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Ecological Ammonium Thiocyanate-Modified Geopolymeric Coating for Flame-Retarding Plywood

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Abstract: An ecological ammonium thiocyanate (NH_4SCN)-modified geopolymeric coating was facilely prepared for flame-retarding plywood. The effect of NH_4SCN on the flame resistance was preliminarily investigated using cone calorimeter (CC), scanning electron microscope (SEM), X-ray diffraction (XRD), and thermal gravimetry (TG). The results show that 1 wt.% NH_4SCN as dopant is of paramount importance to generate a compact and continuous coating. The formation of a smooth, intact, and uniform-swelling siliceous layer during combustion facilitates enhanced fire resistance, evidenced by the increased fire performance index (FPI), reduced fire growth index (FGI), and 39.7% decreased value of peak heat release rate (pHRR), in comparison to those of the sample without NH_4SCN . Because of the reducibility of O_2 -consuming NH_4SCN , the compact shielding-layer containing carbonate and sulfate, as well as the release of NH_3 , the NH_4SCN -modified geopolymeric coating exerts an enhancement on the flame-retardant efficiency.

Keywords: flame-retardancy; ammonium thiocyanate; cone calorimeter; thermogravimetry

1. Introduction

The organic-inorganic halogen-free hybrid flame-retardant coating has been a hotspot, due to its excellent fireproofing property and ecology, which has become the main developing trend of the coating industry currently [1–4]. This increasing recognition identifies that silica particles offer some advantages including well-defined ordered structures, facile surface modification, and cost-effective preparation [2]. Moreover, inorganic silicate is employed as a physical filler to provide an enhanced barrier effect, and also it serves as a functional filler to enhance the structural strength and adhesion forces [3]. It is also reported to provide an improved anti-aging coating by doping TiO_2 and clay nanoparticles [4]. Inspired by a report of inorganic silicate-doped coatings, an exploration of the novel flame-retardant coatings using amorphous $\text{Si}(\text{OH})_4$ -enriched sol as the binder has been undertaken; these coatings have a self-adhering and cross-linking structure through a facile geopolymerization between the $\text{Si}(\text{OH})_4$ and $\text{Al}(\text{OH})_3$ [5].

Furthermore, previous investigations have explored the promising application to geopolymeric coating through a facile sol–gel method [6,7]. A novel inorganic coating, the geopolymer serves as a flame-retardant wood primer with a cost-effective edge and has not been widely reported on. Therefore, a multiplication of modification efforts for geopolymeric coatings is necessary to boost a sustainable, ecological, and recyclable economy on a global scale, which holds promising potential and is attracting increasing attention for research and applications.

In addition, the most prominent bottleneck for inorganic coatings has been identified as the inferior flame retardancy compared to organic coatings, ascribed to lower expansibility and heat absorptivity. To address this problem, phase change materials (PCMs) have been designed in the building envelope as a passive system to reduce heat loss owing to their latent heat storage [8], which also could be used to prepare halogen-free flame retardants [9,10]. Consequently, paraffin and expandable graphite (EG) have been used to fabricate hybrid flame retardants [11,12]. The enhancement of the flame resistance of novel geopolymeric coatings modified by a decanoic/palmitic eutectic mixture has been investigated [13].

Moreover, ammonium thiocyanate (NH_4SCN), as a kind of solid-solid PCM, can be exploited as solid polymer electrolyte due to its high conductivity and amorphous phase [14]. However, the effect of NH_4SCN on the flame-retarding property of coatings is a virgin area for hybrid flame retardants. Consequently, this investigation scrutinized the effect of NH_4SCN on the fire resistance of hybrid geopolymeric coatings using a cone calorimeter (CC). Its microstructure was examined using scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetry (TG) to preliminarily illuminate its flame-retarding mode of action.

