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The role of multi-wall carbon nanotubes in char strength of epoxy based intumescent fire retardant coating

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ABSTRACT

Fire resistance of coatings mostly depends on the formation of char. In this work Multi-wall carbon nanotubes (MWCNTs) were used to improve fire retardant and char properties of the intumescent coating. Different coating formulations were prepared and their heat shielding performance was tested at 950 °C according to ASTM E-119. Char expansion was studied using fire furnace test. Field emission scanning electron microscope was used for char morphology. By means of X-ray Diffraction and Fourier transform infrared spectroscopy the presence of carbon, borophosphate; boron oxide and sassolite in the char was identified. Thermogravimetric analysis results showed that 0.5 wt%MWCNTs enhanced the residual weight of char up to 29.35 wt%. X-ray photoelectron spectroscopy (XPS) confirmed that 0.5 wt% MWCNTs enhanced the carbon content up to 51.90 wt%, lowering oxygen content to approximately 25 wt% in the char that improved the fire resistance performance of the coating. Pyrolysis analysis confirmed that 0.5 wt% MWCNTs formulation released less gaseous products and reduced the decomposition of gaseous products. An accelerated weathering test ASTM D 6695-03 also revealed that 0.5 wt% of MWCNTs sustained its reliability up to 90 days in accelerated weathering chamber.

1. Introduction

Char is formed in the process of the thermal degradation of coating and occurs at the expense of several chemical reactions with the formation of volatiles. A typical char layer consists of an amorphous carbon resulted in the graphitization. The increasing level of graphitization influences the combustibility of the char layer and enhances its thermal stability. If the char layer contains inorganic components in addition to carbon [1,2], the fire resistance of coatings mostly depends on the formation of char initiated by the reactions between the acid, carbon and nitrogen sources. The interaction and decomposition of fire retardant additives and resin at 300–440 °C is the key step for the char formation [3–6]. The charring layer shields the surrounding substance and its protective property depends on the physical and chemical structure of the charring layer [7–10].

The charring structure can be categorized into uniform and asymmetric structures. Uniform structure bears the acceptable temperature gradients in the charring layer and shelter the viscous liquid underlying the matrix material. In the asymmetric structure, there are many pathways and gaps that contribute to evacuate gases and molten mass to enter the fire region due to this isolation effect of heat transfer to the substrate is low-grade [3]. The discovery of carbon nanotube in 1991 marked the emergence of a new class of high-performance polymer composites with nanotubes as the reinforcement material. Multi-wall-carbon-nano tubes (MWCNTs) combined with their low density makes them an excellent candidate for composite reinforcement. These composites are being used to enhance the strength, stiffness and electrical conductivity of structural materials [11–13].

Structurally, MWCNTs consist of multiple layers of graphite superimposed and rolled in the form of a tubular shape. MWCNTs are the most reasonable ones for commercialization as composite additive or coating elements. They offer less attractive properties, but they can be produced on a high scale at a relatively low price [14–18].

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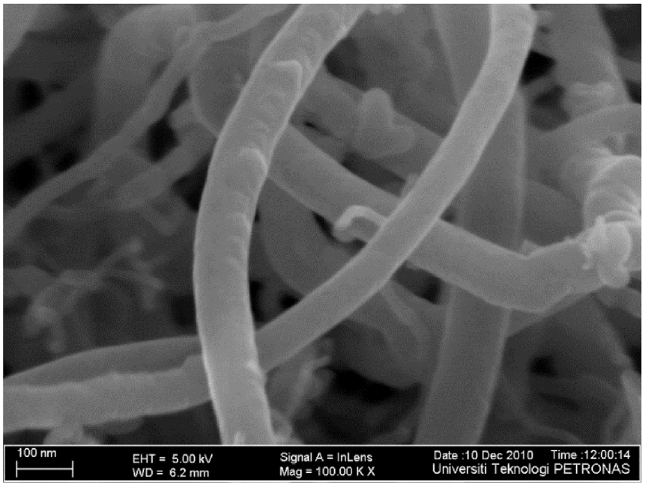

Fig. 1. FESEM image of MWCNTs used in the study.

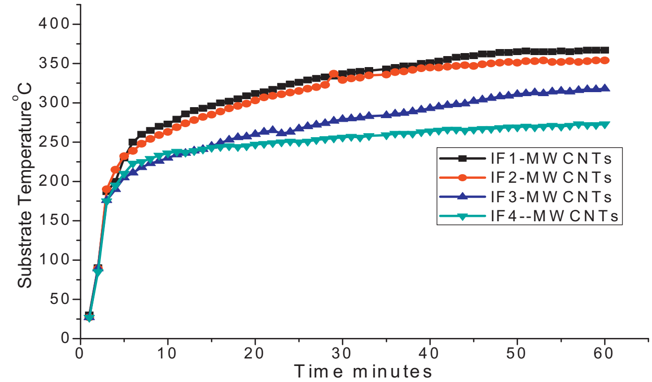

Fig. 2. Substrate temperature dependence versus time and of MWCNTs ICF.

