Effect of Calcium Carbonate Content on the Mechanical and Thermal Properties of Chitosan-Coated Poly(urethane) Foams

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Abstract: *In this work, the effect of chitosan and $CaCO_3$ coating on polyurethane (PU) foam on the mechanical and thermal properties was studied. PU-foams were soaked in a mixture of chitosan- calcium carbonate solution at different concentrations, i.e., 0.1–0.4%. The molecular behaviors due to the incorporation of chitosan/$CaCO_3$ into the PU-foam matrix were investigated by Fourier-Transform Infrared (FTIR) spectroscopy. Field Emission Scanning Electron Microscope (FE-SEM) was utilized to study the effect of chitosan/$CaCO_3$ coat on the pore structure of PU-foam. FTIR spectra show changes in the peak of 1446 and 1413 cm^{-1}, which serve as evidence of molecular interaction between PU and chitosan/$CaCO_3$. FE-SEM images show that the addition of chitosan/calcium carbonate cells was starting to close together, probably due to the increased dispersion of calcium carbonate on the entire surface of PU-foams/chitosan, which indicates that reducing the size of the cell will increase mechanical properties. From this study, it was found that PU-foam soaked in 0.4% $CaCO_3$ had the highest tensile strength. Coating PU-foam with 0.4% $CaCO_3$ also improved its thermal stability, indicated by an increase in its residual mass compared to neat PU-foam.*

Keywords: *coating; polyurethane; chitosan; calcium carbonate*

■ INTRODUCTION

Polyurethane (PU) foams are polymers formed by a reaction between the hydroxyl group of polyol and the polyisocyanate functional group, which has a highly cross-linked three-dimensional closed-cell structure. PU-foams are highly porous, making this material have low density, high energy absorption capabilities, and low thermal conductivity. Because of the low density, good mechanical properties, high energy absorption capabilities, and low thermal conductivity, PU-foams have been used in furniture, bedding, carpet underlay, packaging, and automotive [1].

Automotive applications have shown great attention to the thermal insulation properties of the materials used in the interior design of vehicles, such as headliners. The characteristics of material required for headliners are high rigidity, good thermal insulation, and sufficient thermal stability [2]. PU-foams consist of a soft segment and a hard segment. PU-foams soft segments are usually composed of polyols with a relatively low glass transition temperature, whereas hard segments are generally composed of diisocyanates with a relatively high glass transition temperature [3]. PU-foams are used for crash pads, mattresses, packaging, and automotive interior. The thermal stability of PU-foams is influenced strongly by their chemical and physical properties. Highly porous PU-foams tend to have less rigidity and low thermal stability [4]. The porous structure of PU-foam can provide better insulation properties against heat. Moreover, their lower thermal conductivity is a highly desired property in automotive applications. However, their porous structure makes PU-foams become less rigid and has low thermal stability. Surface modification of PU-foams on coating can increase their rigidity and thermal stability [5].

Chitosan is a deacetylate chitin product and a polysaccharide randomly substituted D-glucosamine and N-acetyl-D-glucosamine in β-(1-4) linkage and the second most abundant natural-based biopolymer after cellulose [6]. D-glucosamine monomer is a rigid unit that makes it potential material for surface coating, and on the other hand, it can increase its crystallinity [7]. Chitosan has been used as a material that can improve polymers' mechanical and thermal properties and diminish their strength to absorb water [8]. The modification of the PU surface to get PU properties both thermally and mechanically by combining PU with chitosan has been studied by Kara et al. [5]. The reaction of chitosan coating to PU showed better compatibility and tensile properties in PU-foams. Previous research using chitosan coating to increase the performance of PU-foam chitosan has been carried out by Centenaro et al., which explained that coated chitosan in PU-foam for absorbent applications gave an excellent performance and was able to reduce costs, but in this study not observed the improvement of the mechanical properties of coated PU-foam [9]. Carosio et al. have studied chitosan-PU foam on cellulose nanofibrils layer products for flame retardant applications. Chitosan coating and the addition of nanofibril cellulose reduce the combustion rate by up to 30%, but the mechanical properties are still not studied [10].

