Thermal Behavior of Nano-TiO$_2$ in Fire-Resistant Coating

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The dispersion state of nano-TiO$_2$ particles was studied by using transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR). Nanoparticles can be fully dispersed by specific hyper-dispersant. The improvement of nano-TiO$_2$ in thermal behavior and flame retardation of acrylic polymer and fire-resistant coating was investigated by differential thermal analysis (DTA), thermogravimetry (TG) and fire-resistant time test. It is demonstrated that nano-TiO$_2$ is helpful for enhancing the thermal stability, anti-oxidation and fire-resistant properties of acrylic polymer and fire-resistant coating.

KEY WORDS: Nano-TiO$_2$; Fire-resistant coating; Thermal stability; Fire-resistant properties

1. Introduction

Acrylic polymer has the poor flame retardation. The incorporation of nanoparticles into the material is one of attractive studies in solving the problem. Nanomaterials with nano-TiO$_2$ have caused extensive attention in material sciences. These nanomaterials exhibit the excellent properties that are different from those conventional materials where the same filler is added to material at micrometer level. Specific content of nano-TiO$_2$ can provide an improvement in fire resistance for polymers or coatings[1–3]. The ammonium polyphosphate-pentaerythritol-melamine (APP-PER-MEL) coatings widely applied in steel structural members are easily oxidized and detached from the substrate. It is necessary to improve anti-oxidation of char structure formed from APP-PER-MEL coating. Nano-technology is a promising way to improve anti-oxidation properties of the coatings[4–6]. This study deals with the preparation and characterization of acrylic polymers and nano-coatings modified by nano-TiO$_2$, and investigates their thermal behavior and fire-resistant performance.

2. Experimental

2.1 Materials

The BD801 thermoplastic acrylic resin (BD801, Shanmu Co., China) was used as the binder of coating. Ammonium polyphosphate (APP50, Xingxing Co., China), pentaerythritol and melamine (supplied by Haiwang Co., China) were used as flame-retardant additives. Nano-TiO$_2$ (primary particle size: 20$\pm$5 nm, specific area: 160$\pm$30 m^2/g) and general TiO$_2$ (particle size: 40$\pm$5 μm) supplied by Zhoushan Nanomaterail Co., China, were used as the fillers. NJ-2 hyper-dispersant (number average molecular weight: 1319, weight average molecular weight: 1412, solvency parameter: 16.2 J$^{0.5}$·cm$^{-1.5}$, length of fatty chain: 32) was used as a modifier of nano-TiO$_2$ particles.

2.2 Preparation of nano-concentrates and nano-coatings

Firstly, 0.08–0.1 g NJ-2 hyper-dispersant was added to 30 g tolune, and then 8 g nano-

TiO$_2$ particles were added to the solution and dispersed at 40°C for 30 min by ultrasonic vibration to obtain nano-solution. The nano-solution and 10 g BD801 acrylic resin were mixed and milled for 3 h in a ball grinder, and then were milled three times in a three-roll mill to obtain nano-concentrates. The nano-concentrates were centrifuged and the precipitate was dispersed with ultrasonic vibration for 1 h and centrifuged at 8$\times$10^3 r/min again. Weight percent of nano-TiO$_2$ in the final nano-concentrates is 40%. 1.25% nano-concentrates (0.5% nano-TiO$_2$) and 5% nano-concentrates (2% nano-TiO$_2$) were respectively added to BD801 acrylic resin to obtain the modified acrylic polymers. 0.5% and 2% general TiO$_2$ was respectively added to BD801 acrylic polymer to comparatively analyze the effect of general TiO$_2$ and nano-TiO$_2$ on thermal stability of acrylic polymers. 26%–28% BD801 acrylic resin, 8%–10% pentaerythritol, 22%–24% ammonium polyphosphate, 8%–10% melamine, 2%–3% glass fiber, 6%–8% titanium dioxide, 7%–8% butyl acetate and 13%–14% dimethyl benzene were dispersed and ground using a Mini Zeta ball mill for 5 h to obtain No.1 coating. Then 4% nano-concentrates (1.6% nano-TiO$_2$ particles) were added to No.1 coating to obtain No.2 nano-coating. The flame retardant coatings were spread to one side of a square steel plate sized 100 mm×100 mm×5 mm. Total thickness of dry film was 1 mm.

2.3 Fire-resistant time test

The fire-resistant time test is aimed to examine fire-resistant property and heat insulation property of fire-resistant coatings. The coated plates were exposed to flame whose temperature increased in accordance with ISO 834 curve (Fig.1). Three thermocouples were placed on the backside of the test plate and the back temperatures of the plate were recorded. When the average of three back temperatures reached 300°C, the time was defined as fire-resistant time.

