

Thermal Degradation Behavior and Stability Assessment of EPDM

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1. Introduction

Non-metallic materials used in nuclear power plants (NPPs) are exposed to temperatures of approximately 40–60°C inside the containment building under normal operating conditions. Additionally, during accident environments such as design basis event (DBE), including loss of coolant scenarios, these materials are exposed to high temperatures. This environment can lead to thermal degradation of non-metallic materials, potentially affecting the functionality of safety-related components. As a result, the degradation of non-metallic materials used in safety-related equipment, such as cable jackets, insulation, and seals, can impact the integrity of the NPP.[1]

Ethylene propylene diene monomer (EPDM) is commonly used as insulation or a jacket for cables. Thermal degradation of EPDM can lead to hardening, cracking, and loss of elasticity, which may compromise the performance of components. Thus, understanding the thermal degradation behavior of EPDM is important. However, research on the thermal degradation behavior of EPDM is relatively insufficient compared to structural materials. In particular, mechanistic studies on degradation behavior in high temperature environments are important for qualifying the functionality of safety-related equipment. [2]

Therefore, this study investigates the thermal degradation and thermal stability of EPDM using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).[3]

2. Experimental

2.1 Thermal analysis

TGA was performed according to ASTM E1131 to evaluate the thermal stability, decomposition behavior, and volatile content of non-metallic materials. EPDM samples were finely ground into ~10 mg powders to optimize thermal contact and measurement accuracy. The temperature was increased from room temperature to 900°C at 10°C/min to balance thermal resolution and experiment duration. High-purity nitrogen gas was used to maintain an inert atmosphere and prevent oxidation. Key thermal parameters, including onset decomposition temperature, maximum decomposition rate, and residual mass at 900°C, were recorded. DSC analysis was

conducted from room temperature to approximately 900°C under a nitrogen atmosphere with a heating rate of 10°C/min.[4]

2.2 Fourier transformed infrared spectroscopy

Fourier-transform infrared (FT-IR) spectroscopy was performed following ISO 4650 and ASTM E1252 to analyze the chemical structure and degradation of selected non-metallic materials. The spectral range was set to 600–4000 cm⁻¹ to identify potential structural modifications, with a resolution of 4 cm⁻¹. The analysis was conducted in attenuated total reflection (ATR) mode using a Ge crystal plate.[5]

2.3 Element analysis

Elemental analysis (EA) was conducted in accordance with ASTM D5291 to determine the carbon, hydrogen, and nitrogen composition of the samples with high precision. This method utilizes a high-temperature combustion process to completely oxidize the sample in an oxygen-rich atmosphere, converting its elemental components into gaseous species CO₂ for carbon, H₂O for hydrogen, and N₂ for nitrogen. The evolved gases were then directed through a drying and purification system to remove potential interferences before being analyzed using gas chromatography (GC). Separation of the gas-phase species was achieved based on their retention times, and quantification was performed using a thermal conductivity detector (TCD), which measures changes in thermal conductivity relative to a reference gas.

3. Results & Discussion

In Stage I, from room temperature to approximately 400°C, a gradual weight loss is observed due to the volatilization of additives present in EPDM, such as water, plasticizers, and oils. Plasticizers, which possess polarity, increase the intermolecular distance between polymer molecules, thereby reducing intermolecular forces. This reduction in intermolecular forces enhances the flexibility of the material, processability, which is the reason plasticizers are commonly added. However, the volatilization of plasticizers increases intermolecular forces and may accelerate crosslinking. Thermal energy is supplied to the EPDM molecules, chemical bonds undergo the process of scission of chemical bonds and generating free radicals. These structures abstract hydrogen atoms from other molecules, accelerating cleavage or combined with other structure. The increased intermolecular forces caused by plasticizer volatilization could further accelerate crosslinking. This crosslinking phenomenon observed in DSC heat flow curve as a low-intensity exothermic peak. However, as the temperature increases, some crosslinked bonds break, increasing molecular mobility, as a result, an endothermic reaction occurs. This endothermic reaction occurs because the partial breakdown of the crosslinked structure allows molecules to move freely, requiring more energy. Additionally, initial thermal decomposition within the polymer chain, where some chemical bonds are cleaved, may contribute to endothermic reactions. Unsaturated bonds (C=C) or hydrocarbon (CH) bonds within the EPDM monomer structure absorb thermal energy and cleave, resulting in an endothermic reaction.

In Stage II, at approximately 460–470°C, thermal decomposition occurs in the main chain of EPDM. TGA results show the major weight loss in this stage, and derivative thermogravimetry (DTG) curve indicates the highest weight loss rate at 469.9°C. This thermal decomposition involves cleavage of the main chain, resulting in an exothermic reaction in the DSC curve. However, as the decomposed fragments interact with atmospheric oxygen, an endothermic reaction peak appears due to oxidation. The decomposition of EPDM main chain leads to the breakdown of organic compounds into CO₂, H₂O, methane, ethane, and other gaseous products, which are subsequently evaporated. Therefore, most significant and rapid weight loss is observed at this stage.

In Stage III, beyond 500°C, where the weight change is relatively minor, the oxidation of char or fillers, such as carbon black, occurs. A gradual weight loss continues, ultimately leading to the complete combustion of all organic components. The combustion of char or fillers appears as an endothermic reaction at approximately 826°C. Subsequently, inorganic additives such as ZnO, SiO₂, and CaCO₃ undergo thermal decomposition and phase transitions. Additionally, at high temperatures,

char undergoes structural modifications, leading to graphitization, which results in an exothermic reaction.

