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# Improvement of ablation resistance of phenolic composites reinforced with low concentrations of carbon nanotubes

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ABSTRACT

Carbon nanotubes (CNTs) were incorporated into a phenolic resin in order to improve its ablation resistance. The CNT-reinforced phenol composites showed enhanced ablation resistance compared to neat phenolic resin, even with a low concentration of CNTs (0.1 wt%). The proposed mechanism of the CNTs for the CNT/Phenolic resin composite's enhanced ablation resistance is that the CNTs functioning as crystal growth nuclei for graphitization of carbonized phenolic resin. The graphitic structures formed around the CNTs improved the composite's resistance to high temperature ablation. X-ray diffraction (XRD) and Raman spectroscopy, scanning electron microscopy (SEM), and Transmission electron microscopy (TEM) were employed to identify the proposed CNT reinforcement mechanism for the enhanced ablative resistance of the CNT/Phenolic resin composites.



## 1. Introduction

Ablation is a heat and mass transfer process in which the material at the surface is consumed due to energy transfer from high temperature source. When a polymer is heated, its surface temperature increases, subsequently vaporizing the material at its surface. During the initial ablation stage, water, solvent, and low molecular weight polymers are vaporized, reducing the temperature increase of the surface by more than 50% [1]. As the temperature is further increased, the thermal agitation of the polymer chains becomes severe, breaking chemical bonds via side chain decomposition. When this phenomenon occurs, if the side chain's decomposition rate is higher than that of the polymer backbone, the majority of the polymer backbones form a char layer, which becomes thicker as the ablation process progresses. The char layer acts as thermal barrier due to its excellent mechanical and thermal resistance properties, and the side facing the inner polymer surface is cooled by the flow of released gas as the polymer decomposes [1].

The main objective of this study was to improve the ablation resistance of a matrix material used in fiber-reinforced composites. A phenolic resin was used as the matrix material in this study, as phenolic resins are known for their thermal stability even after decomposition since they easily form char layers. Hence, phenol resins are widely used as thermal protection materials.

Carbon nanotubes (CNTs) were used as the reinforcement material in this study. Numerous works have examined the mechanical and thermal property enhancement of polymeric composites reinforced with CNTs [2]. Several of these studies reported that the CNTs increase the composite's thermal conductivity by forming heat transfer conduits [3–5]. One study reported an increased composite ablation rate, i.e., decreased ablative resistance, resulting from increased thermal conductivity after CNTs were incorporated [5]. However, it is unlikely that low concentrations ($\leq$1 wt%) of CNTs would dramatically increase the composite's ablation resistance from enhanced thermal conductivity, as low CNT concentrations do not usually increase thermal conductivity drastically [3,4]. In addition, an increase in thermal conductivity may promote a faster decomposition of the resin material [1,6]. Another study reported a 23% increase in ablation resistance by adding only 0.05 wt% CNTs; however, there was no proposed mechanism for the enhanced ablative resistance of samples with CNTs [7].

Another study reported on the enhanced flame retardant properties of CNT/poly(methyl methacrylate) (PMMA) composites. The enhancement was attributed to the formation of nanoparticle networks that reduced crack formation in the PMMA matrix at high temperatures. In their study, 1.0 wt% multi-walled carbon nanotube (MWNT) composites displayed enhanced flame retardant

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properties over the 0.5 wt% MWNT samples [8]. Conversely, in our study, the CNT/phenolic resin (PR) composites with only 0.1 wt% MWNT showed over a 30% increase in their ablation resistance compared to the neat phenolic resin.

The major mechanism for increased ablation resistance of the phenolic composites with low CNT concentrations was hypothesized to be the result of increased graphitization due to the presence of CNTs acting as graphitization nuclei. It is apparent that crystallization (or more specifically, graphitization) of a polymer matrix under exposure to a high heat flux, such as heating in a furnace, should enhance the thermal resistance of the composites [9–11]. One study reported an increased char yield with possible graphitization in the vicinity of the graphite oxide (GO) particles in 0.5 wt% GO/polymer composites, observed using thermogravimetric analysis (TGA) and X-ray diffraction (XRD) measurements [12]. In a different study, CNTs were shown to promote graphitization of electrospun carbon nanofibers (CNFs) containing 1.2 wt% CNTs through an 800 °C oxidative stabilization process [13].

The ablation resistance of phenolic composites with low CNT concentrations was investigated in this study. In order to assess the ablative resistance of the samples, an ablation test setup was built and the ablation rate was measured for the fabricated CNT/PR composite samples. The increase in crystallinity (or degree of graphitization) of the polymer matrix by CNTs' acting as nucleating agents was confirmed by XRD and Raman measurements, and SEM and TEM observation of the nanostructure after the ablation test.

## 2. Materials and experimental

### 2.1. Materials

A resol-type phenolic resin (Durite SC-1008, Momentive Specialty Chemicals Inc., USA) was selected as the matrix material in this study. The resin contains 20 wt% isopropyl alcohol (IPA) to reduce its viscosity. For the reinforcements, MWNTs (CM-150, Hanwha Nanotech Co., Ltd., Korea) were used. The diameter of the MWNTs ranged from 10 nm to 30 nm as shown in Fig. 1.

