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COMPARATIVE THERMAL DEGRADATION BEHAVIOUR OF PRISTINE AND MODIFIED POLYVINYL CHLORIDE: INFLUENCE OF CUO AND FE_3O_4 NANOPARTICLES

СРАВНИТЕЛЬНОЕ ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ИСХОДНОГО И МОДИФИЦИРОВАННОГО ПОЛИВИНИЛХЛОРИДА: ВЛИЯНИЕ НАНОЧАСТИЦ CUO И FE_3O_4

SOF VA MODIFIKATSIYALANGAN POLIVINILXLORIDNING TERMIK PARCHALANISH XUSUSIYATLARINI TAQQOSLASH: CUO VA FE_3O_4 NANOZARRACHALARINING TA'SIRI

Eshtursunov Davron Abdisamatovich[1]
[1]Mirzo Ulug'bek nomidagi O'zbekiston Milliy unversiteti Kimyo fakulteti polimerlar kimyosi kafedrasi tayanch doktoranti

Bekchanov Davronbek Jumazarovich[2]
[2]Mirzo Ulug'bek nomidagi O'zbekiston Milliy unversiteti Kimyo fakulteti polimerlar kimyosi kafedrasi k.f.d., prof.

Muxamediyev Muxtarjan Ganiyevich[3]
[3]Mirzo Ulug'bek nomidagi O'zbekiston Milliy unversiteti Kimyo fakulteti polimerlar kimyosi kafedrasi k.f.d., prof.

Annotatsiya

Mazkur tadqiqotda sof polivinilxlorid (PVX), karbamid bilan modifikatsiyalangan PVX (PPE-2) hamda CuO va Fe_3O_4 nanobirikmalari asosida tayyorlangan funksional nanokompozitlarning termik parchalanish xususiyatlari taqqoslab o'rganildi. Termogravimetrik tahlil (TGA) va differensial skanerlash kalorimetriyasi (DSC) yordamida massa yo'qotilishi, degradatsiya bosqichlari va termik barqarorlik baholandi. Natijalar shuni ko'rsatdiki, PVXning karbamid bilan modifikatsiyasi uning issiqlikka chidamliligini oshiradi, metall oksid nanobirikmalari qo'shilishi esa barqarorlikni yanada kuchaytirib, parchalanish mexanizmini o'zgartiradi. Olingan natijalar CuO va Fe_3O_4 nanobirikmalarining stabilizatorlik rolini tasdiqlaydi va bunday materiallarning yuqori issiqlik va kimyoviy barqarorlik talab etiladigan sohalarda qo'llanish imkoniyatlarini ko'rsatadi.

Аннотация

В данном исследовании сравнительно изучены особенности термического разложения исходного поливинилхлорида (ПВХ), ПВХ, модифицированного мочевиной (PPE-2), а также функциональных нанокомпозитов на основе наночастиц CuO и Fe_3O_4. С помощью термогравиметрического анализа (ТГА) и дифференциальной сканирующей калориметрии (ДСК) были оценены потеря массы, стадии деградatsiu и термическая стабильность. Результаты показали, что модификatsiя ПВХ мочевиной повышает его термостойкость, а введение наночастиц оксидов металлов дополнительно усиливает стабильность и изменяет механизм разложения. Полученные данные подтверждают стабилизирующую роль наночастиц CuO и Fe_3O_4 и демонстрируют перспективы применения таких материалов в областях, где требуются высокая термическая и химическая устойчивость.

Abstract

In this study, the thermal degradation behaviour of pristine polyvinyl chloride (PVC), urea-modified PVC (PPE-2), and functional nanocomposites prepared with CuO and Fe_3O_4 nanoparticles was comparatively investigated. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to evaluate weight loss, degradation stages, and thermal stability. The results showed that urea modification enhances the thermal resistance of PVC, while the incorporation of metal oxide nanoparticles further improves stability and alters the decomposition mechanism. The findings confirm the stabilizing role of CuO and Fe_3O_4 nanoparticles and demonstrate the potential application of such materials in areas requiring high thermal and chemical resistance.

