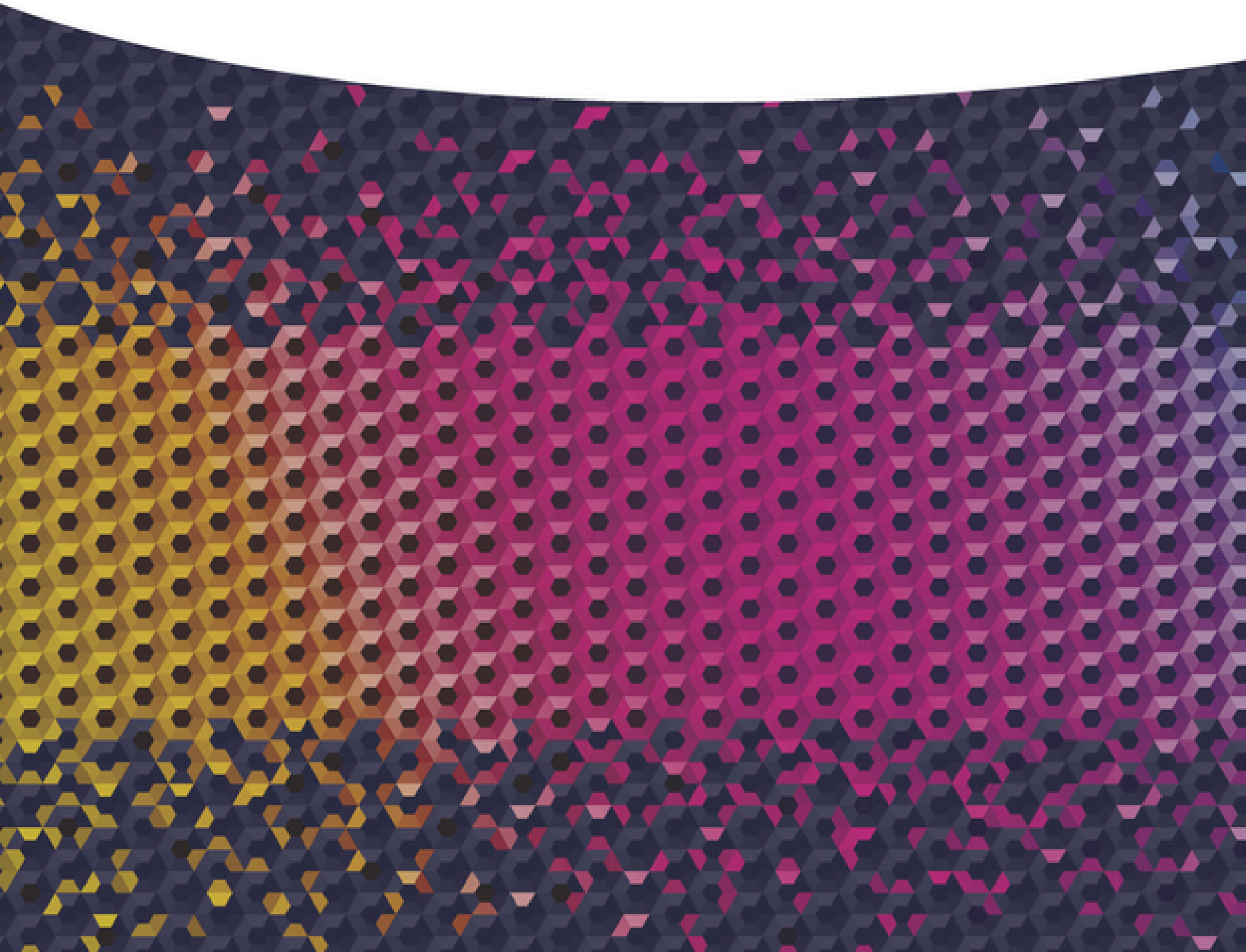
WILEY-VCH

Edited by Senthilkumar Krishnasamy, Senthil Muthu Kumar Thiagamani,
Chandrasekar Muthukumar, Rajini Nagarajan, and Suchart Siengchin