Furthermore, some researchers add inorganic material, such as clay [6], to increase the mechanical and thermal properties of PU. The other inorganic material used is calcium carbonate which is cost-effective and easy to obtain. It has also been widely used as surface coating and applied in the plastic composite industry to improve its thermal properties and rigidity. Researchers have investigated the effect of adding calcium carbonate and chitosan onto polycaprolactone and enhancing the thermal and mechanical properties [11]. Many studies investigated the advantages of blending calcium carbonate into polymers. However, its agglomeration enormously decreases the composite's physical properties, limiting its applications [12]. Conventional surface modification by solution coating can involve interactions between chitosan with calcium carbonate to induce the calcium carbonate's nucleation on the chitosan-coated surfaces [13]. This research aimed to study the effect of adding calcium carbonate in the PU-foams/chitosan coating to increase the thermal stability of PU-foams.

■ EXPERIMENTAL SECTION

Materials

The PU-foams materials with a density of 16 kg/m^3 were produced by Inoac Polytecno Indonesia with the formula composed of polyols, isocyanates, catalyst, blowing agent, and some other additives. Chitosan powder material was obtained from Marine Natural Product, Ltd., Indonesia. Acetic acid with a purity of 99.98% was obtained from Sigma Aldrich.

Instrumentation

Fourier transform infrared (FTIR) analysis

The composite products were characterized using FTIR Perkin Elmer 90325 (Perkin Elmer Inc., Waltham, MA, USA) to study functional groups of molecules in the PU-foams, PU-foams/chitosan, and PU-foams/chitosan/calcium carbonate with various concentrations of calcium carbonate. FTIR spectral analysis was performed within the wavenumber range of 500–4000 cm^{-1} and 30 scans.

Field emission-scanning electron microscope (FE-SEM)

The effect of calcium carbonate and chitosan coating on PU-foam surfaces was investigated by characterizing the composite products' morphology. The morphology observation was carried out using FE-SEM FEI Inspect F50 (FEI Company, Hillsboro, Oregon, USA).

Thermogravimetric analysis (TGA)

The coated PU thermal degradation behavior was recorded using thermogravimetric analyzer STA PerkinElmer STA6000 (PerkinElmer Inc., Waltham, MA, USA), N_2 gas atmosphere, from 40 °C to 500 °C with a heating rate of 10 °C/min.

Procedure

Preparation of coated PU-foams

In the preparation of the coating solution in Fig. 1, chitosan and calcium carbonate were diluted with 5% acetic acid. Chitosan with a concentration of 4% by weight

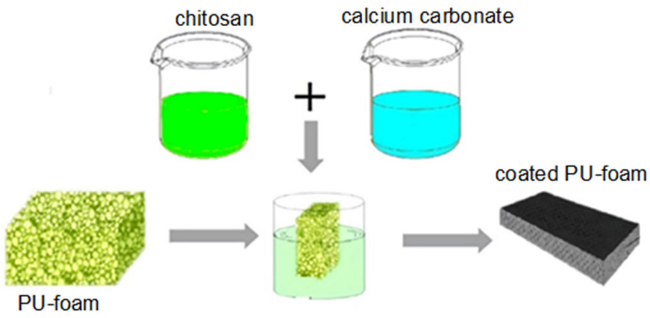

Fig 1. Schematic description of the process preparation of coated PU-foams. Chitosan solution and calcium carbonate were mixed in controlled conditions, then PU-foams cubes were immersed until completely covered

and calcium carbonate concentration ranging from 0.1 to 0.3% by weight are added together, and then the solution is stirred at a temperature of 75 °C until homogeneous. Furthermore, PU-foams were immersed in the solution for 3 min and exposed to air for a few moments. The results were then dried in an oven at 60 °C for 60 min and then cured at 120 °C for 90 min.

