

Influence of Zeolitic imidazolate framework-8 on the thermal stabilization of poly(vinyl chloride)

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ABSTRACT

A zeolitic imidazolate framework material (ZIF-8) was prepared from stoichiometric zinc nitrate and 2-methylimidazole at room temperature in the presence of ammonium hydroxide. The material was characterized by a series of methods and used as a thermal stabilizer for poly (vinyl chloride) (PVC) film. The properties of the stabilized PVC were investigated using Congo red test, thermal aging test and thermal gravimetric analysis (TGA). Compared with the stabilizing efficiencies of some commonly-used reference stabilizers (e.g. CaSt₂ and ZnSt₂), the stabilizers including ZIF-8 [such as CaSt₂/ZnSt₂/ZIF-8 and ZnSt₂/ZIF-8] exhibit better initial color stability and long-term thermal stability for PVC. The static thermal stability time was significantly prolonged from 33.13 min for PVC/CaSt₂/ZnSt₂ to about 128.92 min for PVC/ZIF-8/ZnSt₂ at 180 °C. The superior performance is attributed to the synergistic effect of ZIF-8 and ZnSt₂. The imidazole ligand of ZIF-8 can strongly absorb hydrogen chloride and form complexes with ZnCl₂ generated from ZnSt₂ in the PVC degradation process. In addition, the double bonds of ZIF-8 may help to form stable compounds with polyenes to further retard the PVC degradation. Dynamic mechanical and tensile properties of the PVC films were also studied.

1. Introduction

Poly (vinyl chloride) (PVC), a major commercial thermoplastic film, is prone to degradation at processing temperature [1–3]. This degradation occurs by autocatalytic dehydrochlorination (DHC) of PVC and results in the formation of conjugated double bonds which lead to unacceptable discoloration and property deterioration of PVC [4,5]. The most efficient and practical way to solve this problem is to add a thermal stabilizer to retard the degradation [6]. There are three major categories of industrial stabilizers, which either react with the HCl gas evolved from degradation or exchange the labile chlorine in PVC chains for more stable stabilizer-derived esters or mercaptide groups (e.g. metallic soaps, organic tin/lead salts, and esters or mercaptides of dialkyltin) [7]. However, the application of lead salts and organic tin is limited by toxicity or high cost, despite their high stabilizing efficiency. The nontoxic metal soaps are the most commonly-used stabilizers. The superior synergistic effect between calcium stearate (CaSt₂) and zinc stearate (ZnSt₂) has been found [8,9]. However, an undesirable product, zinc chloride (ZnCl₂) is formed for PVC thermally stabilized with CaSt₂/ZnSt₂, which can catalyze the degradation of PVC to generate a

sudden “zipper DHC” [10]. Therefore, novel high-efficiency zinc-based stabilizers could have negative catalytic effects on the PVC degradation.

Some zinc-based stabilizers could significantly enhance thermal stability of PVC compared to ZnSt₂, and could form stable chelates with ZnCl₂ to delay the sample in a sudden turn black (“zinc-burning”) during PVC processing. For instance, PVC with pentaerythritol–zinc complex (penzinc) as a thermal stabilizer has much longer thermal stability time compared with commercial thermal stabilizers. Aging test showed that the penzinc could significantly retard the discoloration during the long-term PVC decomposition, more importantly, no “zinc-burning” occurred, and this was attributed to the high reactivity of penzinc with the HCl released from PVC degradation [11]. It was reported that, the thermal stability of PVC was significantly enhanced by adding zinc glycerolate (ZnGly) or ZnGly with lanthanum stearate (LaSt₃). Compared with ZnSt₂, the addition of ZnGly could significantly improve the initial color stability and long-term thermal stability of PVC. The high stabilizing efficiency of ZnGly was attributed to its ability to absorb HCl and replace the labile chlorine atoms on PVC chains [12]. Besides, the addition of Zn₃(C₃N₃O₃)₂/ZnO (Zn₃Cy₂ for short) could significantly enhance the thermal stability of PVC (Xu

