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Abstract Clay is a soil component, a ceramic ware component, and a reinforcement in nanocomposites. Its viscoelastic behavior is relevant to vibration damping and slip rheology. The clay studied is hectorite, which is a trioctahedral magnesium-based smectite. Clay compacts with solid contents (50–53) vol% are studied in terms of the dynamic compressive properties at small static strains (3.1–3.5 %), low deformation amplitudes (5–8 μm), and low frequencies (0.2–10.0 Hz). The organic intercalation of hectorite (with basal spacing 12 Å prior to intercalation) to form organoclay (nanoclay in the form of disteardimonium hectorite with basal spacing 29 Å) increases both the loss tangent and the loss modulus of the solid part of the compact by up to about 27 %, while affecting the storage modulus negligibly. At 10.0 Hz, the organic intercalation increases the loss tangent of the solid part from 0.306 ± 0.009 to 0.366 ± 0.021 and increases the loss modulus of the solid part from $(2.69 \pm 0.08) \times 10^4$ to $(3.44 \pm 0.04) \times 10^4$ Pa. The organic intercalation affects the viscous behavior rather than the elastic behavior. The viscous behavior is attributed to the low-amplitude dynamic slippage at the interface between adjacent clay layers in a clay nanoplatelet and that between nanoplatelets in a clay particle. In case of organoclay, it is also due to the nanoscale viscous behavior of the organic component. The viscoelastic properties are essentially independent of the frequency. The viscous character of both unmodified clay and organoclay is weaker than that of carbon black or exfoliated graphite, but the elastic character of both unmodified clay and organoclay is stronger than that of carbon black or exfoliated graphite.

Introduction

Viscoelastic behavior pertains to both the elastic character and the viscous character. The viscous character, in particular, is important for the performance under dynamic loading and is relevant to vibration damping (mechanical energy dissipation), vibration isolation, creep, stress relaxation, and slip rheology (in relation to ceramic ware fabrication by slipcasting). Study of the viscous character is best conducted under dynamic loading. In general, the study of the mechanical properties of materials tends to emphasize the elastic aspect more than the viscous aspect, because the measurement of the elastic properties tends to be more straightforward than the measurement of the viscous properties.

Clay minerals are an important component of clay soils, the vibration damping ability of which is relevant to the performance, durability, and seismic resistance of structures built on the soil [1–6]. Such structures include pavements, foundations, piers, etc. In addition, the vibration damping ability of soil relates to the tendency for settlement [7], which tends to limit the durability of structures, including bridges. Furthermore, clay is effective as an additive in continuous fiber polymer-matrix structural composites for enhancing the damping ability [8, 9].

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Clay is in the form of particles or platelets, in contrast to the bulk form of polymer-matrix nanocomposites containing clay. In a particle compact, the movement of the particles relative to one another involves friction, which results in viscous behavior. Such interparticle movement occurs in addition to mechanisms of energy dissipation that may occur within each particle. Mechanisms within each particle can involve slippage at interfaces within the particle as well as bulk viscous deformation within the particle. Bulk viscous deformation is the most common mechanism used to provide viscous behavior. This mechanism is commonly exhibited by polymers such as rubber.

The viscoelastic properties of a material are commonly described in terms of the loss tangent, the storage modulus and the loss modulus. The loss tangent (loss factor or tan δ, where δ is the phase angle between the stress and strain waves) describes the viscous character. The behavior is purely elastic when $\delta = 0°$ and is purely viscous when $\delta = 90°$.

