# Improving Mechanical Properties of Poly(ethylene oxide) Composites Using RAFT-Modified $SiO_2$ Nanoparticles

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**Abstract:** The objective of this work was to examine the impact of conventional and RAFT-modified $SiO_2$ nanoparticles on the mechanical characteristics and crystallinity of poly(ethylene oxide) (PEO) composites. Preparation of PEO composites included the incorporation of 5 wt% of both unaltered $SiO_3$ and $SiO_3$ that had been changed via reversible addition-fragmentation chain transfer (RAFT) polymerization. We assessed the mechanical characteristics, such as strain at fracture, ultimate tensile strength, and Young's modulus. The inclusion of unaltered $SiO_2$ decreased the strain at fracture (570 ± 18%) and ultimate tensile strength (22.5 ± 0.8 MPa) in comparison to pure PEO (850 ± 25%, 32.0 ± 1.2 MPa). Nevertheless, the inclusion of RAFT-modified $SiO_2$ led to improved tensile characteristics, including a strain at break of 800 ± 30%, ultimate tensile strength of 35.2 ± 2.5 MPa, and Young's modulus of 260 ± 13 MPa. The effective dispersion of RAFT-modified $SiO_2$ in the PEO matrix was verified by X-ray diffraction (XRD), leading to enhanced mechanical characteristics. This research points that the using the RAFT polymerization to alter the surface of nanoparticles is a good strategy to enhance the efficiencies of PEO composite for potential application in versatile electronics, membranes and other polymers technologies.

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# 1 Introduction

Poly(ethylene oxide) (PEO) is a highly valued polymer with a unique set of properties, including high ionic conductivity, elasticity, and wide-spread use in electrochemical and energy storage devices. Its semi-crystalline structure and ability to form complexes with various salts make it an ideal candidate as a solid polymer electrolyte. However, its mechanical stability and ionic conductivity need further improvement to suit the requirements of higher electrochemical applications. It can be improved in terms of electrochemical performance, mechanical strength, and thermal stability by incorporating associative polymers, or by blending PEO with nanofillers, including $SiO_2$, graphene or carbon nanotubes. It is important that these fillers do not cluster and are well compatibilised in the PEO matrix because untreated fillers usually tend to cluster and hence not release the desired output.[1–3] whilst conventional techniques for incorporating these fillers has its limitations because of poor dispersion and poor interfacial adhesion. This decreases mechanical reinforcement and also obstructs the ionic pathways needed for ionic conduction and device performance. Surface modification of fillers has come out as a potential option to these limitations.. Strategies like surface-initiated RAFT polymerization let for the grafting of polymer ancestor on nanofiller to improve compatibility with polymer support. Aerogel and carbon fiber can be prepared by the RAFT polymerization so that better filler distribution and stronger interface adhesion can be realized, and thus the properties such as mechanical strength, thermal stability and ionic conductivity can be enhanced [4,5]. Some new experimental investigations reveal that solution processed PEO composites with short PEO chains on $SiO_2$ nanofibers possess significant enhancements. The over-thing is that the incorporation of both modified and unmodified $SiO_2$ nanoparticles with the PEO matrix can improve the performance of such energy storage devices as fuel cells, electrochemical capacitors, and solid-state batteries. The surface-initiated RAFT strategy alters the properties of the material; the structure is improved, and the efficiency is enhanced compared to the conventional techniques. These mechanical, thermal and electrochemical tests combined with PEO-based coatings assessment corroborate that surface treatment profoundly affects these composites performance, outlining a promising route for PEO-based engineering platforms where reliability, performance and steady-state are critical.[6–8].

