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Interface-derived extraordinary viscous behavior of exfoliated graphite

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ABSTRACT

Exfoliated graphite is obtained by the rapid heating of acid-intercalated graphite flakes. It exhibits a cellular microstructure, with about 60 graphite layers in the cell wall. The recently reported extraordinarily strong viscous behavior of the exfoliated graphite and its cement-matrix composite has been explained in this paper in terms of an interface-derived viscous mechanism, which is in contrast to the well-known bulk viscous deformation mechanism that rubber exhibits. The interfacial mechanism is associated with the dynamic sliding at low amplitudes between the graphite layers in the cell wall of exfoliated graphite during dynamic loading in the elastic regime. The ease of sliding is enabled by the loosening of the interlayer interface that has occurred during exfoliation, in which the cell wall extends greatly like a balloon due to extensive sliding between the graphite layers in the cell wall. The viscous behavior is consistent with the well-known resiliency of flexible graphite, which is a sheet made by greatly compressing exfoliated graphite without a binder. In the cement-matrix composite, the exfoliated graphite is sandwiched with sufficient tightness by the cement matrix in the microstructure of the composite, thereby providing constrained-layer damping in the microscale.

1. Introduction

Viscous behavior that is extraordinarily strong among solids has been recently reported in exfoliated graphite in the small-strain elastic regime [1]. Furthermore, the incorporation of the exfoliated graphite in a cement-matrix composite has been reported to provide a material that exhibits an exceptionally high level of vibration damping [2], provided that the units of exfoliated graphite are sandwiched sufficiently tightly by the cement matrix [3]. Although the behavior has been reported, the scientific origin of the behavior has not been enunciated. This paper is directed at elucidating the scientific origin of the above mentioned phenomena, which have opened up applications for exfoliated graphite in vibration damping, vibration isolation and possibly sound absorption as well.

2. Exfoliated graphite

Exfoliated graphite exhibits a cellular microstructure [4–7] (Fig. 1), which results from the exfoliation of intercalated graphite [4,8,9]. Intercalated graphite is graphite which has been reacted with a foreign species, called the intercalate. The reaction is known as intercalation. The reaction causes the intercalate to enter the space, typically as a monolayer, between the atomic layers in the graphite, thereby forming a layered compound known as an intercalation compound. Due to their crystallinity and low cost, natural graphite flakes

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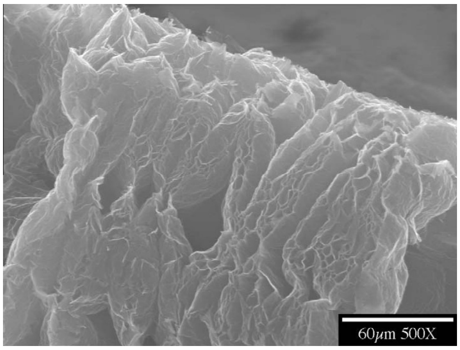

Fig. 1 – SEM microscope photograph of exfoliated graphite used in the discovery of interface-derived extraordinary viscous behavior of exfoliated graphite [1,2]. It shows the well-known cellular microstructure. A worm is a piece of exfoliated graphite obtained by the exfoliation of a single graphite flake. Only a part of a worm is shown. The exfoliation was conducted by rapid heating of acid-intercalated graphite flakes.

are most commonly used to prepare exfoliated graphite. There is typically a charge transfer that occurs between the intercalate and the graphite. Most commonly, the intercalate accepts electrons from the graphite, as in the case of sulfuric acid as the intercalate [10]. In fact, sulfuric and nitric acids are the most commonly used intercalates for preparing exfoliated graphite, due to the large degree of irreversible expansion that stems from the gaseous species generated by the decomposition of the acid molecules during exfoliation [11].