The storage modulus E' is the dynamic elastic modulus, which relates to the stiffness, and is defined as

$$E' = (\sigma_o/\varepsilon_o) \cos \delta, \tag{1}$$

where, σ_o and ε_o are the stress and strain amplitudes, respectively. The loss modulus E'' is the dynamic viscous modulus, which relates to the amount of mechanical energy dissipated per unit volume, and is defined as

$$E'' = (\sigma_o/\varepsilon_o) \sin \delta. \tag{2}$$

The loss tangent is defined as

$$\tan \delta = E''/E'. \tag{3}$$

High values of both the storage modulus and loss tangent are necessary for effective mechanical energy dissipation, which is the essence of vibration damping. This is because (i) a higher value of the storage modulus enables a higher force to be borne and energy relates to the force, and (ii) a higher value of the loss tangent enables more effective reduction of the vibration amplitude. The achievement of high values of both quantities is a challenge. For example, as a thermoplastic polymer is heated past the glass transition temperature, its modulus of elasticity decreases, while its loss tangent increases; as a consequence, the storage modulus is high and the loss tangent is low below the glass transition temperature, and vice versa above this temperature.

Prior work on the viscoelastic behavior of particulate materials has addressed glass spheres of average size 459–4417 μm, polyethylene particles of average size 320–462 μm, rubber particles of average size 219–382 μm, and sand of average size 169 μm [10–12]. Glass and sand give relatively high values of the modulus of elasticity, but relatively low values of the loss tangent (equal to twice the damping ratio in the linear viscoelastic regime), whereas rubber and polyethylene give relatively low values of the modulus of elasticity but relatively high values of the loss tangent.

Prior work on the viscoelastic behavior of particulate materials has also addressed carbon black compacts [13] and exfoliated graphite compacts [14]. Carbon black is in the form of aggregates of nanoparticles. The inter-nanoparticle movement in a carbon black aggregate contributes to the viscous deformation. As a consequence, the loss tangent of the solid part of a carbon black compact increases with increasing aggregate size [13]. On the other hand, exfoliated graphite has a cellular structure with the cell wall being a stack of graphite layers that number about 60 [14]. The viscous character of exfoliated graphite is exceptionally strong, due to the large interfacial area and the easy sliding between the graphite layers in the cell wall [14].

Phyllosilicate clay may be modified by the intercalation of an organic component among the clay layers. The intercalation involves exchanging the original interlayer cations for organocations, which are typically quaternary alkylammonium ions. The resulting surface is hydrophobic, in contrast to the hydrophilicity of the unmodified clay. Organoclay can be used to remove oil from water and is used as antiperspirants. It can also be used as a component in paint formulations, a viscosifier for oil-based drilling fluids, and a nucleating agent in polymer chemistry. The organically modified material is known as organoclay (also known as nanoclay) [15–18].

Sound damping is akin to vibration damping. Montmorillonite clays with and without organic intercalation have been reported to improve the sound/vibration damping ability of polymer-matrix composites [19, 20]. However, the difference in damping ability between clays with and without the intercalation has not been reported.

This paper is aimed at investigating the effect of organic intercalation on the viscoelastic behavior of clay. In addition, it is aimed at improving the vibration damping performance of clay. Although this paper does not address sound damping, the results on vibration damping shed light on sound damping.

Experimental methods

Hectorite and bentonite (montmorillonite) are important among smectite clays because of their swelling properties (valuable for use as rheological additives) and availability. The clay used is hectorite, a trioctahedral magnesium-based smectite clay with composition $Na_{0.33}[Mg_{2.67}Li_{0.33}]Si_4O_{10}[OH]_2$ and a monoclinic crystal structure. It does not contain crystalline silica.

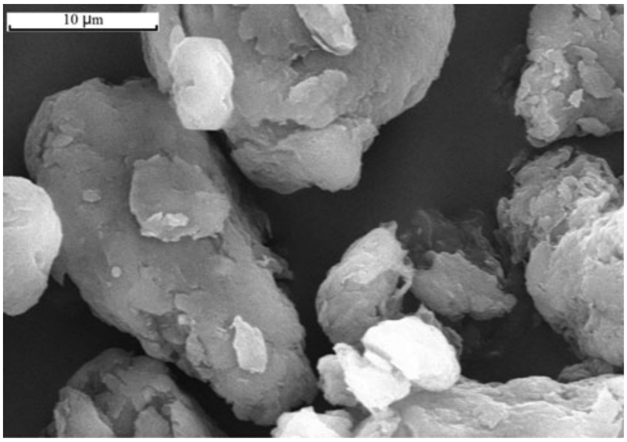

Fig. 1 SEM photograph of organoclay particles

The unmodified hectorite is in the form of nanoplatelets with dimensions 0.8 × 0.08 × 0.001 μm. The iron content is 0.2 %. It is Bentone CT (from Elementis Specialties, Inc., Hightstown, NJ), with 95 % through 200 mesh (75 μm) and density 2.60 g cm^{-3}.