Natural Fiber-Reinforced Composites

Thermal Properties and Applications



Natural Fiber-Reinforced Composites

Natural Fiber-Reinforced Composites

Thermal Properties and Applications

Edited by Senthilkumar Krishnasamy, Senthil Muthu Kumar Thiagamani, Chandrasekar Muthukumar, Rajini Nagarajan, and Suchart Siengchin

WILEY-VCH

Editors

Dr. Senthilkumar Krishnasamy
Department of Materials and Production
Engineering
The Sirindhorn International
Thai-German Graduate School of
Engineering (TGGS)
King Mongkut's University of
Technology North Bangkok
1518 Wongsawang Road, Bangsue
Bangkok, 10800
Thailand

Dr. Senthil Muthu Kumar Thiagamani
Department of Mechanical Engineering
Kalasalingam Academy of Research and
Education
Krishnankoil, 626 126
Anand Nagar, Tamil Nadu
India

Dr. Chandrasekar Muthukumar
School of Aeronautical Sciences
Hindustan Institute of Technology &
Science
Padur, Kelambakkam
Chennai, 603103, Tamil Nadu
India

Prof. Rajini Nagarajan
Department of Mechanical Engineering
Kalasalingam Academy of Research and
Education
Krishnankoil, 626 126
Anand Nagar, Tamil Nadu
India

Prof. Suchart Siengchin
Department of Materials and Production
Engineering
The Sirindhorn International
Thai-German Graduate School of
Engineering (TGGS)
King Mongkut's University of
Technology North Bangkok
1518 Wongsawang Road, Bangsue
Bangkok, 10800
Thailand

Cover Image: © derrek/Getty Images

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-34883-1
ePDF ISBN: 978-3-527-83155-5
ePub ISBN: 978-3-527-83157-9
oBook ISBN: 978-3-527-83156-2

Typesetting Straive, Chennai, India

Printed on acid-free paper

10 9 8 7 6 5 4 3 2 1

Contents

Preface

We are glad to present the book entitled "Natural Fiber-Reinforced Composites: Thermal Properties and Applications" to thermal analysts, materials scientists, materials engineers, material chemists, and researchers working in the field of bio-composites.

This book focuses on exploring the thermal properties of hybrid composites reinforced with natural fibers. As per literature, the thermal properties of these composites could be analyzed by the techniques such as differential scanning calorimetry (DSC), thermomechanical analysis (TMA), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). In lieu of this, all the chapters are designed to cover a broad audience with the aforementioned techniques on hybrid composites reinforced with natural fibers.

This book consists of 18 chapters and is structured as follows: Chapters 1, 2, and 3 present the overview of thermal properties of natural fiber reinforced thermoset and thermoplastic hybrid composites. Chapters 4 to 11 discuss the thermal properties of hybrid composites made up of different natural fibers such as sugar palm, sisal fiber, flax fiber, pineapple leaf fiber, grass/cane fiber, banana fiber, kenaf fiber and hemp fiber. Chapters 12 to 16 provide insights on the effect of nanofillers (e.g. graphene, nanoclay, CNT, metal oxide) on thermal properties of natural fiber reinforced hybrid composites. Chapter 17 discusses the effects of chemical treatments of hybrid composites on thermal properties. Chapter 18 provides an overview of physical, mechanical, and thermal properties of hybrid polymer composites.

We thank our parents and sincerely appreciate the publisher, the typesetting professional associated with this book, and thank all the contributing authors for their valuable time and efforts in submitting their work to this book.