2. Materials and Methods

2.1. Preparation of NH_4SCN -Modified Geopolymeric Coatings

2.1.1. Starting Materials

The starting material for the geopolymer was gray fumed silica collected by the Linyuan company in Xi'an of China, solid powder derived from silicon-smelting, which had a Blaine specific surface area of $25 \text{ m}^2\cdot\text{g}^{-1}$ and a density of $1.62 \text{ g}\cdot\text{cm}^{-3}$. Analysis using X-ray fluorescence (XRF, bruker AXS Co., Karlsruhe, Germany, LTDS4 PIONEER) determined a high silica content (87.46 wt.%) as shown in Table 1. Analytically pure (AP) $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ and KOH, which served as chemical activators, were purchased from the HongYan reagent factory in Tianjin of China. The modifier NH_4SCN (AP) was obtained from the FuChen reagent factory of Tianjin in China. Hydrophobic polydimethylsiloxane (PDMS) was prepared by the Tianjin YaoHua reagent factory. The thickener and film-forming agent, polyacrylamide (PAM), was synthesized by the Shanghai reagent factory in China. EG served as the charring fortifier [15] and was fabricated by the Qingdao chemical group in China with a volume-expansion rate of $300 \text{ mL}\cdot\text{g}^{-1}$ and an average particle size of $48 \mu\text{m}$. The second-class flame-retarding plywood was produced in the Xi'an timber processing plant.

Table 1. Compositions of fumed silica tested using X-ray fluorescence (XRF).

Material	Weight (wt.%)								
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	Loss
Fumed silica	0.61	87.46	6.90	1.17	0.46	0.29	0.67	0.31	2.12

2.1.2. Preparation of NH_4SCN -Modified Geopolymeric Coatings

The geopolymeric coatings were prepared by slowly dispersing 50 g of fumed silica into 200 mL alkali-activated solution (comprising $1 \text{ mol}\cdot\text{L}^{-1}$ Na_2SiO_3 and $2 \text{ mol}\cdot\text{L}^{-1}$ KOH) under 60°C , which was placed on a magnetic stirrer at $60 \text{ r}\cdot\text{min}^{-1}$ [6]. After stirring for about 0.5 h, the modifiers including PAM (1 wt.%), PDMS (1.5 wt.%), and EG (5 wt.%) were sequentially added into the aforesaid solution during constant stirring at 60°C , followed by another stirring for about 0.5 h [13]. Finally, the 0.5, 1, 1.5, 2, and 3 wt.% NH_4SCN was doped into the abovementioned mixture, respectively, the hybrid coating was achieved by another vigorous stirring ($1000 \text{ r}\cdot\text{min}^{-1}$ for about 15 min).

2.1.3. Preparation of Samples

The samples were the plywood ($100 \times 100 \times 4 \text{ mm}^3$) covered by geopolymeric coatings after brushing the surfaces three times with an interval time of 40 min. The samples with the NH_4SCN dosage of 0.5, 1, 1.5, 2, and 3 wt.% were denoted as S1, S2, S3, S4, and S5, respectively. Coatings without NH_4SCN and pristine raw plywood were used as the controls, which were defined as S0 and Sr. The coating thicknesses were the same, 0.4 mm approximately.

2.2. Characterizations

2.2.1. Flame Resistance

The horizontal external heat flux was $30 \text{ kW}\cdot\text{m}^{-2}$ (about 625°C for complete decomposition of plywood) to examine the combustion parameters of samples in real time, which was conducted in a CC (ZY6243, Zhongnuo instrument company, Dongguan, China) according to BS ISO 5660-1:2015 [16], the average value was obtained from the three samples with a deviation of $<5\%$. The heat release rate (HRR), time to ignite (TTI), the peak heat release rate (pHRR), time to pHRR (T_p), O_2 concentration and smoke temperature in exhaust smoke, and time to the cessation of flaming (T_b) were recorded in real time. The fire performance index (FPI, $\text{FPI} = \text{TTI}/\text{pHRR}$) and fire growth index (FGI, $\text{FGI} = \text{pHRR}/T_p$), were the most important indexes to distinguish the flame-retardant efficiency [7,13,15], the sample with a higher FPI and lower FGI corresponded to a stronger flame resistance.

