SPALLATION OCCURRENCE CONTROL BY MIXING PHTHALATE ESTERS IN POLYAMIDE MATERIAL FOR POLYMER ABLATION ASSISTED CIRCUIT BREAKERS

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ABSTRACT

The present paper describes spallation occurrence control from polyamide material by using phthalate esters. The polyamide material is widely used in polymer-ablation assisted type of low voltage circuit breakers. Our previous work had found the spallation occurrence from polyamide materials with water absorption. The spallation phenomena causes micro-sized polymer particles ejections from the polyamide surface by contacting arc plasmas or thermal plasmas, which could be useful to quench the arc plasma. The phthalate esters were confirmed to enhance the spallation phenomena without desorption although the water is inevitably desorbed from the polyamide even at room temperature.

1. INTRODUCTION

Low-voltage or high-voltage circuit breakers often contain polymer materials inside them for electrical insulation or gas flow nozzle. In a current interruption process, an arc plasma is established between the electrodes in the circuit breaker. The arc plasma can contact the polymer material, which inevitably involves polymer ablation. Polymer ablation can generate strong gas flow, and change thermodynamic and transport properties of the arc, increasing the arc interruption ability. Actually, some polymer-ablation assisted types of low-voltage circuit breakers have been developed [1].

Previously, we have fundamentally studied interaction between the thermal plasma and the polymer material using the Ar inductively coupled thermal plasma (ICTP) irradiation technique [2]-[4]. Those results indicated that not only ablated vapor but also "spallation particles" were ejected from polyamide materials surface [3, 4]. Such spallation particles could enter the arc core rather than the ablated vapor. The particles would be ablated

there, which could quench the arc plasma more effectively. Furthermore, we have found that occurrence of spallation can be enhanced by water absorption in the polyamide materials [5]. However, water in polyamide is desorbed from the polyamide even at room temperature, and thus water absorption amount depends on the surrounding environment.

In this paper, we introduce that phthalate ester mixing in polyamide-6 (PA6) can promote spallation phenomena. Four kinds of phthalate esters were selected to be mixed in PA6 instead of water absorption. It was found that PA6 with a phthalate ester effectively ejects spallation particles by contacting thermal plasma. Furthermore, the phthalate ester was confirmed to be stable in PA6 at room temperature.

2. SPALLATION FROM PA6 WITH WATER ABSORPTION

2.1. Spallation phenomenon

In this section, spallation phenomenon is briefly described. Figure 1 shows a high-speed video camera picture during inductively coupled thermal plasma (ICTP) irradiation to a PA6 specimen with water absorption. The ICTP is used instead of arc plasmas for studying interaction between thermal plasmas/arc plasmas and polymer material. This is because the ICTP has good controllability and reproducibility compared to the arcs. In Fig. 1, an Ar ICTP is irradiated to the PA6 specimen from the top side. As seen, the PA6 specimen is ablated to eject ablated vapor with white-bluish light. This white-bluish light is mainly attributed to strong spectral intensity from C_2 Swan system at wavelengths around 450–570 nm according to our previous work [5]. This figure also presents that not only ablated vapor but also spallation particles are ejected from the surface of PA6. The estimated diameters of the spallation particles were in the
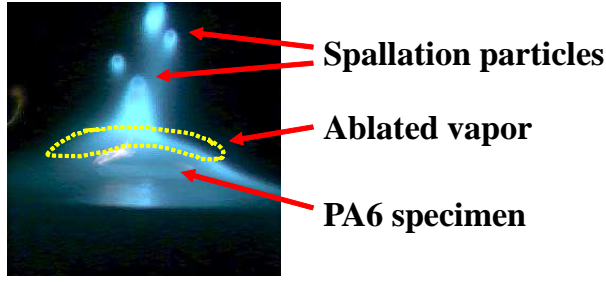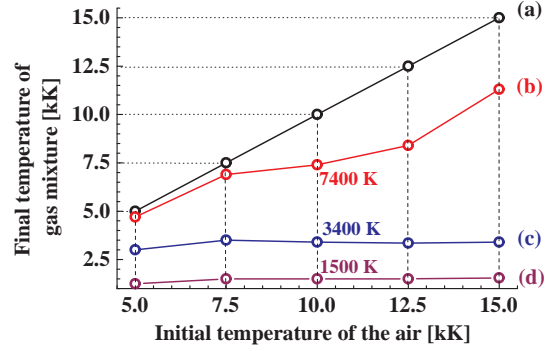
Fig. 1. Spallation from PA6.