■ RESULTS AND DISCUSSION

Molecular Interaction in Coating

The FTIR analysis confirmed distinct groups of PU-foams, chitosan groups, and intermolecular O–H bond groups due to the coating reaction. The groups confirmed to be present before the reaction, namely neat PU-foams, are N–H and C=O, while the FTIR spectrum from the chitosan will be ascertained as hydroxyl, methyl, primary amide, and glycoside [14]. Meanwhile, after the coating reaction occurs, a new group appears, namely the intermolecular hydrogen bond between –O from PU and –H from chitosan, at wavenumbers of 3200–2700 cm^{-1} [15].

Fig. 2 shows a vibrational area characteristic of the urethane group at 2868–3280 cm^{-1}, which is the N–H group region, and the wavenumber of 1640–1718 cm^{-1} corresponding to the C=O group stretching vibration. These test results were in line with the research results by Chalid et al. [16]. Chitosan FTIR spectrum peak has strong and broad at a wavenumber of 3359 cm^{-1}, indicating the presence of O–H that overlaps with the N–H group. Meanwhile, the wavenumber of 1637, 1561, and 1375 cm^{-1} show groups of C=O stretching (primary amide), N–H bending (secondary amide), and C–N (tertiary amide) stretching vibrations, and a weak intensity signal that is a characteristic of the hydrogen bond between O and H [17]. The FTIR results of chitosan-coated PU (Fig. 2) indicate the possibility of the overlapping between characteristic peaks of PU-foams and chitosan structure. A band at 3280 cm^{-1} and 1072 cm^{-1} related to the –NH$_2$ and –OH groups of chitosan, respectively [9].

After PU-foams were coated with chitosan, the result indicated increasing properties by producing intermolecular hydrogen bonds. Furthermore, calcium carbonate is added as a reinforcing additive in PU-foams/chitosan. With this addition, it is expected that its mechanical properties to increase. The compatibility between carbonate groups of calcium carbonate with PU-foams/chitosan with carbonate ions was determined and characterized using FTIR. Carbonate groups in the FTIR spectrum will appear at wavenumbers around 1446 and 1413 cm^{-1}, which is the vibrations of the bending O–H group, according to the report by Reig et al. [18]. This was demonstrated by the presence of these

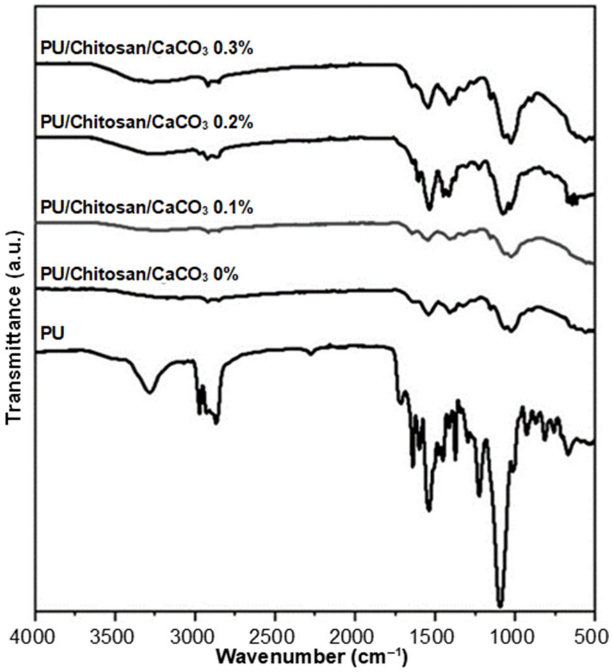

Fig 2. FTIR spectrum of PU-foams, PU-foams/chitosan, and PU-foams/chitosan/calcium carbonate with various concentrations of calcium carbonate

OH groups in all PU/chitosan/calcium carbonate spectrum. The results also explained that there was no shift from the peak of the N–H group and the C=O group by adding calcium carbonate because calcium carbonate was only deposited on the surface of PU-foams, and there was no chemical reaction to form new compounds. It was in accordance with research conducted by Dinararum et al. [19]. Fig. 3 shows the possible interaction between PU-foams, chitosan, and calcium carbonate. From FTIR results, the possible hydrogen bond was between H from chitosan and O from PU-foams and O from carbonyl groups in calcium carbonate with H from hydroxyl groups in chitosan.

