A Coupling Agent's Inclusion Affects Functional Groups and Heat Resistance in Energy Storage Materials

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ABSTRACT

The study of functional groups and heat resistance of energy-importing materials, as well as the inclusion of coupling agents, were the primary subjects of this article. 3-(trimethoxysilyl) propyl methacrylate was the coupling agent employed in this study to alter the surface of the silica in the composite material being created. Furthermore, the emergence of bifunctional organometallic (silane) connecting groups allowed the coupling agent to improve the energy storage material's heat resistance. Through the using of dynamic mechanical analysis, scanning electronic microscopy, and thermal tests. It was determined how the type of coupling material affected the interfacial bond strength. According to the findings, there was a significant interaction between the coupling material and the filler surface that had an impact on the material's heat resistance.

Key word: coupling materials, functional groups, heat resistance.

INTRODUCTION

The most prevalent subject that has caught the attention of many parties is climate change. The accomplishments of sustainable development may be threatened by the effects of climate change. The global accord expressly lists the Sustainable Development Goals (SDGs) for 2030 that include Climate Actions. The Paris Agreement recognized the need for international cooperation to keep the rise in the global average temperature to below 2°C relative to pre-industrial times, and it aimed to make people more resilient to the effects of climate change [1,2]. Consequently, we must use energy responsibly and work to create environmentally acceptable energy storage materials.

Phase Change Material (PCM) is a material that can be a breakthrough in overcoming the current climate change. PCMs are substances that, while undergoing a physical phase shift, have the capacity to store and release heat energy [3] (as shown in Figure 1). Phase changes happen when materials change between the solid, liquid, and gas phases of matter. At a

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particular pressure and temperature, this transformation happens. Applications involving temperature control or thermal energy storage can benefit greatly from PCM.



Figure 1. Melting and solidification process from PCMs [4]

Because PCM can help regulate temperature by lowering the usage of traditional heating or cooling technologies, its use promotes energy efficiency and lowers energy consumption. Organic and inorganic materials are the two primary divisions of phase change materials (PCM) [5,6]. The organic components that make up PCM include lauric acid, paraffin, fatty acids, and hydrocarbons [7]. While salt and metal are examples of inorganic materials [8]. The creation of organic PCM materials offers several benefits, including being inexpensive, non-toxic, and simple to manufacture, yet leaks frequently occur due to the materials' low mechanical strength and high thermal resistance.

Several attempts have been made by previous researchers to improve the performance of organic PCM by adding filler or encapsulation. The use of graphene oxide [9], CuO [10], Al₂O₃ [11], Fe₃O₄ [12] and other nanoparticles has been documented, and other researchers have recommended adding various nanoparticles to PCMs to increase thermal performance. Due to its characteristics, including a better thermal conductivity, low density, and high thermal performance, carbon nanotubes have emerged as one of the most important nanoparticles. The usage of PCM-based TES systems maintains appropriate temperature conditions while being sustainable and reasonably priced [13]. Over the years, various PCM classes have been investigated to match TES applications. Hydrated salts were the first PCM class due to their inexpensive cost, high energy density (60-180 kWh/m³), and melting temperature range of 30°C to 120°C. However, according to the research mentioned above, the filler is made of commercial components, and the surface interaction that results has not been examined. This article focuses on studying the bonding that takes place in PCMs and how it relates to their thermal resistance considering the explanation provided above. To ascertain the interactions that take place between the filler and the polymer matrix, surface analysis was also conducted.

EXPERIMENT

Chemicals and instruments

Chemicals used for research was PEG4000 (HO(C₂H₄O)nH), German company Merck Schuchardt OHG 85662 Hohenbrunn. SDS (C₁₂H₂₅NaO₄S) was provided by Merck KGaA in Germany. A 3-(trimethoxysilyl) propyl methacrylate was the coupling agent. The coprecipitation and titration media, respectively, were sodium hydroxide (NaOH, 98% purity) and HCl, 96% purity. Silica is synthesized from natural materials.

