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Original article

Morphological studies of menthol as a temporary consolidant for urgent conservation in archaeological field

Xiangna Han[a], Xiao Huang[b], Bingjian Zhang[a,*]

[a] Department of Chemistry, Zhejiang University, Hangzhou 310027, China
[b] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

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ABSTRACT

Menthol, a natural organic compound from plant extract, due to its unique aromatic smell and cooling effect, has wide applications in food, cosmetic and pharmaceutical industries. By taking advantage of its volatile ability at room temperature, this compound has the potential to be used as a temporary consolidant in the field of art conservation. In order to evaluate the effectiveness of menthol as a temporary consolidant for urgent conservation in archaeological field, in this paper, laboratory investigations, such as menthol's penetration, consolidation efficacy and morphological changes during sublimation, are carried out on two kinds of organic and inorganic materials respectively, representing four types of fragile archaeological artifacts. In particular, the morphological changes of consolidated substrates during menthol sublimation process are systematically observed. The result shows that menthol's consolidation efficacy is strongly affected by the inherent nature of substrate to be treated. Menthol whisker growth on these substrates surfaces is observed, and a weak intermolecular hydrogen bond is formed between menthol and substrate, which is confirmed by the shift of hydroxyl group stretching bond in the IR spectrum.

1. Introduction

Menthol is a cyclic monoterpene alcohol naturally occurring from corn mint, peppermint or other mint oils. Because of its fairly unique aromatic smell and cooling characteristics, menthol, as a cooling and/or flavor enhancing additive, is widely applied in a variety of consumer products, including pharmaceuticals, cosmetics and tobacco, candies, chewing gum, liqueurs, toothpastes, shampoos and soaps [1–3]. In 2013, it is estimated that more than 20,000 tons of menthol are consumed annually. Commercial menthol is needle-like crystalline substance, clear or white in color. Menthol tends to sublime at room temperature due to its low vapor pressure. This high volatility is usually considered to be a nuisance for menthol's application and its shelf life [4]. However, by taking advantage of its volatile property, menthol may extend its widespread use into a new application field, namely urgent conservation in archaeological field.

With the ongoing work of archaeological excavation, numerous buried objects are exposed to an abruptly changed environment. There is no doubt that it is very important to protect these historical remains immediately; especially some extreme sensitive or/and fragile artifacts are even more badly in need of urgent conservation, so as to rescue the artifacts from any damage risk [5]. In general, the most valuable urgent conservation measurement is pre-consolidating a fragile artifact temporarily, so that it can be moved safely from excavation field to a more condition-controlled workshop. Volatile binders, which will sublimate at room temperature, are preferred by art conservators because they can be regarded as a perfectly reversible adhesive and removed without any additional treatment. Currently, cyclododecane is the most widely used temporary consolidant and is becoming more and more popular [6]. The reports about its use and sublimation kinetics are still increasing rapidly today [7–11].

But, the toxicological data of cyclododecane is a serious concern, and respiratory symptom has been reported immediately after using cyclododecane in unfavorable conditions [12]. Considering menthol has a well-established safety profile from its long-term and numerous usages [13,14], our main interest in recent years has been to explore menthol as a temporary consolidant for archaeological excavation urgent conservation [15,16]. Though some exciting results have been obtained from our previous research, there are still many problems of menthol as temporary consolidant needed to solve. For instance, basically, menthol is applied as a solid coating on archaeological objects surface to

* Corresponding author. Tel.: +86 13 906 518 199.
E-mail address: zhangbiji@zju.edu.cn (B. Zhang).

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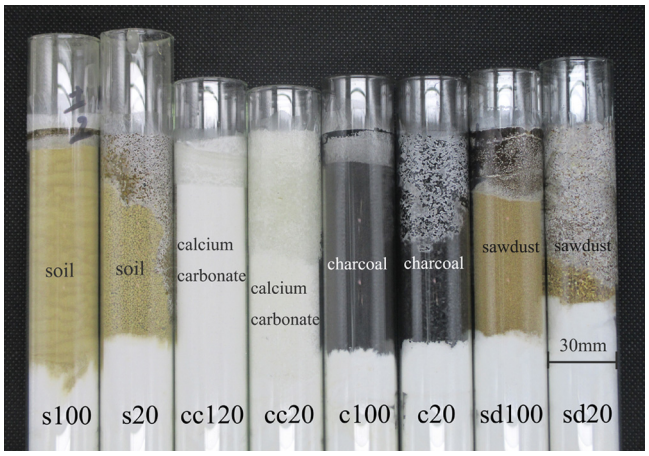

Fig. 1. Picture of substrates after menthol penetration.

