INSTITUTO FEDERAL DE EDUCAÇÃO, CIÊNCIA E TECNOLOGIA DO
RIO GRANDE DO SUL

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Efeito do teor de *carbon dots* de grafeno nas propriedades térmicas, dinâmico
mecânicas, e morfológicas de resina epóxi

FELIZ

2024

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Dissertação apresentada ao Programa de Pós-Graduação em Tecnologia e Engenharia de Materiais para a obtenção do grau de Mestre Profissional em Tecnologia e Engenharia de Materiais.
Área de Concentração: Tecnologia e Engenharia de Materiais
Linha de Pesquisa: Desenvolvimento de Materiais de Engenharia
Orientadora: Profª Drª. Daiane Romanzini Coorientador:
Prof. Dr. Heitor Luiz Ornaghi Jr.

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Trabalho Final apresentado ao Programa de Pós-Graduação em Tecnologia e Engenharia de Materiais do Instituto Federal de Educação, Ciência e Tecnologia doRio Grande do Sul, como requisito parcial para obtenção do título de Mestre Profissional em Tecnologia e Engenharia de Materiais.

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Apresentado e aprovado em: 26 de agosto de 2024.

Local da defesa: Feliz (on-line)

AGRADECIMENTOS

Chegando à conclusão de uma das longas jornadas desafiadora e gratificante,e tenho o prazer de reconhecer as pessoas que tornaram esse percurso possível. Primeiramente, gostaria de expressar minha profunda gratidão a minha orientadora, Profª. Drª. Daiane Romanzini, e em especial ao meu coorientador, Dr.Heitor Luiz Ornaghi Jr, cuja contribuição foi fundamental para a conclusão deste trabalho. Sua dedicação e empenho, tanto na revisão detalhada quanto na organização final do manuscrito, foram cruciais para a realização deste projeto. O seu suporte não se limitou apenas ao aspecto técnico, mas também se estendeu ao fornecimento de valiosos conselhos e orientações ao longo do processo. A sua disponibilidade para discutir questões complexas e o seu comprometimento com a excelência foram verdadeiramente inspiradores. Agradeço profundamente por sua colaboração e pelo impacto significativo que teve na qualidade e no sucesso desta dissertação. Sem a sua ajuda e o seu profissionalismo, este trabalho não teria alcançado o nível de refinamento e precisão.

Agradeço também aos membros da banca examinadora, Profª. Drª. Ana Paula Bilck, Prof. Dr. Édson Luiz Francisquetti e Prof. Dr. Matheus Poletto pelo tempo dedicado à avaliação deste trabalho.

Por fim, agradeço a todos que, de alguma forma, contribuíram para a realização deste trabalho. Sua ajuda e suporte foram inestimáveis.

Com sincero agradecimento, Bárbara Schneider.

RESUMO

Diferentes quantidades de *carbon quantum dots* de grafeno (CQDs) (0,1,2,5, e 5%) foram incorporadas em uma resina epóxi. A condutividade térmica, densidade, morfologia e propriedades térmicas dinâmico-mecânicas (DMTA) foram reutilizadas a partir do estudo de Seibert e colaboradores. O gráfico de Pearson mostrou uma alta correlação entre teor de carga, condutividade térmica e difusividade térmica. Observou-se uma baixa correlação com densidade e capacidade calorífica. Em baixa concentração de CQD (0.1%), a fratura da superfície mostrou-se mais heterogênea, enquanto em quantidades mais elevadas (2.5 e 5%) observou-se superfícies mais homogêneas. O módulo de armazenamento não teve valores alterados com o aumento do CQD. Mas a extensão do platô vítreo aumentou com maiores teores de CQD, com um aumento de ~ 40 °C para os 5% em peso em comparação com os 2,5% em massa e ~ duas vezes em comparação com o epóxi puro. Este resultado é atribuído para as características intrínsecas da carga. Adicionalmente, uma maior quantidade de CQD acarreta em uma menor dissipação de energia e um aumento na temperatura de transição vítrea. A novidade e importância estão relacionadas pelo fato de que, para matrizes mais rígidas (corroborado com a literatura), as propriedades mecânicas não se alteraram, pois o mecanismo das pontes poliméricas não foram apresentadas, apesar da excelente dispersão de CQD, bem como da quantidade de carga. Por outro lado, a condutividade térmica está diretamente relacionada ao tamanho das partículas e à dispersão.

Palavras-chave: carbon dots de grafeno; nanocompósitos epóxi; condutividade térmica; estrutura e relação de propriedade

ABSTRACT

Different amounts of graphene quantum dots (CQDs) (0, 1, 2.5, and 5 wt%) were incorporated into an epoxy matrix. The thermal conductivity, density, morphology, and dynamic mechanical thermal (DMTA) properties were reused from the study of Seibert et al. The Pearson plot showed a high correlation between mass loading, thermal conductivity, and thermal diffusivity. A poorer correlation with density and heat capacity was observed. At lower CQD concentrations (0.1 wt%), the fracture surface showed to be more heterogeneous, while at higher amounts (2.5 and 5 wt%),a more homogeneous surface was observed. The storage modulus values did not change with the CQD amount. But the extension of the glassy plateau increased with higher CQD contents, with an increase of ~40 °C for the 5 wt% compared to the 2.5 wt% and almost twice compared to the neat epoxy. This result is attributed to the intrinsic characteristics of the filler. Additionally, lower energy dissipation and a higher glass transition temperature were observed with the CQD amount. The novelty and importance are related to the fact that for more rigid matrices (corroborated with the literature), the mechanical properties did not change, because the polymer bridging mechanism was not present, in spite of the excellent CQD dispersion as well as the filler amount. On the other hand, thermal conductivity is directly related to particle sizeand dispersion.

Keywords: carbon quantum dots; epoxy nanocomposite; thermal conductivity; structure and property relationship.

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SUMÁRIO

1 INTRODUÇÃO E ESTRUTURA DO TRABALHO

Nos últimos anos, o desenvolvimento de nanomateriais tem se destacado devido às suas propriedades únicas, que variam significativamente em comparação com seus equivalentes em escala macro. Os nanomateriais, com tamanhos que variam de 1 a 100 nm, apresentam uma vasta gama de aplicações que abrangem desde eletrônicos até remediação ambiental, graças à sua alta área de superfície e propriedades distintas, como magnéticas, elétricas, mecânicas e ópticas. Entre esses materiais, os *carbon quantum dots* (CQDs) e os *graphene quantum dots* (GQDs) têm ganhado atenção especial devido às suas promissoras propriedades ópticas e elétricas, além de sua potencial biocompatibilidade e fotoluminescência estável.

Os CQDs podem ser sintetizados por duas abordagens principais: *top-down* e *bottom-up*. A abordagem *top-down* utiliza materiais macroscópicos, como carvão, grafeno e diversos produtos naturais de plantas (como folhas, frutos e caules), que são decompostos para produzir os *carbon dots*. Em contrapartida, a técnica *bottom-up* envolve a modificação química de moléculas menores carbonáceas sob condições específicas de reação para obter *carbon dots* fluorescentes.

Ambas as abordagens têm suas vantagens e desvantagens. Em geral, os métodos *bottom-up* são mais econômicos, enquanto a produção em larga escala é mais fácil com a abordagem *top-down*. No entanto, o método *bottom-up* pode deixar impurezas, exigindo etapas adicionais de purificação, enquanto a abordagem *top-down* raramente necessita de purificação química. Além disso, a abordagem *top-down* tende a produzir uma distribuição de tamanho mais ampla em comparação com a abordagem *bottom-up*.

