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Research paper

Influence of dehydration on the dielectric and structural properties of organically modified montmorillonite and halloysite nanotubes

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ABSTRACT

The dielectric behaviours of organically modified montmorillonite (Cloisite-20) and nanosized tubular halloysite (Dragonite-HP) were investigated using broadband dielectric spectroscopy (BDS) under dehydration conditions up to 200 °C. The thermal and structural properties of both tested clay minerals were also initially examined in the as-received and dehydrated samples. Dragonite-HP was shown to lose 2.2 mass% of the adsorbed and interlayer water up to 200 °C. The dehydration of Dragonite-HP also caused the tightly connected tubular layers to unfold, thereby increasing the specific surface area and the total pore volume. Cloisite-20 lost only 1.1 mass% of its adsorbed water during dehydration due to the presence of an organic modifier, bis(hydrogenated tallow alkyl)dimethyl. Its presence led to decreases in the specific surface area and total pore volume of Cloisite-20 relative to those of pristine montmorillonite. BDS revealed that the dielectric constant (ε') and dissipation factor (tan δ) of the thermally treated Dragonite-HP increased and that the volume resistivity (ρ_v) decreased within one order of magnitude in the temperature range of − 40 to 90 °C. In contrast, the ε' of the thermally treated Cloisite-20 increased by two orders of magnitude, the tan δ increased by more than three orders of magnitude, and the ρ_v decreased by five orders of magnitude. The values of ε', tan δ and ρ_v measured via BDS demonstrate that the dielectric properties of Dragonite-HP at a standard industrial frequency of 50 Hz and under a typical operating temperature range are more advantageous than those of Cloisite-20. This finding is very promising for the possible use of Dragonite-HP as a nanofiller for clay/polymer nanocomposites intended for cable core insulation manufacturing.

1. Introduction

Continuing interest in nanometric structures, including naturally occurring nanosized tubular halloysite and montmorillonite (Mt), has attracted the attention of researchers. The chemical compositions of the two mentioned clay minerals are similar, but their inner structures differ considerably.

Halloysite-(10 Å) is a dioctahedral hydrated polymorph of kaolinite with a monolayer of water molecules between the 1:1 aluminosilicate layers, and the chemical formula of this clay mineral is $Si_2Al_2O_5(OH)_4{\cdot}2H_2O$ (Joussein et al., 2005; Yuan et al., 2012). The interlayer water is weakly bound; thus, halloysite-(10 Å) can irreversibly dehydrate to halloysite-(7 Å) (Alexander et al., 1943; Joussein et al., 2005). Nanosized tubular halloysite, also known as "Hal nanotubes", originates from the curling of layers of naturally occurring halloysite (Hal) under specific geological conditions (Yuan et al., 2012, 2015). The interlayer space in a Hal nanotube can be clearly defined as the space between the Al—O octahedral sheet of the first aluminosilicate layer curvature and the Si—O tetrahedral sheet of the second aluminosilicate layer curvature of the tubular structure. In contrast, Mt is a dioctahedral smectite with the chemical formula $(M_y{}^{+}{\cdot}nH_2O)(Al_{2-y}{}^{3}Mg_y{}^{2+})Si_4{}^{4+}O_{10}(OH)_2$ (Bergaya et al., 2006). The chemical structures of both clay minerals are shown schematically in Fig. 1. Mt is most commonly used as the base material for organoclays (organic-rich clay minerals) due to its high cation exchange capacity (Zhao et al., 2016), while Hal nanotubes are mainly useful for their tubular structure, which enables the development of advanced materials for the paint industry, tissue engineering, drug delivery systems and many other applications (Rawtani and Agrawal, 2012; Liu et al., 2014; Yuan et al., 2015).

Among their other abilities, Mt and Hal nanotubes also possess flame-retardant properties when used as nanofillers in clay/polymer nanocomposites (Jia et al., 2009; Laoutid et al., 2009; Zhao et al., 2014; Majka et al., 2017). This property of the clay/polymer nanocomposites

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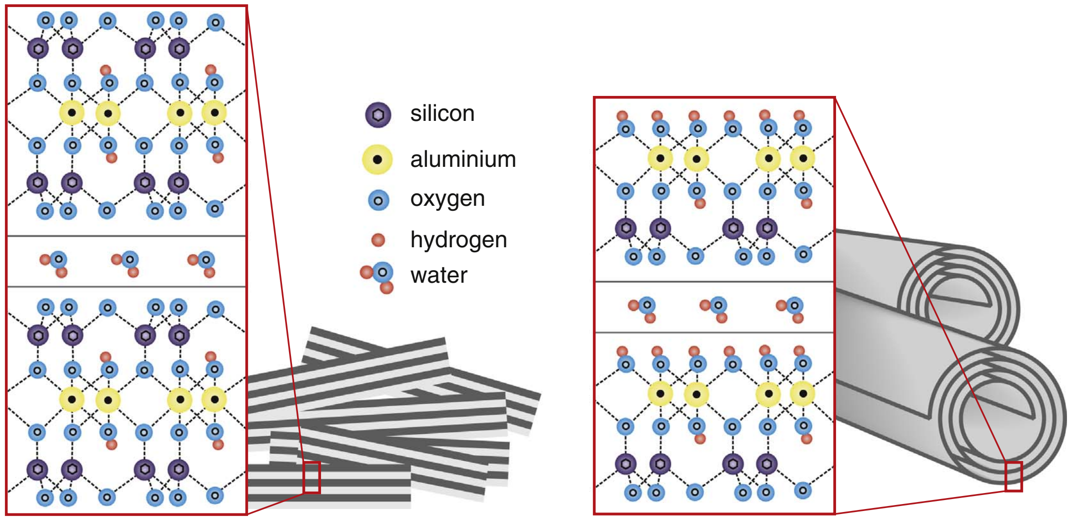

