AI translation · View original & related papers at
chinarxiv.org/items/chinaxiv-202108.00096

Consolidation Model and Its Validation for Wet-Processed Carbon Fiber Reinforced Thermoplastic Composites

Authors: Yan Xin

Date: 2021-08-13T00:00:00+00:00

Abstract

In recent decades, carbon fiber reinforced thermoplastic from the wet-laid process (WL-CTP) appeals to attention for its simplicity and compatibility with recycled carbon fibers. However, there is still no constitutive model for the consolidation of WL-CTP. This study proposes a constitutive model based on the constitutive equation describing the compress behavior of the dry/impregnated CF network. Three deductions raised from the consolidation model were validated by the experiments investigating the effect of molding time, pressure, and temperature on the void volume fraction of the WL-CTP. Flexural testing further investigated the effect of molding time, pressure, and temperature on the flexural modulus and strength of the WL-CTP. It reveals that the molding pressure can be the only factor affecting the consolidation and flexural properties of the WL-CTP, which indicates that the WL-CTP with low void content and qualified mechanical properties can be produced under a relatively low temperature and high productivity.

Full Text

Preamble

A Consolidation Model for Carbon Fiber Reinforced Thermoplastic from the Wet-laid Process and its Validation

Xin YAN, Guang-lei ZHAO, Jin YANG*, Xi-wen WANG**

School of Light Industry and Engineering, State Key Laboratory of Pulp and Paper, South China University of Technology, Wushan Road 381st, Guangzhou City, China

*Corresponding authors: Jin YANG, E-mail: yangjin@scut.edu.cn; Xi-wen WANG, E-mail: wangxw@scut.edu.cn

Abstract

In recent decades, carbon fiber reinforced thermoplastic produced via the wet-laid process (WL-CTP) has attracted attention for its simplicity and compatibility with recycled carbon fibers. However, no constitutive model currently exists for the consolidation of WL-CTP. This study proposes a constitutive model based on equations describing the compressive behavior of dry and impregnated carbon fiber networks. Three deductions derived from this model were validated through experiments investigating the effects of molding time, pressure, and temperature on the void volume fraction of WL-CTP. Flexural testing further examined how these molding parameters affect the flexural modulus and strength of WL-CTP. The results reveal that molding pressure is the sole factor influencing both consolidation and flexural properties, indicating that WL-CTP with low void content and qualified mechanical properties can be produced under relatively low temperatures with high productivity.

Keywords: Carbon fiber reinforced thermoplastic, Wet-laid process, Consolidation, Model, Flexural properties

1. Introduction

The wet-laid process, based on papermaking principles, can be used to produce carbon fiber reinforced thermoplastic (CFRTP) composites. This approach has attracted attention for its simplicity and compatibility with recycled carbon fiber (rCF), offering a solution for low-cost CFRTP production and rCF reuse that broadens CFRTP applications. Since its first application in glass fiber-reinforced thermoplastic manufacturing in the 1990s, various fiber-reinforced thermoplastics have been developed via the wet-laid process in recent decades, ranging from traditional composites to nanocomposites, and from artificial fiber-reinforced to natural fiber-reinforced composites.

The wet-laid process involves two main procedures: (1) Papermaking, where carbon fibers (CFs) and thermoplastic fibers are dispersed in water to form pulp, during which the two fiber types mix evenly, followed by drainage and water removal to produce a preform; and (2) Heat-compression molding, where the preform is placed in a mold. After heat-compression and cooling, the carbon fiber reinforced thermoplastic from the wet-laid process (WL-CTP) is obtained. The papermaking process creates a mixture of carbon and thermoplastic fibers, while heat-compression molding melts the thermoplastic, impregnates the carbon fibers, and endows WL-CTP with strength. Consolidation of WL-CTP occurs during heat-compression molding. Voids are common defects in composites that form during consolidation and degrade mechanical properties. Consequently, constitutive models have been proposed to elucidate how molding conditions influence void elimination and to predict composite consolidation behavior.