Fig. 2. Cooling efficiency by complete evaporation of spallation PA6 particles with a radius of 100 μm in high-temperature air; (a) with no particle, (b) with 1 particle, (c) with 10 particles, (d) with 50 particles.

order of 100-200 μm [4]. These spallation particles jump up to more than 20 mm above from the PA6 specimen surface. This is attributed to the fact that the absorbed water in the PA6 specimen may be first evaporated to increase internal pressure, which could break up a part of the specimen.

We are expecting application of such a spallation phenomenon to circuit breakers. Spallation particles can penetrate into the arc core more deeply than the ablated vapor to quench the arc plasma effectively.

2.2. Arc cooling effects by spallation particles

Here, we estimate the arc cooling effects by spallation particles. Suppose a high-temperature air cylindrical space with a volume of 6 mmϕ × 50 mm at a certain initial temperature T_{air} at atmospheric pressure. It is assumed that in this space, PA6 sphere particles with a radius of 100 μm at 300 K would be injected and completely evaporated at fixed atmospheric pressure. Evaporation of spallation particles would cause mixing of the ablated vapor to the air and decrease the air temperature to the final temperature T_f with a change in volume. The final temperature T_f in this case was obtained by solving the following energy conservation equation:

$$m_{air}h_{air}(T_{air}) = \quad h_{PA6-air}(T_f) \times (m_{air} + m_{PA6})$$
$$+Q_e \times m_{PA6}, \quad (1)$$

where m_{air} is the mass of the high-temperature air, m_{PA6} is the mass of spallation particles, $h_{air}(T_{air})$ is the enthalpy of the air at the initial temperature T_{air}, and $h_{PA6-air}(T_f)$ is the enthalpy of the gas mixture of PA6-air at a final temperature T_f. Q_e is the latent heat of PA6 from 300 K to the thermal decomposition temperature at atmospheric pressure. The enthalpy were calculated by

$$h(T) = \frac{1}{\rho}\sum_i\left(\frac{5}{2}kT + kT^2\frac{\partial}{\partial T}\left(\ln Z_i^{int}\right) + U_i\right)n_i (2)$$

where k is Boltzmann's constant, Z_i^{int} is partition function, U_i is standard enthalpy of formation

and n_i is the number density of molecules or atoms in air-PA6 vapor mixture. For this calculation, the equilibrium composition of air-PA6 vapor mixture was first calculated by minimization of Gibb's free energy of the system at a given admixture ratio of PA6 vapor to the air. Use of this calculated equilibrium composition of air-PA6 mixture allows us to compute the enthalpy of the air-PA6 vapor mixture [6]. The final temperature T_f was obtained for each of the initial air arc temperatures T_{air} of 5000, 7500, 10000, 12500 and 15000 K.

Figure 2 depicts the relation between T_{air} and T_f. The number of PA6 particles is taken as a parameter. For T_{air}=10000 K, the temperature of air-PA6 vapor mixture drops to T_f=7400 K by only 1 spallation particle injection if the particle is completely ablated. Injecting 10 particles into the air at T_{air}=10000 K decreases the air temperature to reach T_f=3400 K. This means that spallation particles have an extremely high cooling ability for the high-temperature air if they are rapidly and completely evaporated.