1

Thermal Characterization of the Natural Fiber-Based Hybrid Composites: An Overview

Chandrasekar Muthukumar[1], Senthilkumar Krishnasamy[2,3], Senthil Muthu Kumar Thiagamani[3], Rajini Nagarajan[3], and Suchart Siengchin[4]

[1] *Hindustan Institute of Technology & Science, Department of Aeronautical Engineering, Kelambakkam, Chennai 603103, Tamilnadu, India*
[2] *King Mongkut's University of Technology North Bangkok, Center of Innovation in Design and Engineering for Manufacturing (CoI-DEM), 1518 Wongsawang Road, Bangsue, Bangkok 10800, Thailand*
[3] *Kalasalingam Academy of Research and Education, Department of Mechanical Engineering, Krishnankoil 626126, Tamil Nadu, India*
[4] *King Mongkut's University of Technology North Bangkok, The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), Department of Materials and Production Engineering, 1518 Wongsawang Road, Bangsue, Bangkok 10800, Thailand*

1.1 Introduction

Hybrid composite is fabricated by adding two or more fibers into a single polymer system [1]. The resulting material has a unique feature that combines the advantages of each fiber. Since different fibers are added together, the benefits of one particular type of fiber property could be compensated with the other fiber lacking a specific property. The performance of hybrid composites could be influenced by many factors [2–7]:

i. Fiber length
ii. Fiber loading
iii. Fiber orientation
iv. Fiber layer sequence
v. Fiber/matrix interfacial bonding
vi. Failure strain of fiber

The hybrid effect is termed as an apparent synergistic improvement of properties due to different fibers in a single matrix system. The selection of fibers and their properties is of main importance to achieve the enhanced properties for the hybrid composites. Besides the physical, chemical, and mechanical stabilities of fiber, the

Natural Fiber-Reinforced Composites: Thermal Properties and Applications, First Edition.
Edited by Senthilkumar Krishnasamy, Senthil Muthu Kumar Thiagamani,
Chandrasekar Muthukumar, Rajini Nagarajan and Suchart Siengchin.

matrix system also defines the strength of the hybrid composites. The different types of hybrid composites are characterized as follows [8–12]:

i. Tow by tow: the fibers are mixed up randomly or regularly.
ii. Sandwich hybrid composites: one material is sandwiched between two different layers.
iii. Inter-ply or laminated: two or more fiber layers are alternatively stacked regularly.
iv. Intimately mixed fibers: various types of fibers are mixed up randomly.

Though the hybrid composites have many advantages, the prime challenges are replacing the synthetic fiber-reinforced composites using biocomposites. Biocomposites exhibit functional and structural stability during storage and degrade upon disposal into the environment. “Engineered natural fiber” is one of the exciting concepts to obtain the enhanced strength in the biocomposites, which involves the blending of the leaf and stem fibers. The correct blending of these two fibers exhibits optimum balance in mechanical properties, resulting in balanced stiffness–toughness properties [13–15].

The mechanical and physical characteristics of the natural fiber are influenced by many factors: (i) maturity of the plant fiber, (ii) harvesting time and region, (iii) soil condition, (iv) rain, (v) sun, etc. Since the natural fibers are nonabrasive and hypoallergenic, they could be processed efficiently. Amongst the various properties of natural fibers, the low density and the cellular structure allow them to exhibit better thermal properties. However, the amorphous hemicellulose on the fiber surface can be a potential threat to the better interfacial bonding between the matrix and the fiber, thereby reducing the properties. Hence, the mechanical and thermal properties of the biocomposites could be further enhanced through chemical treatments [16]. Natural fiber has cellulose, hemicellulose, and lignin susceptible to degradation on exposure to elevated temperature [17–19]. Thus, many studies exploring the thermal properties of the biocomposites have been published over the years [20–22]. By botanical type, the natural fibers are classified into six major types (Table 1.1).

Table 1.1 Classification of the natural fibers.

Seed	Bast	Leaf	Core	Grass and seed	Others
Kapok	Jute	Banana	Flax	Canary	Roots
Coir	Ramie	Pineapple	Kenaf	Barley	wood
Cotton	Flax	Curaua	Hemp	Wheat	
Oil palm	Hemp	Sisal	Jute	Grass	
Rice	Kenaf	Abaca		Corn	

1.2 Thermal Characterization

The thermal analyses encompass a family of techniques that would share a common feature, whereby any material's response could be measured through heating or cooling. Thus, a significant connection is held between the temperature and the physical property of the materials. The most common thermal techniques that have been used by researchers and by industrial organizations for thermal characterization are thermomechanical analysis (TMA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). These techniques are not only used for measuring the physical properties with respect to the temperature changes but also used in the following areas: (i) to substantiate mechanical properties and thermal history of the biocomposites, (ii) to estimate the service life of composites in different environments, and (iii) as one of the quality control approaches in polymers and their manufacturing industries. Figure 1.1 shows some of the essential thermal analysis techniques and the characteristics measured [23–25]. In terms of research, thermal behavior of the biocomposites has been investigated by varying fiber volume fractions [26–28], varying fiber layering patterns [29, 30], using different types of chemical treatments [31, 32], adding different kinds of fillers [19, 33, 34], and using polymer blends [35, 36].