Two primary models are generally used for FRTP consolidation. First, the forced unidirectional infiltration model for deformable porous media treats consolidation as forced molten matrix infiltration into a deformable fiber network, modeling the fiber network as a mat and combining its compressibility and relaxation properties with Darcy’ s law. Michaud et al. applied this model to GMT consolidation from the film-stacking process. Second, the fiber bundle impregnation model treats the fiber network as individual bundles, considering bundle size and distribution in addition to stress-strain behavior and Darcy’ s law. Bernet et al. used this model for GF/PEEK commingled yarn composites. Both models require a clear boundary between fiber network and matrix at the initial consolidation stage. However, in WL-CTP, CFs exist as both single fibers and bundles, commingling with thermoplastic fiber (see Fig 1 [Figure 1: see original paper]). Thus, the carbon fiber network cannot be modeled as either a mat or bundles, and no clear boundary exists between network and matrix (see Fig 1). These characteristics render the two basic models unsuitable for WL-CTP consolidation and make modeling this process complex.

Nevertheless, researchers have studied WL-CTP consolidation. Wei et al. investigated molding pressure effects on WL-CTP with 20% nominal fiber volume fraction (FVF), finding that pressures below 3 MPa could not ensure good consolidation, while pressures above 8 MPa could damage carbon fibers, with an optimal pressure of 5 MPa yielding the best mechanical properties. Tse et al. examined void content in flax fiber-containing WL-CTP, observing decreased void content with increased flax fiber content due to hydroxyl groups promoting fiber interaction. Yeole et al. studied papermaking additive effects on GF/PA6 composites, finding that additives did not affect consolidation because they volatilized during compression molding.

While these studies advance our understanding, no constitutive model for WL-CTP consolidation has been proposed. This study aims to model WL-CTP consolidation and validate the model. We first treat WL-CTP consolidation as compression of an impregnated fiber network, then apply constitutive equations for impregnated fiber network compressibility to model consolidation. Deductions from the model are proposed and experimentally validated. Finally, we investigate how molding parameters affect WL-CTP flexural properties.

2. Theory and Modeling

Fig 1(a) shows the uniform mixture of CFs and PP fibers in a preform containing 50 vol% CF. After heating the preform to melting temperature without pressure and cooling, the matrix spontaneously impregnated the CF network, as shown in Fig 1(b). This spontaneous impregnation is common, as capillary pressure enhances matrix infiltration into fiber networks. This phenomenon indicates that the molten preform can be treated as an impregnated CF network. Thus, WL-CTP consolidation can be regarded as compression of the impregnated CF network, which deforms into a tighter structure under higher pressure, resulting in void closure, as illustrated in Fig 2 [Figure 2: see original paper].

Servais et al. studied impregnated fiber network compressibility and found that impregnated networks behave identically to dry networks, described by the following equation developed by Toll et al.:

$$P_f = \frac{E}{V_{fn}^3} \cdot \frac{\phi}{4} \cdot \left(\frac{V_{fn}}{V_{fn0}} - 1 \right)^5$$

where P_f is pressure applied to the dry/impregnated fiber network, E is fiber tensile modulus, V_{fn} is FVF of the dry/impregnated fiber network, ϕ is the scalar invariant of the fiber orientation distribution function, and V_{fn0} is a parameter related to the mode of fiber orientation distribution: for 3-dimensional distribution, $V_{fn0} = 0.25$; for 2-dimensional distribution, $V_{fn0} = 0.5$.

For WL-CTP containing voids, the ratio of polymer volume fraction to fiber volume fraction, α, can be determined by burning test:

$$\alpha = \frac{W_1 - W_2}{W_2} \cdot \frac{\rho_f}{\rho_p}$$

where W_1 and W_2 are WL-CTP weights before and after burning, and ρ_p and ρ_f are polymer and fiber densities. The theoretical density of WL-CTP, ρ_t, is then:

$$\rho_t = \frac{\rho_f \rho_p (1 + \alpha)}{\rho_p + \alpha \rho_f}$$

Thus, the void volume fraction (VVF) of WL-CTP, X_V, is:

