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Study on Multiphase Pyrolysis Kinetics and Fire Early Warning Characteristics of Cable Sheaths and Insulating Layers

Yujie YIN¹, Lei Lei* Zeyu Wang²

Abstract: This study overcomes a limitation of single-material thermal analysis—which cannot resolve the interdependent, multi-phase degradation of multilayered cables under fire—by integrating STA–FTIR with two model-free kinetic methods (KAS and FWO). This enables mechanistic insight into how graded filler concentrations—low (PVC), medium (ZR-YJLV), and high (N-BV)—govern pyrolytic failure and volatile emissions across outer sheaths and inner XLPE insulation. Kinetic analysis shows filler loading controls apparent activation energy E_a during primary decomposition: E_a decreases from 208.53 kJ/mol (PVC) to 114.0 kJ/mol (ZR-YJLV) and 91.53 kJ/mol (N-BV), confirming a progressive inert dilution effect where dense mineral fillers disrupt polymer continuity and impair thermal homogeneity. N-BV exhibits an E_a increase to 160.96 kJ/mol in the final stage due to endothermic sintering of metal oxides into a refractory ceramic phase. FTIR gas profiling reveals a concentration-dependent suppression: medium–high fillers rely on H₂O vapor for gas-phase dilution; ultra-high fillers form a low-permeability ceramic char barrier that impedes volatile diffusion, reducing CH₄ emissions by over two orders of magnitude. By Integrating these hierarchical inhibition mechanisms and the intrinsic vulnerability of XLPE, established a two-tier early-warning paradigm: Tier I (270–310 °C; HCl and CO) signals sheath degradation; Tier II (450 °C; CH₄, C₂H₄, C₂H₂) marks XLPE breakdown. This framework provides a defensible basis for fire monitoring in urban utility tunnels.

Keyword: Tunnel Cable;STA-FTIR;Pyrolysis Characteristics;Thermodynamic Analysis

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1 Introduction

The ignition and flame spread dynamics of power cables are governed by the thermochemical behavior of insulation and sheath materials under elevated temperatures; unchecked incipient combustion poses a high risk of rapid transition to flashover or structural collapse. Cable fire safety thus integrates electrical insulation performance with essential attributes like flame retardancy and thermal stability. A mechanistically grounded understanding of thermal degradation is fundamental for designing early-warning protocols. Recently, foundational studies by Su et al. utilized TG-FTIR-GC/MS to characterize the pyrolysis kinetics and gas evolution of flame-retardant PVC and PE [1].

Building upon these basic kinetic profiles, researchers have focused on capturing early indicators of thermal failure. Chen et al. analyzed the temperature- and time-resolved gas release from overheated PVC outer jackets, identifying critical volatile markers that emerge prior to macroscopic ignition [2]. To quantify the energy barriers of such degradation, Pan et al. applied model-free kinetic methods to typical high-voltage power cables, confirming that primary mass loss stems from initial backbone cleavage [3]. To further protect cable structures from these intense thermal threats, the application of passive physical barriers has been widely explored. Tang et al. detailed the flame-retardant mechanisms of intumescent fireproof coatings, which form robust carbonaceous layers to shield underlying materials in tunnel environments [4]. Concurrently, the internal insulation layers must maintain their integrity; however, Sun et al. demonstrated that thermal pre-aging significantly accelerates the microstructural degradation and electrical breakdown of XLPE insulation [5]. Translating these thermal vulnerabilities into system-wide safety strategies requires comprehensive macro-scale evaluations. Bai et al. proposed a risk assessment model for dense urban cable channels based on fuzzy mathematics to quantify operational hazards [6]. To improve the precision of such macro-models, a deeper micro-scale understanding of specific pyrolytic reactions is necessary. For example, Meng et al. elucidated the migration and transformation mechanism of chlorine during PVC pyrolysis, highlighting the role of structural defects [7]. Furthermore, He et al. employed molecular dynamics simulations to reveal the complex pyrolytic behavior of polyethylene cable sheaths when subjected to external electric fields [8]. The modulation of these multiphase degradation pathways via the addition of inorganic flame retardants remains a focal point for material optimization. Wu et al. demonstrated that inorganic fillers not only enhance basic thermal stability but also promote the formation of robust ceramic char layers that physically impede heat transfer [9]. Integrating these micro-kinetic and material insights eventually enables the development of highly sensitive, multi-parameter fire hazard detection systems for power cable tunnels, as recently conceptualized by Fu et al. [10].

Although prior research has advanced the understanding of thermal decomposition in individual cable polymers, the prevailing experimental paradigm remains reductionist, focusing on single-component systems and overlooking the compositional modulation of inorganic filler concentration gradients on multiphase pyrolysis thermodynamics and kinetics. In multilayer cables such as ZR-YJLV, three knowledge gaps persist: (i) the absence of a quantitative comparison between degradation kinetics of filler-tuned outer sheaths and thermally robust XLPE insulation under fire-relevant heating conditions; (ii) insufficient insight into how apparent activation energy evolves across reaction regimes and how diagnostic gas species emerge as a function of filler content and thermal history; and (iii) a lack of integrated structure–property–response relationships linking filler-driven microstructural evolution to gas-phase signatures and kinetic barrier shifts. These limitations constrain tunnel cable fire monitoring systems to binary, single-threshold alarm logic, hindering predictive,

multi-parameter early warning architectures. To bridge these gaps, this study systematically compares four materials: conventional PVC sheath, flame-retardant ZR-YJLV sheath (moderate $\text{Mg}(\text{OH})_2/\text{Al}(\text{OH})_3$ loading), fire-resistant N-BV sheath (high filler content), and ZR-YJLV XLPE insulation core. Samples undergo non-isothermal pyrolysis via STA–FTIR at heating rates of 5–20 K/min under nitrogen. Apparent activation energies are determined at 10%–90% conversion using the KAS and FWO methods, ensuring statistical robustness and cross-method consistency.

2 Methods and Materials

2.1 Materials

This study systematically selected four representative cable polymeric materials as model systems: (i) the flame-retardant polyolefin outer sheath of ZR-YJLV cables; (ii) the cross-linked polyethylene (XLPE) insulation layer of ZR-YJLV cables; (iii) the fire-resistant mineral-insulated sheath of N-BV cables; and (iv) the moisture-resistant plasticized PVC outer sheath. Material selection strictly adheres to the functional performance requirements stipulated in two national standards: *Code for Design of Cables in Electric Power Engineering* (GB 50217–2018) [11], which mandates enhanced flame retardancy and thermal stability for cables deployed in confined spaces (e.g., tunnels) and critical emergency circuits; and *Technical Code for Urban Utility Tunnel Engineering* (GB 50838–2015) [12], which specifies stringent moisture resistance and long-term thermal endurance for cables installed in high-humidity underground infrastructure. Sample preparation followed a rigorously controlled protocol: each material was mechanically stripped from its respective cable core under ambient conditions; subsequently, homogenized using a cryogenic ball mill to achieve a uniform particle size distribution with a $D_{90} < 0.2$ mm; and finally dried at 60 °C under a nitrogen purge for 24 h to remove residual moisture and volatiles, ensuring compositional integrity and experimental reproducibility.

2.2 TG-FTIR

Thermogravimetric analyses were conducted on four test specimens: ZR-YJLV outer sheath powder, ZR-YJLV insulating powder, PVC outer sheath powder, and N-BV outer sheath powder. All tests were performed in an air atmosphere, over a temperature range from 30 to 800 °C, employing heating rates of 10, 15, 20, and 25 °C/min.