Diversos estudos destacam aplicações inovadoras dos *carbon quantum dots*. Por exemplo, Lu et al. (2015) relataram uma atividade fotocatalítica aprimorada de GQDs modificados com zinco-porfirina na degradação do azul de metileno sob luz visível. Dang et al. (2022) utilizaram CQDs dopados com ferro para gerar metanol por redução de CO_2. Rahbar et al. (2019) observaram um aumento de três vezes na atividade fotocatalítica com CQDs codopados com enxofre e nitrogênio em comparação com TiO2 na degradação do ácido vermelho 88. Tammina et al. (2019) relataram a utilização de CQDs codopados com nitrogênio e fósforo como sensores fluorescentes para a detecção de dopamina com um limite de detecção de 0,021 M. Além disso, Tammina et al. (2014) descreveram o uso de CQDs dopados com

nitrogênio como plataforma de detecção fluorescente para íons Fe^{3+}.

A escolha de estudar a influência dos pontos quânticos de grafeno em resinas epóxi se justifica pela necessidade de melhorar as propriedades térmicas e mecânicas desses materiais, que são amplamente utilizados em diversas indústrias,incluindo a aeroespacial, automotiva, eletrônica e biomedica. A incorporação de nanomateriais em matrizes poliméricas tem se mostrado uma estratégia eficaz para melhorar características como condutividade térmica, resistência mecânica e estabilidade térmica. No entanto, ainda existem desafios significativos, como a dispersão homogênea dos nanomateriais na matriz polimérica e a formação de uma interface eficaz entre o reforço e a matriz. Acredita-se que os GQDs possam superar alguns desses desafios devido ao seu tamanho nanométrico e propriedades únicas.

Este trabalho é relevante tanto do ponto de vista científico quanto profissional. Cientificamente, contribui para o entendimento das relações entre a estrutura e as propriedades dos reforços com nanocompósitos de GQDs. Ao avaliar a condutividade térmica, morfologia e propriedades dinâmico-mecânicas desses materiais, o estudo fornece *insights* valiosos sobre os mecanismos de reforço e as interações entre os nanomateriais e a matriz polimérica. Profissionalmente, este conhecimento pode ser aplicado no desenvolvimento de materiais avançados com melhor desempenho para diversas aplicações industriais.

Este estudo visa fornecer uma compreensão aprofundada das propriedades dos nanocompósitos de resina epóxi reforçados com pontos quânticos de grafeno, contribuindo para o desenvolvimento de materiais poliméricos com propriedades melhoradas para aplicações avançadas. O trabalho apresenta-se no formato de artigo, publicado pela revista *Polymers* em dezembro de 2023.

1.1   OBJETIVOS

1.1.1 Objetivo geral

- Avaliar a influência de diferentes teores de *quantum dots* de grafeno (CQDs) na condutividade térmica, morfologia e nas propriedades dinâmico-mecânicas de resina epóxi.

1.1.2   Objetivos específicos

- Avaliar quantitativamente o impacto da massa, do tamanho de partícula e da razão de aspecto na condutividade térmica dos CQDs incorporados em matrizes poliméricas, e analisar os efeitos da dispersão e aglomeração no desempenho térmico dos compósitos.

- Investigar as alterações na morfologia da superfície da resina epóxi com a incorporação de CQDs através de mapeamento tridimensional e análise de rugosidade, correlacionando as diferenças observadas com as propriedades mecânicas e térmicas dos nanocompósitos.

- Analisar as propriedades mecânicas e térmicas de nanocompósitos de CQD-epóxi usando DMTA, com foco na influência da massa de CQD sobre o módulo de armazenamento, módulo de perda e tan delta, para entender as mudanças na elasticidade, estabilidade térmica e comportamento viscoelástico do material.

2 APRESENTAÇÃO DO ARTIGO

Evaluation of the influence of different levels of graphene carbon dots in epoxy resin by assessing thermal conductivity, density, morphology and dynamic-mechanical thermal properties (DMTA).

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2.1 INTRODUCTION

Nanomaterials are materials with size ranging from 1 to 100 nm [1] (one nanometer is equivalent to ten H atoms). Many properties are achieved due to their high surface area, which greatly differs from their bulk counterparts, giving distinct magnetic, electrical, mechanical, optical, and other properties. Different nanomaterials, such as fullerenes, carbon nanotubes, nanodiamonds, nanoporous materials, core-shell nanoparticles, and carbon quantum dots, find their role in scratch-free paints, surface coatings, electronics, cosmetics, environmental remediation, and sensors, among others [1]. For the production of the nanomaterials, there are two different approaches: the top-down approach (mechanical milling, etching, laser ablation, sputtering, electro-explosion) or the bottom-up approach (supercritical fluid synthesis, spinning, sol-gel approach, laser pyrolysis, chemical vapor deposition, molecular condensation, chemical reduction, and green synthesis)[2]. The dependent effects are more prominent at the nanoscale than at the meso or macroscale. For example, the mechanical properties of nanomaterials are higher compared to their bulk counterparts due to the increase in crystal perfection or reduction in crystallographic defects, but the stress transfer mechanism also changes. For example, the polymer bridging mechanism mainly causes the tensile deformation of materials containing nanoparticles, where the deformation is avoided even if the interfacial interaction is excellent [3]. For bulk materials, more specifically fibers, if the interfacial interaction is excellent, the tensile property will be higher than the neat matrix because the fiber (more rigid than the matrix) receives all the stress applied and retains most of the stress received.

Carbon-based *quantum dots* (graphene quantum dots and carbon quantum dots) are the shining stars of nanomaterials and present a vast possibility of applications (as can be seen in the schematic representation of Figure 1) [4]. The constant advance of technology and science allows the number of applications to increase even more. Scientists know even more about the strategies (size, modification, synthetic methods) to give the expected properties (optical, luminescent) for biomedicine, optronics, catalysis, and sensor issues.
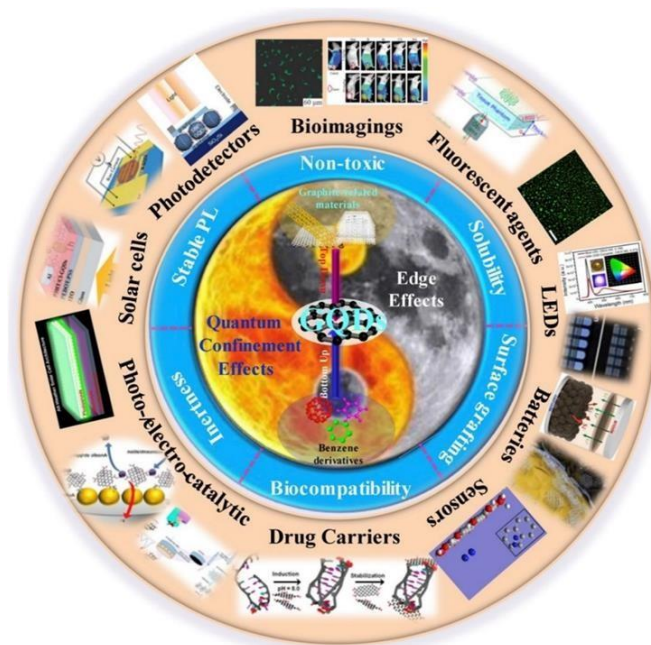
Figure 1. Schematic representation of the carbon quantum dot applications, properties, and fabrication. The figure was used under the Creative Commons License (5).