2.4 Analysis method

The distribution of nanoparticles was examined with a JEM-2000EX TEM at an acceleration voltage of 200 kV. FT-IR (Fourier transform infrared spectroscopy) spectra of the modified nanoparticles were recorded between 4000 and 500 cm^{-1} on a Perkin-

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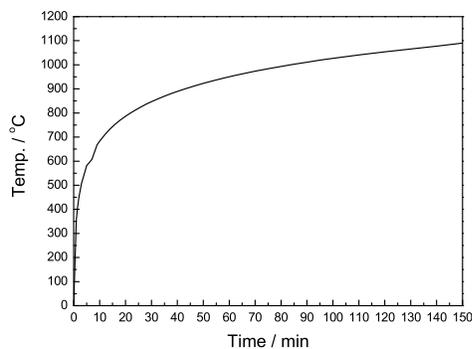† Assoc. Prof., Ph.D., to whom correspondence should be addressed, E-mail: zzyywang@imr.ac.cn.
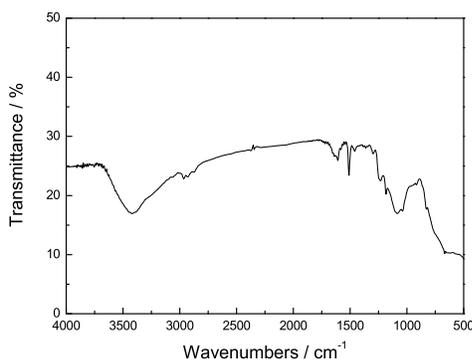
Fig.1 ISO 834 curve

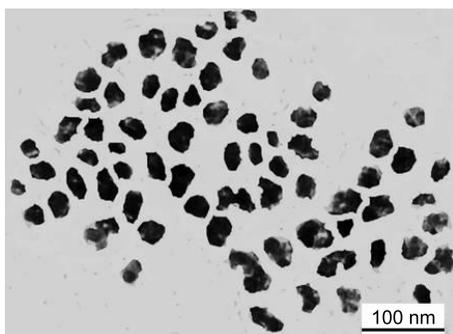**Fig.2** FT-IR spectra of nano-TiO$_2$ particles modified by NJ-2 hyper-dispersant

Fig.3 TEM image of the modified nano-TiO$_2$ particles in nano-concentrates

Elemer 2000FT-IR spectrometer. Differential thermal analysis (DTA) and thermogravimetry (TG) data were collected, respectively with a Setaram Mtb10-8 and a Perkin Elmer from 25°C to 1000°C at a heating rate of 10°C/min under an air.

3. Results and Discussion

3.1 Dispersion analysis of nanoparticles

The FT-IR spectra of the modified nano-TiO$_2$ particles are shown in Fig.2. The two peaks at 1050–1250 cm^{-1} and 1580–1750 cm^{-1} correspond to ester groups (−COOR) and carbonyl groups (C=O). The absorption peak at 2890 cm^{-1} is assigned to methylene groups (−CH$_2$). Unmodified nano-TiO$_2$ particles do not show these specific absorption peaks
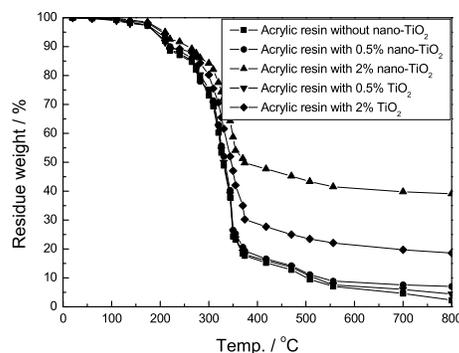

Fig.4 TG curves of acrylic polymers with different content of general TiO$_2$ and nano-TiO$_2$

in FI-IR spectra. This indicates that anchor groups (−COOH) of hyper-dispersant have bonded with hydroxyl groups on the surface of nanoparticles. The long carbon chains of the hyper-dispersant can improve the aggregation of nanoparticles by spatial steric effect[7].

The hydroxyl groups on the surface of nanoparticles form a great many of hydrogen bonds by Van der waals force, and the process causes the aggregation of nanoparticles. Consequently, polymer or coating with the agglomerate nanoparticles exhibits the declined properties. The unmodified nanoparticles are very difficult to achieve a homogeneous dispersion in polymer or coating because of their strong tendency to agglomerate. As presented in the TEM image of Fig.3, the modified nano-TiO$_2$ particles show an excellent dispersion state with nano-scale in nanoconcentrates. The dispersing agent can penetrate into the agglomerated nano-TiO$_2$ particles and bond with the hydroxyl groups of inside and outside the agglomerates. The dispersion state of nano-TiO$_2$ particles can be improved by the bonding action of anchoring groups and steric effect of long carbon chain. The well-distributed nano-TiO$_2$ particles can improve the general properties of coatings[8,9].