The organically modified hectorite is Bentone 38 V CG (also from Elementis Specialties, Inc.), with density 1.70 g cm^{-3}, (95.0–100) % through 200 mesh (75 μm), (36.5–39.5) % loss on ignition, and moisture content up to 3.0 %. Hence, the particle size is comparable for the unmodified and modified materials. For both materials, each particle contains a large number of the clay nanoplatelets. Scanning electron microscopy shows that the organoclay particles have typical size around 10 μm (Fig. 1).

The organoclay is disteardimonium hectorite, i.e., a 1-octadecanaminium, *N*,*N*-dimethyl-*N*-octadecyl-chloride reaction product derived from hectorite. It is a vegetable (non-animal) derived organically modified hectorite that is widely used as a suspending agent in cosmetics. It is synthesized by grafting cationic surfactants to hectorite (i.e., exchanging the interlayer sodium cations with a cationic surfactant). These cationic surfactants are quaternary ammonium compounds, such that at least some of the sodium cations of hectorite have been exchanged for the $[(CH_3)2NRR']^+$ cation, wherein *R* and *R*′ are both octadecyl alkyl chains (i.e., stearyl groups) [21]. The exchange is carried out by the addition of disteardimonium chloride to an alcohol/water slurry of hectorite. This cation exchange shifts the nature of these minerals from being hydrophilic to being hydrophobic (lipophilic).

The organic modification results in an X-ray diffraction (XRD) peak corresponding to interplanar spacing $d_{001} = 29$ Å, compared to the value of 12 Å for the unmodified hectorite (Fig. 2). The increase in the interplanar spacing indicates the occurrence of intercalation and is consistent with the decrease in density upon organic modification. In the completely dehydrated and unmodified state, the spacing is 9.5 Å for hectorite [22].

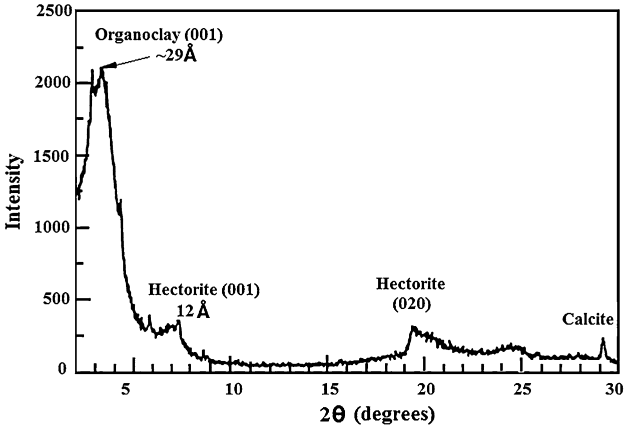

Fig. 2 X-ray diffraction pattern of organoclay. Peaks of hectorite (without organic intercalation) and calcite (calcium carbonate, a common impurity with hectorite) are present in both the organoclay and the hectorite without organic intercalation

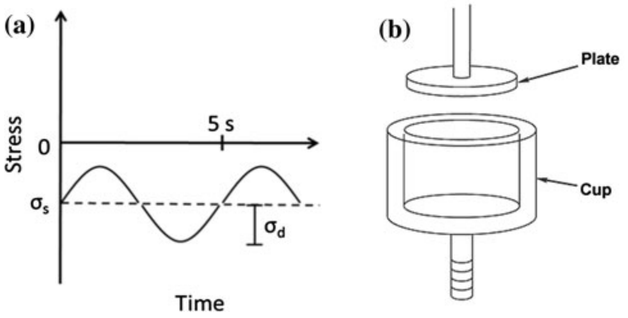

Fig. 3 Method of dynamic compressive testing. **a** Schematic illustrations of the variation of the stress with time during dynamic mechanical compression at 0.2 Hz. The static and dynamic stresses are σ_s and σ_d, respectively. **b** Cup-and-plate specimen holder for dynamic compressive testing