Some reviews have been found regarding the use of carbon-based nanomaterials in different scientific areas. Campuzano et al. [6] studied carbon dots (CDs) and graphene carbon dots (GQDs) in electrochemical biosensing. Zhu et al. [7] debated the current state and future perspective of the photoluminescence (PL) mechanism in carbon dots (CDs), carbon quantum dots (CQDs), and polymer dots, including the four PL mechanisms: quantum confinement effect, surface state, molecule state, and cross-link-enhanced emission. Zheng et al. [8] studied carbon-based nanomaterials for biological applications, including their physicochemical properties, photostability, biocompatibility, and size. Liu et al. [9] compiled the main achievements in the past four decades, paying special attention to the principles behind synthetic chemistry, luminescence mechanisms, and applications. Tian et al. [5] compiled graphene quantum dots from chemistry to applications, including optical, electrical, and optoelectrical properties. Jana et al. [10] explored the use of CQDs for bioimaging and drug delivery in cancer. The authors explained real-time monitoring through fluorescence imaging, CD-based active and passive targeting, tumor microenvironment targeting, multifunctional targeting, in vivo imaging, biodistributions in cancer models, etc. On the other hand, many applications can befound regarding carbon quantum dots. Dall Agnol et al. [2] used spirulina-based carbon dots (bottom-up process) for stimulating agricultural plant growth. The authors studied the

thermodynamic and kinetic mechanisms of the pyrolysis reaction and claimed a mean activation energy of 192.6 kJ/mol, a 10 nm average size, blue photoluminescence emission around 450 nm under a 340–400 nm excitation wavelength, and a high range of solubility when dispersed in a 0.050–1 mg/mL aqueous solution (used for lentil seed growth). Seibert et al. [11] studied the effect of different CQDs (1 wt%, 2.5 wt%, and 5 wt%) on epoxy, and the results showed an increase in the toughness of epoxy by 260%, an increase in the thermal conductivity by 144%, and an increase in the glass transition temperature by 10%, among other improvements. Sun et al. [12] studied the quantum-sized carbon dots for bright and colorful photoluminescence. The authors produced CDs upon simple surface passivation, and the nanomaterials strongly showed photoluminescence in both the solution and the solid state with no blinking effect and were stable against photobleaching.

There are still some challenges regarding the mechanical properties of graphene-based nanocomposites. In spite of considerable advances in research, a lot of work must be done in this research area. The authors seem to be unanimous on the following points: i) scale up the production of high-quality graphene (with the largest aspect ratio and lower number of layers) and related materials; ii) dispersion (must not form aggregates to avoid weak points); iii) filler/matrix bonding (to allow an efficient stress transfer mechanism); iv) functionalization of the filler (which difficults the scale up production due to excessive use of solvents and feedstock); v) use of combined fillers to minimize some drawbacks [13]. Wang et al. [14] studied the thermal conductivity and mechanical properties of graphene nanoplatelet (GnPs)/epoxy composites containing 3 and 5 wt% GnPs using a sonification process followed by three-roll milling.

The authors claimed an increase in tensile and flexural modulus but decreased strength by increasing GnPs concentration. The glass transition and the thermal conductivity were also improved by GnPs concentration, independently of the particle size, but the enhancement was dependent on the particle size. Prolongo et al. [15] achieved an optimum GnP loading of 8 wt% in epoxy matrix using a three-roll mill preparation method and claimed an increase of 22% of the tensile modulus while an increase of 25% of tensile strength was obtained (but at 3 wt% GnP). Using this same preparation method and materials, Chatterjee et al. [16] obtained an increase of 8% of the tensile modulus and 80% of fracture toughness by using 1 wt% GnP, while Ahmadi-Moghadam et al. [17] achieved an increase of 10% of the tensile modulus by using 2 wt% GnP. Regarding graphene carbon dots, most reviews demonstrate that the

applications seem to be restricted to detectors, light-emitting diodes, bioimaging, corrosion protection, or similar [18]. Hence, some properties are clearly affected by the particle size and fabrication method, while others are affected by filler dispersion and characteristics.

In this context, we reused the data from the already-published paper [11] using the freely available data in [19], aiming to improve the available information about CQD not related to the above applications. No additional experimental work was done. In our study, a profound structure-property relationship among the thermal conductivity, density, morphological, and dynamic mechanical thermal properties is discussed. Also, the reinforcement mechanisms for these types of composites are elucidated.

2.2 MATERIALS AND METHODS

The materials and methods are the same of the referenced study [11] and freely available on [19]. Put this, it was not conducted additional experimental work. Figure 2 shows the schematic representation of the method used for production of the nanocomposites. The only difference was that microscopy was used to re-evaluate the surface.
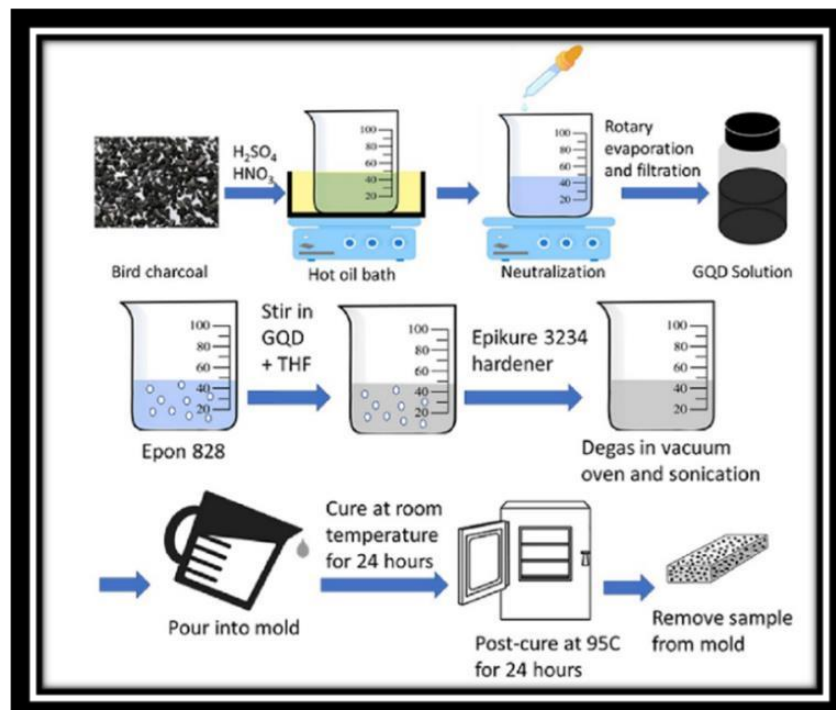
Figure 2. Production of the nanocomposites. The figure was used under the creative commons license [11].

Characteristics using 3D color map surface with projection using OriginPro version 2021. The SEM images were first converted into a matrix, and the Plot > 3D:3D colormap surface with projection, according to Figure 3. All the steps are indicated below. After the construction of the 3D colormap surface graph, the scales were standardized as 0 (the black lower limit) and 255 (the red upper limit) — this selectionis made in the plot details by cliking with the right button of the mouse and selecting color-map/countours >> countour lines. It means that the higher the contrast in the original image, the higher the difference in the colormap created. For the images where the red color appears, it means that more differences in the contrast in the original images are observed. If small differences in the contrast are observed, more similarities in the color pattern are observed.