3.2 TG analysis of acrylic polymer

Figure 4 shows the TG curves of acrylic polymers containing different content of nano-TiO$_2$ and TiO$_2$. The temperatures of the 50% weight loss for acrylic polymer, acrylic polymer containing 0.5% nano-TiO$_2$, and acrylic polymer containing 2% nano-TiO$_2$ are 329, 333 and 365°C, respectively. The final weight of the three acrylic polymers at 800°C is 2.3%, 7% and 39.1%, respectively. The final weight at 800°C of acrylic polymer with 0.5% nano-TiO$_2$ is only 4.7% more than that of acrylic polymer without nano-TiO$_2$. 0.5% nano-TiO$_2$ cannot give the obvious improvement in thermal stability of acrylic polymer. When the content of nano-TiO$_2$ in acrylic polymer increases from 0.5% to 2%, the difference between residue weights of acrylic polymers becomes larger. The final weight of acrylic polymer with 2% nano-TiO$_2$ is 36.8% more than that of acrylic polymer without nano-TiO$_2$. The temperatures of the 50% weight loss for acrylic polymer containing 0.5% general TiO$_2$ and acrylic polymer containing 2% general TiO$_2$ are 331 and 347°C, respectively. Their relative final weight at 800°C
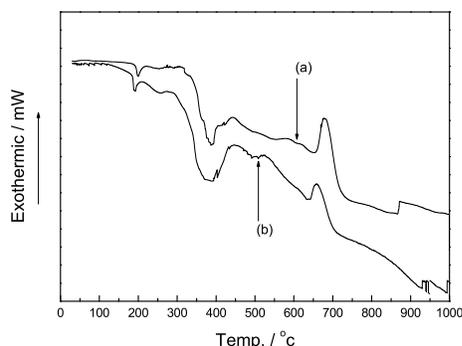
Fig.5 DTA curves of No.1 coating (a) and No.2 nano-coating (b)
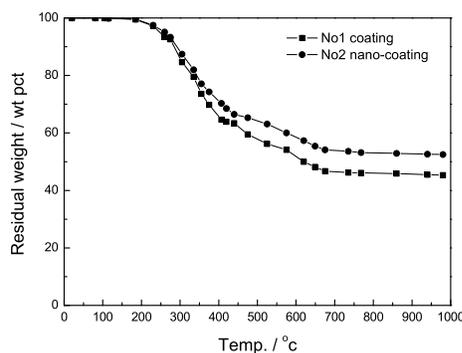
**Fig.6** TG curves of No.1 coating and No.2 nano-coating
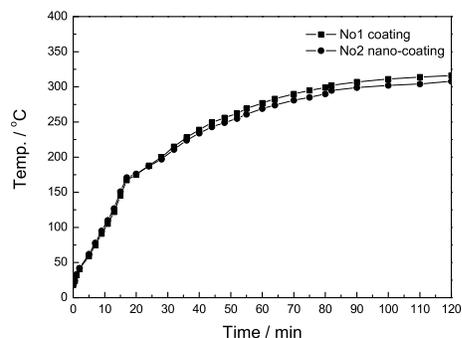
Fig.7 Fire protection curves of No.1 coating and No.2 nano-coating

is 4.4% and 18.6%, respectively. The final weight of acrylic polymer with 2% general TiO_2 is 20.5% less than that of acrylic polymer with 2% nano-TiO_2. It is evident that nano-TiO_2 is more efficient than general TiO_2 in improving thermal stability of polymer. This is because the covalent bonding between nano-TiO_2 and acrylic polymer enhances thermal stability.

3.3 DTA and TG analysis of coatings

DTA curves of No.1 coating and No.2 nano-coating are presented in Fig.5. A distinctive endothermic peak at 300–450°C is attributed to the interaction of APP, PER, MEL and acrylic resin, resulting in the formation of an intumescent charred structure. An exothermic peak at 650–720°C is due to the oxidative degradation of the charred structure. At the temperature higher than 720°C, the inorganic protective layer becomes the main protective material and suppresses

the oxidation trend. A difference in thermal degradation is observed between No.2 nano-coating and No.1 coating. The endothermic peak area and profile of No.2 nano-coating is wider than that of No.1 coating, whereas the exothermic peak area and profile of No.2 nano-coating is narrower than that of No.1 coating. The stronger endothermic effect and the weaker exothermic effect are advantageous to fire-resistant property of No.2 nano-coating[10,11]. Nano-TiO_2 and inorganic filler as a modifier can react with ammonium polyphosphate to form a ceramic-like fused compound at high temperature. The ceramic-like material enhances the char structure and protects the substrate against fire. TiO_2 and $(NH_4)_4P_4O_{12}$ can react as:

$$2TiO_2 + (NH_4)_4P_4O_{12} \rightarrow 2TiP_2O_7 + 4NH_3 + 2H_2O$$
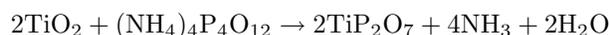
Nano-TiO_2 can form a nano-scale Ti-O-Ti network inside the char structure and a ceramic-like protective material on the surface of char. The nano-scale Ti-O-Ti structure can improve anti-oxidation and thermal stability of No.2 nano-coating at middle and later stage of a fire[12,13].