Figure 1 illustrates the schematic workflow and analytical outputs of the integrated TG-FTIR hyphenated system used in this study. The experimental process commences within the Thermogravimetric Analysis (TGA) module, where a sample undergoes controlled thermal degradation within a microbalance furnace continuously purged by a carrier gas. The evolved volatile products are dynamically swept through a temperature-regulated heated transfer line—specifically configured with heating elements and sensors to prevent premature gas condensation—directly into the optical gas cell of the Fourier Transform Infrared (FTIR) spectrometer for real-time chemical detection. This synchronized hardware configuration generates three comprehensive sets of analytical results: macroscopic TG/DTG curves detailing temperature-dependent mass loss and degradation rates; pyrolysis kinetic profiles mapping the evolution of apparent activation energy across different conversion stages; and time-resolved 3D FTIR surface graphs that provide a continuous, multi-dimensional footprint of the specific pyrolytic gases released during thermal decomposition..

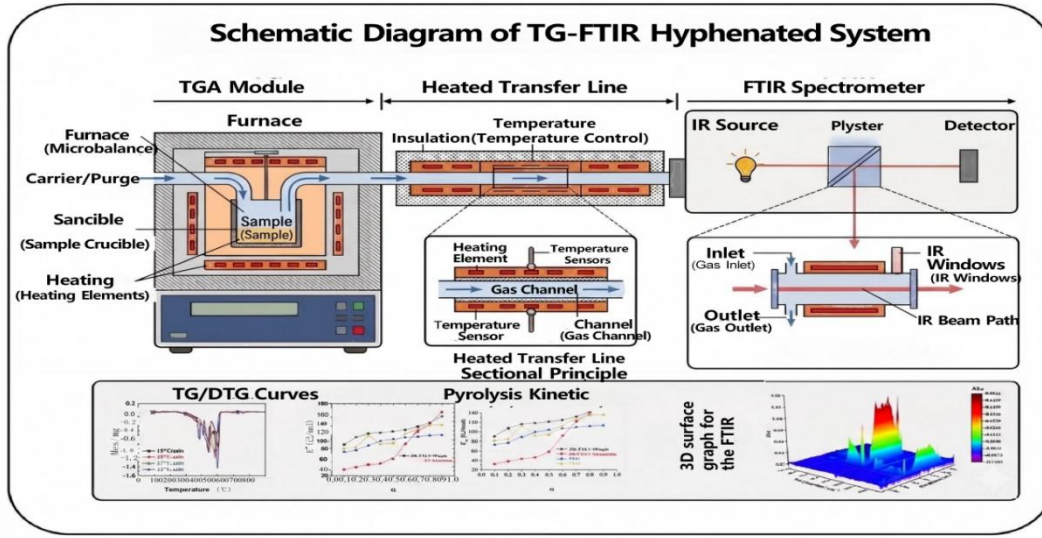


Figure. 1. Schematic diagram of the TG-FTIR experimental setup.

2.3 Dynamic method

Kinetic analysis constitutes a quantitative framework for modeling the time-temperature-composition evolution of thermally driven reactions [21]. For solid polymeric materials, thermal decomposition kinetics are rigorously described by the kinetic triplet: the apparent activation energy E_a , the reaction model function $f(a)$, and the pre-exponential factor A . E_a represents the minimum energetic threshold required to initiate molecular-scale bond dissociation or conformational reorganization—directly correlating with intrinsic thermal robustness and governing the temperature sensitivity of

degradation onset. As formalized in $\frac{da}{dt} = k(T)f(a)$, $f(a)$ is a dimensionless mathematical function that encodes the mechanistic progression of the solid-phase reaction; its functional form reflects the dominant rate-controlling step—whether it be interfacial nucleation, mass transport limitation, or stochastic chain cleavage—thereby enabling mechanistic discrimination among competing degradation pathways:

$$\frac{da}{dt} = k(T)f(a) \quad (1)$$

where α , k is the $k(T)$ rate constant, and $f(a)$ is the kinetic reaction model. The kinetic models used in this study are all based on recommendations proposed by the Kinetics Committee of the International Confederation for Thermal Analysis

and Calorimetry (ICTAC) for dynamic calculations of thermal analysis data [13]. α and $k(T)$ can be expressed as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (2)$$

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Here, m_0 , m , and m_∞ correspond to the initial sample mass, instantaneous mass during decomposition, and residual mass at completion of thermal degradation, respectively. The pre-exponential factor is denoted by A and R is the molar gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). T represents the absolute temperature at which the reaction proceeds. These kinetic parameters are experimentally determined through controlled non-isothermal thermogravimetric analysis under well-defined heating protocols.

Apparent activation energy E_a for thermally degrading composite systems can be extracted using isoconversional (model-free) kinetic techniques, which eliminate the necessity of postulating a reaction mechanism beforehand. These methods are widely accepted in thermal kinetics for their accuracy, reproducibility, and applicability to complex, multi-step decomposition processes under non-isothermal conditions [14]. Prominent among them are the differential Friedman (FR) method [15] and the integral isoconversional approaches—namely, the Flynn–Wall–Ozawa (FWO) [16,17], Kissinger–Akahira–Sunose (KAS) [18,19], and Starink (ST) [20] models—all of which have been rigorously benchmarked across diverse polymeric and inorganic materials. In this investigation, the FWO and KAS methods were selected for parallel analysis to ensure consistency and minimize methodological bias; their mathematical formulations are provided below:

$$\ln \beta = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - 5.3305 - 1.052 \frac{E_a}{RT_\alpha} \quad (4)$$

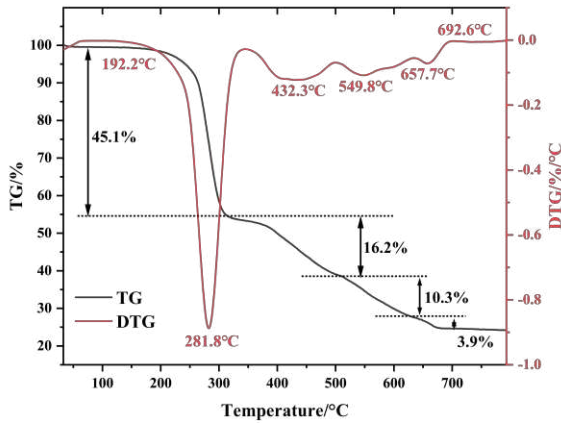
$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT_\alpha} \quad (5)$$

In this formulation, β is the linear heating rate (K/min), T_α is the absolute temperature at which a specific extent of conversion α is reached, A and E_a denote the temperature-independent pre-exponential factor and the apparent activation energy (kJ/mol), respectively, α quantifies the fractional decomposition progress ($0 \leq \alpha \leq 1$), R is the molar gas constant (8.314 J/mol/K), and $g(\alpha)$ corresponds to the integral reaction model function—derived from the differential form $f(a)$ via integration over the conversion domain.