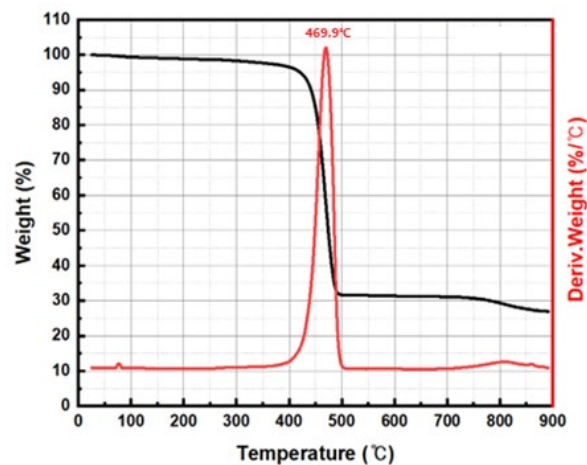


Fig. 1. Thermogravimetric analysis (TGA) and 1st derivative weight loss curves of EPDM

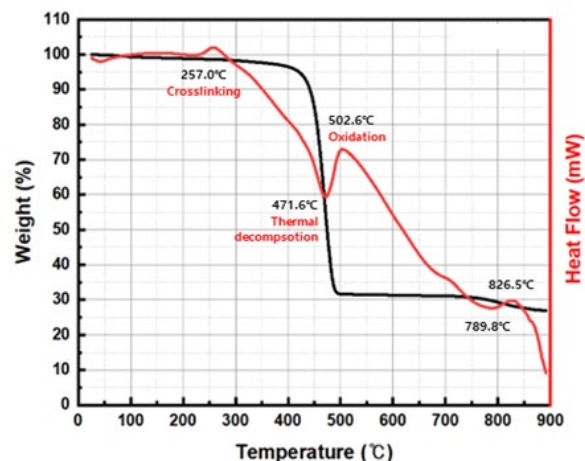


Fig. 2. Thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) Analysis of EPDM

For EPDM, characteristic absorption peaks were observed at 719 cm⁻¹ (CH₂ bending vibration), 1375 cm⁻¹ (CH₃ bending), and 1463 cm⁻¹ (CH₂ bending). Strong stretching vibrations of CH₂ and CH₃ groups were also detected at 2850 cm⁻¹ and 2919 cm⁻¹, confirming that the polymer backbone structure is shown in Figure 3.

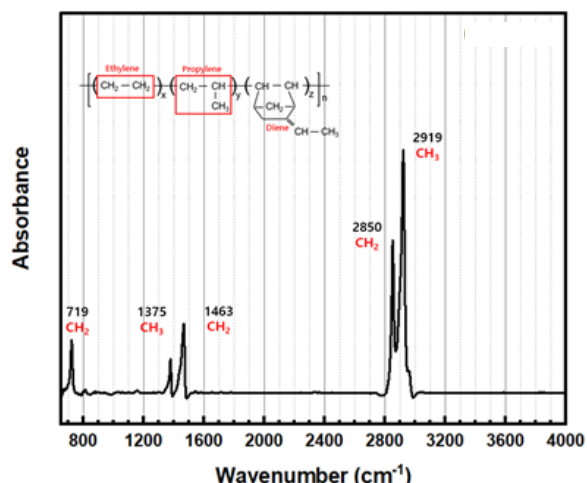


Fig. 3. FT-IR spectral analysis results and chemical bond structures

Table. 1. Elemental analysis results (Carbon, Hydrogen, Nitrogen, and Oxygen) of EPDM

Element	Composition(wt.%)
Nitrogen	5.16
Carbon	80.31
Hydrogen	6.49
Oxygen	3.85

As shown in Table 1, the high carbon content of EPDM is attributed to CH, CH₂, and CH₃ groups, as well as the added carbon black. Additionally, a small amount of oxygen, presumed to originate from plasticizers and other additives, was also analyzed.

Characteristic FT-IR absorption peaks of EPDM appeared at 719 cm⁻¹ (CH₂ bending vibration), 1375 cm⁻¹ (CH₃ bending vibration), 1463 cm⁻¹ (CH₂ bending vibration), and strong stretching vibrations at 2850 cm⁻¹ and 2919 cm⁻¹ (CH, CH₂, and CH₃ groups). These peaks confirm the hydrocarbon polymer structure (CH, CH₂, CH₃) of EPDM, along with the presence of added carbon black. Such characteristic absorption peaks serve as important references for identifying the chemical structure of EPDM and evaluating its initial structural properties prior to thermal degradation.

4. Conclusions

In Stage I (room temperature to ~400°C), volatilization of plasticizers increases intermolecular forces in EPDM, and thermal energy causes chemical bond scission generating radicals that initiate additional crosslinking reactions, initially reflected as a low-intensity exothermic peak in DSC results, followed by partial breakdown of crosslinked structures. In Stage II (460–470°C), EPDM main polymer chains undergo significant thermal decomposition, releasing gases such

as CO₂, H₂O, methane, and ethane, characterized by substantial weight loss and both exothermic and endothermic reactions due to oxidation. In Stage III (above 500°C), oxidation of residual fillers such as char or carbon black occurs, resulting in gradual weight loss and ultimately complete combustion of organic materials.

To ensure the integrity of EPDM, it is essential to conduct in-depth studies on its thermal degradation mechanism or thermal decomposition behavior. Additionally, future analyses of EPDM subjected to thermal degradation under various environmental conditions are necessary to establish a comprehensive database on material degradation.

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