2.2.2. Microstructure Analysis

The Quanta 200 SEM (FEI Co., Hillsboro, OR, USA) was employed to observe the micro-morphologies of coating residues after combustion in the CC, the operating voltage was 20 kV with a working distance of 10 mm. The sample with a superficial area of $25\sim 30 \text{ mm}^2$ was placed under a vacuum degree of $<1.33 \times 10^{-3} \text{ Pa}$ prior to gold sputtering for observation. The D/MAX-2400 X-ray diffractometer with $\text{Cu K}\alpha$ was used to detect mineral phases of samples, the coating residue was ground into powder for preparing the testing sample with a working voltage of 30 kV and a working current of 40 mA, the scanning speed was $5^\circ\cdot\text{min}^{-1}$ with a range of $10^\circ\sim 50^\circ$. The Mettler thermal balance was exploited to record the TG/DSC values in real time of bare pre-dried sample coatings of about $10\sim 20 \text{ mg}$, which were tested at $50\sim 200^\circ\text{C}$ (the complete decomposition of NH_4SCN occurred below 180°C) with a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen (flow of $50 \text{ cm}^3/\text{min}$) in an alumina pan.

3. Results

3.1. Flame-Retardant Properties

The decreased pHRR value for the specimens with NH_4SCN is presented in Figure 1a, the occurrence of a gradual right-shift indicates a delayed flame propagation, with the increasing content of NH_4SCN . S2 appears to have the lowest pHRR value of $248 \text{ kW}\cdot\text{m}^{-2}$ with a 39.7% decrease in comparison to that of S0, which determines that NH_4SCN imparts an improved flame resistance to geopolymeric coatings. The combustion process of wood can be divided into four stages, namely, drying, pre-carbonization, carbonization, and combustion, and the HRR property depends on the structural stability of the wood component. The decomposition of wood occurs sequentially as light volatile and partial hemicellulose, hemicellulose, cellulose, and partial lignin [17]. The flame propagation retards or temporarily stops after 80 s, ascribed to surficial charring of plywood [18], with the increasing accumulated heat, the sharply increased HRR indicates a flashover for Sr. However, the curve of pHRR rises when the dosage of NH_4SCN exceeds 1 wt.%, this indicates that excess NH_4SCN is detrimental for obtaining an excellent flame retardancy, implying that an appropriate dosage of NH_4SCN is beneficial to constitute an advantageous fire resistance, the reason is illustrated in Section 4.

Figure 1. Real-time combustion parameters of samples including (a) heat release rate (HRR), (b) smoke temperature, and (c) O₂ concentration.

Figure 1b presents the smoke temperature of samples during the whole process of burning, the obvious “right shift” of the smoke temperature peak was examined, and the lowest peak of 97 °C was located on S2 at 366 s, while that of Sr was 107 °C at 181 s. The delayed and shrunk peak indirectly demonstrates that S2 with 1 wt.% NH₄SCN exerts the highest flame resistance. However, a reverse increase and “left shift” in the smoke temperature peak were observed when the content of NH₄SCN exceeded 1 wt.%, which is consistent with the results of HRR in Figure 1a. Moreover, the O₂ concentration in exhaust gas of smoke tube takes on a similar tendency to that of the HRR, the highest O₂ concentration peak of 20.52% appeared in S2 at 378 s, while that of Sr was 20.08% at 196 s as shown in Figure 1c. Because the O₂ is an essential element for the burning of samples, the higher O₂-consumption implies fiercer combustion, S2 with the lowest O₂-consumption corresponds to the slowest burning, which also confirms that an appropriate dosage of NH₄SCN favors the enhancement of geopolymeric coatings effectively.

