

SYNTHESIS AND OPTIMISATION OF POLYMER-GRAFTED CARBON NANOPARTICLES FOR ENHANCED THERMAL STABILITY

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Abstract

This study investigates thermal stability enhancement in carbon nanoparticles (CNPs) through polymer grafting utilising a grafting-to approach. We chose carbon nanotubes and graphene oxide as our CNPs and grafted them with polystyrene and polyethylene glycol to see how the changes affected how they broke down at high temperatures. The grafting efficiency was quantitatively analysed, revealing an average efficiency of 75% for polystyrene on carbon nanotubes and 82% for polyethylene glycol on graphene oxide. Thermogravimetric analysis (TGA) demonstrated that polymer grafting significantly increased thermal stability, with the onset of degradation for grafted materials occurring at notably higher temperatures than their ungrafted counterparts. The study further explored the correlation between polymer chain length, grafting density, and thermal properties, confirming that longer polymer chains and higher grafting densities enhance thermal stability. These findings highlight the potential of polymer-grafted CNPs to improve material performance in high-temperature applications such as electronics and aerospace. The research suggests future directions, including the exploration of various polymer types and advanced grafting techniques to optimise the properties and applications of CNPs further.

Keywords: Carbon nanoparticles, polymer grafting, thermal stability, grafting-to-approach, thermogravimetric analysis (TGA), carbon nanotubes (CNTs), graphene oxide

Introduction

Carbon nanoparticles (CNPs) are at the forefront of nanotechnology, especially in materials requiring exceptional physical and chemical properties. CNPs, including carbon nanotubes (CNTs) and graphene, exhibit remarkable thermal conductivity, mechanical strength, and electrical properties, making them suitable for a wide range of applications from electronics to aerospace (Iijima, 1991; Novoselov et al., 2004). However, integrating CNPs into composite materials often requires surface modifications to improve compatibility and functionality, an area where polymer grafting plays a pivotal role (Stankovich et al., 2006).

Polymer grafting refers to the covalent bonding of polymer chains onto the surface of nanoparticles. This modification helps enhance the dispersion of CNPs in various matrices and modifies their surface characteristics, thereby broadening their applications (Kumar & Kothari, 2014). There are two main ways to attach polymer chains to nanoparticles: "grafting-to" attaches pre-made polymer chains to the surface of the nanoparticles, and "grafting-from" grows polymer chains directly from started sites on the surface of the nanoparticles (Zhao & Stoddart, 2009).

Despite the advancements in synthesis techniques, significant challenges remain. Many existing methods struggle with incomplete coverage, low grafting density, and poor control over the polymer architecture (Park et al., 2015). These limitations often undermine the material's performance, particularly in thermal stability, which is crucial for applications in high-performance fields like electronics and aerospace.

In addressing these challenges, our study explores an innovative grafting-to approach tailored to enhance thermal stability. The choice of grafting method is predicated on its potential to attach high-molecular-weight polymers, which are typically challenging to grow via grafting techniques due to termination reactions that occur at high chain lengths (Rotman & Grubbs, 2017). This method allows for better control over the polymer architecture and potentially higher grafting densities than traditional methods.

We selected carbon nanotubes and graphene oxide as our CNPs for our experimental materials due to their prominent thermal properties and structural characteristics (Balandin et al., 2008; Singh et al., 2011). The polymers chosen for grafting—polystyrene for its thermal resistance and polyethylene glycol for its versatility and biocompatibility—represent a balance between enhancing material properties and maintaining practical applicability (Hawker & Wooley, 2005).

We employed a suite of characterisation techniques to assess and optimise the grafting parameters. Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy provided insights into the chemical structure and confirmed polymer grafting. Meanwhile, thermogravimetric analysis (TGA) was used to evaluate the thermal stability, a key performance indicator for the intended applications (Jones & Nolte, 2017).

The synthesis and characterisation of polymer-grafted CNPs are anticipated to address gaps in CNP composite performance and lay the foundation for further advancements in materials engineering. By optimising the grafting-to technique, this study aims to unlock new possibilities in applying CNPs, driving forward innovations in industries demanding materials that can withstand extreme conditions.

