarized optical microscopy and rheology as investigative techniques.

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Gregory R. Yandek, Patrick N. Ruth, Joseph M. Mabry

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Exfoliation of Layered Magnesium Aluminum Silicate Platelets in Polymer Hosts Enabled by Cation Chemistry and Temperature

Gregory R. Yandek[1], Patrick N. Ruth[2], and Joseph M. Mabry[1]

[1]Air Force Research Laboratory, Space and Missile Propulsion Division, Edwards AFB, CA, gregory.yandek@edwards.af.mil.

[2]ERC, Inc., Air Force Research Laboratory, Edwards AFB, CA

INTRODUCTION

Montmorillonite-smectite clay consists of anisotropic clay platelets, generally a nanometer in thickness by hundreds of nanometers laterally, bound together by charge balancing cations. Clay dispersion in polymer hosts has been shown to impart a number of improvements including increased barrier properties, fire resistance, reduced coefficient of thermal expansion, and superior mechanical properties all in relation to the neat host polymer.[1-3] The dispersion of clay in a host material occurs first by intercalation, where the host medium penetrates the galleries causing an increase in inter-plate distance, followed by exfoliation, where the clay platelets migrate away from each other disrupting long range order. A high degree of exfoliation can be difficult to achieve in many polymer hosts due to the polarity of the clay platelet and the inorganic nature of naturally occurring cations such as sodium. Dispersion may be facilitated by imparting organic character to the clay through a cation exchange with an organic ammonium salt, and also by introducing polar nature to the intended polymer host. Recently, it has been shown that clay with certain organic cations exhibits spontaneous room temperature and temperature-initiated exfoliation in hydroxyl- and carboxyl-terminated liquid polybutadiene rubbers (CTPB and HTPB, respectively) in the absence of shear.[4-6] These observations represent a simple process to achieve sought after barrier properties in polymer materials in a relatively simple and reproducible manner. The following represents a more comprehensive examination of the attempted dispersion of a number of different grades of clay in HTPB using polarized optical microscopy and rheology as investigative techniques.

EXPERIMENTAL

Materials. Liquid HTPB (Poly bd R45-HTLO) was purchased from Sartomer. Cloisites Na^+ (naturally occurring), and 10A, 20A, 25A, and 30B were acquired from Southern Clay Products, each possessing a unique cation- exchanged alkyl ammonium salt. The chemical structures of the cation are shown in Figure 1 where HT designates high tallow content (i.e. ~65% C18, ~30% C16, and ~5% C14).

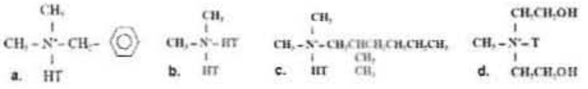

Figure 1. Chemical structures of the exchanged alkyl ammonium cations in a) Cloisite 10A, b) 20A, c) 25A, and d) 30B.

Blending Methodology. All grades of clay were mixed into HTPB in glass beakers using an overhead stirrer at a concentration of ten percent by weight.

Investigative Techniques. Polarized optical microscopy (POM) was conducted using a Zeiss microscope with the polarizer and analyzer oriented perpendicular to each other. Rheological investigations were performed with an Anton Paar parallel plate rheometer using a plate diameter of 25 mm, a spacing of 1 mm, and a continuous purge of nitrogen within the sample chamber. During non-isothermal scans from room temperature to 120°C back to room temperature at a rate of 2°C/minute, a steady shear of $0.05\ s^{-1}$ was imposed on the material, less than the shear rate required for the orientation of the HTPB polymer chains.

RESULTS AND DISCUSSION

Polarized optical microscopy images of the HTPB/clay mixtures after room temperature stirring are shown in Figure 2a, demonstrating poor miscibility in all cases as evidenced by intense light scattering from the crystalline micro-sized particles of aggregated clay platelets. However, after overhead stirring during a temperature ramp to 90°C, a reduction of scattering was observed by the HTPB/Cloisite 20A mixture whereas little morphological changes were observed in the other blends (Figure 2b).

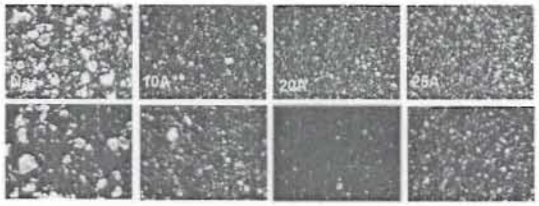

Figure 2. Polarized optical microscopy images of HTPB/clay mixtures: a (top set of images) micrographs after room temperature stirring, and b (bottom set of images) after overhead stirring during a ramp to 90°C.

To further investigate these optical observations, viscosity measurements were taken according to the conditions described in the experimental section. A temperature ramp imposed on the room temperature stirred mixtures during low shear revealed the onset of gradually increasing viscosity for the HTPB/Cloisite 20A mixture at approximately 50°C and a similar behavior for the 10A containing mixture at 95°C, below the upper temperature limit investigated in the POM experiments, supporting temperature driven exfoliation (Figure 3). The other blends exhibit only limited increases in viscosity. Cooling the mixtures in the rheometer indicated that the viscosity increases for the 20A and 10A containing mixtures were irreversible.

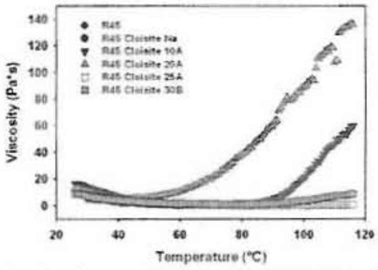

Figure 3. Viscosities of HTPB/clay blends with temperature.

CONCLUSIONS

A combination of cation and blending temperature selection can provide a facile route to exfoliating clay in certain polymer hosts.

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