Dynamic compressive testing (ASTM D 4065-94) using a sinusoidal stress wave at controlled frequencies of 0.2, 1.0, 5.0, and 10.0 Hz is conducted at room temperature using a dynamic mechanical analyzer (DMA7E, Perkin Elmer Corp., Shelton, CT). The variation of stress with time is illustrated in Fig. 3a for 0.2 Hz. The dynamic stress σ_d ranges from 64 to 75 % of the corresponding static stress σ_s. The stresses are chosen, so that different specimens are tested at comparable values of the static and dynamic strains. The static stress ranges from 1200 to 1400 Pa, the dynamic stress is 900 Pa, the static strain ranges from 3.1 to 3.5 %, and the deformation amplitudes ranges from 5 to 8 μm. The deformation amplitude is kept low in order to avoid other vibration modes. The frequencies (0.2–10.0 Hz) are far from any vibration resonance frequency. Low frequencies are relevant to soil applications.

Table 1 Dynamic compressive properties of hectorite clay particle compacts and their fractional increase due to the organic intercalation of the clay

Frequency (Hz)		Unmodified	Organically intercalated	Fractional increase due to the organic intercalation (%)
	Density of compact (g cm^{-3})	1.286 ± 0.001	0.900 ± 0.001	
	Solid content of compact (vol%)[a]	49.46 ± 0.01	52.94 ± 0.01	
	Static stress (Pa)	1400	1200	
	Dynamic stress (Pa)	900	900	
0.2	Static strain (%)	3.10 ± 0.05	3.15 ± 0.05	/
	Deformation amplitude (μm)	6.0	8.2	/
	Loss tangent	0.136 ± 0.005	0.168 ± 0.007	23 ± 11
	Storage modulus (10^4 Pa)	8.95 ± 0.14	9.06 ± 0.34	2 ± 5
	Loss modulus (10^4 Pa)	1.22 ± 0.05	1.60 ± 0.09	31 ± 13
	Loss tangent/solid content	0.274 ± 0.010	0.317 ± 0.013	14 ± 11
	Storage modulus/solid content (10^4 Pa)	18.1 ± 0.3	17.1 ± 0.6	−6 ± 5
	Loss modulus/solid content (10^4 Pa)	2.47 ± 0.10	3.02 ± 0.17	23 ± 12
1.0	Static strain (%)	3.49 ± 0.11	3.22 ± 0.08	/
	Deformation amplitude (μm)	6.6	7.2	/
	Loss tangent	0.138 ± 0.008	0.182 ± 0.012	32 ± 16
	Storage modulus (10^4 Pa)	9.33 ± 0.04	9.14 ± 0.34	−2 ± 4
	Loss modulus (10^4 Pa)	1.29 ± 0.03	1.66 ± 0.09	29 ± 10
	Loss tangent/solid content	0.279 ± 0.016	0.344 ± 0.023	24 ± 15
	Storage modulus/solid content (10^4 Pa)	18.9 ± 0.1	17.3 ± 0.6	−9 ± 3
	Loss modulus/solid content (10^4 Pa)	2.61 ± 0.06	3.14 ± 0.17	20 ± 10
5.0	Static strain (%)	3.53 ± 0.09	3.52 ± 0.09	/
	Deformation amplitude (μm)	5.5	8.2	/
	Loss tangent	0.145 ± 0.011	0.191 ± 0.012	33 ± 18
	Storage modulus (10^4 Pa)	8.95 ± 0.07	9.34 ± 0.24	4 ± 3
	Loss modulus (10^4 Pa)	1.30 ± 0.08	1.78 ± 0.03	37 ± 10
	Loss tangent/solid content	0.286 ± 0.008	0.360 ± 0.022	26 ± 11
	Storage modulus/solid content (10^4 Pa)	18.1 ± 0.1	17.6 ± 0.5	−3 ± 4
	Loss modulus/solid content (10^4 Pa)	2.63 ± 0.16	3.36 ± 0.06	28 ± 10
10.0	Static strain (%)	3.56 ± 0.07	3.40 ± 0.06	/
	Deformation amplitude (μm)	5.9	7.5	/
	Loss tangent	0.151 ± 0.004	0.194 ± 0.011	28 ± 11
	Storage modulus (10^4 Pa)	8.83 ± 0.11	9.37 ± 0.12	6 ± 3
	Loss modulus (10^4 Pa)	1.33 ± 0.04	1.82 ± 0.02	37 ± 4
	Loss tangent/solid content	0.306 ± 0.009	0.366 ± 0.021	20 ± 10
	Storage modulus/solid content (10^4 Pa)	17.8 ± 0.2	17.7 ± 0.2	0 ± 3
	Loss modulus/solid content (10^4 Pa)	2.69 ± 0.08	3.44 ± 0.04	27 ± 6