Instrumentation applied for analysis were FTIR (Fourier Transform Infrared Spectroscopy), DMA (Dynamic Mechanical Analysis), DSC (Differential Scanning Calorimetry), and TEM (Transmission Electron Microscopy). The functional groups formed in the composites are characterized using FTIR, the thermomechanical response to the material's heat resistance is determined using DMA and DSC, and the morphology and surface contact area formed between the matrix and filler are determined using TEM. Knowing the nature of heat resistance was done in the energy storage composites' operating temperature range, specifically from room temperature to 80°C.

Synthesis procedure

Through immersion in a 1.0 M of HCl, silica made from natural materials was created through a chemical process. In order to modify the surface and neutralize the resultant silica, 3-(trimethoxysilyl) propyl methacrylate was added as a coupling agent. After adding SDS as a dispersion agent and combining the surface-modified silica with the PEG polymer, the composite is prepared for printing. In order to maximize the effect of the centripetal force in promoting the spread of filler, this composite was prepared under melted PEG conditions.

RESULT AND DISCUSSION

Natural silica has been effectively added to composites in the form of filler in polymer matrix materials. A representative FTIR pattern of the 20% CQ composite that exhibits the functional group bonding pattern of PEG and silica as illustrated in Figure 2 serves as evidence of this success. The presence of silanol groups (1004.85 cm⁻¹) on the silica particles following preparation with the addition of a coupling agent is what makes Figure 2 fascinating. One silicon atom (Si) is connected to three hydrogen atoms (H), one hydroxyl group (OH), and three oxygen atoms (O) to form the chemical functional group known as silanol [14–16]. The typical formula for this group is R₃SiOH, where R stands for an organic or inorganic substituent group.



Figure 2. The representative FTIR pattern of the 20% CQ composite that exhibits the functional group bonding pattern of PEG and silica. Red circles indicate the presence of silanol groups.

Silanol (Si-OH) can occasionally play a significant role in fortifying the relationship between a substance and other surfaces, such as on the surface of ceramic or silica (SiO₂) materials that include silicon-oxide bonds [17]. The ability of silanols to create hydrogen bonds

with other surfaces that contain accessible hydroxyl groups or oxygen atoms makes this particularly true. However, it is important to note that the nature of these silanol bonds can depend heavily on the specific chemical and physical environment, such as humidity, pH, temperature, and surface composition. In some cases, silanols can also become weak points in the material structure and can contribute to material degradation or cracking [18,19].

According to earlier research [20,21], the two weak intramolecular interactions of the PEG polymer, specifically the hydrogen bonds $OH \cdots O$ and $CH \cdots O$, are what give PEG its flexibility. As a result, in general, composites made of polymers need to have greater mechanical strength. Silanol plays a significant influence in enhancing the mechanical performance of compost and lowering modulus loss when applied external stresses. These outcomes are shown in Figure 3.

A more comprehensive analysis was hold by dynamic mechanical analysis. Here, we focused on damping (tan δ). The component of a material's reaction related to the material's capacity to dampen vibrations, is represented by the damping (tan δ) [22,23]. It describes how much of the mechanical energy used to distort the material is converted into heat. The damping, which is related to the viscoelastic behavior of the material, is a gauge of the material's damping capacity. Figure 2 reveals that the damping is reduced below T_m because the PEG molecular components are closely packed and very stiff in this area. Since molecular parts cannot move freely, the damping properties are poor. The chain segments can store additional energy in this stiff area. The micro-Brownian motion [24,25] stimulated to the PEG chain slippage and coordinated in the amorphous phase, resulting in the maximum damping (around Tm), where all of the polymer chains participate in the complicated motion, with further rises in temperature. Additionally, because there is no molecular barrier to large-scale polymer chain movement, the reduced damping values are once more discernible in the final region (liquid state).