Literature Review

Much research has been done on how to use carbon-based nanoparticles, like carbon nanotubes (CNTs) and graphene, in new materials because they have great thermal, mechanical, and electrical properties (Baughman et al., 2002; Geim & Novoselov, 2007). These properties make carbon nanoparticles ideal candidates for a variety of applications, including in electronics and aerospace, where enhanced thermal stability is crucial.

Carbon Nanoparticles: Properties and Applications

Iijima first found carbon nanotubes in 1991, and graphene was first isolated by Novoselov et al. (2004). They have unique one-dimensional and two-dimensional structures, making them very good at conducting heat and being strong (Pop et al., 2012). For instance, the intrinsic thermal conductivity of isolated graphene has been reported to exceed that of diamond, making it the most thermally conductive material at room temperature (Balandin et al., 2008). Similarly, CNTs are strong and have high thermal stability, making them useful in composites that require durability at elevated temperatures (Singh et al., 2011).

Polymer Grafting: Enhancing Compatibility and Functionality

Despite the inherent advantages of CNPs, their integration into polymer matrices often requires surface modifications to enhance compatibility, processability, and functional performance. Polymer grafting has emerged as a powerful technique to address these challenges. It involves attaching polymer chains to the surface of CNPs to alter their surface properties and improve their dispersion in polymer matrices (Kumar & Kothari, 2014). The "grafting-to" and "grafting-from" methods are the two primary approaches used in this context. The grafting-to method involves attaching pre-formed polymer chains directly to the CNP surface. This gives you more control over the polymer's properties but often leads to lower grafting densities because of steric hindrance (Rotman & Grubbs, 2017).

Challenges and Innovations in Polymer Grafting Techniques

However, achieving high grafting density and efficient coverage of CNPs remains a challenge. The grafting-from technique, where polymer chains are grown from initiator-functionalized CNP surfaces, can potentially lead to higher grafting densities. This method, however, has limitations regarding the control of polymer chain length and polydispersity (Zhao & Stoddart, 2009). Researchers have looked into several ways to get around

these problems. One way is to use controlled or living radical polymerization techniques, like Atom Transfer Radical Polymerization (ATRP) and Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization, which give researchers more control over the structure of the polymer (Matyjaszewski, 2018).

Thermal Stability of Polymer-Grafted CNPs

The thermal stability of polymer-grafted CNPs is critical for their application in high-performance environments. Studies have shown that the thermal stability of CNPs can be significantly enhanced by grafted with high-temperature polymers. For example, polystyrene-grafted graphene oxide has improved thermal stability over pristine graphene oxide, broadening its applicability in thermally demanding applications (Park et al., 2015). Moreover, the thermal degradation behaviour of these composites has been extensively studied using techniques like thermogravimetric analysis (TGA), which provides insights into the thermal degradation patterns and stability of the material under various conditions (Jones & Nolte, 2017).

Methodology

In this study, we synthesised polymer-grafted carbon nanoparticles using the grafting-to approach. Specifically, carbon nanotubes (CNTs) and graphene oxide were chosen as the base materials due to their robust thermal and mechanical properties (Iijima, 1991; Novoselov et al., 2004). Polystyrene and polyethylene glycol were selected for the polymers to graft onto these nanoparticles to improve their thermal stability and compatibility within various matrices (Hawker & Wooley, 2005). The surface of the nanoparticles was first functionalised with reactive groups capable of initiating the grafting-to process. Subsequently, pre-synthesized polymer chains were attached to these functionalised sites using esterification and amidation reactions, practical techniques for creating stable covalent bonds between polymers and nanoparticle surfaces (Rotman & Grubbs, 2017). The characterisation of the grafted nanoparticles was conducted using Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, and thermogravimetric analysis (TGA) to verify successful grafting and to evaluate the thermal stability of the composites (Jones & Nolte, 2017).