The loss tangent decreases with increasing static strain, while the storage modulus increases with increasing static strain. Comparison between unmodified and organically intercalated clay at each frequency is conducted at similar values of the static strain and deformation amplitude

[a] Calculated based on the known density of the solid and the measured density of the compact

Specimens are obtained by manual compaction of the clay particles in a stainless steel cylindrical cup of inside diameter 18.00 mm (Fig. 3b). The thickness of the specimen in the direction of the compressive stress is 3.51 mm. The density is obtained from the measured mass and the measured volume, which relates to the thickness. Dynamic compressive stress is applied via a stainless steel circular plate of diameter 15.00 mm, such that the plate is parallel to the bottom plane of the cup and is centered at the axis of the cup. The set of the cup and the plate is an accessory of the dynamic mechanical testing equipment. Three specimens are tested for each combination of specimen type and loading condition.

Powder XRD is conducted with CuKα radiation (40 kV, 30 mA) using a Siemens Kristalloflex D500 diffractometer with a diffracted-beam graphite monochromator. The basal spacing is thus obtained.

Results and discussion

Comparison of clays with and without organic intercalation is conducted at similar values of both the static strain and the deformation amplitude, as obtained by adjusting the static stress and dynamic stress. As shown in Table 1 (0.2 Hz, static strain 3.1 %, deformation amplitude 6–8 μm), the organic intercalation increases the loss tangent from 0.136 ± 0.005 to 0.168 ± 0.007 [i.e., an increase of (23 ± 11) %], increases the storage modulus from $(8.95 \pm 0.14) \times 10^4$ Pa to $(9.06 \pm 0.34) \times 10^4$ Pa [i.e., an increase of (2 ± 5) %], and increases the loss modulus from $(1.22 \pm 0.05) \times 10^4$ Pa to $(1.60 \pm 0.09) \times 10^4$ Pa [i.e., an increase of (31 ± 13) %)]. Hence, the fractional increase in the storage modulus is much smaller than the fractional increases in both the loss tangent and the loss modulus. In other words, the increase in loss modulus due to the organic intercalation is mainly associated with the increase in the loss tangent.

The loss tangent divided by the solid content (corresponding to the loss tangent of the solid part of the compact if the rule of mixtures is obeyed), the storage modulus divided by the solid content (corresponding to the storage modulus of the solid part of the compact if the Rule of Mixtures is obeyed), and the loss modulus divided by the solid content (corresponding to the loss modulus of the solid part of the compact if the Rule of Mixtures is obeyed) are also increased by the organic intercalation, and the fractional increases (0.2 Hz, static strain of 3.1 %, deformation amplitude 6–8 μm) are (14 ± 11), (−6 ± 5), and (23 ± 12) %, respectively. These percentage increases mean that the presence of the organic component due to the organic intercalation of the clay promotes the viscous character, but essentially does not affect the elastic character, and confirm that the increase in loss modulus due to the presence of the organic component is mainly associated with the increase in the loss tangent. This further means that the storage modulus of the solid part of the compact is essentially independent of the solid content, which differs between clays with and without organic intercalation, in agreement with the Rule of Mixtures, and the organic modification essentially does not affect the stiffness of the solid part.