Figure 3. The damping factor of the composite formed by the addition of 3-(trimethoxysilyl) propyl methacrylate as a coupling agent.



Figure 4. The π bond mechanism becomes interlocking and secondary bonding between silica and PEG.

In detail, the coupling agent mechanism that can improve the mechanical performance and heat resistance of compost above T_m can be explained in Figure 4. The presence of silica filler displaces some of the volume in the matrix, which reduces the number of weak π bonds and introduces new interlocking bonds between matrix and filler due to roughness filler form (as shown from Figures 4 and 5). In addition, silica has a higher latent heat than PEG (238 J/g [26] vs. 209 J/g [27]). According to Duquesna et al [5], latent heat is a method of storing heat energy through a phase change. The rubbery state that forms between the two transitions, namely the glass transition (T_g) and melting (T_m) temperatures, is represented in this study by region with the temperature range (room temperature -38°C). The way by which external thermal energy moves from the matrix to the filler is impacted by the interaction of the silica-PEG chain. The majority of the heat energy absorbed by the filler during thermal treatment can be attributed to the presence of silica filler. It makes sense why composites' tan δ is decreasing at a slower rate than pure PEG. The same justifications hold true for other compositions.

In addition, a peak in the temperature range of 38 to 60 °C denotes a polymer melting transition. Tm is associated with the first-order transition phenomena, showing that polymer has changed from a solid to a liquid [28]. T_m is a measure of how well molecular rearrangements and internal friction contribute to energy loss in a material. The existance of silica particle in the PEG matrix built more interfacial bonding between filler and matrix where energy could be damped. The domination of silica-polymer chain interaction, located in the surface of matrix and filler, reduce that results the highest T_m of 20% silica. However, the micoparticles of filler will be have the free motion at the interfacial bonding, because there is a large space filled PEG (matrixdominated region) with hight free volume. Consequently, more energy is released into heat and makes lower T_m values and higher tan δ peak.

Further inspection of Figure 3 shows the tan δ peak broadening of composites compared with pure PEG. This broadening can quantify the inhibition of stress relaxation due to rigid filler will absorb some energy from external loading forwarded through the matrix. It can also been remarked that the addition of silica content caused changes in relaxation temperatures of the composites. In the peak broad of tan δ implies stres from external loading will be muffled by silica filler before continuing into polymer matrix. So, these composites will need more time to through trasition temperature. Total energy dissipation in the composites depends on the filler content, their fractions in the composite and the interfacial bonding between filler and matrix.



Figure 5. Typical interface region of silica-filled composites with TEM.



Figure 6. DSC profiles of energy storage composites by the addition of 3-(trimethoxysilyl) propyl methacrylate as a coupling agent.

During phase transitions, such as crystallinity transitions in polymers or phase shifts in solids like solid solvents, heat changes that take place in DSC can reveal information regarding alterations in crystal or phase structure. This could have an impact on the DMA analysis's (tan δ). The peak of tan δ will be impacted by certain phase transitions in a sample that indicate changes in the material's elasticity and viscosity at a specific temperature. The composite

transition temperature on DSC exhibits a peak location identical to the DMA result, as illustrated in Figure 6. The DSC results support the DMA results, which demonstrate that the synthetic composites exhibit heat resistance in the temperature range of 38 to 60°C.

The ratio of energy absorbed to energy stored during deformation cycles is represented by the peak (tan) in DMA. While in DSC, heat changes caused by phase transitions or modifications to the molecular structure may have an impact on the sample's viscoelastic characteristics and, consequently, the peak (tan δ).

CONCLUSION

The findings of this study suggest that silica, a filler, can have its surface modified by 3-(trimethoxysilyl)propyl methacrylate to strengthen its binding with the polymer. It has been demonstrated that the addition of silane improves the heat resistance of composite materials where the coupling silica filler displaces some of the matrix volume, reducing the number of weak links and introducing new interlocking bonds between the matrix and filler due to filler roughness.

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