### 2.2. Sample processing

The CNTs were added into the phenolic resin by a solution mixing method with IPA as the solvent since it was also incorporated into the phenolic resin.

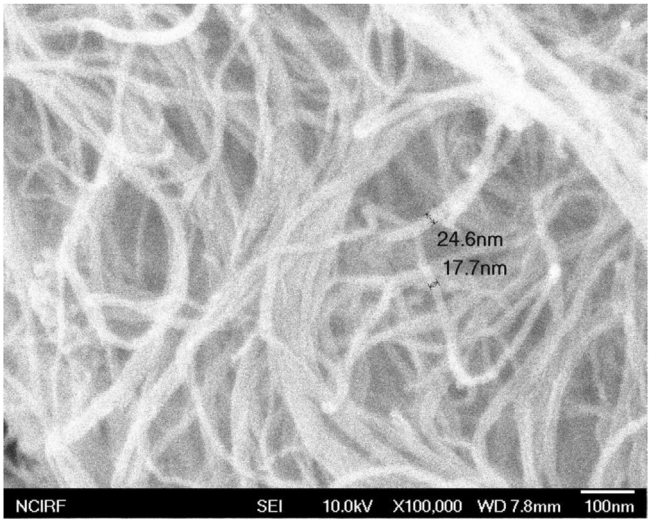


**Fig. 1.** SEM image of the MWNTs used in this study.

For dispersion of the CNTs into the phenolic resin, the IPA and phenolic resin were first mixed in a 1:1 weight ratio and CNTs were added to the solution. The CNTs were then dispersed using a conical ultrasonicator (CV 505 power supply and CV 33 converter from Sonics & Materials, Inc., USA) for 2 h. The added IPA was then evaporated using a stirrer and hot plate at 50 °C until it was fully removed from the mixture. Finally, the mixture was degassed in a vacuum oven at 50 °C for 30 min.

A mold was manufactured to fabricate samples for the ablation tests. Each mold had dimensions of 50 mm × 50 mm × 7 mm (length × width × thickness). The CNT/PR mixture was poured into each open mold, followed by placing the mold in a vacuum oven for an additional degassing process (50 °C, 30 min).

The samples were cured at 75 °C for 12 h and at 85 °C for 24 h in a convection oven, followed by a postcure step at 120 °C for 2 h. The CNT concentrations in the samples were varied at 0.05, 0.1, and 0.3 wt%, respectively.

### 2.3. Measurements

Ablation properties of materials in re-entry condition can be investigated by ballistic flight experiment, however this method can hardly be used due to considerable cost. Instead, ground-based ablation tests are more often used. Some researchers used a plasma torch test [14,15]. This method uses an argon/nitrogen mixture and partially simulate the re-entry environment, but has a limitation in varying parameters. Oxy-acetylene torch test is the most common method with reasonable cost and provides primary evaluation for the ablative properties of materials [16–21]. This device is able to produce both high temperature flame (up to 3000 °C) and high heat flux. The essential device consists of gas vessels, pressure gauges, flux meters, and the torch. The oxy-acetylene torch flame is classified as carburizing flame, oxidizing flame, or neutral flame depending on the ratio of oxygen to acetylene. Some other studies used high velocity oxygen fuel (HVOF) torch to simulate Solid Rocket Motor (SRM): an HVOF torch is basically an oxy-kerosene burner in which alumina particles injected into the plume to simulate the particle-laden of SRM exhaust [22,23]. Some authors investigated the ablation rate of the materials by exposure to combustion gases in a mock solid rocket motor firing rig [24].

The electrolytic oxy-hydrogen (EOH) gas torch was used for ablation tests in this study. The EOH gas is a stoichiometric mixture of hydrogen and oxygen produced by the electrolysis of water. The adiabatic flame temperature of oxyhydrogen gas can reach over 3000 °C. And the flame of the oxy-hydrogen jet occupies very narrow volume compared with any other hydro-carbon gases because the flame speed of the hydrogen gas is much greater. In short, the oxy-hydrogen flame can induce high temperature to the sample within the concentrated region and can effectively decompose the specific spot with less heat conduction to the adjacent regions of the sample.

The EOH gas is produced continuously by using a water electrolyzer (Model BB-2000, Best Korea Co., Ltd.). The gas generator is designed to maintain the gas in the range of 0.8–1.0 bar automatically. The gas flow is controlled by a mass flow controller (MFC) (TSC-230, MKPrecision Co., Ltd.) located after the air filter. It maintains the flow rate of the EOH gas to 1 L/min. A tube burner with nozzle diameter 0.7 mm was used for burning the EOH fuel.

The ablation test apparatus was setup as shown in Fig. 2. $H_2$ and $O_2$ gases at a 2:1 weight ratio were generated by electrolysis using a Brown gas generator (BK-6000, BEST KOREA Co., Ltd., Korea) and fed into the torch at a constant flow rate of 1000 $mm^3$/min. The flame's temperature was measured using a C-type thermocouple. The temperature is dependent on the distance from the torch's tip