Kalit so'zlar: *polivinilxlorid, PPE-2, CuO nanozarrachalari, Fe_3O_4 nanozarrachalari, TGA, DSC, termik barqarorlik.*

Ключевые слова: *поливинилхлорид, PPE-2, наночастицы CuO, наночастицы Fe_3O_4, TGA, DSC, термическая стабильность.*

Key words: *Polyvinyl chloride, PPE-2, CuO nanoparticles, Fe_3O_4 nanoparticles, TGA, DSC, thermal stability.*

INTRODUCTION

Polyvinyl chloride (PVC) occupies a special place among synthetic polymers worldwide due to its high production volume[1]. By 2025, its production is expected to reach approximately 56 million tons, making PVC one of the most important polymers globally[2]. PVC is distinguished by its versatile properties, which include high dielectric permittivity, flame resistance (oxygen index OI = 47), low cost, and resistance to environmental influences[3]. These characteristics ensure the widespread application of PVC in various fields.

However, its thermal stability remains a critical issue, particularly at elevated temperatures (>200 °C), where the dehydrochlorination process occurs with the release of HCl, thereby limiting its recyclability[4,5]. Therefore, to improve PVC properties, it is necessary to modify it using thermostabilizers, plasticizers, fillers, and various additives, including polymer ligands as well as metals and metal oxides[6,7].

Polymer–metal complexes have attracted significant research interest in recent ears due to their ability to combine the properties of both organic and inorganic components[8]. Such complexes can enhance catalytic activity, improve thermal resistance, and increase the chemical stability of materials[9,10]. For example, composites of polyvinyl chloride with various amines can act as effective ligands for forming ion–coordination compounds with metal ions, thereby influencing the reactivity and stability of the material[11].

In this study, polyvinyl chloride was modified with urea (PPE-2)[12], and iron oxide (Fe_3O_4)[13] and copper oxide (CuO)[14] were immobilized on its structure via an in-situ method. The effect of these modifications on thermal stability was investigated using TGA/DSC analysis, providing an opportunity to assess the practical applicability of such composite materials.

Thermogravimetric analysis (TGA) provides information on the decomposition process and thermal stability of polymers, allowing the evaluation of mass loss as a function of increasing temperature. The thermal stability of the modified polymer is determined by heating the material to high temperatures until the final low-molecular-weight product is released. Thermal analysis is thus an essential tool for studying the properties of polymer composites, including PVC modified with urea.

MATERIALS AND METHODS

Thermogravimetric analysis (TGA) combined with differential scanning calorimetry (DSC) was employed to investigate the thermal stability and degradation behaviour of the samples. Simultaneous TGA/DSC measurements were performed using a Linseis STA PT 1600 instrument (Linseis Messgeräte GmbH, Selb, Germany). For each run, approximately 10 ± 0.1 mg of sample was weighed into 70 μL alumina crucibles, chosen for their thermal stability and chemical inertness. The analyses were conducted in the temperature range of 25–800 °C at a constant heating rate of 10 °C/min under a nitrogen atmosphere (99.99% purity) with a flow rate of 30 mL/min to suppress oxidation. The instrument was calibrated prior to measurements using standard reference materials. Temperature accuracy was within ±0.1 °C. Both mass changes and heat flow data were recorded simultaneously, allowing identification of degradation steps, mass loss, and associated thermal effects.

Thermal Stability of Polyvinyl Chloride (PVC) and PPE-2 Anion Exchanger

The thermal stability of polyvinyl chloride (PVC) was studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the results are presented in Fig 1.