Morphological Behavior of Coating

Characterization was then carried out using FE-SEM to understand the details of the coating mechanism and compatibility in PU-foams/chitosan coating materials and the effect of adding calcium carbonate. The presence of solid chitosan particles in the PU-foams matrix network affected PU-foam's morphology. A study showed that chitosan's presence affected PU-foams' porosity and surface roughness [20].

Fig. 4(a) showed the 250× magnification result for PU-foams having a stretchy and porous surface. The resulting pores had a large size and were open cells. Furthermore, PU-foams were coated with chitosan, resulting in a cell structure shown in Fig. 4(b). The pore size was smaller compared to PU-foams without chitosan coating. The addition of calcium carbonate to PU-foams/chitosan affected the cell structure, as shown in Fig. 4(c). The cells were starting to close together, probably due to the increased dispersion of calcium carbonate on the entire surface of PU-foams/chitosan.

The addition of calcium carbonate in PU-foams/chitosan was analyzed (Fig. 5). The various concentrations of calcium carbonate aimed to optimize calcium carbonate concentrations that give the desired results. The SEM results of neat PU-foams, PU-foams/chitosan, and PU-foams/chitosan/calcium carbonate can be seen in Fig. 5. It was shown that the addition of calcium carbonate could reduce the size of the cell. The shape of the structure was also tidier and more uniform than PU-foams because the addition of inorganic material increased the bulk viscosity so that it could resist cell growth. This result was in accordance with the research conducted by Chuayjuljit et al. [21].

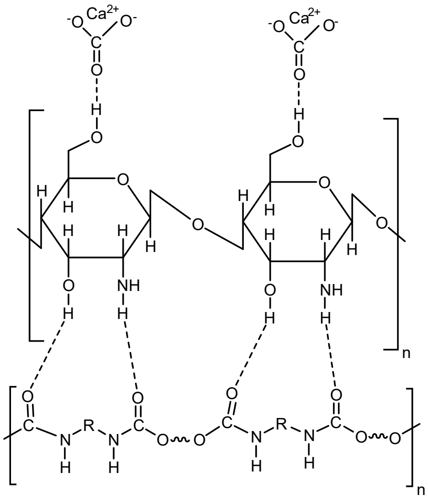

Fig 3. Proposed intermolecular hydrogen bond interactions between the PU-foam-chitosan and chitosan-calcium carbonate

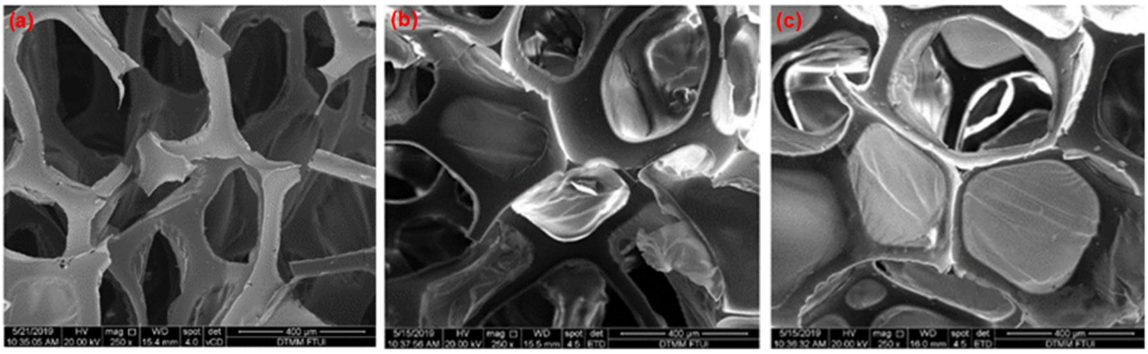

Fig 4. Comparison of morphology (a) PU-foams, (b) PU-foams/chitosan, and (c) 0.1% calcium carbonate in PU-foams/chitosan with a magnification of 250×