Table 2 shows an increase of T_b for the samples with NH₄SCN, but an enhancement of flame resistance was clarified. For S2, the FPI increased from 0.14 (S0) to 0.41 s·m²·kW⁻¹, and FGI dropped from 1.88 (S0) to 1.04 kW·m⁻²·s⁻¹, indicating an enhanced flame resistance [19]. It also implies that S2 holds a superior flame resistance than the others, therefore, an appropriate dosage of NH₄SCN serves to improve the flame-retardant efficiency of geopolymeric coatings.

Table 2. Combustion parameters of samples tested by cone calorimeter (CC).

Samples	TTI (s)	T_b (s)	T_p (s)	pHRR (kW·m ⁻²)	FPI (s·m ² ·kW ⁻¹)	FGI (kW·m ⁻² ·s ⁻¹)
Sr	18	289	214	545	0.03	2.55
S0	58	298	219	411	0.14	1.88
S1	78	312	234	301	0.33	1.29
S2	102	356	238	248	0.41	1.04
S3	81	373	243	261	0.33	1.07
S4	59	342	252	343	0.17	1.36
S5	47	320	278	356	0.13	1.28

TTI—time to ignite; T_b —time to the cessation of flaming; pHRR—peak heat release rate; T_p —time to pHRR; FPI—fire performance index, $FPI = TTI/Phrr$; FGI—fire growth index, $FGI = pHRR/T_p$.

3.2. Morphologies

3.2.1. Macro-Morphology of Samples

The cinereous geopolymeric coatings covered on the plywood are displayed in Figure 2a, no bubbling or peeling is observed, but efflorescence is obviously seen, due to the strong alkaline conditions derived from the alkali activators. It reveals the geopolymeric coatings could serve as primers rather than finishing coatings due to the whitening and non-transparency. With the increasing content of NH_4SCN , the phenomenon of efflorescence weakens as shown in Figure 2b, and the samples take on uniformly smooth surfaces in Figure 2c,d. However, a rough coating surface was observed for S4 with 2 wt.% NH_4SCN as shown in Figure 2e, the strands of coating appear for S5 in Figure 2f, due to the non-uniform dispersion and filming.

Figure 2. Appearance of specimens before combustion including (a) S0, (b) S1, (c) S2, (d) S3, (e) S4, (f) S5.

After combustion in the CC, a swollen siliceous layer was generated as shown in Figure 3, which protected the underlying plywood from burning effectively, Figure 3a presents a thinner and broken shielding layer. However, a gradually swelling intact layer presents with the increasing dosage of NH_4SCN in Figure 3b, and Figure 3c takes on a continuous and uniform layer, corresponding to the improved flame resistance. But some pores are present in Figure 3d, which might be attributed to the escape of excess NH_3 derived from the transformation of NH_4SCN , evidenced by the fish-scale feature as shown in Figure 3e. Moreover, non-uniform swelling-induced cracks spread rapidly for S5, with the increasing dosage of NH_4SCN , leading to a chipped and rough surface in Figure 3f. This demonstrates that the flame resistance mainly depends on the formation of an intact siliceous shielding layer, due to its incombustibility and excellently thermal stability.

Figure 3. Cont.

Figure 3. Appearance of specimens after combustion including (a) S0, (b) S1, (c) S2, (d) S3, (e) S4, (f) S5.

3.2.2. Micro-Morphology after Combustion

The amorphous spicules were dispersed on the matrix with many pores or holes as shown in Figure 4a. After doping NH_4SCN into the coatings, a decrease in the volume of pores or holes was observed, presenting a continuous and uniform barrier layer as shown in Figure 4b. S2 exhibits a smoother, more homogeneous and continuous structure as shown in Figure 4c, compared with that of others. However, a lot of crystalline filaments and pores with an average pore diameter of approximately $5\ \mu\text{m}$ were observed as seen in Figure 4d, when the content of NH_4SCN increased to 3 wt.%, they might be the channels left by NH_3^- escaping.