# 2 EXPERIMENTAL

## 2.1 Materials

The pellet-shaped polymer matrix consisted of poly(ethylene oxide) (PEO), with an average molecular weight of about 600,000. The silica filler material was 99% trace

metals base and had a particle size of less than 50 nm[9–11]. The surface of the SiO2 nanoparticles was altered by employing anhydrous dichloromethane (DCM, 99.99%) in the presence of triethylamine (TEA, ≥99%) to graft 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPADB, 97%) onto them. The initiator in the polymerization process was 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%) and the monomer used was ethylene oxide (EO). The chain transfer agent was CPADB.Acetone (p.a.), toluene (p.a.), and 100% anhydrous ethanol (p.a.) were all used in the polymerization and modification processes. In order to dry and purify the substance, dimethylformamide (DMF) and diethyl ether (ACS reagent, anhydrous, ≥99%) were used. Deionized water (DW) was used in every cleaning stage and to prepare aqueous solutions as needed.

## 2.2 Modification of SiO2 Particles

This study employed a surface-initiated reversible addition-fragmentation chain transfer (RAFT) polymerization method to modify silica nanoparticles ($SiO_2$). Precise measurements of the $SiO_2$ dispersion were achieved using a calibrated Schlenk flask, which contained a specific quantity of nanoparticles suspended in anhydrous dichloromethane (DCM) within an argon atmosphere. To successfully polymerize the monomers, the RAFT agent was prepared using fluoro acetic acid CPADB and triethylamine as the catalyst. A presumably suitable method for the separation of dissolved gases from a reaction mixture is a cycle of freezing and pumping the solution followed by its thawing. When gas formation ceased, free radical polymerization was initiated using 2,2’-azobis(2-methylpropionitrile) (AIBN) under argon atmosphere.The polymerization process was monitored in a high temperature for 24 hours with the temperature being 70◦C. After the reaction was full-borne, the liquid was cooled in order to remove any unreacted material. The above modified $SiO_2$ particles were further purified by filtration and solvent extraction using acetone, ethanol, and toluene solvents. Last, the modified silica nanoparticles were placed under vacuum drying at a temperature of 50°C for a whole night ready to be incorporated into composite materials.[12–14].

## 2.3 Preparation of PEO/SiO2 Composites

Polyether/silica composites were prepared from using polyether and silica glycols through a state-of-art melt blending process. First, poor-quality polyethylene pellets were melted in a twin-screw processor at 100°C while the screw speed was 60 rpm. For dispersion of the particles, both modified and unmodified silica nanoparticles were added incrementally into the molten polyethylene oxide and at the same time the rate of stirring was gradually increased to 100 RPM. This process of mixing was continued up to a total of 10 minutes for preparation of the mixed batches.

After both coarse and fine aggregates were mixed together in the mixer, they were then tipped out and left to cool down before they were broken into smaller pieces. Three distinct composite formulations were prepared: PEO, PEO with 5 wt% of untreated Silica and PEO solution with 5 wt% of chemically treated Silica. To form thin films of each composite, the applied materials have been exposed to heat treatment in a modern hydraulic press at 120 C for 3 minutes. After this, the films

were rapidly cooled on a water cooled press to ensure that the surface of the films and their quality and structural characteristics were preserved. Having a high-quality die cutting machine, different samples were made-owing to intense mechanical characterisation, Fourier transform infrared (FTIR), and X-ray diffraction tests in the paper.

### 2.4 Characterization

Confirming changes in silicon dioxide (SiO2) nanoparticles and identifying the chemical composition of synthesized compounds was done via Fourier Transform Infrared Spectroscopy. In this work we have utilized ATR spectra which were collected from the highly specified diamond crystal. A special concern was the analysis of the PEO polymer matrix crystallographic structure regarding its crystallinity quality upon SiO2 nanoparticles dispersion, with the help of XRD methods. (XRD). Thus, an X-ray source of Copper Kα was utilized to obtain XRD patterns at various 2θ angle from 10 to 60 degree. The two sophisticated techniques may be used to analyze in more detail the molecular intersactions that exist in the polyethylene oxide/silica compounds.