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et al.), and this was attributed to the cyanurate anions of Zn_3Cy_2 which can strongly absorb the HCl released from PVC degradation. In addition, $CaSt_2/Zn_3Cy_2$ was also found to exhibit excellent synergistic effects with commercial auxiliary stabilizers [13]. Moreover, zinc norfloxacin [$Zn(C_{16}H_{17}FN_3O_3)_2 \cdot 4H_2O$, represented as $ZnNo_2$] could also extend the thermal stability of PVC and had a good synergetic effect with $CaSt_2$ on decelerating the release of HCl [14]. The excellent thermal effect of $ZnNo_2/CaSt_2$ was attributed to the HCl absorbing ability of the norfloxacin anions. Enrofloxacin complexes [e.g. binary Co(II)-(1), Ni(II)-(2) complexes with enrofloxacin drug (HL1) and ternary Co(II)-(3), Ni(II)-(4) complexes] were investigated as thermal stabilizers and co-stabilizers for rigid PVC, and compared with some of the commonly-used reference stabilizers. Blending these complexes with the reference stabilizers at different ratios all presented synergistic effect, and could enhance the induction period, along with better initial color stability and long-term thermal stability. The stabilizing efficiency was attributed partially to the ability of the metal complex stabilizer to incorporate in the polymeric chains, disrupting the chain degradation and replacing the labile chlorine atoms on PVC chains by a relatively more stable moiety [15].

The application of zeolitic imidazolate frameworks (ZIFS) as PVC thermal stabilizers was not reported. Herein we report the incorporation of ZIF-8 into the Ca/Zn system to embody the long-term thermal stabilizing effect on PVC.

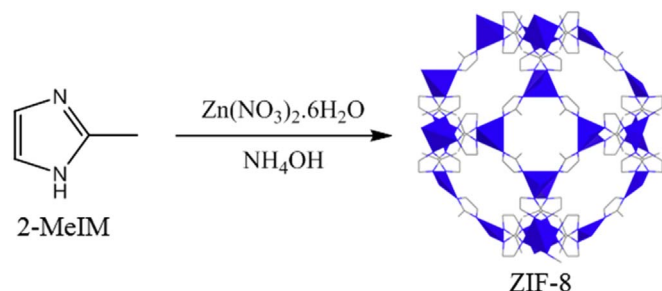
ZIF is a novel class of metal–organic frameworks (MOFs) formed from self-assembly. ZIF-8, resulting from the reaction between Zn^{2+} and 2-methylimidazole (2-MeIM), has a porous crystalline structure with metal atoms linked through N atoms by ditopic imidazolate ($C_3N_2H_3^- = Im$). The Metal–Im–Metal angle links together at 145° and coincides with the Si–O–Si angle commonly found in zeolite [16,17]. Great efforts have been made to synthesize nano- or micro-scale ZIF-8 crystals by using solvothermal [18], microwave [19], ultrasound [20], thermochemical [21] or accelerated aging [22] methods. ZIF-8 possesses many advantages such as excellent chemical stability against polar and nonpolar solvents, high-pressure structural reorientation, and high mechanical strength [23].

In this work, ZIF-8 was prepared using highly-diluted zinc salt and 2-MeIM at room temperature in the presence of ammonium hydroxide (NH_4OH) (Scheme 1). The thermal stabilizing effects of ZIF-8 and its combination with $CaSt_2$ and $ZnSt_2$ on PVC were investigated, and compared with some commonly-used stabilizers including $CaSt_2/ZnSt_2$, LTS-Ca/Zn (LTS: liquid thermal stabilizer) and C36DA-Ca/C36DA-Zn (C36DA: dimer fatty acid).

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 99% purity] was purchased from Alfa Aesar Chemicals. 2-MeIM ($C_4H_6N_2$), TEA (99.5% purity) and NH_4OH (28–30% aqueous solution, Sigma–Aldrich) were purchased from Sigma–Aldrich, Australia and used without further purification. Liquid thermal stabilizer [LTS-Ca/Zn (2.40% Ca, 2.41%



Scheme 1. Synthesis routes of ZIF-8.