Figure 3. Schematic representation of the conversion of the SEM image into a 3D colormap surface with projection.

2.3 RESULTS

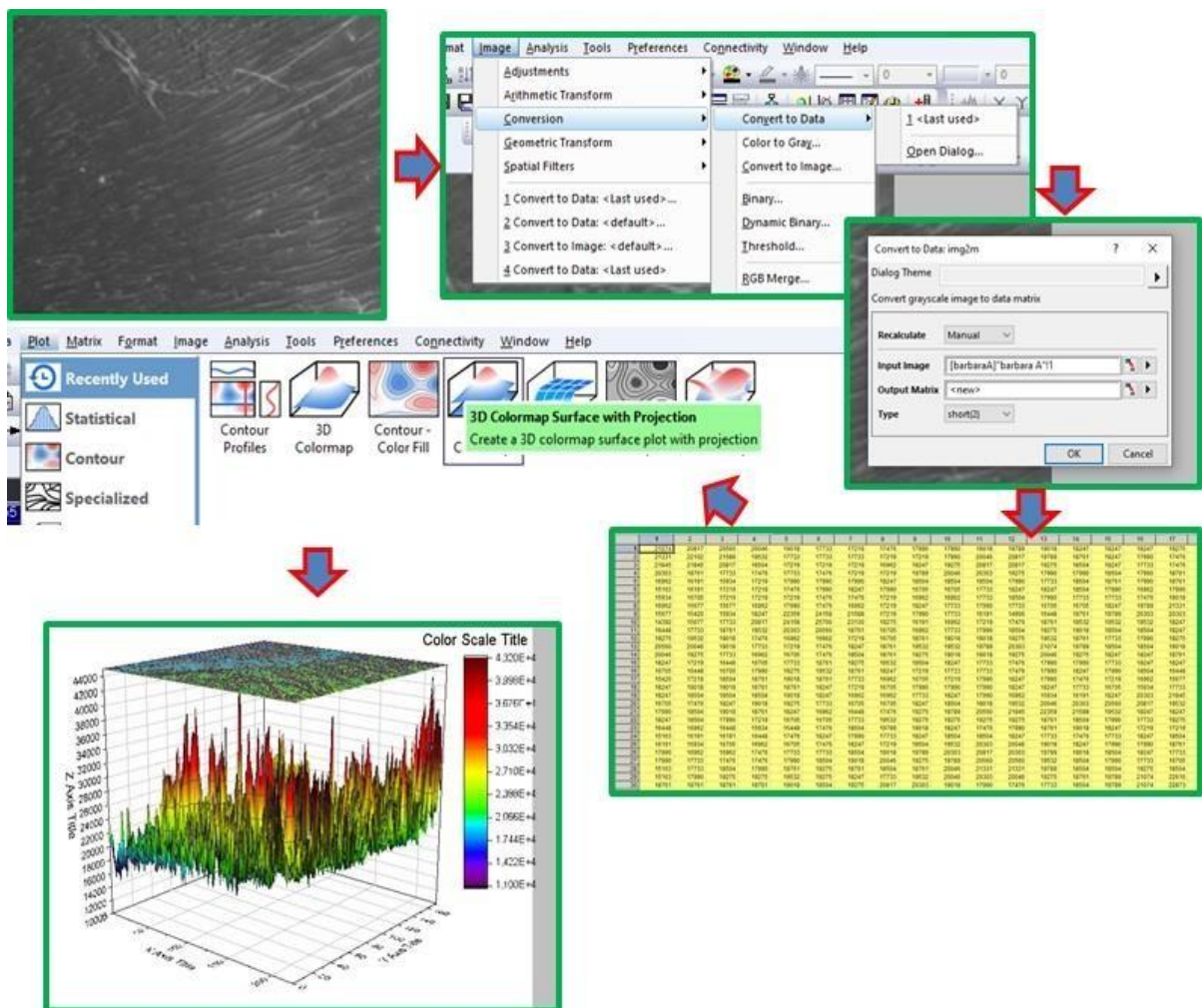The graphene quantum dots have the behavior associated with i) quantum confinement effects, and ii) edge effects. In other words, the behavior is associated with the dimensions of the particle [20]. In our case, since the size is constant, the discussion is done with respect to the dispersion of the nanoparticles and the possible changes in the crosslinking density of the epoxy.

2.3.1. Thermal Conductivity

Figure 4 shows the correlation plot (higher part) with the correlation coefficient (lower part) from Table 1. Five different variables were analyzed: mass loading (0, 1, 2.5, and 5 wt%), thermal conductivity (0.206, 0.259, 0,369, and 0,503 W/m.K), heat capacity (Cp) (1.26, 1.41, 1.38, and 1.36 J/g.K), density (0.981, 1.001, 1.005, and 0.983), and thermal diffusivity (0.167, 0,185, 0.264, and 0.376 mm2/s). The red color represents a positive correlation, while the blue color represents a negative correlation. Also, the more elliptic the figure, the higher the correlation. It is noted that there is a high correlation between the mass loading and the thermal conductivity (0.98) and thermal diffusivity (0.97). This is due to thermal conductivity,which refers to the ability of a given material to conduct or transfer heat, while thermal diffusivity is considered the thermal conductivity divided by the density and specific heat at constant pressure. High diffusivity means that heat transfers rapidly [21].

These results are directly related to the mass loading content due to the intrinsic characteristics of the graphene quantum dot. In addition, a high correlation between thermal conductivity and thermal diffusivity is noted (0.99).
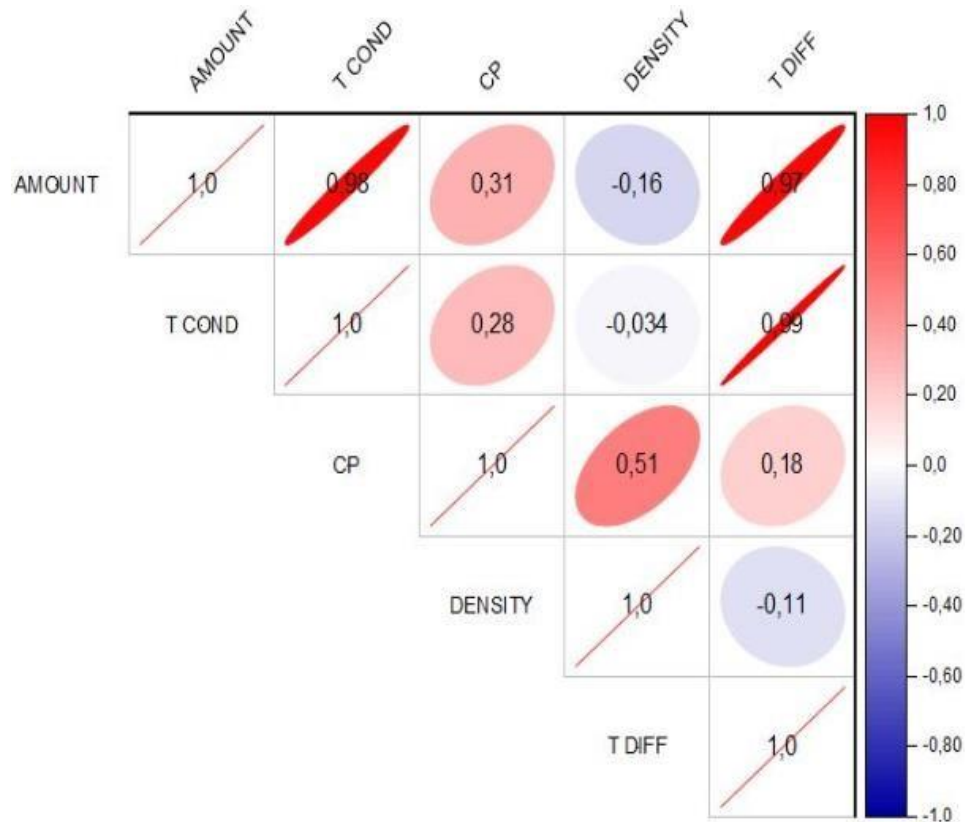
Figure 4. Correlation plot of the different variables studied considering the thermal conductivity. Amount – amount of CQDs, T COND – Thermal conductivity, CP – heat capacity, DENSITY – density of the samples, T DIFF – Thermal diffusivity.