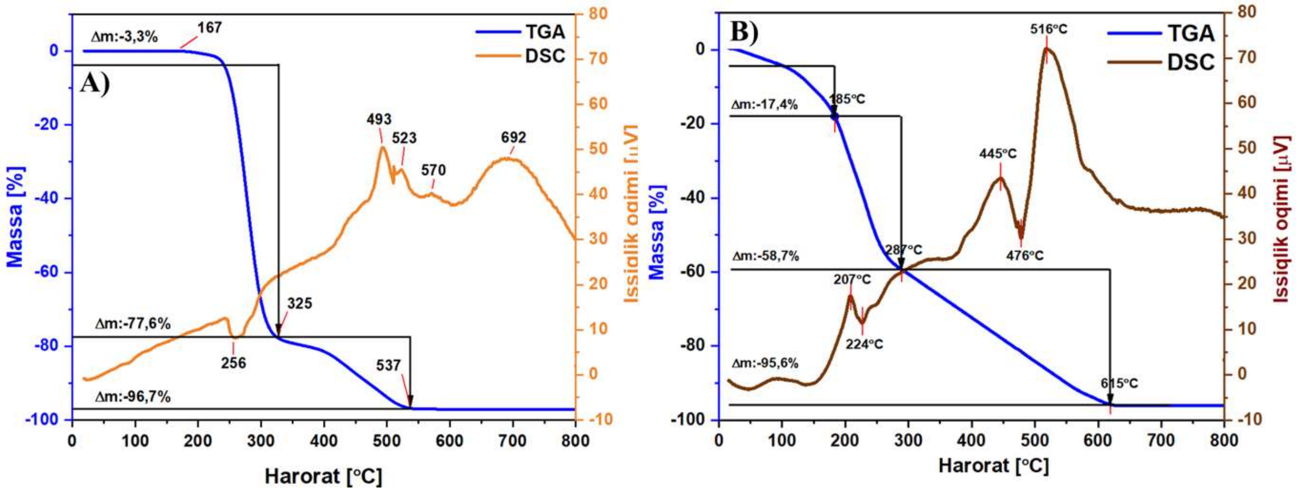

Figure 1. *Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves of PVC and PPE-2 anion-exchanger.*

The investigated samples contained commercial-grade PVC plastisols, which are manufactured with plasticizers, fillers, thermostabilizers, and other additives. The type and concentration of these components are selected depending on the required functional properties of the material.

As shown in the TGA curve of Figure 1A, PVC undergoes a two-step thermal degradation process. The first stage, observed at lower temperatures, corresponds to the major weight loss caused by HCl elimination and polymer chain scission. The second stage, at higher temperatures, is associated with the complete decomposition of the carbonaceous skeleton and the release of volatile products.

The first stage occurs within the 25–167 °C range, characterized by a minor weight loss (Δm = –3.3%), which can be attributed to the evaporation of adsorbed residual moisture, plasticizers, or other volatile organics. The second major degradation stage appears between 167–325 °C, during which the mass decreases by 77.6%. This process is linked to dehydrochlorination, where chlorine atoms are eliminated from the polymer backbone, leading to the formation of conjugated polyene structures[15].

Beyond 325 °C, the rate of mass loss significantly slows down and stabilizes around 537 °C, leaving a final residue of ~3.3%, which corresponds to the carbonized phase of the polymer.

The DSC analysis results (Figure 1A) are consistent with TGA data. An endothermic peak at 256 °C was detected, which could correspond to the release of adsorbed moisture or the glass transition of PVC. However, considering the significant mass loss observed in TGA, this peak is primarily attributed to the dehydrochlorination process, since HCl release is endothermic in nature. At higher temperatures — 493 °C, 523 °C, 570 °C, and 692 °C — several exothermic peaks were recorded, which may be associated with crystallization, oxidation, or structural rearrangements of the polymer[16]. According to Krongauz et al.[17], such exothermic processes can result from the cyclization of polyenes via Diels–Alder reactions, producing short-chain structures.