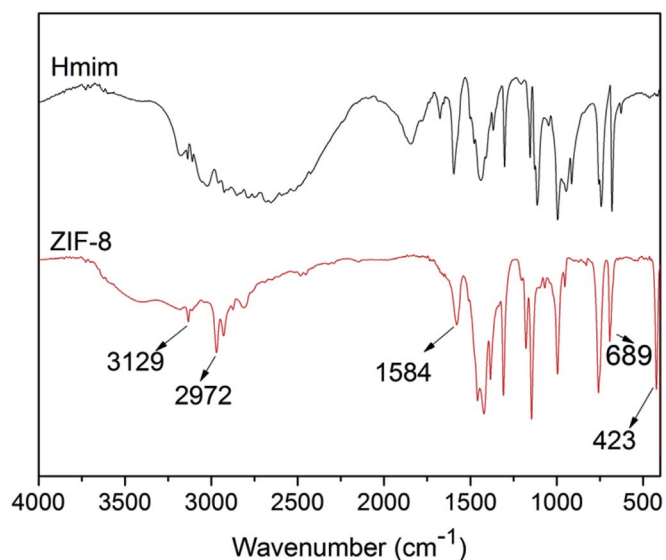


Fig. 1. FT-IR spectra of the as-synthesized ZIF-8.

Zn]) was offered by Changzhou Jia Ren Wo Chemical Company. Di (2-ethylhexyl) terephthalate (DOTP) was purchased from Shanghai Aladdin Industrial corporation, China. $CaSt_2$ and $ZnSt_2$ were purchased from Shandong Huike Additives Co., Ltd., China. Polyvinyl chloride (PVC, S-1000) was supplied by Shandong Qilu Co., Ltd., China. C36DA-Ca and C36DA-Zn were homemade [24]. All reagents and solvents were used as received.

2.2. Synthesis

2.2.1. Synthesis of ZIF-8

ZIF-8 was synthesized as described elsewhere [25,26]. In a typical process, 5.94 g of zinc nitrate hexahydrate (0.02 mol) was dissolved in 30 mL of deionized water. At the same time, 3.28 g of 2-MeIM (0.04 mol) was dissolved in 37.6 g of NH_4OH solution (0.64 mol NH_3). Then zinc nitrate and 2-MeIM solutions were mixed together. The final synthesis solution had a Zn: 2-MeIM: NH_3 : H_2O molar composition of 1: 2: 32: 157. After stirring for 30 min at room temperature ($25^\circ C$), the crystallization was completed. The product was collected by centrifugation and washing with deionized water several times until the final product had pH value of 7, then dried at $80^\circ C$ overnight. Finally, ZIF-8 was obtained as a white solid (yield: 83.18%) [25,26].

2.3. Preparation of PVC films

For comparison, commercial $CaSt_2/ZnSt_2$, LTS-Ca/Zn, C36DA-Ca/C36DA-Zn stabilizers were chosen as control. 100 g PVC, 50 g DOTP, 3.6 g thermal stabilizers (3.6 pph based on resin) were milled into a homogeneous film using a Haake torque rheometer at $160^\circ C$ for 5 min.

2.4. Characterization of ZIF-8

The Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet iS10 FT-IR (Nicolet Instrument Corp., USA) infrared spectrophotometer by KBr disc method.

The metal (Ca and Zn) content of the thermal stabilizer was measured using an Optima 7000 inductively coupled plasma atomic emission spectrometer (ICP-AES) (PerkinElmer, America).

X-ray diffraction (XRD) patterns were recorded on Y-4Q X-ray power diffractometer (Shimadzu 6000) with $Cu K\alpha$ radiation (40 mA and 40 kV) at a scan rate of $2^\circ/min$ with a step size of 0.02° .

Scanning electron microscopy (SEM) images were obtained by using a FEI-NOVA Nano SEM 450 scanning electron microscope operated at 5

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