TG curves of the two coatings are shown in Fig.6. The weight loss of No.1 coating and No.2 nano-coating takes place at 180–670°C, and the two coatings produce very little weight loss at the temperature higher than 670°C. The final residue weight of No.1 coating and No.2 nano-coating is 45.3% and 52.5%, respectively. It is seen that the final residue weight of No.2 nano-coating with 1.6% nano-TiO_2 is 7.2% more than that of No.1 coating without nano-TiO_2. A tough and stable nano-scale ceramic-like material can be formed from nano-TiO_2 at high temperature[10]. The ceramic-like material enhances anti-oxidation properties of protective char structure in a fire, which results in an increase in residue weight. Fire resistance of coatings is connected with residue weight of coatings. It is concluded that only 1.6% nano-TiO_2 can significantly improve residue weight and anti-oxidation properties of the coating in a fire[14].

3.4 Fire-resistant time

The fire protection curves are presented in Fig.7. The fire-resistant time of No.2 nano-coating increases from 81 min of No.1 coating to 96 min. An increase in fire-resistant time indicates the improvement of fire-resistant properties due to the presence of nano-TiO_2. The well-dispersed nano-TiO_2 particles can form an interpenetrating nanoparticle network in char structure, and the network can enhance anti-oxidation of char structure and protect the metal substrate at the middle and later stage of a fire. As a result, 1.6% nano-TiO_2 can effectively improve fire protection properties of fire-resistant coating[15,16].

4. Conclusion

Nano-TiO_2 particles modified by hyper-dispersant can be well dispersed in acrylic polymer and coating. 2% nano-TiO_2 can greatly enhance the thermal stability of acrylic polymer, and nano-TiO_2 is more efficient than general TiO_2 in improving thermal stability of polymer. 1.6% nano-TiO_2 can enhance anti-oxidation, endothermic effect and fire protection properties of fire-resistant coating because of formation of

the nanoscale ceramic-like protective materials in char structure.

REFERENCES

[1] C.N.R.Rao and A.K.Cheetham: *J. Mater. Chem.,* 2001, **12,** 2887.

[2] Z.Y.Wang, E.H.Han and W.Ke: *Prog. Org. Coat.,* 2005, **53,** 29.

[3] R.B.Donald, E.B.Paul and A.E.Anter: *Prog. Org. Coat.,* 2003, **47,** 342.

[4] M.B.Le, S.Bourbigot and D.Christelle: *Fire Mater.,* 1996, **20,** 191.

[5] Jianjun CAO: *Iron Steel Vanadium Titanium,* 2004, **25**(4), 1. (in Chinese)

[6] Z.Y.Wang, E.H.Han and W.Ke: *Polym. Degrad. Stabil.,* 2006, **91,** 1937.

[7] J.Lin and J.A.Siddiiqui: *Polym. Advan. Technol.,* 2001, **12,** 285.

[8] E.Reynaud, T.Jouen and C.Gauthier: *Polymer,* 2001, **42,** 8759.

[9] A.Tsutsumi, M.Ikeda and W.Chen: *Powder Technol.,* 2003, **138,** 211.

[10] Z.Y.Wang, E.H.Han and W.Ke: *Surf. Coat. Technol.,* 2006, **200,** 5706.

[11] Lin LIU, Guojian WANG and Tiebao WANG: *Paint Coat. Industry,* 2006, **34,** 1. (in Chinese)

[12] D.J.Chaiko and A.A.Leyva: *Chem. Mater.,* 2005, **17,** 13.

[13] K.P.O.Mahesh, M.Alagar and S.A.Kumar: *Polym. Adv. Technol.,* 2003, **14,** 137.

[14] Lingmei GE, Aiping DAI and Tianliang LI: *J. Xi′an Univ. Sci. Technol.,* 2002, **22,** 12. (in Chinese)

[15] Jianke DU, Yanping LU and Jian CHEN: *Mater. Protect.,* 2002, **35,** 5. (in Chinese)

[16] Z.Y.Wang, E.H.Han and W.Ke: *Can. Metall. Quart.,* 2006, **45,** 485.