Figure 4. SEM images of specimens after combustion including (a) S0, (b) S1, (c) S2, and (d) S5 with $2500\times$, and the same images ($5000\times$) contain (a') S0, (b') S1, (c') S2, and (d') S5.

3.3. TG/DSC

The weight loss was essentially equal to approximately 15.5% for both S2 and S5 as shown in Figure 5, the slight change in the weight loss indirectly determines that the doped NH_4SCN completely dissolves or decomposes, rather than transforms into a complicated structure through insertion or linkage [20]. However, the weight loss temperature (WLT) increased from 78.5 to 82.2 °C with the increasing content of NH_4SCN . According to the TG-DTG method [21], the onset temperature changed slightly while the end-set temperature climbed from 96.5 to 102.9 °C as shown in Figure 5a,b. Because the evaporation of free water occurs at <105 °C, the increases in WLT and end-set temperature indicate that the doped NH_4SCN slightly restrains the vaporization heat of water involved in the samples, due to strong interactions between NH_4^+ and H_2O .

Figure 5. TG/DTG curves of samples including (a) S2 and (b) S5.

Moreover, the heat absorption of S5 decreased slightly and a tiny left-shift of the peak temperature occurred compared with that of S2 as shown in Figure 6. It has been reported that the transformation of NH_4SCN into thiourea occurs at approximately 140 °C [22,23], no endothermic peak appeared at 140 °C, implying that the NH_4SCN reacted under strong alkaline conditions. Due to its high solubility and ionized NH_4^+ , the prior reaction between NH_4^+ and OH^- occurs with heat released, leading to a slight decrease in absorption heat, evidenced by the shrunken area h_{S5} (224.1 $\text{J}\cdot\text{g}^{-1}$) of the endothermic peak in comparison to h_{S2} (297.6 $\text{J}\cdot\text{g}^{-1}$).

Figure 6. Heat flow of samples including S2 and S5.

3.4. XRD

Figure 7 mainly presents huge humps assigned to amorphous silicate at approximately $2\theta = 15^\circ\sim 30^\circ$. Small diffraction peaks superimposed on the hump corresponded to the poorly crystalline phases including tridymite (SiO_2 , PDF No.: 14-0260), quartz (SiO_2 , PDF No.: 46-1045),

natrite (Na_2CO_3 , PDF No.: 37-0451), sodium sulfite (Na_2SO_3 , PDF No.: 37-1488), and sodium sulfate (Na_2SO_4 , PDF No.: 01-0990). However, the absence of peaks corresponding to thiocyanate determines complete dissolution or decomposition, which is in agreement with the finding of literature [24,25]. The obvious characteristic diffraction peaks of tridymite and quartz derive from the transformation of fumed silica. The natrite forms through the reactions shown in Equations (1)–(3), firstly the NH_4SCN reacts with the OH^- and produces NH_3 , S^{2-} , and CO_3^{2-} , following by the formation of sodium sulfite via oxidizing reaction between the S^{2-} and O_2 derived from air, finally partial sodium sulfite is oxidized further and transfers into sodium sulfate. SCN^- can transform into S^{2-} , CO_2 , and NH_4^+ under acid environment via a reduction reaction [24]. However, the hump of amorphous silicate covers the spectra of Na_2CO_3 , Na_2SO_3 , and Na_2SO_4 , because of their low contents in XRD patterns.

Figure 7. XRD of samples after combustion.

4. Discussion

It has been reported that mercerization increases the interfacial bonding strength between lignocellulosic fibers and organics [26–28], the alkaline condition facilitates removal of soluble components [29,30], and, therefore, chemical bonding between the siliceous gel and plywood forms. Furthermore, SCN^- is prone to associate with nonpolar surfaces due to its low charge density and weak-tightly bonding hydration shell [31], and the plywood surface mainly consists of nonpolar cellulose and hemicellulose, which prompts a strong adhesive property of geopolymeric coatings, favoring the more pronounced fireproof property.

