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Effects of titanium dioxide on the flammability and char formation of water-based coatings containing intumescent flame retardants

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ABSTRACT

Rutile-type TiO_2 (r-TiO_2) or anatase-type TiO_2 (a-TiO_2) in association with a conventional intumescent flame retardant system which contains ammonium polyphosphate/pentaerythritol/melamine (APP–PER–MEL) was introduced to silicone-acrylate coatings to improve the fire resistance. The effect of TiO_2 on the fire-resistance and thermal properties of APP–PER–MEL coating has been investigated by using big panel method and thermogravimetry (TG). The limit of fire-resistance of the sample containing 30 phr rutile-type TiO_2 (73 min) is much longer than that of the sample containing 30 phr anatase-type TiO_2 (34 min). The morphology and structure of charring layers were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The relationship between charring process and melt flow rate (MFR) of silicone-acrylate was also discussed. It is suggested that MFR value can significantly affect the formation of char, and a moderate silicone-acrylate MFR is required to form good quality char.

1. Introduction

The low-toxicity water-based coatings have become more and more popular due to its inherent environmental friendly characteristics [1].

There are generally two types of conventional halogen-free fire resistant coatings: alkali metal silicate or borate containing coatings and aluminum or magnesium containing coatings. The former coatings usually have low smoke production, good fire resistance and high strength of char when heated, but have poor toughness and water resistance. The latter ones have higher stability and lower generation of volatile and toxic gases. However, they have large solid contents and are apt to meet problems on compatibility between fillers and bonders.

Currently, intumescent flame retardants are widely used in the field of fire resistant coatings, and they exhibit prominent flame-retarding performance when applied on steel, wood, cables and so on. The carbonization mechanisms result from an intumescence phenomenon between APP and PER, development of intumescence (the protective cellular carbon-based coating) occurs between 280 °C and 350 °C, and the degradation of the intumescent coating takes place between 350 °C and 430 °C. At higher temperatures, structural changes lead to the formation of new carbonaceous species (established in the temperature range between 420 °C and 560 °C). Some researchers demonstrated that the dynamic properties of the char could be explained by the chemistry of the system (aromaticity, thermal polymerization of aromatic molecules, etc.) [2,3]. As one of the most economical and commonly used intumescent flame retardants (IFR), APP–MEL–PER system can significantly enhance the flame-retarding property because of the synergistic effect among the three additives when heated, thus producing a “foamed” and light char layer, which is a poor conductor of heat, to effectively insulate fire spread and heat/fuel/oxygen transfer from the substrate [4].

In recent years, mineral fillers such as titanium dioxide (TiO_2) in IFR coating have attracted much concern. TiO_2 is an additive that is commonly used in coating industry as pigments. A novel IFR coating was prepared using APP-MEL-PER-TiO_2 system and white material appeared at the surface of the charring layer during combustion [5,6]. However, the effects of TiO_2 structure on the fire resistance of IFR coating have not been investigated. Rutile-type TiO_2 and anatase-type TiO_2 have different size distribution and crystalline forms, and the former tends to be more stable and easier to be dispersed evenly in the polystyrene matrix than the latter.

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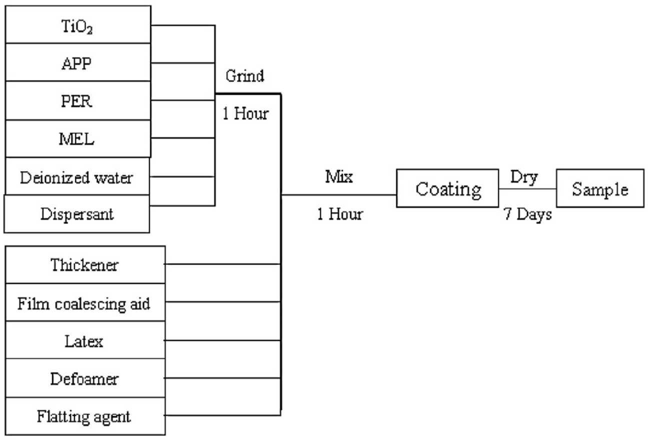

Fig. 1. Flow chart of sample preparation.