3. MIXING OF PHTHALATE ESTER TO PA6 TO PROMOTE SPALLATION

3.1. Phthalate esters

Our previous work showed that the occurrence of spallation can be enhanced by water absorption to PA6 [5]. However, water absorption amount in PA6 depends on the surrounding environment with a temperature and a humidity. At room temperature, the absorbed water in PA6 can be vapor-

ized from the specimen. It is thus necessary to find another additional material instead of water to enhance spallation phenomena for their practical applications. The additional material should have the boiling temperature between the pyrolysis temperature of PA6 (717.6 K) and the boiling temperature of water (373 K) because it should be ablated more easily than PA6 but is should hardly be vaporized at room temperature. Moreover, the additional material should have a polarity to make hydrogen-bonds with amide groups (-CONH-) in PA6.

We eventually found that the phthalate esters are candidates for this use. Generally, some kinds of phthalate esters are widely used as plasticizer for polyvinyl chloride materials. The phthalate esters have carbonyl groups (-CO-) with polarity. We chose four kinds of phthalate esters as indicated in Tab. I: Dimethyl phthalate (DMP), Dibutyl phthalate (DBP), Dioctyl phthalate (DOP) and Di-isononyl phthalate (DIP). Using these phthalate esters, phthalate ester-kneaded PA6 specimens were prepared at a fraction of phthalate ester of 20 wt%.

3.2. Desorption properties of phthalate esters in PA6

Before ICTP irradiation test, the desorption properties of the phthalate esters in PA6 specimen were investigated. The specimens with the four phthalate esters were kept in a desiccator with silica gel as a desiccant for 300 hours at room temperature. At the specified time, the weight of the specimens were measured. Figure 3 indicates the temporal variations of the weight fraction of the phthalate esters in the specimens. In this figure, the measured water adsorption property were also plotted for comparison. All of the phthalate esters were found to be hardly evaporated to decrease their masses for 300 hours. This means that phthalate esters is extremely stable in PA6 specimens at room temperature compared to water.

3.3. Ar thermal plasma irradiation test
3.3.1. Experimental setup

Figure 4 depicts the experimental setup for the experiment. The ICTP torch is 345 mm long, and 70 mmϕ in inner diameter. It is composed of two coaxial water-cooled quartz tubes. From the top of the torch, Ar gas is supplied along the inner wall of the inner quartz tube as a sheath gas at a flow
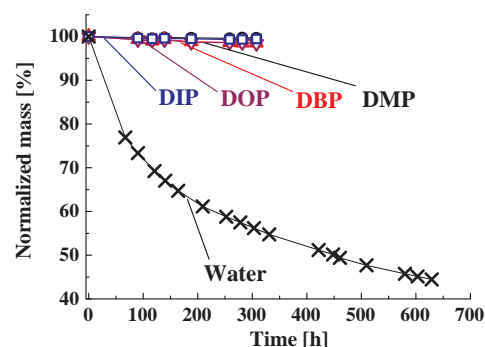

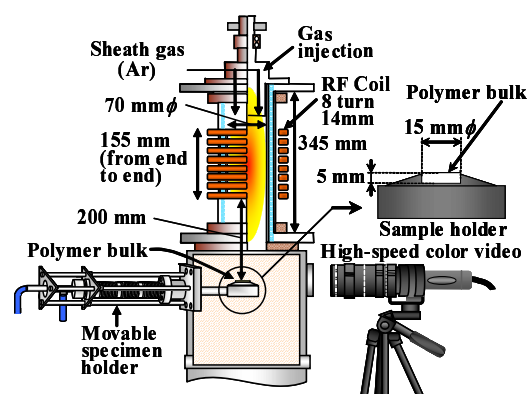Fig. 3. Desorption of phthalate esters mixed in PA6.

Fig. 4. RF plasma torch and observation system for polymer ablation test.

rate of 30 L/min. The pressure inside the chamber was fixed at atmospheric pressure. Around the torch, an eight-turn induction coil is located to generate a thermal plasma inside the torch. The input power to the plasma was set to 8.5 kW. A color high-speed video camera was used to observe polymer ablated vapor and spallation particles near the polymer surface from the observation window. The observation frame rate was 1000 fps.