For instance, Table 1.2 presents some of the experimental works carried out on thermal properties using different natural fibers.

1.2.1 DMA

Figure 1.2 presents the step-by-step process involved in the DMA of the polymers and polymer-based composites. Output parameters such as storage modulus (E' or G'), loss modulus (E'' or G''), and damping factor (tan δ) obtained as the function of temperature are shown in Figure 1.3a. As the polymer or composite is heated in the temperature range with the simultaneous application of oscillatory load, it undergoes displacement or strain where some energy gets stored in the material,

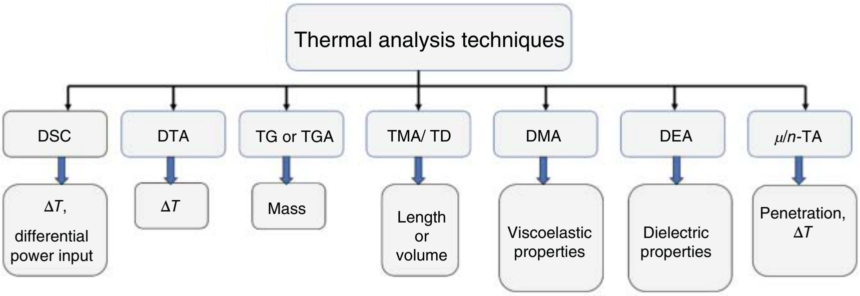


Figure 1.1 Various thermal analysis techniques and their applications. DFA, dielectric analysis.

Table 1.2 Reported thermal based works of natural fiber-reinforced hybrid composites.

Hybrid composites	Details of study	References
Thermoset polymers		
Flax/sugar palm/epoxy	DMA	[6]
Flax/woven aloe vera/epoxy	TGA, DMA	[20]
Sisal/cattail/polyester	Thermal conductivity	[37]
Date palm/coir fiber/epoxy	TGA	[38]
Sisal/jute/sorghum/polyester	TGA	[39]
Coir/*Luffa cylindrica*/epoxy	DMA	[40]
Bamboo/kenaf/epoxy	TGA, DMA, DSC	[41]
Ramie/sisal/epoxy Sisal/curaua/epoxy	TGA, DSC	[42]
Flax/aloe vera/hemp/epoxy	TGA, DMA	[43]
Kenaf/pineapple leaf fiber/phenolic	TGA	[44]
Thermoplastic polymers		
Sugar palm/roselle/polyurethane	TGA	[45]
Jute/bamboo/polyethylene	DSC, TGA	[46]
Sugar palm/roselle/polyurethane	TGA	[47]
Seaweed/sugar palm fiber/thermoplastic sugar palm starch agar	TGA	[48]
Coir/pineapple leaf fiber/polylactic acid (PLA)	TGA	[49]
Coir/pineapple leaf fiber/ PLA	TGA, TMA	[50]
Biodegradable polymers		
Sisal/hemp/bioepoxy	DMA, TGA	[29]
Kenaf/sisal/bioepoxy	TGA, DSC, DMA	[51]
Sisal/hemp/bioepoxy	TGA	[52]

while some energy is dissipated as heat due to the internal friction. The resultant strain measured by applying the oscillatory load is represented as loss modulus, storage modulus, and phase angle or damping factor. The ability of the tested material to store the energy is termed as the storage modulus while the tendency of the material to dissipate heat energy is termed as the loss modulus. Storage modulus represents the stiffness of a polymer or composite and is often related to Young's modulus. Loss modulus is related to the molecular chain motions such as transition and relaxation within the polymer during the heating process and applied load. Tan δ is a dimensionless number obtained through the ratio of loss modulus to the storage modulus. Lower tan δ indicates higher stiffness and better interfacial bonding between fiber and polymer matrix, which restricts the molecular mobility within the polymeric chains.