Fig. 1. Chemical structures of Mt and the Hal nanotubes.

may be useful in the cable industry, where safety requirements are becoming increasingly strict to guarantee the functionality of safety and emergency systems in areas with an increased risk of fire or high population. The relatively high flammability of unmodified polymers is one of the main problems limiting their use in such applications. For this reason, polymers are commonly incorporated with various organic and inorganic flame-retardant additives (Laoutid et al., 2009). Considering that halogenated additives are being phased out due to their adverse effects on the environment, proven or suspected inorganic filler materials, such as metal hydroxides ($Al(OH)_3$ or $Mg(OH)_2$), are becoming widely used (Laoutid et al., 2009). These fillers decompose endothermically to release water, absorbing energy from the combustion zone and producing char and a metal oxide coating that can act as a protective layer during combustion (Hull et al., 2003). However, a large portion (e.g., 60–70% according to Hull et al., 2008) of metal hydroxides in polymer compounds dramatically degrades their dielectric and mechanical properties and limits their application. Hence, these compounds are acceptable, for example, for manufacturing cable sheaths or cable bedding but not as a material for cable core insulation, which requires excellent dielectric and mechanical properties.

Currently, unmodified and low-polarity polymers, such as polyethylene (PE), more specifically low-density polyethylene (LDPE) or cross-linked polyethylene (XLPE) (Rawtani and Agrawal, 2012; Polanský and Polanská, 2015), possess the dielectric properties required for core insulation. Nevertheless, such materials are highly flammable. Therefore, under fire conditions, their sudden ignition can dramatically influence the fire-proof functionality of the whole cable, mechanically destroying the protective layers previously formed by metal hydroxides from the cable sheath and bedding (Polanský and Polanská, 2015). For this reason, modification the polymers primarily used for cable core insulation is required to achieve improved flame retardancy. The modification must also maintain the main dielectric properties within acceptable limits; thus, filling with a high proportion of metal hydroxides is undesirable. Although the flame-retardant properties of small amounts of Mt and Hal nanotubes in various polymer compounds have been widely reported (e.g., Du et al., 2006; Jia et al., 2009; Majka et al., 2017), the number of studies on their respective dielectric properties has been limited (Ishida et al., 2000; Adamczyk et al., 2014; Vasilyeva et al., 2014). Moreover, both clay minerals dehydrate at polymer extrusion temperatures (200 °C or more for polyethylene according to Hedley et al., 2007); thus, understanding their dielectric behaviour during dehydration would be valuable.

Therefore, the main objective of this study is to explore the dielectric behaviour of organically modified Mt and Hal nanotubes during dehydration using broadband dielectric spectroscopy (BDS). The thermal and structural properties of the tested clay minerals were initially examined to provide further insight into their structural behaviours at typical temperatures of both clay/polymer nanocomposite production and applications.

2. Experimental

2.1. Description of the tested clay minerals

Organically modified montmorillonite (marketed as Cloisite-20), supplied by BYK-Chemie GmbH (Wesel, Germany), and nanosized tubular halloysite (marketed as Dragonite-HP), supplied by Applied Minerals, Inc. (New York, NY, United States), were used in this study. Cloisite-20 and Dragonite-HP are additives for plastics intended to improve various physical properties, such as mechanical strength and flame retardancy.

Cloisite-20 was chosen as a representative of common planar organoclays used as fillers in nanocomposites with a polymeric matrix. Mt without modification exhibits a pronounced tendency towards moistening and agglomeration (Basara et al., 2005). Therefore, its use without modification is inappropriate in practice. In contrast, the natural clay Dragonite-HP, consisting of particles with a non-planar structure, has a lower tendency to form large particle aggregates. It is important to note that every organic modification of clay is time consuming and costly in industrial production. For this reason, the non-planar clay Dragonite-HP is used in the presented research without modification. The determination of whether the use of Dragonite-HP is sufficient for application as a filler in clay/polymer nanocomposites intended for electrical engineering is very important. Modification of Hal nanotubes, for example, by γ-aminopropyltriethoxysilane, as discussed in Yuan et al. (2008), may represent a further step in this research.

Cloisite-20 is a natural montmorillonite treated with bis(hydrogenated tallow alkyl)dimethyl, hereinafter referred to as an organic modifier, according to BYK Additives and Instruments (2013). Cloisite-20 has a median particle size (d_{50}) of 10 µm and a moisture content below 3% (BYK Additives and Instruments, 2013). Dragonite-HP is an unmodified high-purity natural aluminosilicate clay with a hollow tubular morphology produced by the Dragon Mine, Tintic District (Silver City, Utah, United States). Dragonite-HP has a halloysite content greater than 95%, a median particle size of 1 µm and a moisture content of 3–4% below 105 °C (Applied Minerals Inc., 2011, n.d.). A study by García et al. (2009) indicated that natural halloysite from the Dragon