$$X_V = 1 - \frac{\rho_a}{\rho_t}$$

where ρ_a is the actual density of WL-CTP. Since WL-CTP consists of CF, matrix, and voids (air), the FVF of WL-CTP, V_{fc}, is:

$$V_{fc} = \frac{\rho_a}{\rho_t} \cdot \frac{1}{1 + \alpha}$$

Since WL-CTP consolidation can be regarded as compression of the impregnated CF network:

$$P_a = P_f$$

where P_a is applied pressure for WL-CTP consolidation. Combining Eq (1) with Eqs (5)-(7), we obtain:

$$P_a = \frac{E}{V_{fc}^3} \cdot \frac{\phi}{4} \cdot \left(\frac{V_{fc}}{V_{fc0}} - 1 \right)^5$$

Wan et al. used X-ray scanning to examine WL-CTP internal structure and found CFs were primarily distributed in-plane. Therefore, the theoretical value of ϕ in Eq (8) can be determined as 5, giving the constitutive model for WL-CTP consolidation:

$$P_a = \frac{5E}{4V_{fc}^3} \cdot \left(\frac{V_{fc}}{V_{fc0}} - 1 \right)^5$$

From Eq (9), we make three deductions: (1) Since no term representing molding time appears, molding time does not affect WL-CTP VVF; (2) VVF decreases with increasing molding pressure, and $\log(P_a)$ and $\log(X_V)$ have a linear correlation with coefficient 5; (3) Since no term representing molding temperature appears, molding temperature does not affect WL-CTP VVF. Experiments were designed to validate these deductions.

3.1. Composite Preparation

Fig 3 [Figure 3: see original paper] shows the sample preparation schematic. CFs (ZOLTEK PX35 Wet-Type, 6 mm length, 1.91 g/cm^3 density) and PP fibers (Zhejiang Yijiahui Co., Ltd, 4 mm length, 3 dtex fineness, 0.90 g/cm^3 density) were jointly disintegrated in water using a blender (Lorentzen & Wetter 991509, Sweden) for 10 min to form a fiber suspension containing 0.1 wt% raw materials. Although WL-CTP' s compatibility with rCFs is an advantage, we used virgin CFs because we needed to determine the tensile modulus of CF as a critical constant in the consolidation model from Eq (9). The tensile modulus of rCFs can vary considerably due to complex raw material supply and mechanical property degradation during recycling, so we selected virgin CFs to avoid potential batch-to-batch variations.

The fiber suspension was poured into a laboratory papermaking machine (Lesson Ind. Co., Ltd, 398AS, China Taipei). Drainage and squeezing produced wet nonwoven fabric, which was dried at 105°C for 6 h to form the dry preform. Final dry preforms had a basis weight of approximately 400 g/m^2. Sufficient preform was placed in a matched-die mold (home-made; details in supplementary material) so that the prepared WL-CTP would have a theoretical thickness of 2 mm without voids. Molding pressure was applied after preheating the mold for 1 h in a platen press. The mold was then transferred swiftly to another platen press at room temperature and cooled for 20 min, with molding pressure maintained during cooling. Finally, a square WL-CTP sample (100 mm side length) was obtained. Fig 4 [Figure 4: see original paper] shows the heat-molding procedures.

3.2. Testing

3.2.1. Burning Test and VVF Determination

WL-CTP samples were placed in an oven at 350°C for 4 h to burn off the PP matrix, and weights before and after burning were recorded. The polymer-to-fiber volume fraction ratio was calculated using Eq (2). Actual density was measured with a density balance and applied in Eq (4) to calculate VVF. All VVF standard deviations were calculated from three parallel experiments.

3.2.2. Flexural Properties

Flexural testing followed GB/T 9341-2008. Rectangular specimens (40 mm length × 25 mm width) were cut from WL-CTP samples. A load frame (Shimadzu AGS10KNI) with a 10 kN load cell tested specimens in three-point bending at 1 mm/min cross-head speed with a 32 mm span length. All flexural property standard deviations were calculated from five parallel tests.

3.2.3. Micro Observation

All SEM images were obtained using a Scanning Electron Microscope (Zeiss EVO18).