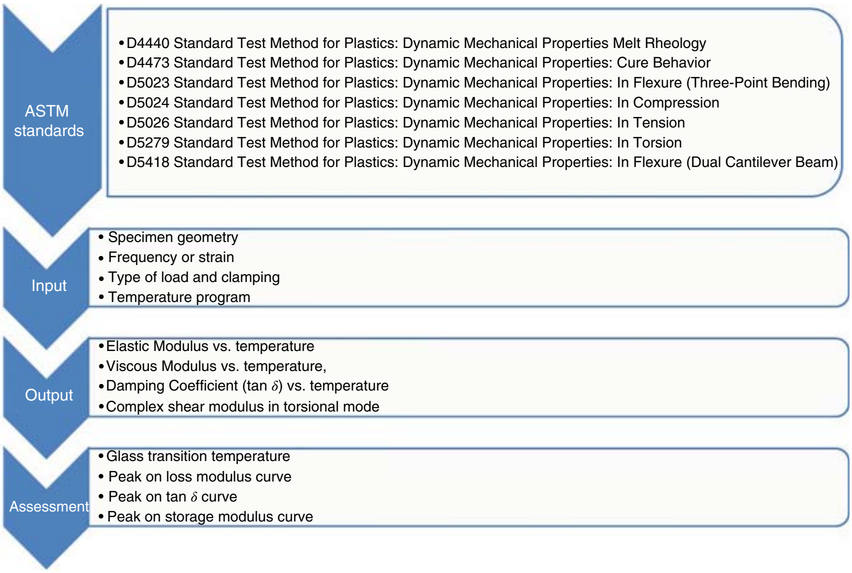


Figure 1.2 Thermal characterizations of the polymer and polymer-based composite through DMA, step-by-step process.

Polymers are viscoelastic and can be classified into crystalline, amorphous, and semicrystalline (has both crystalline and amorphous characteristics) depending upon the composition. It is because of this characteristic that polymers or polymer-based composite undergoes phase change during the simultaneous application of the load and heating process (Figure 1.3b). Figure 1.3a shows the typical data obtained from DMA. Glass transition temperature (T_g) is the tangent obtained in the phase change region between glassy state and rubbery state. T_g can be below the melting temperature for a polymer, which has both crystalline and amorphous characteristics. The material tends to get softer rather than melting at T_g. DMA is particularly useful in identifying the cross-linking density of the polymer, as shown in Figure 1.3b. It can be noticed that polymers with a high cross-linking density have higher T_g and greater loss modulus and storage modulus, while it is vice versa for polymers with low cross-linking density [53].

1.2.2 TMA

TMA is a common technique used for investigating the dimensional change of material under the combination of temperature and a fixed load. Figure 1.4 presents the step-by-step process involved in the TMA of the polymers and polymer-based composites. Dimensional change of material (at nanoscale) under the influence of temperature and load can be measured in various testing modes shown in Figure 1.5. Changes in the free volume of material depending upon the heat absorption or heat release with respect to the temperature can also be determined with this technique.

Figure 1.6a–c shows that the T_g measurement for a polymer or a polymer composite can be derived from the TMA, DSC, and DMA.