The thermal conductivity of graphene quantum dots is dependent on the mass loading of graphene quantum dots, which is different from some graphene nanoplatelets [11, 22]. It seems that there is a clear correlation between particle size and thermal conductivity. The thermal conductivity will only be affected if the particle is incorporated into the polymeric matrix. Lower the particle size higher the thermal conductivity. This occurs due to an increase in the Brownian motion and in the surface area to volume ratio. Hence, the thermal conductivity is expected to increase with decreasing nano-particle size (as well as with increasing temperature and a less viscous solution). Even if an eventual agglomeration is presented, the thermal conductivity tends to increase with the CQD amount. Figure 5 shows a schematic representation of the thermal conductivity as a function of particle size and aspect ratio. By analyzing Figure 5, it is only prudent to affirm that similar thermal conductivities can be obtained even when different aspect ratios of particles are used, but for nanoparticles, the thermal conductivity is more homogeneous compared to the microcomposites. Hence, the thermal conductivity seems to be more dependent on the type of reinforcement

compared to its own dispersion. It is noteworthy to mention that the effectiveness is improved with dispersion. The combination of the different nanoparticles can also increase the thermal conductivity[23, 24]. It is noteworthy that the thermal conductivity of the graphene quantum dot has a high relative error (30%), and hence the measurements are done consideringthe epoxy resin as the starting point material.
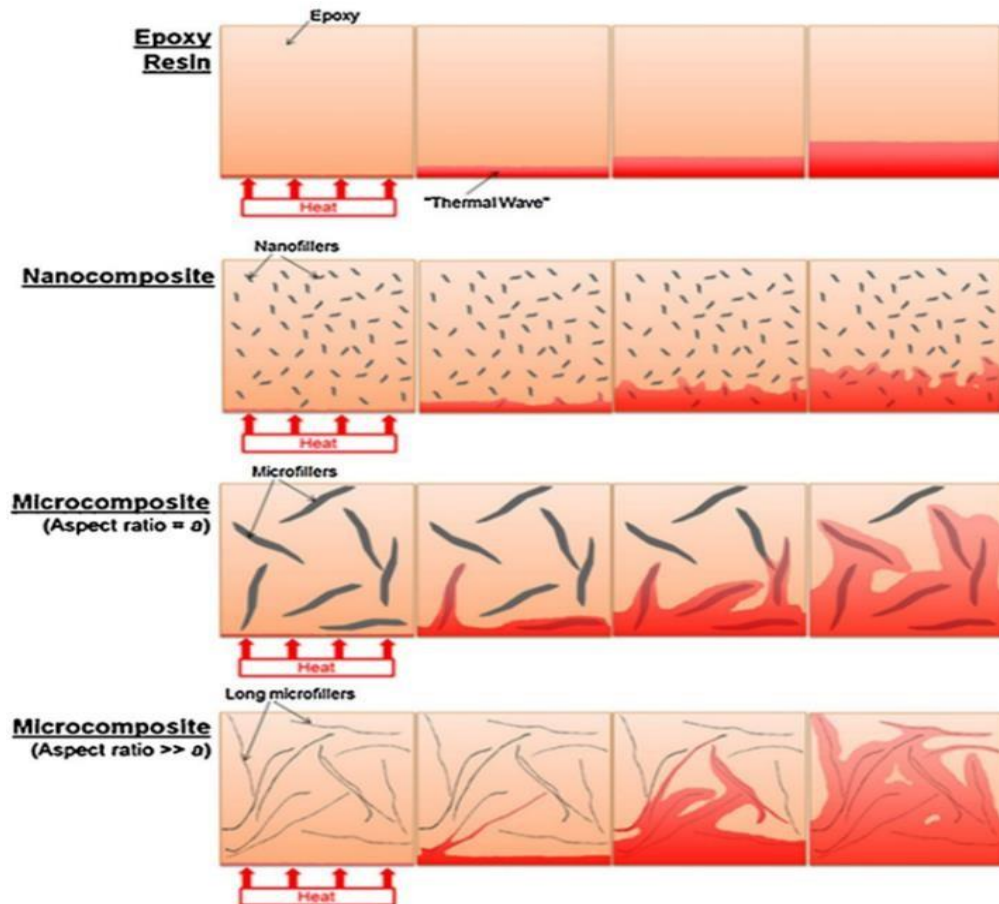
Figure 5. Thermal conductivity in function of the size and aspect ratio of the nanoparticles. Figure was used with kindly permission of [21].

Many drawbacks are expected to be found when the thermal conductivity is measured in polymer matrices of nanomaterials. When the size of the object decreases to a certain value, the uncertainties of the measurement also increase, and many variables, which were not considered for fibers, for example, must be accounted for [25]. The presence of functional groups and chemical reactions tendsto reduce the thermal conductivity because of the reduction of the surface area (more groups have connected each other, and the bulk increases). Anyway, as a comparative test, the values can be considered. It is not well known how the thermal conductivity is affected

by the dispersion state of the nanoparticles. Also, knowing the aspect ratio and the good contact between the different surfaces involved are also necessary for any particle [26]. Han et al. [27] compared the same volume content of reinforcement and an increase of two-fold in thermal conductivity by changing the scale from micro to nano. The authors claimed that when a percolationnetwork is formed, more effective thermal conductivity is achieved, even for very lowloadings. For conductive graphene-polymer composites, Shtein et al. [28] studied the effect of particle size on graphene-polymer composites, and the authors claimedan ultrahigh thermal conductivity of 12.4 W/m K (vs. 0.2 W/m K for neat polymers) with a percolation threshold of φ 0.17. As shown in the schematic representation inFigure 5, the thermal conductivity differs depending on the aspect ratio and size.