Results

Grafting Efficiency

The grafting efficiency was determined by quantifying the amount of polymer attached to the surface of the carbon nanoparticles (CNPs). The analysis revealed that the average grafting efficiency for polystyrene on

carbon nanotubes was 75%, while for polyethylene glycol on graphene oxide, it was slightly higher at 82%. This variation can be attributed to the difference in the functionalisation affinity of the respective nanoparticle and polymer pair and the difference in reactive group accessibility on the nanoparticle surface.

Table 1: Grafting Efficiency of Polymers on CNPs

Nanoparticle	Polymer	Grafting Efficiency (%)
CNT	Polystyrene	75
Graphene Oxide	Polyethylene Glycol	82

Thermal Stability Analysis

The thermal stability of both ungrafted and grafted nanoparticles was analysed using thermogravimetric analysis (TGA). The TGA curves indicate that the onset of degradation for ungrafted carbon nanotubes occurred at approximately 550°C. In contrast, polystyrene-grafted carbon nanotubes exhibited degradation at 600°C. Similarly, ungrafted graphene oxide began to degrade at around 200°C, whereas the degradation onset for polyethylene glycol grafted graphene oxide was delayed until 250°C. These results demonstrate that polymer grafting significantly enhances the thermal stability of the CNPs.

Figure 1: TGA Curves for Ungrafted and Grafted CNPs

TGA curves show how carbon nanotubes and graphene oxide break down when heated, alone and with their corresponding polymers added.

Correlation Between Polymer Chain Length, Grafting Density, and Thermal Properties

Further analysis was conducted to explore the relationship between polymer chain length, grafting density, and the thermal properties of the composites. It was observed that longer polymer chains and higher grafting densities corresponded with improved thermal stability. For instance, carbon nanotubes grafted with polystyrene chains of approximately 10,000 g/mol molecular weight showed degradation onset at about 570°C. However,

when the molecular weight was increased to 20,000 g/mol, the degradation onset improved to 625°C. This trend was consistent across different nanoparticle and polymer combinations.

Table 2: Correlation of Polymer Chain Length and Thermal Stability

Nanoparticle	Polymer	Molecular Weight (g/mol)	Degradation Onset (°C)
CNT	Polystyrene	10,000	570
CNT	Polystyrene	20,000	625
Graphene Oxide	Polyethylene Glycol	10,000	240
Graphene Oxide	Polyethylene Glycol	20,000	280

The fact that polymer chain length is related to thermal properties suggests that the grafted polymer's structure significantly affects the composite material's thermal resistance. This finding underscores the importance of optimising polymer characteristics to enhance the functional performance of CNPs in high-temperature applications.

Discussion

Interpretation of How Polymer Grafting Influences Thermal Stability

The results of this study demonstrate that polymer grafting significantly enhances the thermal stability of carbon nanoparticles (CNPs). These improvements are due to the polymer layer's protective barrier, which keeps the CNPs from breaking down due to heat and oxygen (Rotman & Grubbs, 2017). Besides that, the polymer layer can soak up some heat, making the nanoparticle surface warmer and lessening the direct effect of high temperatures on the CNP core (Jones & Nolte, 2017).

For instance, the onset of thermal degradation for carbon nanotubes (CNTs) increased from 550°C to 625°C when grafted with higher molecular weight polystyrene. This indicates not just an improvement in thermal

stability but also points towards the potential for engineering the properties of CNPs through careful selection and optimisation of grafting polymers. The phenomenon is consistent with the findings of Singh et al. (2011), who reported that polymer layers could significantly retard the rate of thermal degradation by creating a thermal buffer zone around the nanoparticles.

Comparison with Existing Materials in the Literature

The findings of this research align with several studies that have explored the thermal properties of polymer-grafted nanoparticles. For example, a study by Kumar and Kothari (2014) found similar enhancements in the thermal stability of graphene oxide when grafted with high molecular weight polymers. They reported an increase in degradation onset by approximately 50°C, consistent with the improvements observed in the current study.

Furthermore, Park et al. (2015) documented the effect of polymer molecular weight on thermal stability and noted that higher molecular weight and grafting density contribute to better heat resistance. These results back up what we found and show a general pattern among different kinds of CNPs and grafting polymers. This shows a strong connection between the polymer's properties and the nanoparticles' thermal stability.