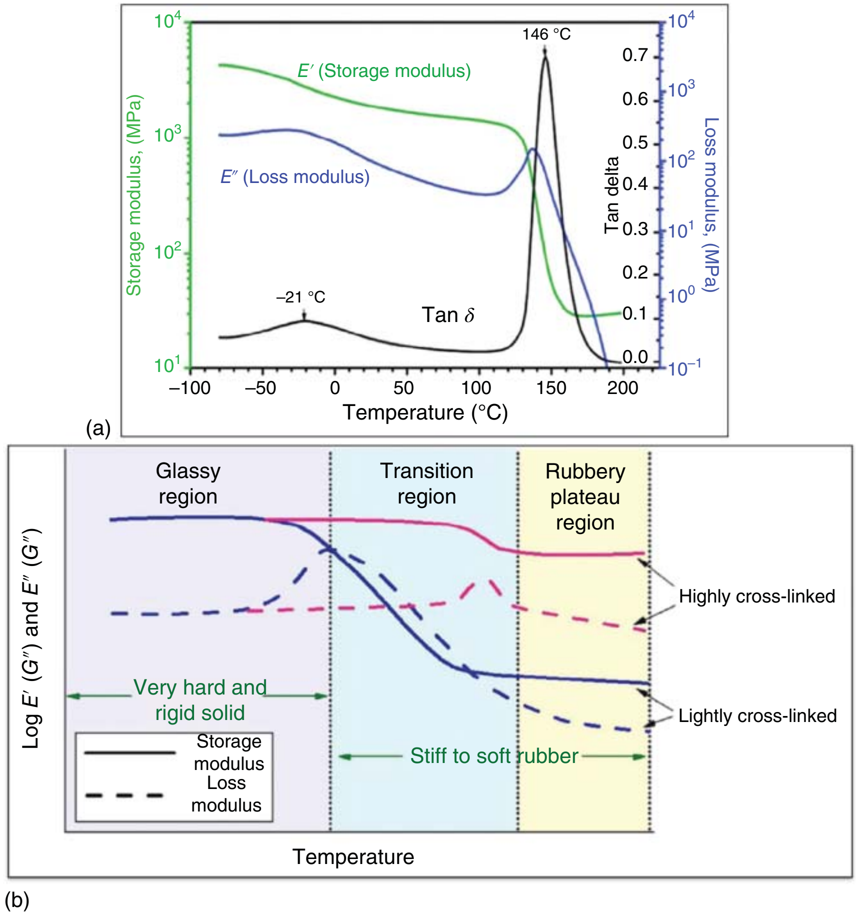


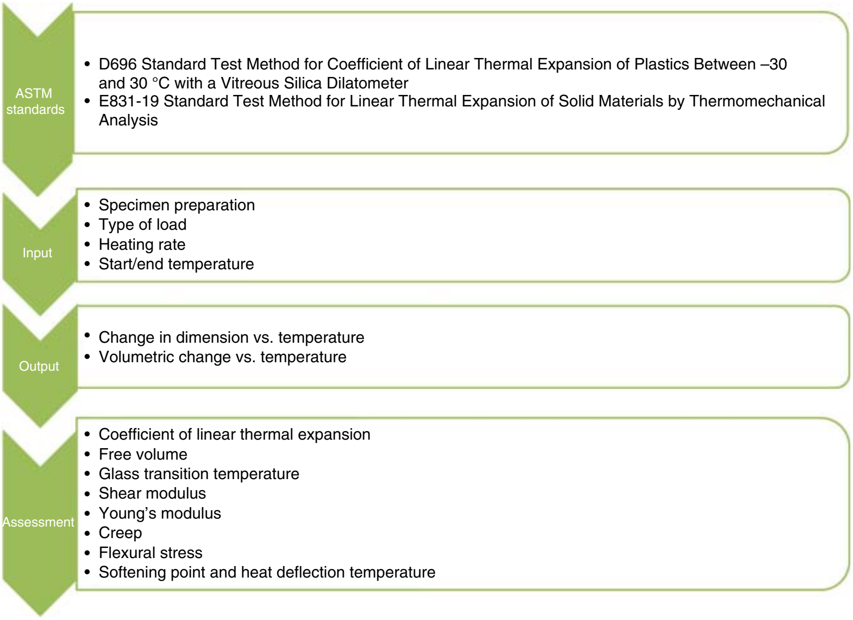
Figure 1.3 Thermal characterization of polymer and polymer-based composite with DMA. (a) Typical curve. (b) Viscoelastic characteristics of the polymer. Source: Saba et al. [53].