## 3 Methodology

In this work, we chose to use the Surface initiated RAFT Polymerisation technique to graft $SiO_2$ nanoparticles. This technique was to allot a RAFT agent onto the nanoparticle surfaces, thus enabling the polymerization of short polyethylene oxide (PEO) chains. After the functionalisation process the nanoparticles were purified and characterised to confirm successful modification. In order to obtain composites, melt blending was used in order to ensure the incorporation of both modifed and unmodified $SiO_2$ nanoparticles in to the PEO matrix. The last process involved in preparation of the PEO composite included the use of a high-shear mixer to facilitate good dispersion of the nanoparticle filler in the PEO. Differences in the composite properties were studied when using different concentrations of $SiO_2$ nanoparticles, which enabled the elaboration of the researched filler loading effectfully. Tensile strength and elongation at break were measured by an automated testing procedure and stress-strain curves were plotted in order to examine how the modified $SiO_2$ nanoparticles influence the overall mechanical performance of the composites. Further, we studied the DSC analysis of the PEO matrix for the thermal transition of the material including the melting and crystallization of PEO matrix to determine the effect of $SiO_2$ nanoparticles on thermal properties. The PEO/$SiO_2$ composites' phase structure was investigated by X-ray diffraction or XRD analysis. This work was intended to evaluate the PEO crystallinity and characterize the impact of $SiO_2$ nanoparticles thereon. Using this multi-pronged approach, we could perform a comprehensive analysis of the mechanical, thermal, electrochemical and structural characteristics of PEO/$SiO_2$ composites and thereby have a better understanding of how changes in the nanoparticles alter the performance of the resulting material.

**3. Result and Analysis**

### 3.1 Mechanical Properties

The tensile properties of PEO and PEO/$SiO_2$ composites are presented in the following table, based on mechanics characterization of the samples. The data also showed that the incorporation of $SiO_2$ nanoparticles, whether unaltered or modified by RAFT, affected the mechanical properties of PEO matrix.

- **Strain at Break:** The maximum strain at break (850 ± 25%) was seen in Neat PEO. The incorporation of unaltered SiO2 nanoparticles greatly decreased the strain at fracture to 570 ± 18%, suggesting that the inflexible nanoparticles impeded the elongation of the polymer chains. Nevertheless, the SiO2 nanoparticles treated with RAFT (PEO/5% SiO2-RAFT) exhibited enhanced ductility, as shown by a rise in strain at break (800 ± 30%)[20–22]. This observation implies that the surface modification has contributed to a better compatible relationship between the filler and the matrix.
- **Ultimate Tensile Strength**: The measured ultimate tensile strength of pure PEO was 32.0 ± 1.2 MPa. The incorporation of unaltered SiO2 resulted in a decrease in tensile strength to 22.5 ± 0.8 MSa. By contrast, the addition of RAFT-modified SiO2 nanoparticles (PEO/5% SiO2-RAFT) led to a significant increase in tensile strength, reaching 35.2 ± 2.5 MPa, which exceeded the strength of pure PEO. The observed rise may be ascribed to the improved dispersion and interfacial adhesion between the modified nanoparticles and the PEO resin matrix[23–25].
- **Young's Modulus**: Upon adding unaltered SiO2, the Young's modulus of clean PEO rose from 200 ± 10 MPa to 230 ± 11 MPa, showing an increase in rigidity. The composite with RAFT-modified SiO2 had the greatest modulus (260 ± 13 MPa), indicating that the surface modification enhanced the transmission of stress between the polymer matrix and the nanoparticles, thereby increasing the mechanical strength of the composite.