The intercalate is typically present in the form of islands, in accordance with the Daumas-Herold model [12], in which the graphite layers bend, thereby resulting in domains, each of which is an intercalate island (Fig. 2). This model has been confirmed by electron microscopy [13,14]. It means that, for stages greater than 1, the intercalate layer does not necessarily extend all the way from one end of the graphite crystal to the other. The in-plane length of an island depends on the intercalate species and the intercalate activity during intercalation. For the same intercalate species, the lower is the intercalate activity (as obtained by increasing the intercalation temperature or decreasing the intercalate concentration in the reaction vessel during intercalation), the larger are the intercalate islands [15].

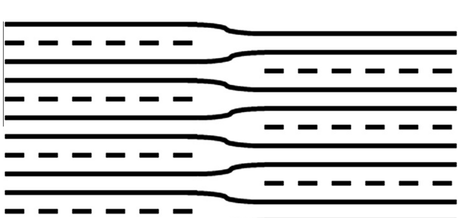

Fig. 2 – Daumas-Herold Model [12] as illustrated for a stage-2 graphite intercalation compound. The stage refers to the number of graphite layers between nearest intercalate layers in the superlattice along the c-axis. The graphite layers are indicated by solid lines; the intercalate layers are indicated by dotted lines.

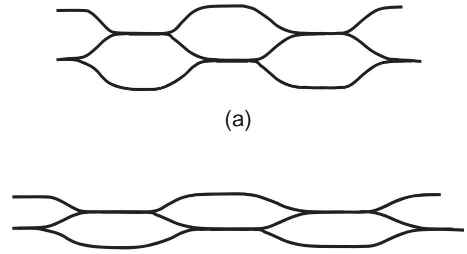

Fig. 3 – Schematic illustration (not to scale) of the cellular structure of exfoliated graphite. The cell wall, which is a nanoscale multilayer that consists of about 60 graphite layers, can stretch greatly due to the sliding of the graphite layers with respect to one another. The solid line denotes the cell wall. The individual layers in the multilayer are not shown. (a) Before loading. (b) During loading.

During the heating of intercalated graphite, each intercalate island expands tremendously along the c-axis of the graphite. The larger are the intercalate islands, the greater is the degree of expansion [15]. Thus, for a high degree of exfoliation, the lateral size of the graphite flakes must be large enough to accommodate at least several islands in the plane of the flake. The expansion can be up to a few hundred times, depending on the choice of intercalate and the size of the intercalate islands [10,15–17]. The driving force of the expansion is the vaporization or decomposition of the intercalate upon heating [10,15]. Thermal decomposition that causes an intercalate molecule to decompose into multiple molecules helps enhance the gas evolution during exfoliation, thereby increasing the driving force. An exfoliated graphite flake is known as a worm, due to its shape.

In order for the large expansion to be able to occur during exfoliation, the graphite layers that make up the wall of an intercalate island must be able to stretch greatly – akin to the stretching of the wall of a balloon as it expands (Fig. 3). The stretching of the wall enables an intercalate island to expand like a balloon. A wall consists of multiple layers of graphite, such that each layer does not necessarily extend all the way across the length of an island and different layers may overlap one another to various degrees (Fig. 4). The structure of the wall has not been adequately addressed. There are about 60 graphite layers (on the average) in the cell wall of the exfoliated graphite used in the discovery of the extraordinary viscous behavior of exfoliated graphite [1]. The stretching of a wall is made possible by the sliding of the graphite layers with respect to one another within the wall. This sliding requires the overcoming of the van der Waals' forces between the graphite layers. The vapor-related driving force for exfoliation is adequate for overcoming these forces, thereby allowing exfoliation to occur. If the heating rate during exfoliation is high enough and the vapor evolution during exfoliation is significant enough, the expansion is substantially irreversible, so that the expanded state remains upon subsequent cooling. This is the case when acids are used as the intercalates [10,11,15], since an acid molecule decomposes upon heating. The term "exfoliated graphite" typically refers to the irreversibly expanded form.