3.3.2. Spallation occurrence from phthalate ester mixed PA6

Figures 5(a) − 5(d) show the accumulated images of 100 pictures captured by the high speed video camera in 0.1 s. For a PA6 specimen with DMP, no spallation particle but only ablated vapor was observed to be ejected. On the other hand, specimens with DBP, DOP and DIP eject several spallation particles by ICTP irradiation. In particular a PA6 specimen with DBP ejects much more spallation particles.

Table I. Phthalate esters chosen for test.

Abbreviations	DMP	DBP	DOP	DIP
Molecular formula	$C_{10}H_{10}O_4$	$C_{16}H_{22}O_4$	$C_{24}H_{38}O_4$	$C_{26}H_{42}O_4$
Boiling temperature	555 K	613 K	657 K	676 K
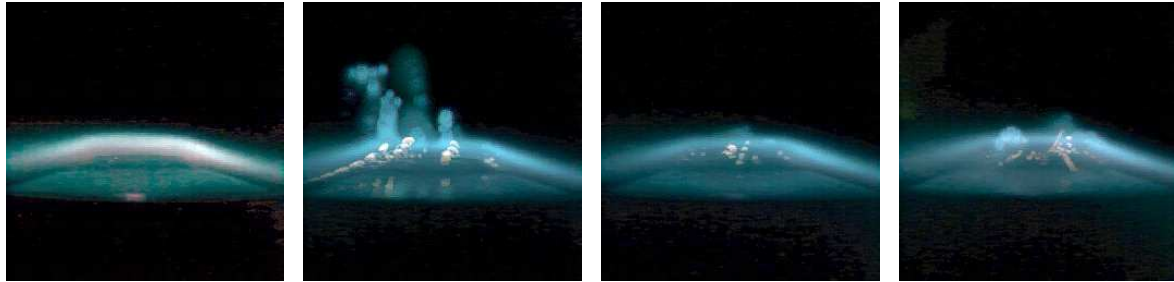
(a) 20 wt% DMP   (b) 20 wt% DBP   (c) 20 wt% DOP   (d) 20 wt% DIP

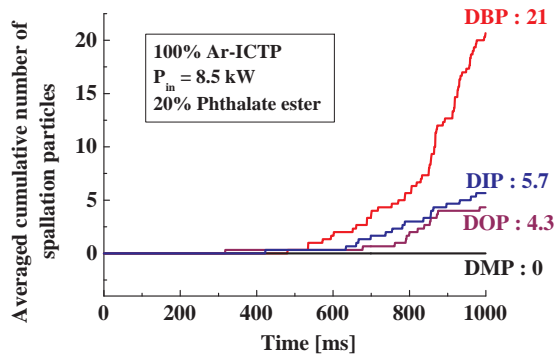Fig. 5. Accumulated 100 images of phthalate esters mixed PA6 irradiated by Ar plasma.

Fig. 6. Cumulative number of spallation particles from phthalate ester mixed PA6 specimens.

Spallation particles jumping up to 5 mm above from the surface of specimens were counted from the high-speed video images. Figure 6 indicates the cumulative numbers of spallation particles ejected from specimens. These cumulative numbers in this figure are the averaged values from three tests under the same condition. The time on the horizontal axis indicates the time from ICTP irradiation initiation. As seen in this figure, the PA6 specimen with DOP, DIP or DBP ejects spallation particles from 500 ms after irradiation. Among them, the specimen with DBP has 21 spallation particles per second, which is much higher than those for the other specimens.

4. SUMMARY

In this paper, we found that PA6 specimens with phthalate esters could eject spallation particles by contacting thermal plasmas. In particular, the PA6 specimen with dibutyl phthalate (DBP) ejected much more particles. The spallation particles could be effective to decrease the temperature of air arcs according to our thermodynamic calculation. Furthermore, the phthalate esters were observed to be kept in the PA6 specimen at room temperature. These properties could be useful for application to low-voltage circuit breakers.

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