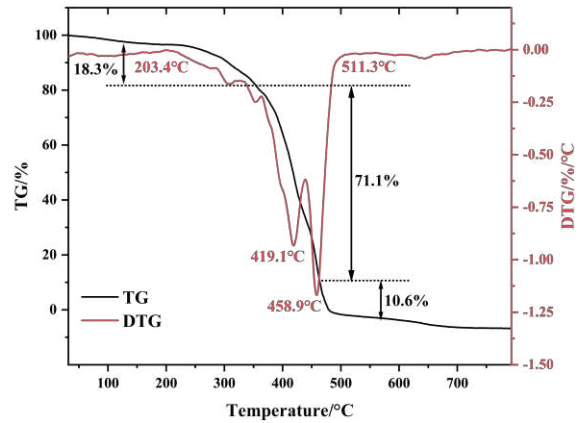
3 Results and Discussion

3.1 Thermogravimetric analysis

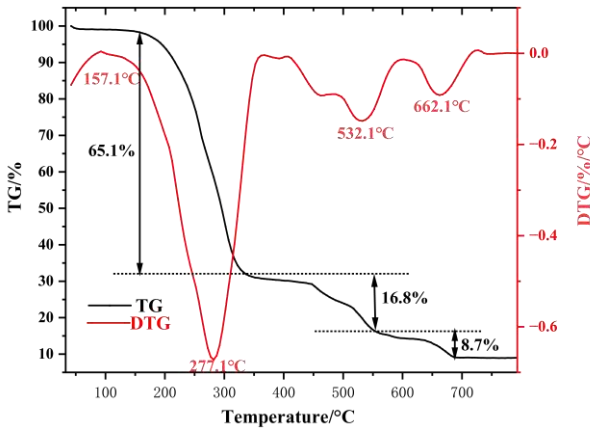
Figures 2 – 4 present the thermogravimetric (TG) and derivative thermogravimetric (DTG) profiles of the insulation layer of ZR-YJLV crosslinked polyethylene cable and three representative outer sheath materials—standard polyvinyl chloride (PVC), flame-retardant ZR-YJLV, and fire-resistant N-BV—recorded under non-isothermal conditions at heating rates of 10, 15, 20, and 25 °C/min. Comparative analysis reveals marked differences in pyrolysis behavior between the insulation core and the outer sheathing layers. The ZR-YJLV insulation exhibits a dominant single-step decomposition process across all heating rates, indicating structural homogeneity and the absence of distinct multi-stage degradation pathways. Specifically, at $\beta = 10$ °C/min, the DTG curve displays an initial low-intensity shoulder peak (weight loss $\approx 18.3\%$) below 300 °C, attributable to the evaporation of plasticizers and low-molecular-weight additives; the principal mass-loss event occurs sharply between 400 and 500 °C, with a maximum rate at 458.9 °C. This high-temperature exothermic degradation stage is mechanistically associated with extensive random scission of the crosslinked aliphatic backbone—a signature of thermal instability onset in crosslinked polyolefins—leading to rapid, concerted depolymerization and substantial structural collapse.



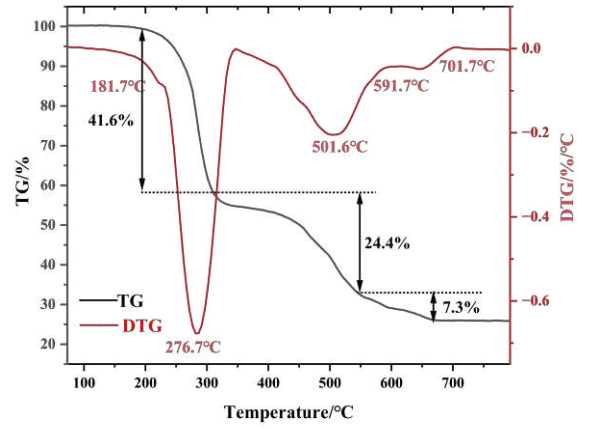
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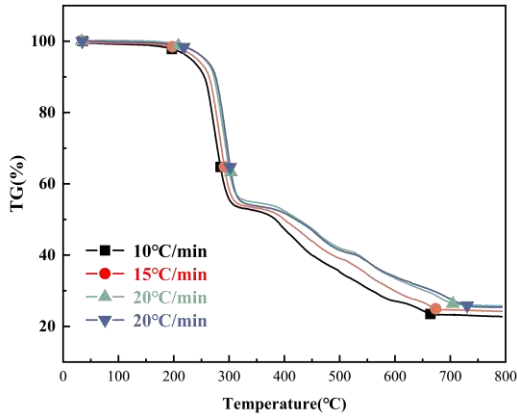


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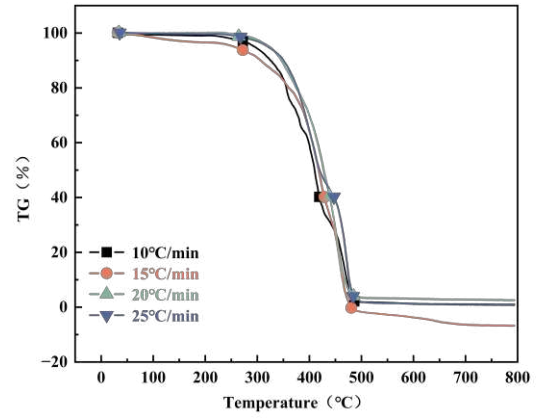


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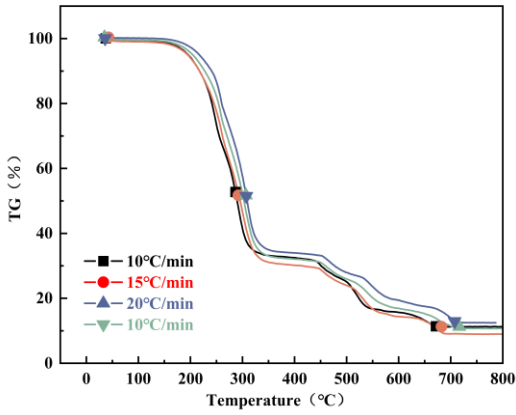
Figure. 2. TG/DTG curves of four cable materials at a heating rate of 15 K/min (a) Outer sheath of ZR-YJLV cable (b) Insulation material of ZR-YJLV cable (c) PVC outer sheath material (d) N-BV outer sheath material.



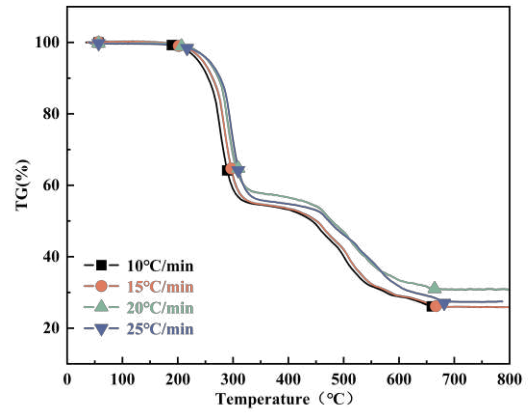
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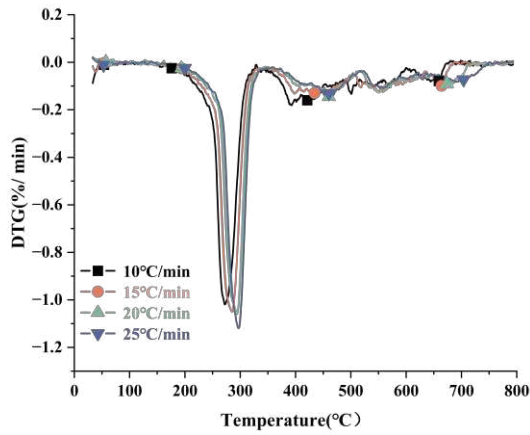