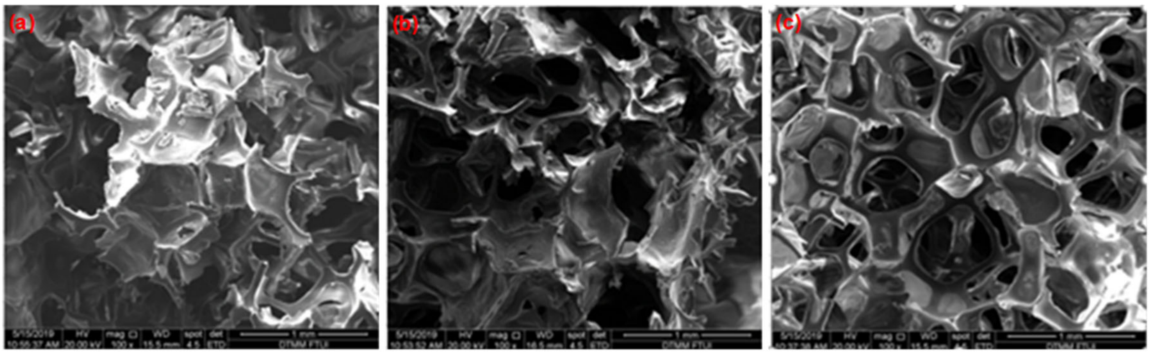

Fig 5. Morphological comparison of (a) 0.1%, (b) 0.2%, and (c) 0.3% calcium carbonate in PU-foams/chitosan with a magnification of 250×

Thermal Behavior of Coating

Thermogravimetric analysis (TGA) of coated PU samples was analyzed to observe the effect of coating on PU-foams' thermal stability in a nitrogen gas atmosphere at the heating rate of 10 °C/min. TGA and derivative thermogravimetric DTG curves obtained for PU-foams, PU-foams/chitosan, and PU-foams/chitosan/calcium carbonate were represented in Fig. 6. They corresponded to the sample's weight loss upon continuous heating to 500 °C. It was clarified from the TGA thermograms and data in the summarized table that the thermal stability of the PUs sample was slightly raised after being coated with calcium carbonate. This enhanced thermal stability was due to the homogenous calcium carbonate coating on the surface of PU, as shown in SEM images. This increase in decomposition temperature indicated increased PU-foams/chitosan/calcium carbonate's thermal stability.

TGA results for PU-foams/chitosan and PU-foams/chitosan/calcium carbonate had an initial weight loss below 100 °C regardless of their water content. The initial change was ascribed to the vaporization of water because of the chitosan's hydrophilic character and the remaining solvent used to dilute chitosan and calcium carbonate. TGA results showed that all the PUs samples showed two-step degradation, with the initial step degradation appearing in the range of 200–340 °C and the subsequent step degradation occurring at 320–430 °C. The first degradation step was known as the initial degradation temperature (T^{d1}), where the degradation temperature of all samples occurred at temperatures of