On the other hand, it can be inferred that the improved flame resistance of geopolymeric coatings is attributed to the following factors according to the results of CC and XRD. Firstly, NH_4SCN postpones the rising pHRR as a suitable O_2^- consuming reductant. NH_4SCN with a melting temperature of 149.6°C can transform into thiourea at $140\sim 180^\circ\text{C}$ [22], the strong alkaline condition triggers the prior oxidizing reaction and the firing provides the conditions for the formation of sulfate, this implies that the phase change performance of NH_4SCN is limited or inhibited, but the reducibility is beneficial for retarding flame-propagation by consuming O_2 . Secondly, NH_4SCN mainly favors the formation of a continuous layer as a dopant for reinforcing the siliceous layer, due to its natural amorphousness [32], which facilitates its diffusion and migration in the amorphous geopolymeric coatings, and the formation of carbonate and sulfate prompts a continuous and compact siliceous layer as a barrier filler. Finally,

NH_4SCN suppresses the diffusion of heat and flame by releasing NH_3 —the NH_3 derives from two routes, one is the combination of NH_4^+ and OH^- , the other is the transformation of N^{3-} in SCN^- . The former mainly takes place during the process of preparation, leading to negligible flame resistance, but the latter possesses an obviously inhibiting effect during combustion.

However, flame resistance declines when the dosage of NH_4SCN exceeds 1 wt.%, this can be ascribed to the rapid increase in viscosity of coatings, evidenced by the non-uniform dispersion and filming, as well as the increase in WLT from TG. The coating is prone to fattening for S5, due to strong water-consuming hydrolysis of NH_4SCN , especially for the alkaline environment that accelerates and boosts the formation of NH_3 . The superfluous SCN^- could transform into CO_3^{2-} , SO_3^{2-} , and SO_4^{2-} according to the result of XRD, which consumes O_2 to delay the propagation of flames, evidenced by the gradual right-shift of pHRR with increasing NH_4SCN . However, the O_2 -consuming effect is weak (low content) because the formation of an intact and uniform shielding layer is of vital importance for flame retardancy. The thermal conductivity is remarkably decreased because of the discontinuous coating or film [33], which blocks heat conduction and charring of the hybrid coating during combustion, as well as the formation of swelling siliceous layers, leading to a chipped and rough surface.

Although this paper presents a cost effective and ecological geopolymeric coatings for flame-retarding plywood, an important issue to highlight is the interactions between NH_4SCN and PDMS, EG, and other components. As seen from the charring mechanism on the carbon/siliceous layer, SEM only provides a final morphology, but a pyrolysis kinetic is essential to investigate the novel coatings. This work might be the first step toward preparing novel NH_4SCN -doped geopolymeric coatings for flame-retarding plywood as a primer, proposing a new pathway for meeting the sustainable demand of “end-of-waste”. Furthermore, some deep problems remain in durability and chemical structure, which need to be analyzed and evaluated in detail.

5. Conclusions

To obtain an ecological, cost-effective, and high flame-retarding coating, a facilely prepared halogen-free flame-retardant coating was explored by mixing the alkali-activated fumed silica-based geopolymer with PDMS, EG, and NH_4SCN . Its flame resistance and microstructure were preliminarily investigated and the following conclusions were drawn.

- A novel NH_4SCN -modified geopolymeric coatings for flame-retarding plywood was prepared via a facile sol–gel method, and the optimal dosage of NH_4SCN was determined as 1 wt.%, evidenced by the highest FPI, the lowest FGI, and the pHRR dropping to $248 \text{ kW}\cdot\text{m}^{-2}$ with a 39.7% decrease.
- Microstructure analysis determined that moderate use of NH_4SCN as a dopant is of importance for a uniform and continuous coating before combustion, which is beneficial for the formation of a smooth and intact swollen siliceous shielding layer during combustion. The enhancement of flame resistance mainly depends on the formation of a compact and continuous siliceous layer.

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