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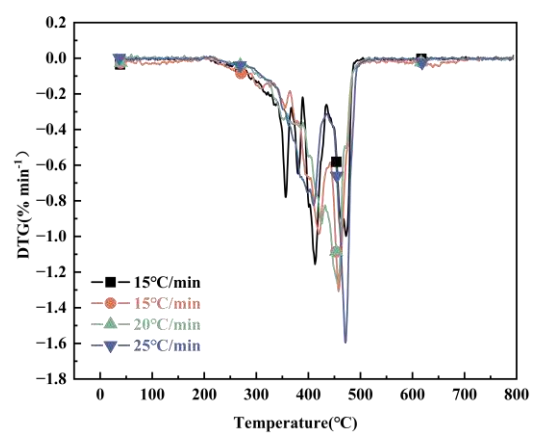


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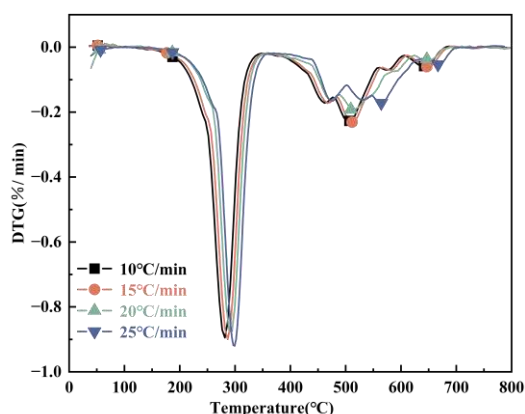
Figure. 3. TG curves of four materials at heating rates $\beta = 10, 15, 20$, and 25 °C/min: (a) ZR-YJLV outer sheath (b) ZR-YJLV insulation layer (c) PVC outer sheath material (d) N-BV outer sheath material.



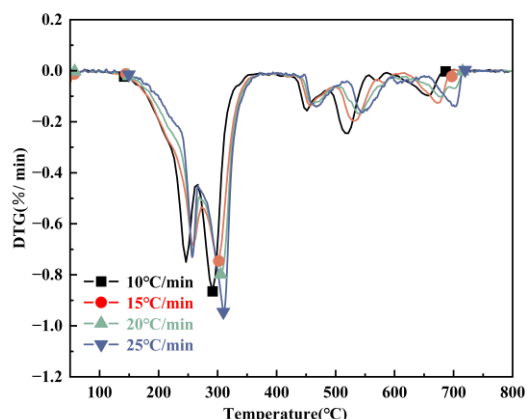
(a)



(b)



(c)



(d)

Figure. 4. DTG curves of four materials at heating rates $\beta = 10, 15, 20$, and 25 °C/min: (a) ZR-YJLV outer sheath (b) ZR-YJLV insulation layer (c) PVC outer sheath material (d) N-BV outer sheath material.

In contrast, all three PVC-based outer sheath materials undergo multi-step thermal degradation, with pronounced inter-material differences primarily manifested in the characteristics of the initial major DTG peak—centered between 270 and 300 °C and predominantly attributable to dehydrochlorination. For the unfilled conventional PVC sheath, the first DTG maximum occurs at 277.1 °C under a heating rate of 10 °C/min, accompanied by an abrupt mass loss of 65.1%, reflecting inherently low thermal resilience during early-stage decomposition. Incorporation of flame-retardant additives—particularly inorganic fillers—systematically modulates the kinetics and extent of this primary degradation event. Both the flame-retardant ZR-YJLV sheath (peak temperature: 281.8 °C) and the fire-resistant N-BV sheath (peak temperature: 276.7 °C) exhibit broader decomposition intervals surrounding the main DTG peak and markedly reduced mass-loss rates in the initial stage compared to conventional PVC. Quantitatively, the first-stage weight loss decreases progressively across the series: conventional PVC (65.1%) > flame-retardant ZR-YJLV (45.1%) > fire-resistant N-BV (41.6%). This trend underscores distinct stabilization mechanisms: the unfilled PVC permits unimpeded volatilization of HCl and low-MW fragments; the ZR-YJLV formulation attenuates gas-phase release through matrix dilution and the formation of transient gas–solid diffusion barriers; whereas the highly loaded N-BV system achieves superior suppression of early gaseous effluents via synergistic effects—including intense physical dilution by refractory fillers, rapid solid-phase sintering, and in situ ceramization that yields a thermally stable, low-permeability char layer.

These results collectively establish that the thermal protection capability of cable outer sheaths is principally governed by the ability of functional fillers to attenuate the reaction intensity during the initial dehydrochlorination-dominated degradation step. Conversely, the subsequent high-temperature decomposition stage—arising from the identical polymeric backbone—shows negligible dependence on filler content; its fundamental pyrolysis mechanism remains unchanged, thereby preserving the characteristic thermochemical degradation profile inherent to the base polymer Pyrolysis kinetics analysis.

The isoconversional (model-free) approach was applied to quantify the apparent activation energy E_a of the cable insulation material across its two principal decomposition stages. Figure 5 displays the evolution of E_a with conversion degree α , computed over the α range of 0.10 – 0.90. This interval was deliberately selected to exclude the initial and final extremes of decomposition, where experimental uncertainties—arising from instrumental noise, baseline drift, and incomplete mass-loss resolution—tend to amplify kinetic parameter errors. Excellent agreement is observed between the E_a profiles derived from the FWO and KAS methods, confirming methodological robustness and obviating the need for differential interpretation.

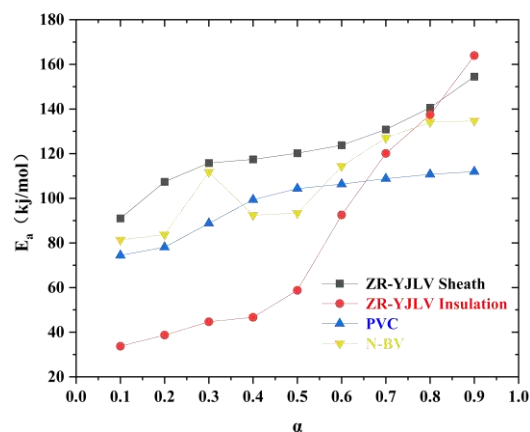
The apparent activation energy E_a exhibits pronounced non-isothermal variation with conversion degree α , deviating markedly from constancy and instead displaying sharp, stepwise transitions at critical α values that demarcate distinct decomposition stages. This dynamic E_a profile provides compelling evidence that the thermal degradation of all four cable materials proceeds not via a single elementary reaction but through heterogeneous, multi-step mechanisms involving concurrent and sequential reaction pathways. Crucially, the α -intervals wherein E_a undergoes abrupt shifts align quantitatively with the characteristic weight-loss segmentation observed in the TG and DTG traces (Figures 2 and 3): each inflection in the E_a curve corresponds precisely to a change in the dominant mass-loss regime. For the three PVC-based outer sheaths—conventional PVC, flame-retardant ZR-YJLV, and fire-resistant N-BV—the principal transition points occur near $\alpha \approx 0.45 - 0.50$ and $\alpha \approx 0.80$. Within the initial interval ($\alpha = 0.10 - 0.50$), degradation is dominated by low-temperature processes: evaporation of plasticizers and stabilizers, dehydrochlorination initiated by C – Cl bond homolysis, or endothermic dehydration of hydrated metal hydroxides. Upon surpassing the first transition ($\alpha > 0.50$), the system enters a mid-temperature regime ($\alpha = 0.50 - 0.80$) characterized by progressive conjugated polyene formation and extensive random scission of the polymer backbone. Finally, in the high-conversion domain ($\alpha > 0.80$), the steep rise and subsequent decline in E_a mirror the high-temperature DTG tail peak, reflecting oxidative consumption of residual carbonaceous char and concurrent refractory filler sintering/ceramization. In stark contrast, the crosslinked polyethylene (XLPE) insulation layer (ZR-YJLV core) displays a singular, uni-modal evolution: it ascends rapidly to a plateau value and remains elevated and narrowly distributed over $\alpha = 0.20 - 0.70$ —a range that coincides exactly with the intense, single-peaked main degradation event in its TG/DTG curves, attributable to concerted cleavage of the crosslinked aliphatic network.