The fractional increase in the loss tangent divided by the solid content due to the organic intercalation [(14 ± 11) %, 0.2 Hz] is slightly less than that in the loss tangent itself [(23 ± 11) %, 0.2 Hz]. This means that an increase in solid content, as associated with the change from unmodified clay to organically modified clay, contributes to causing the increase in the loss tangent, but the presence of the organic component due to the organic intercalation also contributes to increasing the loss tangent.

The enhancement of the loss tangent of the solid part by the organic intercalation is attributed to the nanoscale viscous deformation provided by the nanoscale organic component, which amounts to approximately 60 vol% [(29 − 12)/29] of the clay. It is probably also partly due to the increased ease of slipping between the clay layers when the layers are separated by the organic component between the layers. Based on the increase in the basal spacing by the organic intercalation, the organoclay may be roughly modeled as 40 vol% inorganic component and 60 vol% organic component. The loss tangent of the inorganic component of the solid part of the organoclay compact is taken as that of the solid part of the unmodified clay compact, i.e., 0.27 (0.2 Hz, Table 1). With the loss tangent of the solid part of the organoclay compact at 0.32 (0.2 Hz, Table 1), it may be estimated, based on the Rule of Mixtures, that the loss tangent of the organic component of the solid part of the organoclay compact is 0.35. This calculation gives an over-estimate, as it neglects the interfacial contribution to the loss tangent. The validity of the Rule of Mixtures for the calculation of the loss tangent is actually questionable [23, 24]. Nevertheless, this calculation suggests that the organic component contributes substantially to the viscous behavior of the organoclay.

Comparison of the data in Table 1 for various frequencies shows that an increase in frequency in the range from 0.2 to 10.0 Hz does not cause any statistically significant trend in the change of the loss tangent, storage modulus, loss modulus, loss tangent divided by the solid content, storage modulus divided by the solid content, and loss modulus divided by the solid content, whether the clay has been intercalated or not. In other words, the frequency has little, if any, effect on the viscoelastic behavior. This is in contrast to conventional bulk viscous behavior, which is exhibited by bulk polymers and which tends to vary with the frequency [25]. Thus, the viscous behavior provided by the unmodified clay and by the organic component of the organoclay differs from that of bulk viscous behavior, probably because of the interfacial friction mechanism associated with the interface between adjacent clay layers and because the organic component in the organoclay is present in a nanoscale.

The nanoscale thickness of the organic component is attractive for constrained-layer damping, in which the inorganic component of the clay serves as the constraining layer, while the organic component serves as the constrained layer. Conventional constrained-layer damping involves constrained layers that are macroscopic in thickness. A thinner constrained layer facilitates the load transfer needed to shear the entire constrained layer. On the other hand, with the constraining layer fixed in thickness, as in the case of organoclay, a thinner constrained layer decreases the volume fraction of the viscous component. Therefore, an optimum thickness of the constrained layer is expected to be most attractive. A systematic study of the effect of the thickness of the organic component in organoclay on the viscoelastic behavior would be useful for both science and technology, though it is outside the scope of this work.

The ease of interlayer movement of organoclay is expected to increase with increasing temperature, due to the increasing fluidity of the organic component. However, the maximum temperature is limited, due to the inability for the organoclay to withstand high temperatures.

The effect of the organic intercalation on the loss tangent (as well as the loss tangent divided by the solid content), the storage modulus (as well as the storage modulus divided by the solid content), and the loss modulus (as well as the loss modulus divided by the solid content), as shown by the fractional increases (last column of Table 1), also does not show any systematic dependence on the frequency. This is in contrast to conventional bulk viscous behavior, which tends to vary with the frequency. Thus, the viscous behavior provided by the organic component of organoclay differs from that of bulk viscous behavior, as explained above.