2.3.2. Morphological analysis

The SEMs from the original study were reused to create a 3D color map surface with projection (Figures 6A–H) to better visualize the differences in the surface of the epoxy with the incorporation of the CQDs. As the CQs are incorporated into the matrix, more differences among the peaks are observed (represented by the colors red and purple). For the 2.5 wt% CQD nanocomposite, the difference is slightly lower, while for the 5 wt% CQD, the difference decreases considerably, being more similar to the neat epoxy. If the surface is less rough, it means that the fracture is more brittle, as in the case of neat epoxy and 5 wt% CQDs. It can be hypothesized that for the latter, a higher amount of crosslinking occurs since the increase in the crosslinking density leads to a more brittle material (as can be seenin the next section with the extension of the glassy plateau). The nanocomposite with 1 wt% CQD shows a rough surface, indicating that this amount of CQD promotes more differences in the structure. Physically, a more similar "structure" leads to a narrower relaxation time distribution, and the fractal structure formed needs more energy to achieve molecular mobility, increasing the main thermal transition to hightemperatures. Another analogy is that for the 5 wt% CQD, the more homogenous structure is strongly indicative of a dominant interphase (CQD/epoxy interaction) being formed. If this is true, a lower tan delta peak has to be observed in DMTA analysis (as confirmed in the next section).
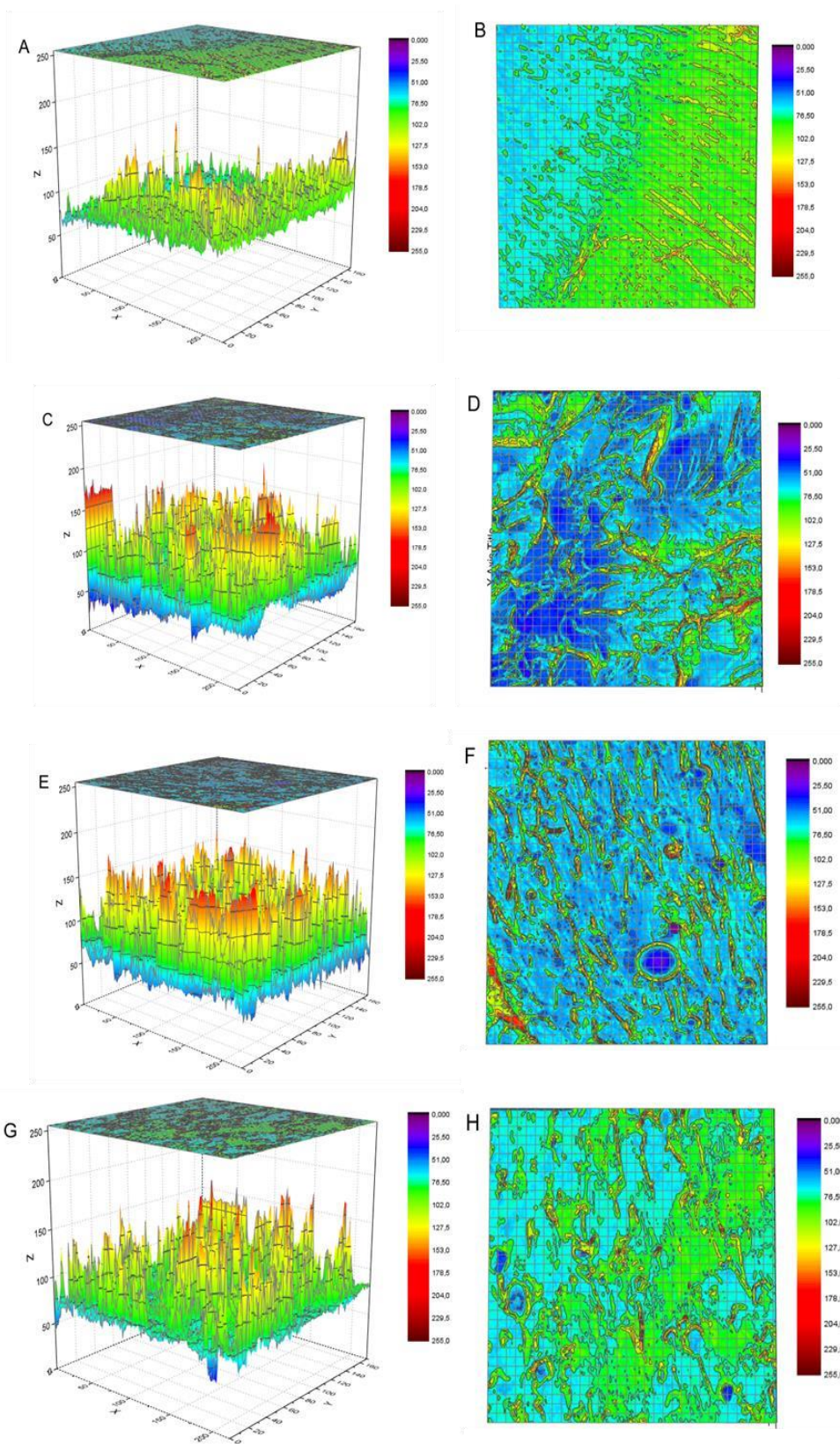
Figure 6. 3D color surface maps with projection with the respective upper view of A-B) neat epoxy, C-D) 1 wt% CQD, E-F) 2.5 wt% CQD, and G-H) 5 wt% CQD. The original SEM images were obtained from reference [11] with kindly permission.

2.3.3 Dynamic mechanical thermal analysis

Figure 7 shows a representative curve of the storage modulus, loss modulus, and tan delta, representing the main transitions analyzed, and Figure 7 shows the DMTA curves of the neat epoxy and the 1 wt%, 2.5 wt%, and 5 wt% nanocomposites studied. The samples were done in triplicate, and a representative curve is shown.

The storage modulus (E') curves can be analyzed separately in three distinct regions: the glassy region, the glass transition region, and the rubbery (elastomeric) region. Figure 7 shows the representative curve of the neat epoxy, showing the main transitions aforementioned. It is noted that the behavior is not necessarily the same when comparing the same nanocomposite. It is important to mention that the cross-linking density is not controllable; hence, it is expected that the behavior will not be the same.

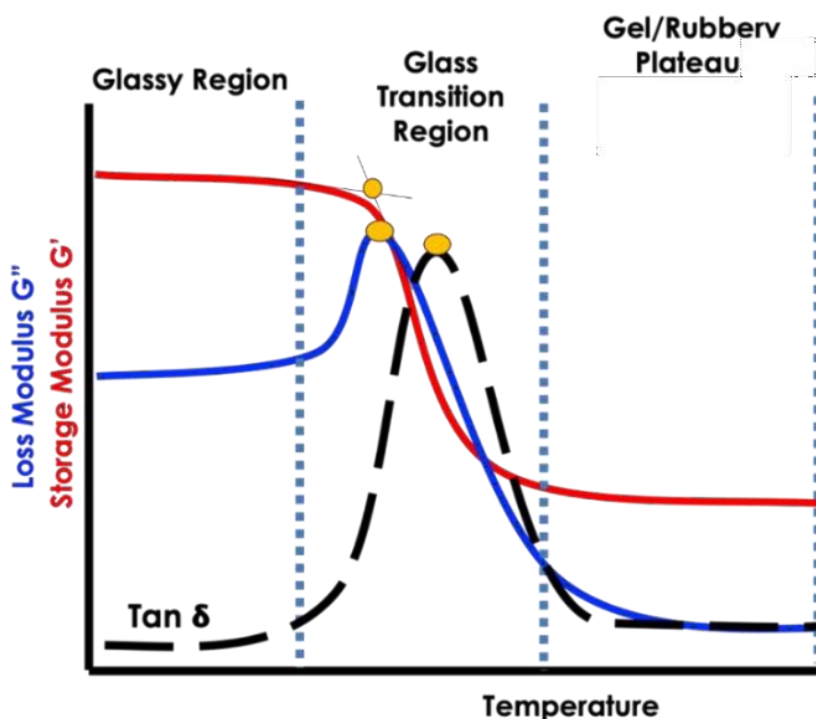Figure 7. Representative curve of the storage modulus, loss modulus and tan delta representing the main transitions analyzed. Figure was adapted from [29]. The yellow circles represent the glass transition temperature of the storage modulus, loss modulus, and tan delta.