4.1. Effect of Molding Time on VVF

WL-CTPs were prepared under molding pressures of 2 MPa and 5 MPa, with molding temperature fixed at 190°C. VVF variation with molding time was examined. The experimental design is summarized in Table 1 , with results plotted in Fig 5 [Figure 5: see original paper].

At 2 MPa molding pressure, VVF decreased with molding time up to 10 min, then stabilized at ~20 vol%. This occurred because a dry CF network existed at the initial consolidation stage (Fig 6 [Figure 6: see original paper]), which was spontaneously impregnated by molten polymer, causing VVF to decrease initially. After complete impregnation, no further pressure was applied to deform the fiber network, preventing additional void closure and resulting in stable VVF. At 5 MPa molding pressure, VVF did not decrease initially and stabilized at ~11 vol% for all molding times. This indicates that the fiber network was compressed much tighter under 5 MPa, making the spontaneous impregnation stage too brief to observe. Therefore, Deduction (1) is validated: molding time does not affect WL-CTP VVF.

4.2.1. Compressive Behavior of Dry Fiber Network

Consolidated WL-CTP was heated at 350°C for 4 h to burn off polymer, yielding a dry CF network. The network’ s weight and dimensions were measured, and it was compressed using a load frame (Shimadzu AGS10KNI, 10 kN load cell) at

1 mm/min. The load-strain curve was recorded and transformed into a P_f-V_{fn} curve using:

$$P_f = \frac{F}{A}, \quad V_{fn} = \frac{m}{\rho_f A h_0 (1 - s)}$$

where F is load, s is strain, and A, m, and h_0 are compressed area, weight, and initial height of the dry CF network. Fig 7 [Figure 7: see original paper] shows the P_f-V_{fn} curve in logarithmic coordinates. Linear fitting of the linear portion yielded:

$$\log(P_f) = 5.02 \log(V_{fn}) + 8.27$$

The slope (5.02) is very close to 5, confirming Eq (1) applicability. From Eqs (8) and (9), the intercept is intrinsic to the preparation method, so it was fixed at 8.27 for linear fittings in Sections 4.2.2 and 4.3.

4.2.2. Effect of Molding Pressure on VVF

WL-CTPs were prepared under different molding pressures while temperature and time were fixed at 190°C and 10 min. The platen press minimum pressure was 2 MPa, so pressures of 2, 3, 4, 5, and 6 MPa were used. VVF variation with molding pressure was examined. Table 2 summarizes the experimental design, with results plotted in logarithmic coordinates in Fig 8 [Figure 8: see original paper].

The fitting line slope in Fig 8 was 4.64, close to the theoretical value of 5, with an Adj-R^2 of 0.99989 indicating excellent agreement. Thus, Deduction (2) is validated: VVF decreases with increasing molding pressure, and $\log(P_a)$ and $\log(X_V)$ have a linear correlation with coefficient 5.

4.3. Effect of Molding Temperature

The experiments in Section 4.2.2 validated the WL-CTP consolidation model directly. If the $\log(P_a)$-$\log(X_V)$ relationship in Fig 8 can be reproduced under different molding temperatures, then molding temperature does not affect WL-CTP consolidation or VVF. Therefore, experiments from Section 4.2.2 were repeated at 180°C and 200°C, with the design summarized in Table 3 and results plotted in logarithmic coordinates in Fig 9 [Figure 9: see original paper].

Linear fitting showed good agreement for both 180°C and 200°C cases, with fitting equations close to each other and to the equation in Fig 7. Thus, Deduction (3) is validated: molding temperature does not affect WL-CTP VVF.

4.4. Effect of Molding Parameters on Flexural Properties

From the above results, molding pressure is the only factor affecting WL-CTP VVF among the parameters studied. This suggests molding pressure may also be the sole factor affecting mechanical properties. Therefore, we investigated how molding parameters affect flexural properties as a representative mechanical property.

Flexural properties of WL-CTPs from Section 4.1 were tested to examine molding time effects, with results plotted in Fig 10 [Figure 10: see original paper]. At 2 MPa molding pressure, both flexural modulus and strength increased with molding time and stabilized after 10 min, mirroring VVF behavior in Fig 5. Fig 10(b) shows minimal molding time impact at 5 MPa, also consistent with VVF behavior. Therefore, molding time does not affect WL-CTP flexural properties.