The data in Figure 1B show that the thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses of PPE-2, synthesized by modification of PVC with urea, demonstrate improved thermal stability compared to pure PVC. TGA results revealed that PPE-2 undergoes a three-step degradation process. The first stage, in the range of 100–185 °C, accounts for a weight loss of 17.4%, mainly due to moisture and volatile gaseous components. The second stage, occurring between 185–287 °C, corresponds to a weight loss of 58.7%, which is attributed to the thermal decomposition of PVC-urea polymer chains and the release of low-molecular-weight fragments. This process is supported by the exothermic DSC peak at 207 °C, which reflects chain scission. The third stage, between 287–615 °C, corresponds to the degradation of carbonaceous residues into small molecular species, resulting in a total mass loss of 95.6%, with a final residue of 4.4%.

The results indicate that the thermal decomposition of PPE-2 occurs at higher temperatures compared to pristine PVC, confirming its enhanced thermal stability. According to DSC, PPE-2 shows endothermic peaks at 224 °C and 476 °C, as well as exothermic peaks at 207 °C, 445 °C, and 519 °C, corresponding to the glass transition of PVC, subsequent transformations of the polymer matrix, and the decomposition of carbonaceous residues, respectively.

TGA and DSC Analysis of the Fe_3O_4/PPE-2 Functional Material

The thermal behavior of the Fe_3O_4/PPE-2 functional composite material was evaluated using TG–DSC analysis. Within the temperature range up to 800 °C, the stepwise mass loss occurred through four main thermal degradation stages (Fig. 2).

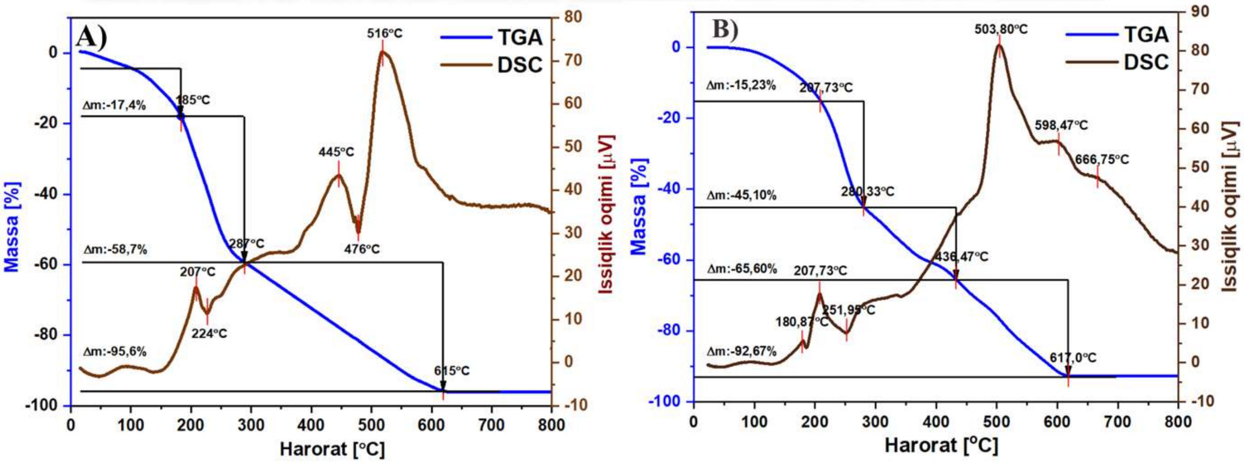

Figure 2. *Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves of PPE-2 anion-exchanger and Fe_3O_4/PPE-2 functional material.*

First stage (25–208 °C). In this interval, the material lost approximately 15.23% of its mass. This process is attributed to the evaporation of hygroscopic moisture and low-molecular-weight volatile components in the polymer matrix modified with Fe_3O_4 particles[18]. The absence of significant thermal events on the DSC curve indicates that the process is predominantly of physical nature.