The apparent activation energy E_a distribution curves obtained from the model-free kinetic calculation in Figure 6 quantitatively demonstrate and confirm that the gradient effect of inorganic filler concentration (general PVC < ZR-YJLV < N-BV) in outer sheath systems specifically regulates the pyrolysis kinetics of condensed phases. In the second stage of pyrolysis, the apparent activation energy of the three types of sheath materials exhibits a distinct decreasing trend, following the order: general PVC outer sheath (208.53 kJ/mol) > ZR-YJLV outer sheath (114.07 kJ/mol) > N-BV outer sheath (91.53 kJ/mol). This kinetic differentiation essentially reflects the physical dilution effect and mass transfer phase regulation of the

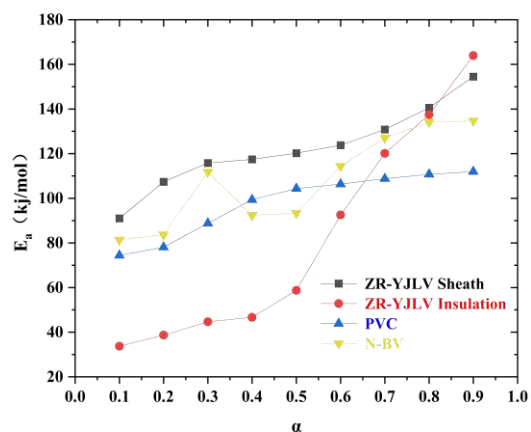
polymer system by inorganic fillers: unmodified PVC requires concentrated dissociation of the conjugated polyene skeleton with high bond energy at high temperatures, exhibiting an extremely high apparent depolymerization energy barrier; as the filling concentration of inorganic mineral fillers increases significantly, the stable solid-phase minerals do not participate in gasification and mass loss, which greatly dilutes the concentration of combustible organic matrix in the reaction region. Moreover, densely distributed inorganic particles divide the continuous degradation of macromolecules into localized microdomain reactions, thereby significantly reducing the apparent energy barrier required for macroscopic total mass loss. In addition, in the third stage of pyrolysis, the apparent activation energy of the N-BV fire-resistant outer sheath with ultra-high filler concentration jumps to 160.96 kJ/mol, which strongly verifies the phase transition mechanism of high-concentration silicate and ceramic-forming fillers at high temperatures, that is, the high energy consumption characteristic that a large amount of inorganic powder overcomes solid-phase migration resistance, undergoes microscopic sintering, and solidifies into a dense ceramized skeleton.

In contrast, the ZR-YJLV cable's insulation layer—composed of cross-linked polyethylene (XLPE)—functions as the protected core and displays a unimodal kinetic profile characterized by an initial increase followed by a subsequent decrease in activation energy. This behavior stems from the thermal stability conferred by its highly saturated, cross-linked aliphatic C - C backbone, which yields a peak activation energy of 115.33 kJ/mol during the second stage (i.e., the primary pyrolysis phase). However, upon exceeding the depolymerization threshold, extensive random chain scission occurs across the macromolecular network. Owing to the lack of a condensation-phase carbon retention mechanism—and consequently, no substantial char formation—the activation energy declines sharply to 94.90 kJ/mol in the third stage, reflecting kinetic destabilization and structural collapse following the breakdown of the thermal barrier.

The staged evolution of apparent activation energy with conversion not only represents the difficulty of chemical bond cleavage but also accurately quantifies the complete kinetic evolution law of the material transition. from homogeneous chain scission depolymerization of the pure polymer matrix to physical barriers of high-filled multiphase systems and high-temperature solid-phase sintering of inorganic residues dominated by inorganic filler concentration gradients; these staged energy barriers and critical decomposition thresholds reshaped by different filler concentrations directly determine the temperature and kinetic response rate of thermal degradation and characteristic volatile release in each protective layer of cables.

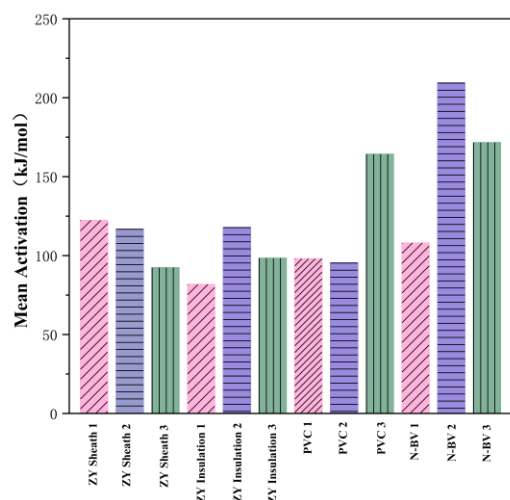


(a)

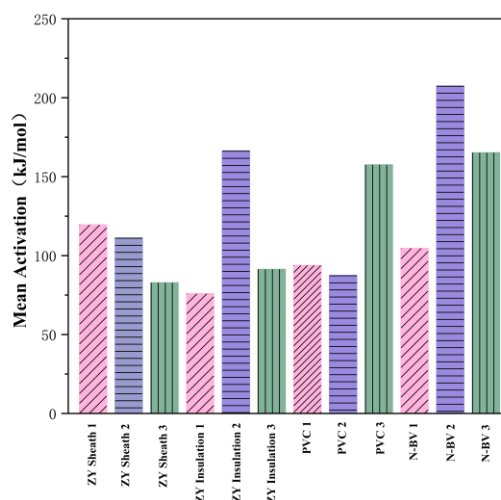


(b)

Figure. 5. Relationship between activation energy and conversion rate during the pyrolysis of ZR-YJLV sheath, ZR-YJLV insulation, PVC, and N-BV determined (a) FWO method (b) KAS method.