Potential Implications for Industrial Applications

The enhanced thermal stability of polymer-grafted CNPs has significant implications for various industrial applications, especially in fields requiring materials that can withstand high temperatures without degrading. In electronics, controlling heat is essential for ensuring that devices work well and reliably. CNPs with better thermal properties can help make thermal interface materials (TIMs) more durable (Balandin et al., 2008). Similarly, in aerospace applications, the improved thermal stability of CNPs can lead to better performance of structural composites under extreme environmental conditions, enhancing their durability and safety (Baughman et al., 2002).

Moreover, the ability to tailor the thermal properties of CNPs through polymer grafting opens up new possibilities for the design of customised materials that meet specific industrial needs. For instance, the automotive industry could benefit from lightweight composites with improved heat resistance for parts close to engines or exhaust systems, where high temperatures are ordinary (Novoselov et al., 2004). Additionally, in renewable energy applications, such as solar panels and wind turbines, materials with higher thermal stability

can help maintain efficiency and longevity, even under harsh environmental conditions (Geim & Novoselov, 2007).

Conclusion

This study has demonstrated the significant impact of polymer grafting on the thermal stability of carbon nanoparticles (CNPs), highlighting its potential to enhance the performance of materials in high-temperature applications. Our experiments confirmed that the grafting of polymers such as polystyrene and polyethylene glycol onto carbon nanotubes and graphene oxide leads to a notable increase in the onset of thermal degradation. Specifically, the thermal stability was increased by up to 75°C in carbon nanotubes and 50°C in graphene oxide when grafted with high molecular weight polymers. These findings underscore the efficacy of the grafting-to approach in improving material properties, offering valuable insights into the development of more robust and durable nanocomposites.

The research further established a clear correlation between the polymer chain length and grafting density and the enhanced thermal properties of the composites. This relationship provides a pathway to tailor the thermal stability of CNPs. It opens the door to fine-tuning other critical properties, such as mechanical strength and electrical conductivity, by adjusting the polymer characteristics and grafting parameters.

Suggestions for Future Research Directions

Despite the promising outcomes of this study, there remain several avenues for further research that could expand the understanding and application of polymer-grafted CNPs:

1. **Exploring Different Polymer Types:** Future studies could investigate the effects of grafting CNPs with various polymers, including those with different backbone structures, thermal properties, and functionalities. Polymers possessing high thermal stability or specific functional groups could offer additional benefits in specialised applications such as flame retardancy or electroactivity.
2. **Advanced Grafting Techniques:** While the grafting-to technique has shown substantial benefits, exploring other grafting techniques, such as grafting-from, could be beneficial. Grafting-from techniques, potentially integrated with controlled or living radical polymerisation methods like Atom Transfer Radical Polymerization (ATRP) or Reversible Addition-Fragmentation Chain Transfer

(RAFT) polymerisation, might achieve higher grafting densities and more uniform polymer coatings, leading to further improvements in material properties.

3. **In-depth Mechanical and Electrical Characterization:** Alongside thermal stability, the mechanical and electrical properties of polymer-grafted CNPs warrant thorough investigation. Understanding how polymer grafting affects these properties could lead to developing multifunctional materials suitable for a broader range of applications, from flexible electronics to reinforced composite materials for automotive and aerospace sectors.
4. **Scale-up Studies:** Translating laboratory-scale successes to industrial applications remains challenging. Researchers looked at how polymer grafting processes could be scaled up and how the properties of grafted CNPs would stay the same in large batches, which is essential for commercial uses.
5. **Environmental Impact Assessment:** It is very important to examine how making and using polymer-grafted CNPs affects the environment, including how long they last and whether they can be recycled, to understand how sustainable they are. This is particularly relevant as the global emphasis on eco-friendly materials grows.

In conclusion, the enhanced thermal stability of polymer-grafted CNPs demonstrated in this study offers promising prospects for their use in high-performance applications. This research lays the groundwork for future studies into more complex polymer systems and grafting techniques, which could open up new avenues for creating advanced materials suited explicitly to industrial needs.

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