The formation of intumescent char is actually a process of char foaming. It has been proved that melt flow rate (MFR) is closely related to foaming [7]. Therefore, a close relationship between IFR char formation process and MFR may exist.

In this work, two types of TiO_2 were introduced to the flame retardant silicone-acrylate coating in order to improve the fire performance. The flammability was characterized by the big panel method. Char morphology was characterized by SEM, FTIR and XRD. MFR was firstly used to characterize the char's intumescing process in this work.

2. Experimental

2.1. Materials

Silicone-acrylate emulsion, thickener, film coalescing aid, dispersant, defoamer, and flatting agent were purchased from Health Chemical Co., Ltd., Nantong. APP was provided by Jinan Enter Chemical Co., Ltd. PER was purchased from Shang Shan Chemical Co., Ltd., Jinan. MEL was provided by Jinan Enter Chemical Co., Ltd. Rutile-type TiO_2 with an average particle diameter of 0.17 μm and anatase-type TiO_2 with an average particle diameter of 0.30 μm were purchased from Shanghai Titanos Industry Co., Ltd.

2.2. Preparation of coatings

The preparation process was shown in Fig. 1. Silicone-acrylate emulsion, rutile-type TiO_2/anatase-type TiO_2, and APP–PER–MEL were milled for 1 h in a ball grinder. The flame-retardant coatings were then coated on the surface of one side of a plywood plate with a size of 100 × 100 × 5 mm. Interval time of spreading between the coatings was 24 h and the coated plates were dried at 25 °C for 1 week in the ventilated environment. The thickness of coated dry film was 1.00 ± 0.05 mm.

Fig. 2. Schematic diagram of big panel method.

The mass ratio of APP-MEL-PER was fixed at 20:12:9 based on the initial experience data. Formulations of IFR coatings samples were listed in Table 1.

2.3. Fire resistance test: big panel method

Fire resistance test was an examination of heat insulation of flame-retardant coatings. When cracks appeared on the wooden test plate, the time was defined as fire-resistant time. The curves of samples' thickness vs time were obtained by on-line measurement during the test. Fig. 2 shows schematic diagram of big panel method. The detailed procedure is described in "Big panel method" (GB/T 12441-2005).

2.4. Melt flow rate

The melt flow rates (MFR) of the sample Ref with and without TiO_2 (see Table 1) were measured under different temperatures within 150–450 °C by a Melt Flow Indexer (Chengde Jinjian Testing Instrument Co., Ltd) according to the procedure described in ISO 1133.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed in a TAQ-5000 (Mettler Toledo) with a heating rate of 10 °C/min at a temperature range of 20–800 °C under air atmosphere at the flow

Table 1
Formulation of IFR coating samples[a]

Components Samples	Latex/phr	APP/phr	PER/phr	MEL/phr	Deionized water/phr	R-TiO_2[b]/phr	A-TiO_2[b]/phr	Fire-resistant time/min
Ref	100	0	0	0	0	0	0	2
IFR	100	150	68	90	250	0	0	43
IFR/15r-TiO_2	100	150	68	90	250	15	0	46
IFR/30r-TiO_2	100	150	68	90	250	30	0	73
IFR/45r-TiO_2	100	150	68	90	250	45	0	56
IFR/60r-TiO_2	100	150	68	90	250	60	0	52
IFR/15a-TiO_2	100	150	68	90	250	0	15	26
IFR/30a-TiO_2	100	150	68	90	250	0	30	33
IFR/45a-TiO_2	100	150	68	90	250	0	45	46
IFR/60a-TiO_2	100	150	68	90	250	60	60	49

[a] Each formulation also contains thickener, flatting agent, dispersant, defoamer and film coalescing aid.
[b] R-TiO_2 and A-TiO_2 represent rutile-type TiO_2 and anatase-type TiO_2 respectively.