Flexural properties of WL-CTPs from Sections 4.2 and 4.3 were tested to examine molding pressure and temperature effects, with results plotted in Fig 11 [Figure 11: see original paper]. At all three temperature levels, flexural modulus and strength increased with molding pressure, corresponding to VVF decrease as pressure deformed the CF network into tighter structures and closed voids. At each molding pressure, molding temperature did not affect flexural modulus or strength, consistent with the consolidation behavior observed in Section 4.3.

These results demonstrate that molding pressure is the only factor affecting WL-CTP mechanical properties, just as it is the only factor affecting VVF. This means that once molding temperature reaches the polymer melting point and molding pressure satisfies Eq (9), WL-CTP with low void content and qualified mechanical properties can be produced under relatively low temperature and high-speed production. Therefore, as a discontinuous CFRTP, WL-CTP can be an affordable product for large-scale automotive interior and covering applications requiring lightweight design.

5. Conclusion

A constitutive model for WL-CTP consolidation was proposed based on equations describing dry/impregnated CF network compressive behavior. Three deductions from the model were validated experimentally, revealing that molding pressure is the sole factor affecting WL-CTP consolidation among time, pressure, and temperature. Flexural testing further confirmed that molding pressure is the only factor affecting flexural properties. Overall results indicate that WL-CTP with qualified mechanical properties can be produced under relatively low molding temperature with high productivity, making WL-CTP a promising candidate for affordable CFRTP products.

Acknowledgment

We acknowledge Toray and ZOLTEK for supplying PX35 carbon fiber, and appreciate Guangzhou Congyuan Instruments for manufacturing and maintaining

the matched-die mold.

References

[1] Hemamalini T, Giri Dev V R. Wet Laying Nonwoven Using Natural Cellulosic Fibers and Their Blends: Process and Technical Applications. A Review[J]. Journal of Natural Fibers, 2019: 1-11.

[2] Pakdel E, Kashi S, Varley R, et al. Recent progress in recycling carbon fibre reinforced composites and dry carbon fibre wastes[J]. Resources, Conservation and Recycling, 2021, 166: 105340.

[3] D. F. Hiscock D M B. Long fiber reinforced thermoplastic matrix composites by slurry deposition[J]. Polym Compos, 1989, 10: 145-149.

[4] D. M. Bigg D F H, J. R. Preston, E. J. Bradbury. The Properties of Wet-Formed Thermoplastic[J]. Polym Compos, 1993, 14: 26-34.

[5] Lu Y. Mechanical Properties of Random Discontinuous Fiber Composites Manufactured from the Wetlay Process[D]. Virginia Polytechnic Institute and State University Blacksburg, Virginia.

[6] Caba A C. Characterization of Carbon Mat Thermoplastic[D]. Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 2005.

[7] Nakagaito A N, Fujimura A, Sakai T, et al. Production of microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from sheets obtained by a papermaking-like process[J]. Compos Sci Technol, 2009, 69 (7-8): 1293-1297.

[8] Lee J-C, Lee J-A, Lim D-Y, et al. Fabrication of Cellulose Nanofiber Reinforced Thermoplastic Composites[J]. Fibers and Polymers, 2018, 19 (8): 1753-1759.

[9] Johnson R K, Zink-Sharp A, Renneckar S H, et al. Mechanical properties of wetlaid polypropylene[J]. Composites Part A: Applied Science and Manufacturing, 2008, 39 (3): 470-477.

[10] M. Honma A T, N. Hirano, T. Hashimoto. Novel carbon-fiber-reinforced stamped thermoplastic sheet with high strength[C]. 18th International Conference on Composite Materials, 2011.

[11] Wei H, Nagatsuka W, Lee H, et al. Mechanical properties of carbon fiber paper reinforced thermoplastics using mixed discontinuous recycled carbon fibers[J]. Adv Compos Mater, 2017, 27 (1): 19-34.