(a)



(b)

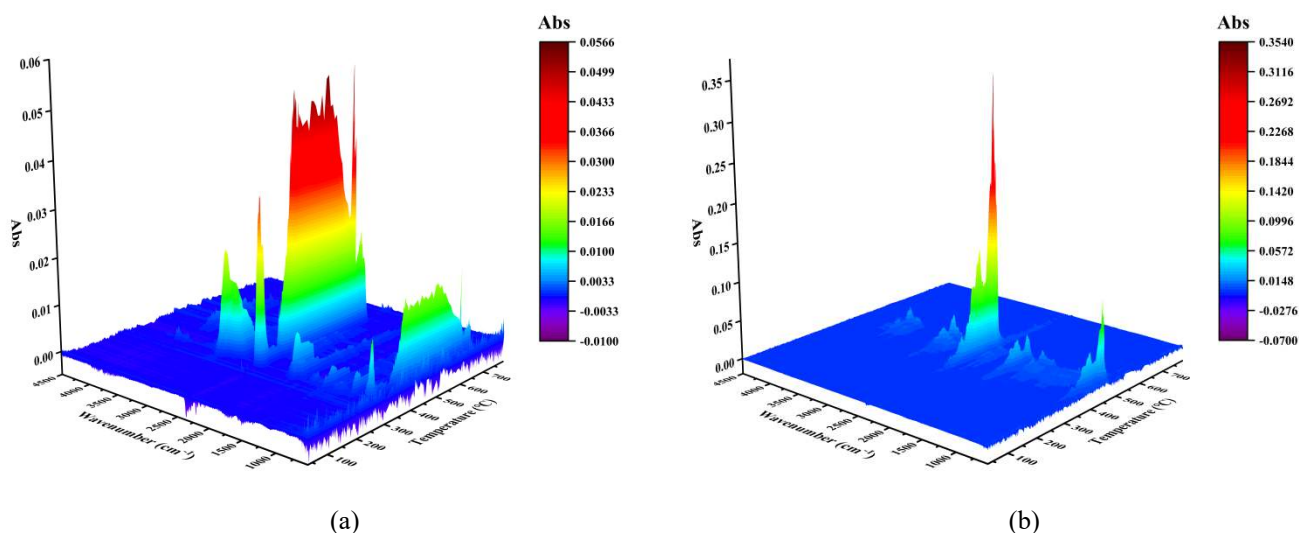
Figure. 6. Average activation energy values calculated via model-free methods: (a) FWO method; (b) KAS method. Wherein: ZV Sheath 1: the first stage of ZR-YJLV outer sheath; ZV Sheath 2: the second stage of ZR-YJLV outer sheath; ZV Sheath 3: the third stage of ZR-YJLV outer sheath; ZV Insulation 1: the first stage of ZR-YJLV insulation layer; ZV Insulation 2: the second stage of ZR-YJLV insulation layer; ZV Insulation 3: the third stage of ZR-YJLV insulation layer; PVC 1: the first stage of PVC outer sheath; PVC 2: the second stage of PVC outer sheath; PVC 3: the third stage of PVC

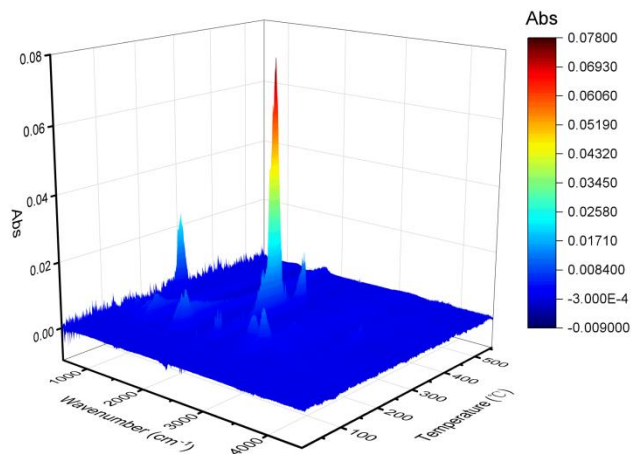
outer sheath; N-BV 1: the first stage of N-BV outer sheath; N-BV 2: the second stage of N-BV outer sheath; N-BV 3: the third stage of N-BV outer sheath.

3.2 FTIR spectrum analysis

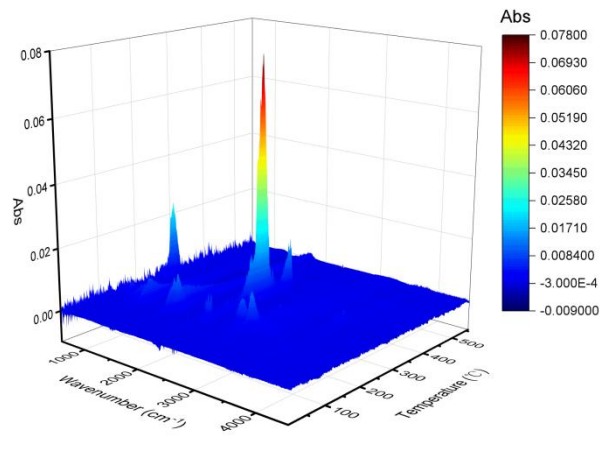
Figure 7 presents three-dimensional surface plots of the FTIR spectra corresponding to volatile pyrolysis products evolved from the four cable materials under a constant heating rate of 15 K/min. As illustrated in Figs. 7(a) – (d), the temperature range of concentrated gaseous product evolution closely coincides with the primary mass loss region observed in the TG and DTG curves presented in Figs. 2 and 3, with the minor temporal lag between mass loss onset and gas-phase detection—previously attributable to gas transmission delay in the FTIR coupling system—effectively eliminated. Notably, due to fundamental differences in pyrolysis mechanisms across the investigated formulation systems, their three-dimensional FTIR absorption profiles exhibit pronounced stage-dependent variations in both peak intensity and thermal distribution width.

Although the infrared spectra of various chlorine-containing polymer sheath materials exhibit intrinsic similarity in the positions of characteristic peaks, their absorption intensities profoundly reflect the gradient regulation effect of inorganic filler concentrations. Spectral analysis demonstrates that during the first stage (approximately 270–310 °C) of the three types of outer sheath materials with polyvinyl chloride matrices, obvious characteristic gas release is detected near the 2700–3000 cm^{-1} .



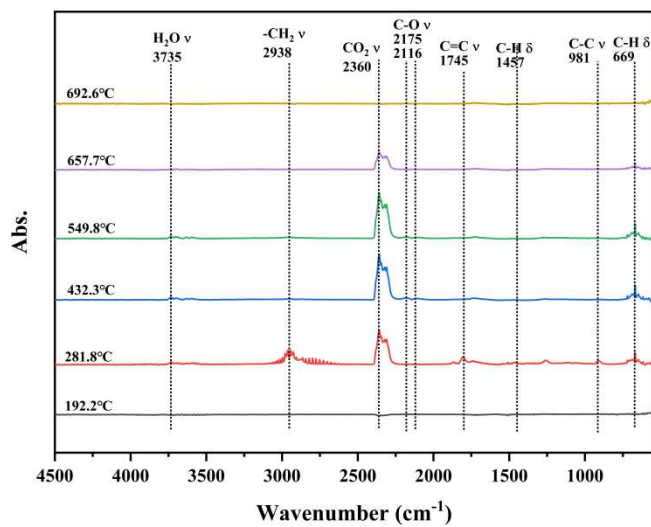


(c)