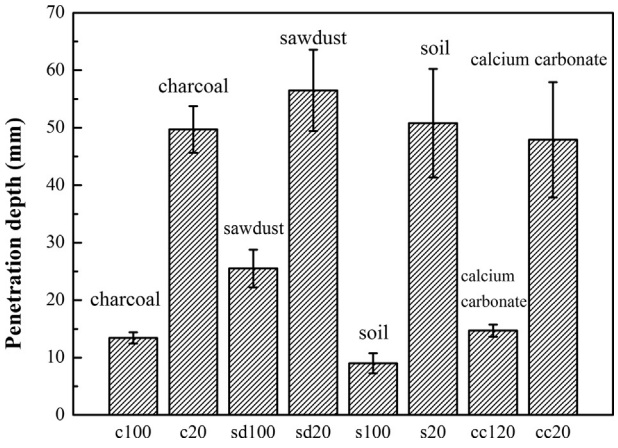

Fig. 2. Penetration depths of menthol into various substrates.

provide protection action. The coating is usually formed by cooling molten menthol. Whereas, as termed "volatile binder", sublimation of menthol coating, especially morphology changes of menthol solid coating formed on surface of applied object throughout the whole process of sublimation, has not been carefully studied. Whether menthol crystal formed from recrystallization during the sublimation–condensation process has any threat to the fragile archaeological object is unknown.

As a results of its widely applications, there are numerous researches about menthol, but very few of them concern the sublimation of menthol. In our previous work, it has been found that whisker-like objects emerge during sublimation in some cases. In the literature, the growth of menthol whiskers has also been reported [17–19]. Morphological changes are usually accompanied with stress generation and volume changes, which are potential threats to those fragile archaeological artifacts. So, morphological changes of menthol during sublimation need to be taken serious accounts in art conservation.

Real archaeological artifacts are very precious. It is almost impossible to perform experimental studies on real artifacts. Normally artificially simulated samples are used instead. Meanwhile, the material used in real artifacts are quite complex. In order to better understand the correlations among the experimental data, four commercial materials charcoal, sawdust, soil and calcium carbonate, with very simple and clear composition, are selected as simulated samples instead of real archeological artifacts.

The morphological changes of menthol on these consolidated substrates during sublimation are systematically examined on four artificial substrates by three-dimensional microscopy, XRD and IR. The penetration and consolidation efficacy of menthol on these substrates are also examined.

2. Materials and methods

2.1. Materials

L-menthol (98%, melting point 42 °C) was purchased from Aladdin Co. and was used as received. Four materials were selected as representative archaeological substrates to be applied with menthol:

- commercial available apple tree charcoal, simulating the weathered archaeological carbon remains;
- oak sawdust, simulating piecemeal of archaeological wood object;
- soil from ancient Liangzhu City Wall relics (3000 B.C.) in Hangzhou, China;
- calcium carbonate (99%, AR, Aladdin), simulating powdery products of limestone.

Apple tree charcoal and Liangzhu soil were smashed beforehand. Apple tree charcoal, oak sawdust and Liangzhu soil were sieved with 20, 30 and 100 mesh number griddle. Materials were collected between 20–30 and under 100 mesh sieves and named

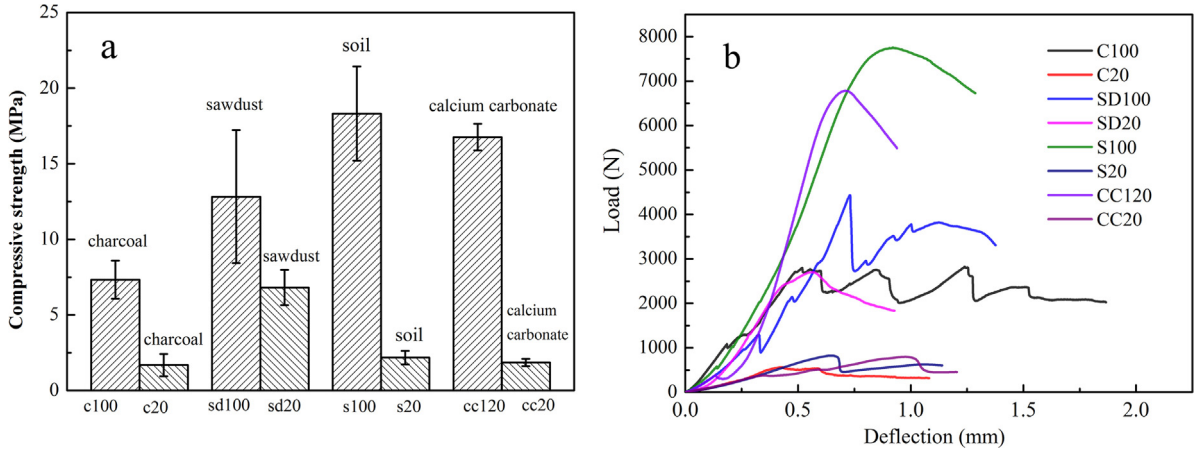

Fig. 3. Compressive strength (a) and load-deflection curves (b) of menthol consolidated substrates.