Second stage (208–280 °C). A sharp mass loss of about 45.10% was observed. An endothermic peak at 252 °C on the DSC curve corresponds to the degradation of functional groups in the polymer chains, particularly $-NH_2$ groups, cleavage of C–Cl bonds in PVC, and the release of HCl. This process leads to weakening of the polymer chain segments.

Third stage (280–436 °C). The maximum weight loss of 65.60% occurred in this range. Exothermic peaks were recorded on the DSC curve, associated with the decomposition of the main PPE-2 polymer backbone, cleavage of C–C bonds, and the onset of carbonization. At this stage, Fe_3O_4 nanoparticles partially act as stabilizing factors against thermal degradation.

Fourth stage (436–617 °C). During the final decomposition stage, the material lost a total of 92.67% of its mass, leaving a residue of 7.33%, which corresponds to the magnetic inorganic oxide phase of Fe_3O_4. Endothermic/exothermic peaks at 503.80 °C, 598.47 °C, and 666.75 °C on the DSC curve reflect phase transitions and oxidation processes of residual components. With increasing temperature, the remaining polymer fraction undergoes complete carbonization, while the crystalline structure of iron oxide is preserved. Additionally, DSC analysis revealed a glass transition temperature (Tg) at 180.87 °C, corresponding to the softening point of the PPE-2-based resin.

TGA and DSC Analysis of the CuO/PPE-2 Functional Material

The thermal behavior of the PPE-2 functional material modified with CuO nanoparticles was investigated using TG and DSC methods. The results demonstrated that the stepwise thermal decomposition of the material within the temperature range up to 800 °C proceeds through four main stages (Fig 3).

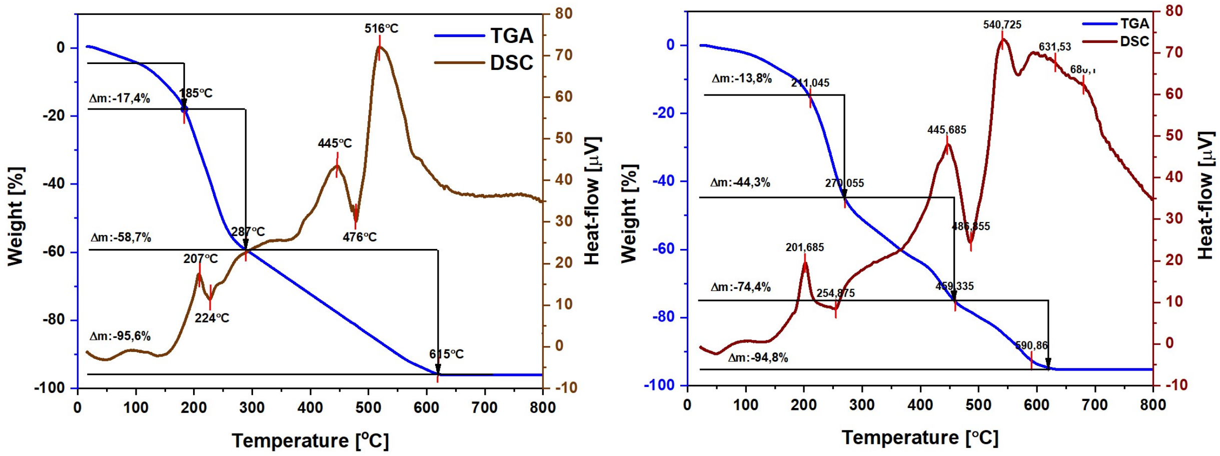

Figure 3. *Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves of PPE-2 anion-exchanger and CuO/PPE-2 functional material.*

First stage (25–211 °C). A total mass loss of 13.8% was observed in this interval. This loss is associated with the evaporation of adsorbed moisture, low-molecular-weight volatile compounds, and substances weakly bound to CuO particles. An exothermic peak at 201.68 °C was detected on the DSC curve, which corresponds to low-energy reactions of moisture and amino groups within the polymer matrix.

