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# Influence of acid and alkali pre-treatments on thermal degradation behaviour of polyisocyanurate foam and its carbon morphology

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ABSTRACT

The thermal degradation of polyisocyanurate foam samples were studied by TG/DTA, FTIR, and SEM. All samples with different isocyanate index (NCO/OH = 100, 200, 300) were pre-treated by $H_2SO_4$, $K_2CO_3$, and NaOH before heating. The measurements of DTG and DTA presented corresponding variability for different acidic and alkaline treatments. The activation energy of thermal decomposition was calculated based on kinetic reaction evaluation. The pronounced polyol and isocyanate regenerations were observed over degradation. Further FTIR measurements at elevated temperatures suggested the possibility of acidic hydrogen bonding catalyzation and alkaline reversible amide regeneration during degradation by chemical treatments. The morphology and growth mechanism of localized corrosion and microcrystallization were characterized based on SEM micrographs.

## 1. Introduction

Polyisocyanurate (PIR) is an extraordinary type of rigid polyurethane foams (PUR) derived from stoichiometric excessiveness of isocyanate over polyol which can be characterized by parameter of isocyanate index (NCO/OH > 100). This material is typically used as fire resistant thermal insulation barrier attributable to its high efficient charring from thermal stable homocyclized isocyanurate trimer structures. The trimerized ring structure was reported to be able to decompose at higher temperature range from 300 to 325 °C with approximate char yield of 30% [1]. The homogenous carbonaceous structure of generated char layer can provide effective protection against thermal degeneration into gaseous pyrolyzates and shield the underlying substrate from further burning oxidation.

Polyurethane carbonizations have been widely studied based on thermogravimetry (TG) measured weight loss over thermal degradation [2,3] which can be instrumental to understanding thermodynamics from differential kinetics evaluation but not informative about the decomposition mechanism. To better understand the carbonization evolvement, instrument aided analyses on both solid remains and gaseous release need to be performed. Therefore, in-situ FTIR has been employed to monitor the carbonization progression by analysing the functional groups changes in carbonaceous residues [4,5]. GC-MS measurements can also provide clues on chemical composition of released volatile gaseous pyrolyzates from dehydration and scission [6,7]. Nonetheless, these analyses are often complicated by formulation variability for different commercial applications [8–10]. Furthermore, the morphology characterizations of carbonaceous residues are rarely reported in polyurethane thermal degradation research. Only few studies show carbon microporous morphology with few details on formulation impact on carbonization. For instance, Einhorn et al. [1] reported a visual inspection on cell skeletons morphology of polyisocyanurate foam oxidative degradation at elevated temperature. Branca et al. [11] reported morphological changes of rigid polyurethane foams exposed in thermal radiation. But these are not sufficient to support polyurethane carbonization mechanism in heating.

Studies have shown polyurethane decomposition scheme contains three stages: primary stage of polyurethane depolymerization and polyol/isocyanate regeneration, secondary stage of

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dehydration producing water and carbon dioxide, and tertiary stage of small molecule pyrolyzates liberation [12–14]. This three-stage scheme can degenerate into two-stage when the degradation condition changes from oxidative air carbonization to non-oxidative nitrogen pyrolysis. The thermal degradations of polyurethane foam are under the influence of two major constituents – polyol and isocyanate. The isocyanate index (NCO/OH ratio) can dictate the functionality of derived carbons which can provide a potential use for electrochemical supercapacitors. Furthermore, the activation of chemical pre-treatment on foam precursors can have further extensive impact on thermal degradation and create carbons as expected. Usually the chemicals being used for activation are strong acid and base, or salt [15] which can promote the carbon porosity and make carbonization easy to proceed at lower temperature with less time exposure.

The purpose of this study is to understand the thermal degradation and carbonization performance of polyisocyanurate foams under condition of chemical activation. The test samples with different isocyanate index were selected in order to better understand if there are any positive or negative impacts the isocyanate excessiveness could have bring to. The pyrolysis processes were progressively monitored by thermogravimetric and thermodynamic measurements. The chemical function variability was investigated by FTIR at elevated temperature. Carbon morphology was also characterized to provide understanding on acidic and alkaline effectiveness on carbonization.