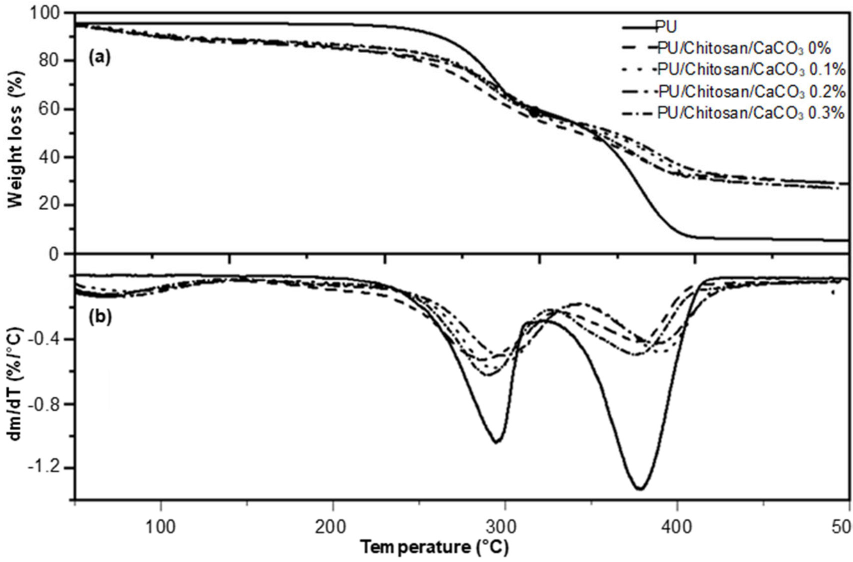

Fig 6. (a) TGA and (b) DTG curves of PU-foams, PU-foams/chitosan, and PU-foams/chitosan/calcium carbonate

200–340 °C. This was due to the decomposition temperature of urethane bonds to form CO_2, alcohols, aldehydes, amines, and solvent evaporation [22], the decomposition of diisocyanate as the hard segment of PU, and the decomposition of chitosan hydroxyl groups [23]. The second decomposition step (T^{d2}) was between 320–430 °C, representing the decomposition of the polyol molecules as the soft segment of PU. Meanwhile, the subsequent degradation was the degradation temperature of complex polyol molecules and other inorganic materials, including calcium carbonate [24].

The neat PU-foams have T^{d1} and T^{d2}, respectively, at around 294.7 °C and 376.1 °C, with a residual weight of 5.52%. As shown in Fig. 7, all the PUs samples with calcium carbonate showed thermal stability compared to samples without calcium carbonate at all stages. Therefore, it was concluded that the use of calcium carbonate and the incorporation of chitosan in the PU matrix enhanced the thermal stability and thermal degradation behavior of samples. This aspect was further reflected by the significant increase in the residual mass of neat PU-foams (5.52%) at 500 °C compared to PU-foams/chitosan (30.33%) and PU/chitosan/calcium carbonate (28.42–30.74%). As also reported in the research by Barikani et al. [25], compared with neat PU-foams and PU-foams/chitosan, the sample coated with calcium carbonate showed considerably higher thermal stability, especially at higher temperatures.

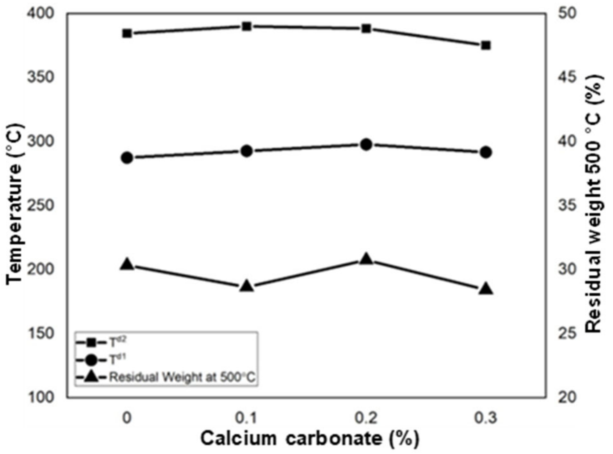

Fig 7. Degradation temperature and residual weight from PU-foams, PU-foams/chitosan, and PU-foams/chitosan/calcium carbonate

■ CONCLUSION

In a nutshell, we show a simple technique for preparing chitosan-calcium carbonate to improve the thermal and mechanical properties of PU-foams. From FTIR results, the possible hydrogen bond was between H from chitosan and O from PU-foams and O from carbonyl groups in calcium carbonate with H from hydroxyl groups in chitosan. Field Emission Scanning Electron Microscope (FE-SEM) shows that the shape of the structure was tidier and more uniform than PU-foams because the addition of inorganic material increased the bulk viscosity so that it could resist cell growth. It was clarified from the TGA thermograms that the thermal stability of the PU-foams sample was slightly raised after being coated with chitosan-calcium carbonate. The PU-foam coated with chitosan-added calcium carbonate can find potential applications requiring flame retardancy and good mechanical properties, such as automotive parts.

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