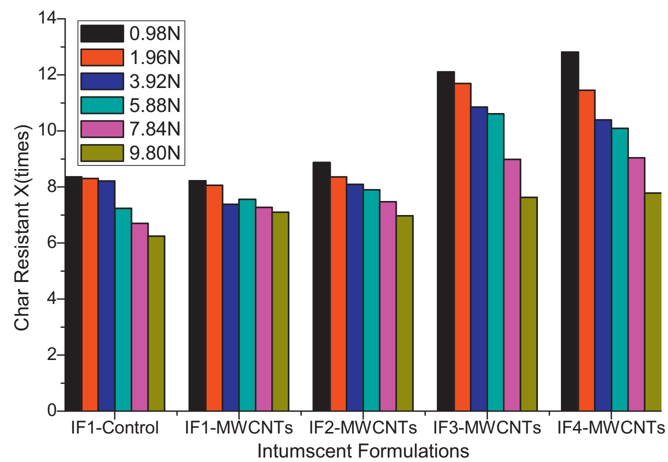

Fig. 3. Comparison of char resistance at different load on the char of MWCNTs ICFs.

Previous research has shown that nanoparticle fillers are highly attractive for the purpose of making a material more flame retardant because they can simultaneously improve both the physical and non-flammable properties of the polymer nanocomposite [19–21]. MWCNTs are promising flame retardant nano-additives due to their geometry. MWCNTs provide a good balance between the effect of thermal conductivity and shielding performance of external radiant flux and heat feedback from the flame. Their excellent mechanical properties combined with their nano-size and low bulk density of 2.6 g/cm^3 makes them attractive as reinforcing phase in a variety of polymers, ceramics and metallic matrices in designing high-performance composite materials [22]. It is also believed that CNTs can provide innovative materials for thermal control applications with their high thermal conductivity, and high aspect ratios as well as the mechanical strength [13]. It is expected that flame retardant coatings reinforced with CNTs will enhance the char density [14,20]. Florentina et al. [23] combined carbon nanotubes with ATH (alumina trihydrate), DECA (decabromodiphenyl oxide), antimony oxide (Sb_2O_3) and resorcinol diphosphate (RDP) and concluded that there is an interaction between ATH and CNT which provokes an increase of the char quantity and reduces accordingly the values of peak heat release. It is considered that CNTs have a potential advantage in combining with fire retardants in some polymers [24].

The use CNTs instead of other low-cost materials such as clay and carbon nanofibers may be considered as an interesting alternative. Published literature showed that nanoparticles improve the material non-flammability with relatively small concentration compared to other fillers. CNTs exhibit average diameters in the range of 38–69 nm whereas the length varies from 0.65 to 1.3 mm. Günter Beyer [25] stated that MWCNTs act as very efficient flame retardants at low filler contents in Ethylene-vinyl acetate (EVA). They developed and optimized formulation for flame retardant insulated wires based on filler which was blended with MWCNTs/organoclays. The results showed that the char was strengthened by the reinforcement of higher aspect ratio MWCNTs. This improved fire retardancy and enhanced the insulation of wire. Takashi Kashiwaghi [26] reported that the lowest heat release rate curve for Polypropylene-Multi-walled Carbon Nanotubes (PP/MWCNTs) was achieved with 1% by mass of MWCNT. The peak heat release rate was increased when the concentration of MWCNTs was used more than 1% and it is considered due to an increase in thermal conductivity of the nanocomposite. However, CNTs can be used as a carbon source in the intumescent coating and may provide protective layers of char on the material surface. The char of CNT reinforced reduces the diffusion of evaporated gaseous compounds and simultaneously the diffusion of oxygen from the closed environment toward the surface of the underlying substrate. The char provides an efficient thermal barrier to reduce the rate of heat transport to the substrate [27]. In turn, it slows down the melting of the coating and its evaporation in comparison to the unprotected one and the produced char are much denser. CNTs can enhance the char strength and reduces the thermal conductivity, electrostatic discharge features, electrical conductivity and thermal conductivity, all of these give significant impact on product performance and quality [28,29]. The scaffold of CNTs reduces

Table 1
The mass% of ingredients used to study the reinforcement of MWCNTs in ICFs .

Formulation No	EG	APP	MEL	Boric Acid	MWCNTs	Epoxy	Hardener
IF1-control	5.8	11.76	5.76	11.5	0.00	43.43	21.75
IF1-MWCNTs	5.8	11.76	5.76	11.5	0.2	43.32	21.66
IF2-MWCNTs	5.8	11.76	5.76	11.5	0.3	43.25	21.63
IF3-MWCNTs	5.8	11.76	5.76	11.5	0.4	43.18	21.60
IF4-MWCNTs	5.8	11.76	5.76	11.5	0.5	43.12	21.56