Second stage (211–270 °C). Approximately 44.3% of the mass loss occurred in this range, attributed to the initial degradation of PPE-2 polymer chain segments. An endothermic peak at 255 °C on the DSC curve is related to the cleavage of C–Cl bonds, HCl release, and decomposition of weak chain segments. CuO nanoparticles may act here as factors that intensify the thermal effect.

Third stage (270–459 °C). The major decomposition occurred in this interval, with up to 74.4% of total mass loss. This stage corresponds to the breakdown of the main PPE-2 polymer backbone, including the carbon skeleton and amino-containing segments. An exothermic peak at 445 °C on the DSC curve reflects the release of energy during C–C bond cleavage. A sharp change in the TGA curve at 459 °C indicates the transition to the final stage of decomposition.

Fourth stage (459–591 °C). In the final stage, the material exhibited a total mass loss of 94.8%, with the remaining 5.2% corresponding to the thermally stable inorganic oxide residue of CuO. In this temperature range, the DSC curve displayed three distinct exothermic peaks at 540.73 °C, 631.53 °C, and 680.10 °C, which are associated with phase transitions of residual components, carbonization, and oxidation processes.

Comparative thermal analysis of pure polyvinyl chloride (PVC) and its modified polymer-composite materials showed that modification significantly improved the thermal resistance of PVC-based materials. Specifically, pure PVC completed its main degradation process at 537 °C, leaving 3.3% residue. PPE-2 exhibited stability up to 615 °C and an increased glass transition temperature (Tg) of 144 °C. Nanocomposites synthesized with CuO and Fe_3O_4 underwent four-stage thermal decomposition with residual masses of 5.2–7.33%. The peaks identified in DSC analysis confirm the phase stability and segmental mobility of the polymer skeleton and modified structures. The summarized results are presented in **Table 1**.

Table 1

Based on the TG analysis, the percentage of mass losses corresponding to the decomposition of individual components of each functional material was determined.

Material	Δm_1 (%)	T_1 (°C)	Δm_2 (%)	T_2 (°C)	Δm_3 (%)	T_3 (°C)	Δm_4 (%)	T_4 (°C)	Residue	Tg (°C)	DSC Peaks (°C)
PVX	−3.3	167	−74.3	325	−19,1	537	–	–	3.3	90	256,493,523,570,692
PPE-2	−17.40	185	−41.3	287	−36.9	615	–	–	4.4	144	224, 445, 476, 516
CuO/PPE-2	−13.80	211	−30,5	270	−30.1	459	−20.4	590	5.2	132	254.87, 445.69, 486.86, 540.73, 631.53, 680.10
Fe_3O_4/PPE-2	−15.23	207	−29.87	280	−20.5	436	−27.07	617	7,33	133	207.73, 251.95, 503.80, 598.47, 666.75

In general, the incorporation of metal oxides not only enhanced the thermal and mechanical strength of the polymers but also improved their resistance to aggressive environments[19–21].

CONCLUSIONS

In this study, the thermal degradation behaviour of pristine PVC, urea-modified PVC (PPE-2), and their nanocomposites with CuO and Fe_3O_4 nanoparticles was systematically investigated using TGA and DSC techniques. The results revealed that:

1. Urea modification of PVC improved its thermal resistance by shifting the main degradation steps to higher temperatures and increasing the stability of the polymer matrix.
2. Incorporation of metal oxide nanoparticles (CuO and Fe_3O_4) further enhanced the thermal stability, as evidenced by higher residual mass and delayed decomposition onset.
3. CuO and Fe_3O_4 acted as effective stabilizers, altering the decomposition mechanism and suppressing mass loss during the major degradation stages.
4. Comparative analysis confirmed that nanocomposite formation is a promising strategy for tailoring the thermal and chemical durability of PVC-based materials.

Overall, these findings demonstrate the significant role of nanoparticle incorporation in improving the stability of functional polymers and suggest potential applications of such nanocomposites in areas where enhanced thermal resistance and durability are required.

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