[12] Wei H W, Nagatsuka W, Ohsawa I, et al. Influence of small amount of glass fibers on mechanical properties of discontinuous recycled carbon fiber-reinforced thermoplastics[J]. Adv Compos Mater, 2019, 28 (3): 321-334.

[13] Bullions T A, Gillespie R A, Price-O' brien J, et al. The effect of maleic anhydride modified polypropylene on the mechanical properties of feather fiber,

kraft pulp, polypropylene composites[J]. J Appl Polym Sci, 2004, 92 (6): 3771-3783.

[14] Bullions T A, Hoffman D, Gillespie R A, et al. Contributions of feather fibers and various cellulose fibers to the mechanical properties of polypropylene matrix composites[J]. Compos Sci Technol, 2006, 66 (1): 102-114.

[15] Christina Froemder K K, Neil Reynolds, Peter R. Wilson, Felipe C. Fernandes, Stuart R. Coles. Investigation of the processability of hybrid thermoplastic nonwoven including recycled carbon fibre through fast stamping[C]. SAMPE Europe Conference, 2018.

[16] Sousa S, Costa A P, Simões R. Poly(lactic acid) composites reinforced with kraft pulp fibres: Production by a papermaking process and characterisation[J]. Composites Part A: Applied Science and Manufacturing, 2019, 121: 273-282.

[17] Sommer J L, Mortensen A. Forced unidirectional infiltration of deformable porous media[J]. J Fluid Mech, 1996, 311: 193-217.

[18] Michaud V, Manson J a E. Impregnation of compressible fiber mats with a thermoplastic resin. Part I: Theory[J]. J Compos Mater, 2001, 35 (13): 1150-1173.

[19] Michaud V, Tornqvist R, Manson J a E. Impregnation of compressible fiber mats with a thermoplastic resin. Part II: Experiments[J]. J Compos Mater, 2001, 35 (13): 1174-1199.

[20] Kim T W, Jun E J, Um M K, et al. Effect of pressure on the impregnation of thermoplastic resin into a unidirectional fiber bundle[J]. Adv Polym Tech, 1989, 9 (4): 253-260.

[21] Bernet N, Michaud V, Bourban P E, et al. Impregnation model for the consolidation of thermoplastic composites made from commingled yarns[J]. J Compos Mater, 1999, 33 (8): 751-772.

[22] Tse B, Yu X, Gong H, et al. Flexural Properties of Wet-Laid Hybrid Nonwoven Recycled Carbon and Flax Fibre Composites in Poly-Lactic Acid Matrix[J]. Aerospace, 2018, 5 (4).

[23] Yeole P, Ning H, Hassen A A, et al. The Effect of Flocculent, Dispersants, and Binder on Wet-laid Process for Recycled Glass Fiber/PA6 Composite[J]. Polym Polym Compos, 2018, 26 (3): 259-269.

[24] Servais C, Michaud V, Manson J a E. The packing stress of impregnated fiber mats[J]. Polym Compos, 2001, 22 (2): 298-311.

[25] Toll S. Packing mechanics of fiber reinforcements[J]. Polym Eng Sci, 1998, 38 (8): 1337-1349.

[26] Toll S. Note: On the tube model for fiber suspensions[J]. J Rheol, 1993, 37 (1): 123-126.

[27] S. Toll J a E M. Elastic Compression of a fiber network[J]. Journal of Applied Mechanics, 1995, 62 (1): 223-226.

[28] Wan Y, Takahashi J. Deconsolidation behavior of carbon fiber reinforced thermoplastics[J]. J Reinf Plast Compos, 2014, 33 (17): 1613-1624.

[29] Meng F, Mckechnie J, Turner T, et al. Environmental Aspects of Use of Recycled Carbon Fiber Composites in Automotive Applications[J]. Environ Sci Technol, 2017, 51 (21): 12727-12736.

[30] Wan Y, Takahashi J. Development of Carbon Fiber-Reinforced Thermoplastics for Mass-Produced Automotive Applications in Japan[J]. Journal of Composites Science, 2021, 5 (3): 86.

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.