The loss tangent of the solid part of clay compacts is up to 0.37 (Table 1), which is much lower than the corresponding value of a carbon black compact (up to 1.2 [13]) and that of an exfoliated graphite compact (up to 25 [14]), all similarly tested under dynamic compression at 0.2 Hz. The viscous character is stronger for carbon black and exfoliated graphite than organoclay, in spite of the absence of an organic component in carbon black or exfoliated graphite. For carbon black, the viscous behavior increases with increasing aggregate size [13], indicating the importance of the inter-nanoparticle interface in a carbon black aggregate to the viscous behavior. The stronger viscous character of carbon black compared to clay means that the inter-nanoparticle movement in a carbon black aggregate is more effective than the interfacial movements in clay for providing viscous character. Moreover, the very strong viscous character of exfoliated graphite compared to clay means that the interlayer movement in the cell wall of exfoliated graphite is much more effective than the interfacial movements in clay for providing viscous character. The interfacial movements in clay include the interlayer movement within a clay nanoplatelet and the inter-nanoplatelet movement within a clay particle. The strong viscous character of carbon black and exfoliated graphite compared to clay probably relates to the larger area and the greater ease of slippage of the associated interfaces in carbon black or exfoliated graphite compared to clay.

The storage modulus of the solid part of clay compacts is up to 18×10^4 Pa (Table 1), compared to 4.4×10^4 Pa for carbon black [13] and 4.6×10^4 Pa for exfoliated graphite [14], all similarly tested by dynamic compression at 0.2 Hz. Hence, clay gives greater stiffness than carbon black or exfoliated graphite. The greater stiffness is attractive for dimensional stability of a particle packing.

The loss modulus of the solid part of clay compacts is up to 3.0×10^4 Pa (Table 1), compared to 3.2×10^3 Pa for carbon black [13] and 4.5×10^7 Pa for exfoliated graphite [14], all similarly tested by dynamic compression at 0.2 Hz. Hence, clay is intermediate between carbon black and exfoliated graphite in relation to the loss modulus. Although clay is inferior to carbon black in terms of the loss tangent, it is much superior to carbon black in terms of the storage modulus. As a consequence, clay is superior to carbon black in terms of the loss modulus. Although clay is superior to exfoliated graphite in terms of the storage modulus, it is much inferior to exfoliated graphite in terms of the loss tangent. As a consequence, clay is much inferior to exfoliated graphite in terms of the loss modulus. A high value of the loss modulus is attractive for vibration damping.

Conclusion

Hectorite clay compacts with solid contents (50–53) vol% have been studied in terms of the dynamic compressive properties at small static strains (3.1–3.5 %), low deformation amplitudes (5–8 μm), and low frequencies (0.2–10.0 Hz). The organic intercalation of hectorite (basal spacing 12 Å) to form organoclay (disteardimonium hectorite, basal spacing 29 Å) increases both the loss tangent and loss modulus of the solid part of the compact by up to about 27 %. The fractional increase in the storage modulus due to the organic intercalation is negligible, so that the loss modulus increase is associated with the loss tangent increase. In particular, at 10.0 Hz, the organic intercalation increases the loss tangent of the solid part (at a static strain of 3.5 %) from 0.306 ± 0.009 to 0.366 ± 0.021 and increases the loss modulus of the solid part from $(2.69 \pm 0.08) \times 10^4$ to $(3.44 \pm 0.04) \times 10^4$ Pa.

The viscous behavior is attributed to the low-amplitude dynamic slippage at the interface between adjacent clay layers in a clay nanoplatelet and the interface between nanoplatelets in a clay particle. In case of organoclay, it is also due to the nanoscale viscous behavior of the organic component. The viscoelastic properties are essentially independent of the frequency.

The viscous character of both unmodified clay and organoclay is weaker than that of carbon black or exfoliated graphite, but the elastic character of both unmodified clay and organoclay is stronger than that of carbon black or exfoliated graphite. As a consequence, the clays are superior to carbon black but inferior to exfoliated graphite in terms of the loss modulus.

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