**Table 1.** Mechanical properties of our material

| Blend | Strain at Break (%) | Ultimate Tensile Strength (MPa) | Young's Modulus (MPa) |
|---|---|---|---|
| PEO | 850 ± 25 | 32.0 ± 1.2 | 200 ± 10 |
| PEO/5% SiO2 | 570 ± 18 | 22.5 ± 0.8 | 230 ± 11 |
| PEO/5% SiO2-RAFT | 800 ± 30 | 35.2 ± 2.5 | 260 ± 13 |

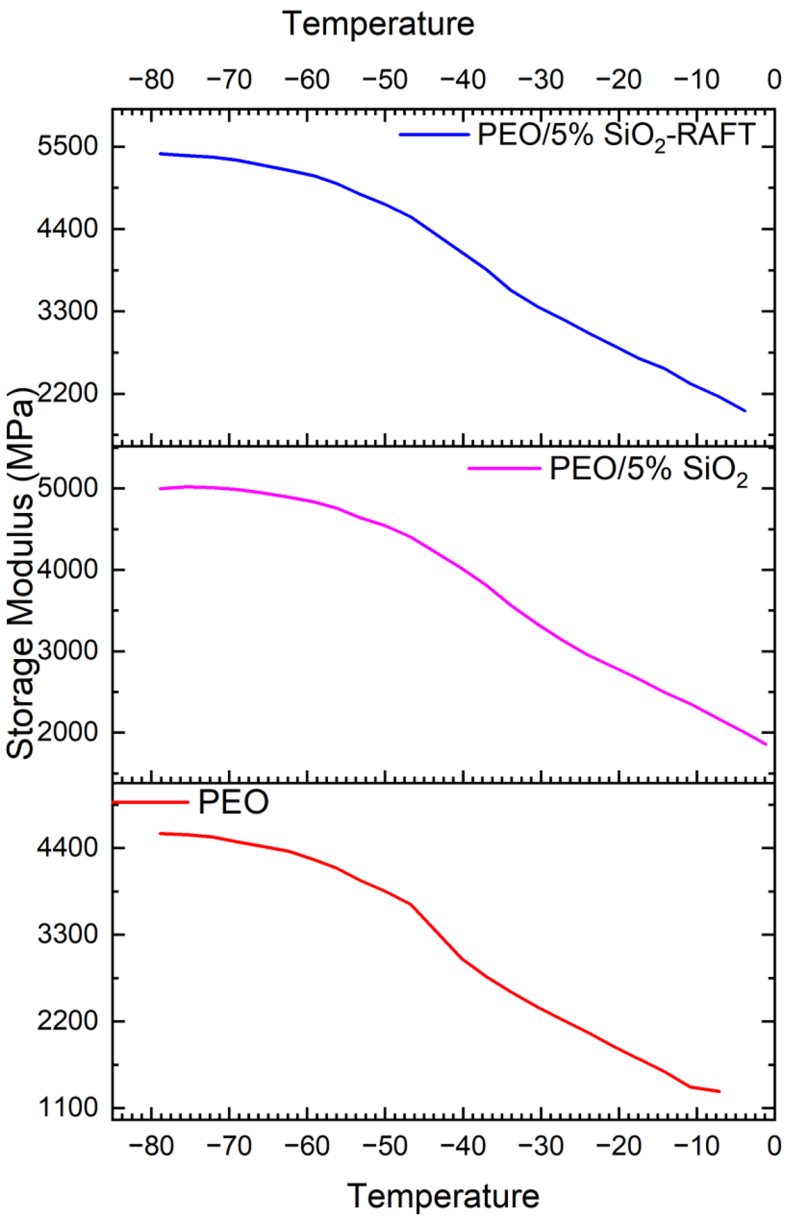


**Fig. 1.** Mechanical Properties of our material

### 3.2 XRD Analysis

The X-ray diffraction (XRD) patterns of neat PEO, PEO/5% SiO2, and PEO/5% SiO2-RAFT are shown in the figure below. The following observations can be made:

- **PEO:** Particularly in the 2θ region of 19° to 23°, the black curve illustrating the X-ray diffraction pattern of pure PEO shows clear crystalline peaks that are peculiar to the semi-crystalline structure of PEO. These peaks indicate the composition of PEO, which is defined by its orthorhombic crystal structure.
- **PEO/5% $SiO_2$**: A clear peak at around 22 degrees was seen, as shown by the red curve, as a result of adding unmodified SiO2 to the PEO/5% SiO2 combination. It is possible that the presence of silicon dioxide nanoparticles is responsible for the observed peak. The nanoparticles inside the PEO matrix have probably compressed due to insufficient dispersion, thus the peak is not very strong. Because of the presence of SiO2, the intensity of the PEO crystalline peaks was somewhat reduced, indicating that the crystallization process of PEO was disrupted.
- **PEO/5% $SiO_2$-RAFT:** A more consistent dispersion of nanoparticles inside the material was suggested by the RAFT-modified SiO2's noticeable SiO2 peak at 22 degrees (blue curve). The PEO's crystalline peaks are still visible, however they aren't quite as bright as they are when the PEO is polished. These results indicate that the modified SiO2 nanoparticles did not significantly affect the PEO crystallization, allowing for an appropriate ratio of filler to matrix crystallinity.

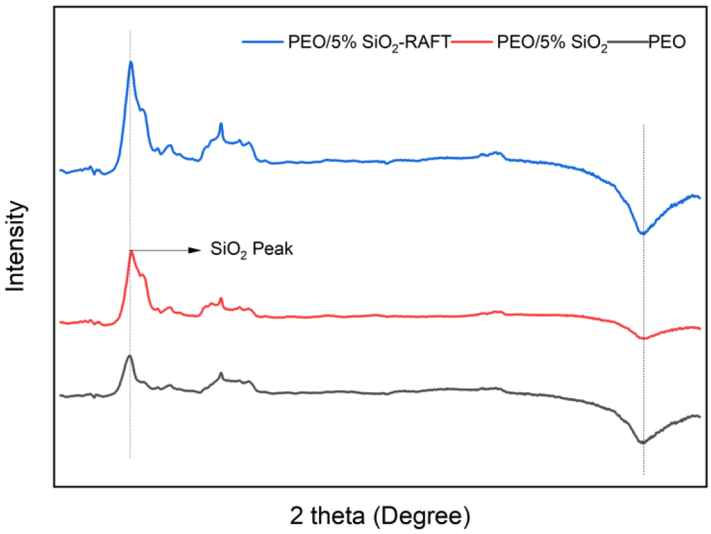


**Fig. 2.** XRD analysis of Experiment

## 4 Conclusion

The aim of this study was to analyze the structural and mechanical properties of PEO composites with 5 weight percent of either unmodified SiO2 or SiO2 nanoparticles transformed via RAFT. According to the empirical findings, the mechanical

characteristics of PEO are significantly affected by the addition of unmodified $SiO_2$. The Young's modulus was to be 230 ± 11 MPa, the ultimate tensile strength of 22. 5 ± 0. 8 MPa and the fracture strain of 570 ± 18%. The reason for the deterioration of the performance was identified to be the incompatibility and poor distribution of the uncoated $SiO_2$ in the PEO matrix. As a support to these results, X-ray diffraction (XRD) investigations revealed that the $SiO_2$ nanopixels aggregate. Furthermore, the mechanical properties of the material were enhanced by adding of RAFT-modified SiO2 nanoparticles. When it was broken, the material exhibited different performances in terms of strain of 800±30 percent, the ultimate tensile strength of 35.2±2.5 megapascals, and Young's modulus of 260±13 megapascals of the $SiO_2$ nanoparticles, the one which was subjected to the RAFT process further exhibited increased homogeneity of the composition as determined from the XRD result. A more compatible filler gave better mechanical performance and better stress transfer with the PEO matrix. The enhanced improvement happened for both the mechanical properties and the dispersion of the $SiO_2$ nanoparticles within the PEO matrix to change its surface by RAFT polymerization. Thus, the aim of the presented study is to prove that PEO-based composite materials might improve by using RAFT-modified $SiO_2$ in high-performance polymer technologies like flexible electronics and membranes.

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