Figure 8 a-c) shows the storage modulus, loss modulus and tan δ curves. Storage modulus: the storage modulus represents the elasticity portion of the

polymer. When a polymer receives an external stress (electrical, mechanical, etc.) the backbone chain deforms, aiming to dissipate the energy. The higher the energy received, the greater the deformation caused in the polymer chains. The stronger the chemical interaction, the higher the modulus, since the elastic modulus is dependent on the way the chains are packed and the intermolecular forces [30–32]. In the case of composites or nanocomposites, unless the reinforcement acts as a barrier to polymer chain deformation, no effect of the reinforcement is observed. For fiber-reinforced composites, the fiber size is always higher in comparison to the polymer chains, but for nanoparticle-reinforced composites, the reinforcement has a more similar size compared to the polymer chains. Hence, the stress-transferring mechanisms differ from each other. For fiber-reinforced composites, the higher dimension (length) is responsible for the tensile strength, while the extremities act as compression forces and weakening points [33, 34]. Also, the lower the diameter of the fiber, the higher the efficiency of the reinforcement.

For nanoparticle-reinforced composites, the reinforcement mechanism is via polymer bridging, leading to a nanoparticle network similar to colloidal structures [35]. If well-dispersed and having favorable particle-polymer interactions forms fractal structures via polymer bridging, A molecular dynamics simulation confirms this hypothesis [36]. Put simply, and comparing the storage modulus in the glassy state, it is noted that the incorporation of CQD did not significantly influence the elasticity of the epoxy. Hence, no reinforcement effect can be attributed to the incorporation of the CQDs. But the extension of the glassy plateau increases with CQDs. This behavior can be attributed to: i) CQDs are more thermally stable compared to the polymer, and hence a higher amount of CQDs leads to higher thermal stability; or ii) an increase in the crosslinking density [5, 37–39]. For lightly crosslinked systems, the increase in the crosslinking density reflects an increase in the density (not noted here), while for heavily crosslinked systems, the density is not altered by increasing the crosslinking density. In the case of this study, the maintenance of the density values probably indicates a heavily crosslinking system (this is the reason why the density values are not altered with CQDs), in which the CQDs help in the crosslinking formation. Considering that chemical crosslinking is already more stable than physical crosslinking, when CQDs are included and become part of the system, the system becomes more stable due to the intrinsic higher thermal stability of the nanoparticles [40, 41].
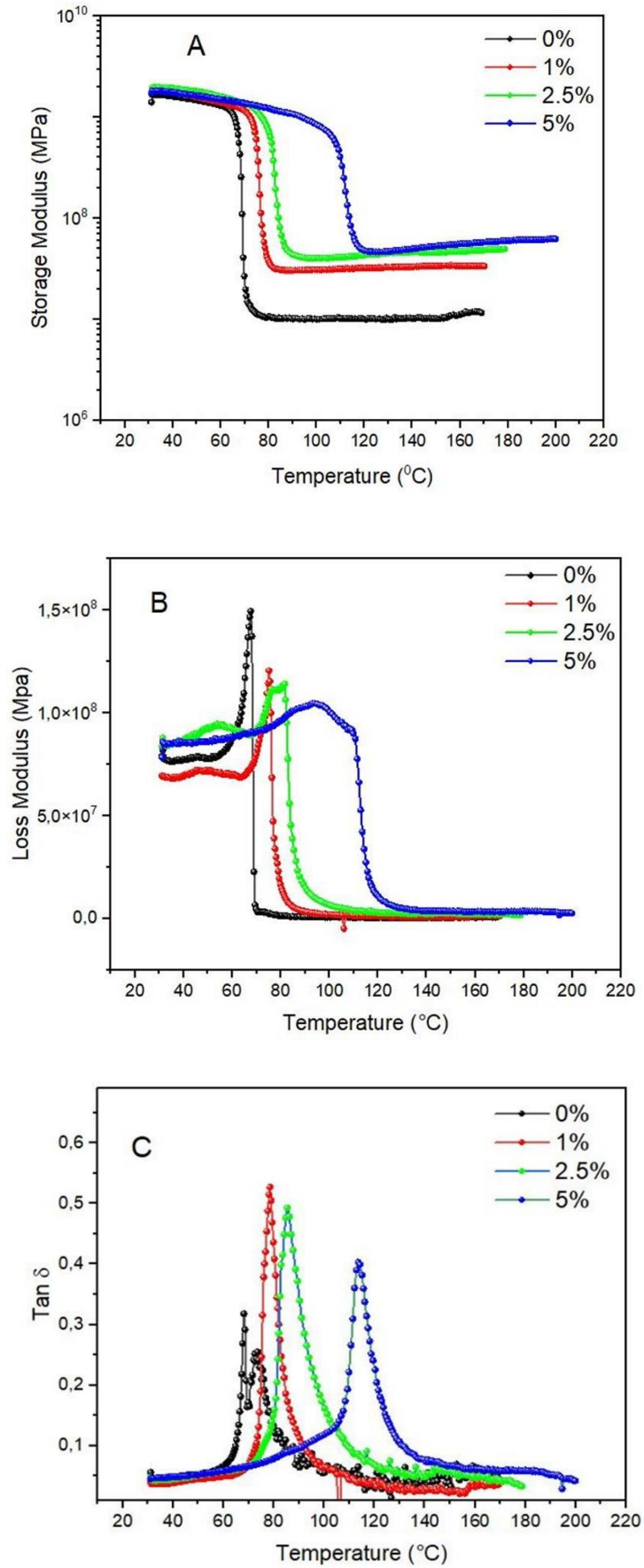
Figure 8. Representative curve of the storage modulus, loss modulus and tan delta representing of the neat epoxy, 1 wt% CQDs, 2.5 wt% CQDs, and 5 wt% CQDs.

Another important feature is that the rubbery region has a less abrupt decay when incorporating CQDs compared to the neat epoxy. This is also a strong indication of a more crosslinking system. Physically, when the molecular chains have enough thermal energy to considerably increase the free volume (in the glass transition region), the polymer chains are apart from each other [4, 42]. If no chemical joints are formed, the loss of property is higher compared to a system where a chemical network is formed because this network hinders further deformation. The glass transition temperature also increases with CQD incorporation, indicative of a more crosslinked system.

Loss modulus and tan delta: the loss modulus represents the energy lost by a cycle of deformation. The energy is only dissipated when the backbone chain cannot support the energy stress imposed. The loss modulus increases by increasing molecular motion, achieving a maximum peak after a new decrease. The tan delta (the same behavior with the loss modulus but the main events shift to higher temperatures) represents the viscoelastic behavior of the polymer (E''/E') and represents the curve similar to the loss modulus but shifted at higher temperatures[43].