## 2. Materials and methods

### 2.1. Materials

The polyisocyanurate foam samples (PUR100, PIR200, PIR300) with different isocyanate index (NCO/OH = 100, 200, 300) were supplied by Stepan China (Table 1). The flame retardants were removed deliberately from generic formulation to eliminate the negative distraction of extra thermal resistance on thermal degradation measurement. Usually TCPP and DMMP are two commonly used flame retardants in rigid polyurethane foam formulation. Both of them are phosphate and phosphonate complexes which can produce charring intumescent to insulate further oxidation during carbonization. They are considered to create inflated amorphous carbonaceous layer on surface from burning that will affect the evaluation on isocyanate impact. Furthermore, to mitigate other possible impacts such as crosslink degree, the foam core densities were kept constant at 42 kg/m$^3$ for all test samples. The isocyanate parts by weight (pbw) were calculated directly from the index. Sulfuric acid ($H_2SO_4$), potassium carbonate ($K_2CO_3$), and sodium hydroxide (NaOH) were selected as activation chemicals for pre-treatment. All chemicals were diluted in deionized water and made into solutions of pH = 1, pH = 11, and pH = 13 respectively. The test foam samples were impregnated by these three solutions for 3 h and then dried at room temperature for 48 h.

### 2.2. Methods

TG weight loss measurements were performed on SII TG/DTA 6300 (SII Nano Technology Inc) with elevating temperature from 25 °C to 1000 °C at heating rate 10 °C/min under a nitrogen flow at 200 ml/min. The sample weights were constant at 5 mg. The weight loss rate was calculated by differential thermogravimetry (DTG). The temperature differences between the sample and reference during tests were also recorded by differential thermal analysis (DTA) which can transform heat into electropotenital signals. The morphological characterizations were performed by SEM Sigma VP ZEISS with magnifications 100X, 500X and 3.00 KX on carbonized samples at two different temperatures (450 °C and 700 °C) under nitrogen flows. FTIR spectrum analyses were conducted by Brucker Vertex 70 with ATR platform. The measurement temperatures were set at the maximum and minimum weight loss points from DTG measurements. All carbonized samples were heated at 40 °C for 24 h before measurement to remove possible water hydration.

## 3. Results and discussion

### 3.1. Thermogravimetry

The typical two-stage nitrogen thermal degradation of polyurethane was observed as potentially escalating to obscure three-stage degradation with different slopes (~350–550 °C) under chemical pre-treatment. In non-activated nitrogen pyrolysis (Fig. 1A), the typical two-stage polyurethane thermal degradation was obtained which suggests the reactions of primary depolymerization and continuous dehydration with combination of regenerated isocyanates [5]. For all the three activated samples, $H_2SO_4$ treatment (Fig. 1B) presents the steepest descent compared with the remaining two indicating the most aggressive carbonization. This was followed by NaOH treatment (Fig. 1D) with a reduction in descent, while $K_2CO_3$ treatment presented the least thermolysis among the three. Furthermore, the samples with higher isocyanate index treated with $H_2SO_4$ (PIR300 in Fig. 1B) presented some remarkable three-stage degradation during temperature rise, which was an indication to the carbonization in air at almost the same temperature ranges for each stage. This suggests more volatile small molecules release from the carbonization under activation by $H_2SO_4$ for polyisocyanurates with increasing isocyanates. The samples pre-treated by $K_2CO_3$ and NaOH exhibited obscure three-stage with light slide shoulder slightly different from non-activation (Fig. 1C/1D).

There are significant discrepancies between all three chemical treatments from DTG measurements from previous studies. Usually rigid polyurethane foams display immediate sharp weight loss when the heating starts which is attributable to vaporization of blowing agents. In this study, the blowing agent being used to produce foam samples is hydrochloroflurocarbonate (HCFC-141b) which has boiling point of 32 °C. Nonetheless, the cell gas is a

**Table 1**
Generic formulations for test samples.

| Materials | Chemical | PUR100 | PIR200 | PIR300 |
|---|---|---|---|---|
| Polyol | Phthalate Polyester | 100 | 100 | 100 |
| Isocyanate | p-MDI | 65 | 131 | 184 |
| Amine Catalyst 1 | Cyclohexylamine | 0.1 | 0.1 | 0.1 |
| Metal Catalyst 2 | Potassium Caprylate | 1.2 | 1.2 | 1.2 |
| Surfactant | Siloxane | 2 | 2 | 2 |
| Blowing agent | Hydrochloroflurocarbonate | 14 | 22 | 22 |
| Water | – | 0.6 | 0.6 | 0.6 |
| Core Density (kg/cm$^3$) | | 42 | 42 | 42 |