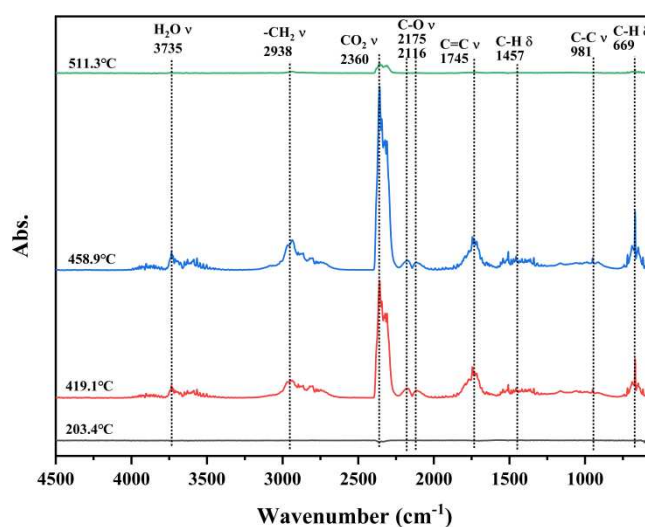


(d)

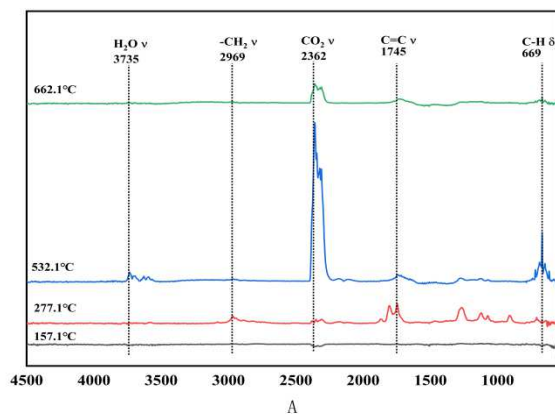
Figure. 7. Three-dimensional surface plots of FTIR spectra corresponding to volatile pyrolysis products evolved from four cable materials under a constant heating rate of 15 K/min: (a) ZR-YJLV outer sheath (b) ZR-YJLV insulation layer (c) PVC outer sheath (d) N-BV outer sheath.



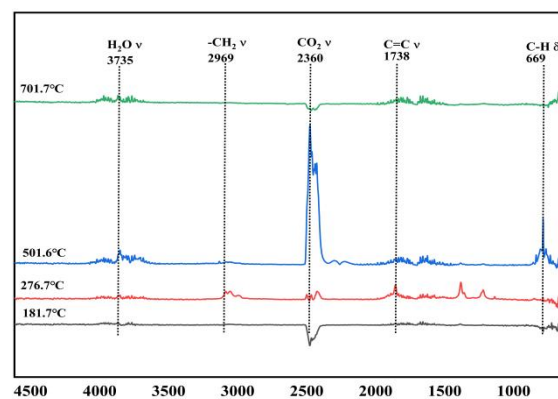
(a)



(b)

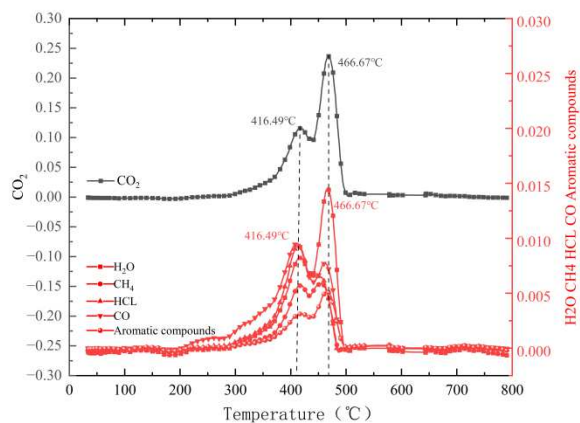


(c)

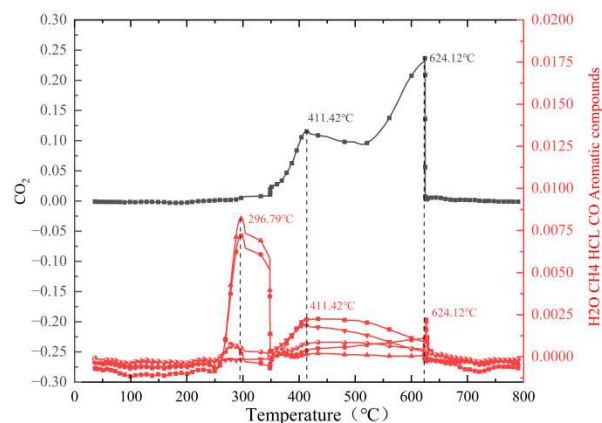


(d)

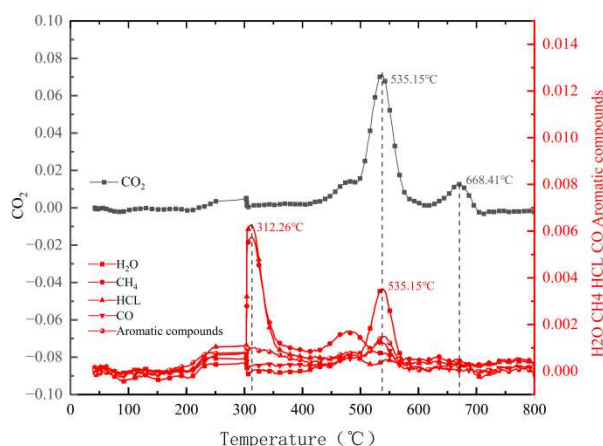
Figure. 8. Spectra of mining cable insulation at the temperature corresponding to the maximum mass loss rate for four materials: (a) ZR-YJLV outer sheath (b) ZR-YJLV insulation layer (c) PVC outer sheath (d) N-BV outer sheath.



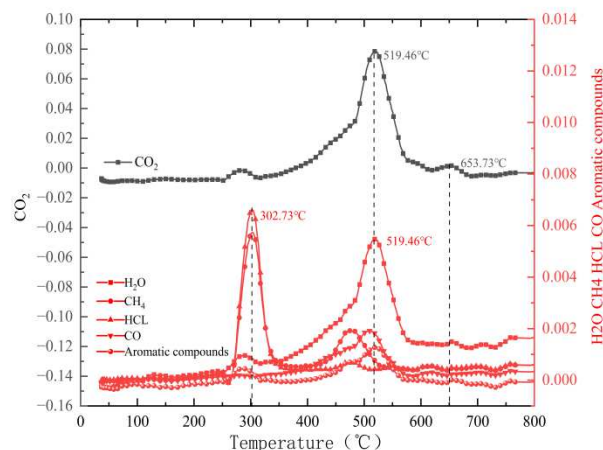
(a)



(b)



(c)



(d)

Figure. 9. Temperature variation curves of main pyrolysis components of four cable materials: (a) Outer sheath of ZR-YJLV (b) Insulation layer of ZR-YJLV (c) Outer sheath of PVC (d) Outer sheath of N-BV.

Figure 8 compares the two-dimensional FTIR absorption spectra of the four materials at their respective maximum mass loss temperatures. Furthermore, the peak at 3735 cm^{-1} corresponds to H_2O stretching vibration; the peaks at $2969/2938\text{ cm}^{-1}$ correspond to aliphatic $-\text{CH}_2$ stretching vibration; the sharp peak at 2360 cm^{-1} corresponds to CO_2 asymmetric stretching vibration; the peaks at $1745/1738\text{ cm}^{-1}$ correspond to $\text{C}=\text{O}$ or $\text{C}=\text{C}$ skeleton vibration, while the peak at 669 cm^{-1} is assigned to $\text{C}-\text{Cl}$ or $\text{C}-\text{H}$ deformation vibration. Notably, with the significant increase in inorganic filler content (conventional PVC < ZR-YJLV < N-BV), the absorbance of various characteristic peaks corresponding to hydrocarbon skeleton fracture (such as $-\text{CH}_2$ and $\text{C}-\text{Cl}$ vibrations) is significantly inhibited, which is attributed to the organic matrix dilution effect in high-filling systems and the mass transfer barrier effect of the dense residue network. Meanwhile, ZR-YJLV and N-BV sheaths exhibit enhanced H_2O absorption bands at the early peak positions, which confirms the initial endothermic dehydration mechanism of inorganic flame retardants and refractory ceramization additives from the perspective of pyrolysis products.