The Tg of the loss modulus of the neat epoxy resin is 70 °C. Lower dissipation is obtained as more CQDs are incorporated, indicating a more effective interface. In other words, when the stress is imposed through the nanocomposites by the matrix, the CQDs retain part of the energy (polymer/CQD interface), hindering the heat from dissipating and hence showing a lower peak. If a crosslinked system is presented (as probable by the storage modulus characteristic curve), more stress can also be borne [43, 44]. The peak maximum (Tg) did not change with CQD, indicating that the segmental immobilization of the amorphous chains is similar among the CQD nanocomposites.

The glass transition of the tan delta (δ) curves was affected by the CQD content (from 70 °C for the neat resin to 120 °C for the 5 wt% CQD), followed by a significant change in the peak height (decreasing, in general). The decrease is indicative of a stronger polymer/matrix interface, causing a reduction in energy dissipation. According to Ornaghi Jr. et al. [45] and Chirayil et al. [46], lower the tandelta peak height, higher the constrained region amounts, representing lower molecular vibrations of the epoxy amorphous chains and a decrease in the dissipation energy. This trend is almost linear among the CQD nanocomposites [47].

Lin et al. [48] studied the origin of mechanical enhancement in polymer nanoparticle composites with ultrahigh nanoparticle loading and claimed (> 50%). In this particular case, a marked improvement in the mechanical properties is obtained

compared to the analogous matrices. For small amounts of NPs, the mechanical properties can also be improved, but they are highly dependent on the particle size, dispersion, preparation method, and mechanical properties of the filler.

2.4   CONCLUSIONS

In this study, freely available data was re-used to better understand the profound structure-versus-property relationship among the thermal conductivity, density, morphological, and dynamic mechanical thermal properties of an epoxy resin with different graphene carbon dot contents (0, 1, 2.5, and 5 wt%). The main results indicate that the higher the CQD content, the higher the thermal conductivity, compared to other studies from the literature. The elastic modulus values were not altered with CQD content, but the extension of the plateau showed a considerable improvement of almost 40 °C from 2.5 wt% to 5 wt%. The mechanical properties seem not to be improved by this type of system, but other properties such as thermal conductivity and thermal electricity seem to be directly dependent on particle size and concentration.

The surface of the neat resin and the CQD/epoxy nanocomposites were evaluated by SEM. The 5 wt% CQD nanocomposite showed a less rough surface and a more brittle fracture, similar to the neat epoxy sample. At lower CQD concentrations (1 and 2.5 wt%), a rough surface is presented, reflecting the extension of the glassy plateau on DMTA curves.

In the glassy state, it is noted that the incorporation of CQD did not significantly influence the elasticity of the epoxy. But the extension of the glassy plateau increases with CQDs, probably due to the higher thermal stability of CQDs if compared with the polymer, and hence a higher amount of CQDs leads to higher thermal stability or an increase in the crosslinking density. Regarding the loss modulus results, lower dissipation is obtained as more CQDs are incorporated, indicating a more effective interface. The glass transition of the loss modulus and tan delta curves increases with increased CQD content, and a decreased peak height was observed due to the stronger polymer/matrix interface causing a reduction in energy dissipation.

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3 CONSIDERAÇÕES FINAIS

O primeiro tipo de *carbon dots* (CQDs) foi sintetizado por acaso em 2004, o que torna essa tecnologia relativamente nova. As possibilidades de utilização desses materiais são bastante amplas, abrangendo diversas áreas como biomedicina, energia, meio ambiente, armazenamento de energia e liberação controlada de medicamentos, entre outras.

Considerando o atual estudo, pode-se dizer que a variação do teor de GQDs apresentou correlação com condutividade térmica e difusividade térmica de uma resina epóxi, e baixa correlação com densidade e capacidade calorífica. Além disso, mudanças na extensão do platô vítreo, verificadas na curva do módulo de armazenamento, foram reportadas, aumentando também a temperatura de transição vítrea. Não foram verificadas alterações significativas na matriz termorrígida, em relação às propriedades mecânicas, com a incorporação de diferentes teores de GQDs, sendo um ponto positivo, visto que as partículas podem apresentar melhorias nas propriedades térmicas, por exemplo, sem comprometer as propriedades mecânicas.

Desta forma, pode-se dizer que este estudo contribuiu de forma significativa para o entendimento das relações entre a estrutura e as propriedades dos reforços com nanocompósitos de GQDs, considerando os mecanismos de reforço e as interações entre os nanomateriais e a matriz polimérica. Além disso, este conhecimento pode ser aplicado na indústria, atendendo a demanda por materiais mais eficientes e duráveis, bem como para produtos implantáveis dentre eles cateteres e dispositivos de distribuição de medicamentos.

Dado o potencial de desenvolvimento e produção dos CQDs, uma alternativa promissora para beneficiar a sociedade seria a conversão de resíduos sólidos em CQDs. Esta abordagem não só aproveita materiais residuais, mas também contribui para a redução da poluição global, alinhando-se aos princípios de gerenciamento sustentável de resíduos e aos objetivos de desenvolvimento sustentável (ODS) estabelecidos pela Organização das Nações Unidas (ONU).

3.1   POSSIBILIDADES DE TRABALHOS FUTUROS

Há muitos aspectos dos *carbon dots* que ainda precisam ser explorados, sendo um dos principais a conversão de resíduos sólidos em *carbon dots*. A gestão sustentável desses resíduos é um desafio significativo devido ao alto custo, à falta de organização e às dificuldades associadas, o que impede o avanço da urbanização e a melhoria dos padrões de vida. Portanto, o método de gestão proposto deve ser econômico, simples, sustentável, ecologicamente viável, além de legal e socialmente permissível.

Atualmente, os *carbon dots* ainda não são amplamente utilizados em aplicações práticas devido à sua baixa reprodutibilidade durante a síntese em larga escala. Isso representa uma oportunidade para pesquisadores desenvolverem métodos avançados de síntese e novas aplicações. Além disso, a conversão de grandes volumes de resíduos sólidos gerados em áreas rurais e urbanas em carbon dots ambientalmente benignos pode ter um impacto positivo significativo. Os *carbon quantum dots* têm sido empregados em várias aplicações, como agentes de entrega de medicamentos, genes e outros fármacos em estudos in vivo e in vitro. Esses materiais são especialmente úteis para a detecção celular e têm potencial em armazenamento de energia, baterias e detecção de elementos tóxicos, íons, moléculas e explosivos, devido à sua alta fluorescência e lacuna de banda ajustável.

No entanto, os *carbon quantum dots* (CQD) ainda não são considerados completamente seguros, e mais pesquisas são necessárias para garantir sua pureza e segurança toxicológica. Os processos existentes frequentemente resultam em produtos de baixa qualidade, limitando sua aplicação em nanomedicina. A seletividade dos CQDs para a absorção de certos elementos, íons e moléculas tóxicas ou radioativas é baixa, e os mecanismos para ajustar suas características de fotoluminescência ainda precisam ser melhor compreendidos. Embora algumas técnicas, como dopagem e funcionalização de superfície, tenham mostrado potencial, as características físicas e químicas dos CQD ainda não foram claramente descritas. A pesquisa sobre a entrega de genes usando CQD está em fase inicial e requer mais atenção, e suas capacidades de detecção podem ser efetivamente exploradas em contextos como o diagnóstico e monitoramento da COVID-19.

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