Figure 9 presents quantitative temperature-resolved evolution profiles of major pyrolytic volatiles— CO_2 , H_2O , CH_4 , HCl , CO , and aromatic compounds—evolved from the insulation and sheath materials, thereby elucidating their distinct thermal degradation mechanisms. The inner ZR-YJLV insulation layer undergoes a single-step, sharp decomposition event centered at $\approx 455\text{ }^\circ\text{C}$, accompanied by the instantaneous release of substantial quantities of gaseous hydrocarbons (notably CH_4) and aromatic species. This behavior is consistent with catastrophic backbone cleavage via random scission of its highly crosslinked polyethylene network. In contrast, the bimodal gas evolution profiles observed for the outer sheath materials quantitatively demonstrate the physicochemical suppression conferred by inorganic filler loading: the unfilled conventional PVC sheath exhibits an intense, low-temperature HCl and combustible hydrocarbon release peak at $\approx 312\text{ }^\circ\text{C}$ —the hallmark of dehydrochlorination-dominated degradation; conversely, the fire-resistant N-BV sheath, featuring

high inorganic filler content, not only markedly attenuates the intensities of HCl and aromatic compound emissions but also shifts the principal volatile release peak to a higher temperature regime ($\approx 360\text{--}380\text{ }^{\circ}\text{C}$), resulting in a substantial reduction of the overall gaseous product evolution flux.

Based on the dynamic evolution behavior of gaseous products characterized in prior sections, the cumulative mass yield of volatile pyrolysis species over the complete thermal decomposition range follows a material-specific ranking. For the ZR-YJLV insulation layer, the descending order of total evolved gas mass is $\text{CO}_2 > \text{CH}_4 > \text{aromatic compounds} > \text{CO} > \text{H}_2\text{O}$. For the outer sheath materials, the corresponding rankings are: ZR-YJLV outer sheath— $\text{CO}_2 > \text{HCl} > \text{H}_2\text{O} > \text{aromatic compounds} > \text{CH}_4 > \text{CO}$; conventional PVC outer sheath— $\text{CO}_2 > \text{HCl} > \text{aromatic compounds} > \text{CH}_4 > \text{H}_2\text{O} > \text{CO}$; and N-BV outer sheath— $\text{CO}_2 > \text{HCl} > \text{aromatic compounds} > \text{H}_2\text{O} > \text{CH}_4 > \text{CO}$.

The pronounced differences in the evolution sequence of these gaseous products arise fundamentally from intrinsic disparities in the polymer matrix architecture and the compositional modulation imparted by inorganic filler concentration. Specifically, the structural contrast between the halogen-free, aliphatic crosslinked polyethylene backbone of the insulation layer and the chlorine-rich polyvinyl chloride-based network of the sheath materials dictates the dominant emission profiles: hydrocarbon gases (e.g., CH_4) prevail in the former, whereas HCl dominates in the latter. A comparative analysis across the three outer sheath systems further demonstrates a systematic shift in volatile evolution behavior with increasing inorganic filler loading: under low-filler conditions (conventional PVC), rapid and abundant CH_4 release reflects unimpeded thermal degradation of the organic matrix; at medium-to-high loading ZR-YJLV, enhanced H_2O evolution emerges as the principal gas-phase signature, attributable to endothermic dehydration of hydrated mineral fillers (e.g., $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$); and under ultra-high loading N-BV, CH_4 evolution is markedly suppressed—both in intensity and rate—due to kinetic retardation imposed by a thermally stable, ceramized char barrier that impedes volatile diffusion.

4 Conclusion

The study employs synchronized TG-FTIR analysis combined with model-free kinetic methods (FWO and KAS) to evaluate the thermal decomposition of four cable components: PVC outer sheath, flame-retardant ZR-YJLV outer sheath, fire-resistant N-BV outer sheath, and ZR-YJLV crosslinked polyethylene insulation, dynamic heating conditions. Results reveal that increasing inorganic filler loading induces a dual-mode failure: progressive layered protection in outer sheaths versus abrupt structural collapse in inner insulation. Based on this mechanism, a three-tiered, spatially resolved grading framework is established, integrating time-, temperature-, and composition-dependent kinetic signatures. This framework provides fundamental thermo-kinetic parameters for early fire identification, risk assessment, and adaptive mitigation strategies in underground utility corridors.

(1) The insulation layer and the three outer sheath materials exhibit distinct thermal decomposition temperature ranges and kinetic behaviors. The insulation layer undergoes a single-stage degradation centered at $400\text{--}500\text{ }^{\circ}\text{C}$, whereas the primary DTG peaks for conventional PVC, ZR-YJLV, and N-BV outer sheaths occur at $270\text{--}310\text{ }^{\circ}\text{C}$. Inorganic filler loading predominantly governs the mass loss rate during the initial stage: volatile yield decreases from 65.1 wt% (unfilled PVC) to 41.6 wt% (highly filled N-BV). In the second stage, apparent activation energy systematically declines from 208.53 to 91.53 kJ/mol with increasing filler content, without altering the fundamental polymer scission pathway.

(2) The evolution of gaseous pyrolysis products is governed by polymer composition and filler loading. The XLPE

insulation layer releases CH₄ and aromatics via backbone scission. Outer sheaths (PVC, ZR-YJLV, N-BV) emit HCl at 270–310 °C due to dehydrochlorination. Filler loading modulates volatiles: medium-to-high filler in ZR-YJLV enhances H₂O from endothermic dehydration; ultra-high filler in N-BV suppresses CH₄ via a ceramized char barrier.

By integrating time-resolved temperature profiles with real-time gas evolution, this study establishes a hierarchical monitoring and early warning framework for cable fire hazards. Based on experimentally observed stepwise degradation—driven by multiphase physicochemical retardation in outer sheaths and thermal instability of inner insulation—a two-stage warning protocol is formulated: Stage I (precursor alert, 270–310 °C) employs HCl and nascent CO as indicators of dehydrochlorination and incipient oxidative cleavage; Stage II (critical escalation alert, > 450 °C) uses abrupt CH₄ release as a marker of irreversible insulation failure. This framework overcomes the limitations of conventional single-parameter alarms by incorporating kinetic, thermal, and chemical dimensions into a unified decision logic, providing theoretical support for early detection, risk stratification, and adaptive intervention in underground utility tunnels.

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Author contributions

[Yujie Yin]: Conceptualization; **[Zeyu Wang]:**Data curation; **[Yujie Yin]:**Formal analysis; **[Lei Lei]:**Funding acquisition; **[Yujie Yin]:**Investigation; **[Yujie Yin]:**Methodology; **[Lei Lei]:**Project administration; **[Lei Lei]:**Supervision; **[full name]:**Validation; **[Yujie Yin]:**Visualization; **[Yujie Yin]:**Writing—original draft; **[Lei Lei]:**Review and editing.

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