1.2.3 DSC

Figure 1.7 presents the step-by-step process involved in the DSC of the polymers and polymer-based composites. In DSC, the sample is heated around 30 to the elevated temperature beyond 300 °C with the constant supply of liquid nitrogen in a controlled chamber. Heat flow from the sample is measured as a function of the temperature shown in Figure 1.8. The changes in crystalline properties (T_g), melting temperature (T_m), and cold crystallization temperature (T_c) due to the introduction of two or more natural fibers in the hybrid composite can be evaluated.

1.2.4 TGA

Figure 1.9 presents the step-by-step process involved in the TGA of the polymers and polymer-based composites. It is an effective technique for evaluating thermal


ASTM standards

- D696 Standard Test Method for Coefficient of Linear Thermal Expansion of Plastics Between –30 and 30 °C with a Vitreous Silica Dilatometer
- E831-19 Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis

Input

- Specimen preparation
- Type of load
- Heating rate
- Start/end temperature

Output

- Change in dimension vs. temperature
- Volumetric change vs. temperature

Assessment

- Coefficient of linear thermal expansion
- Free volume
- Glass transition temperature
- Shear modulus
- Young's modulus
- Creep
- Flexural stress
- Softening point and heat deflection temperature

Figure 1.4 Thermal characterizations of the polymer and polymer-based composite through TMA, step-by-step process.

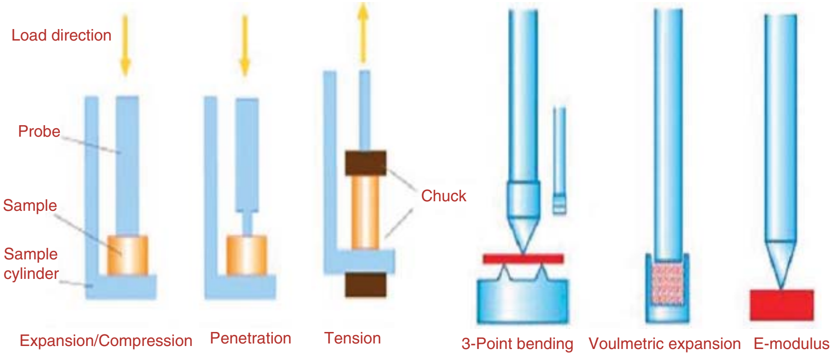


Figure 1.5 Test modes in TMA. Source: Saba and Jawaid [54].

decomposition characteristics of the polymers and polymer composite reinforced with the natural fibers or the synthetic fibers. It provides the quantitative mass change of the sample due to the heating under the controlled atmosphere. A natural fiber obtained from the plants and trees is made up of the constituents such as cellulose, hemicellulose, lignin, pectin, wax, moisture, and ash. The percentage of constituents can vary from one fiber to another, which has a significant influence on the thermal decomposition characteristics of natural fiber and their composites. Also, these fiber constituents are volatile and can decompose at elevated temperatures.

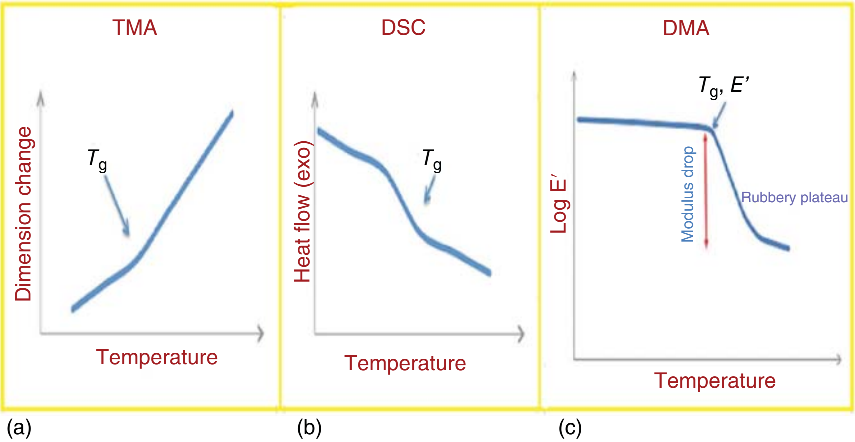
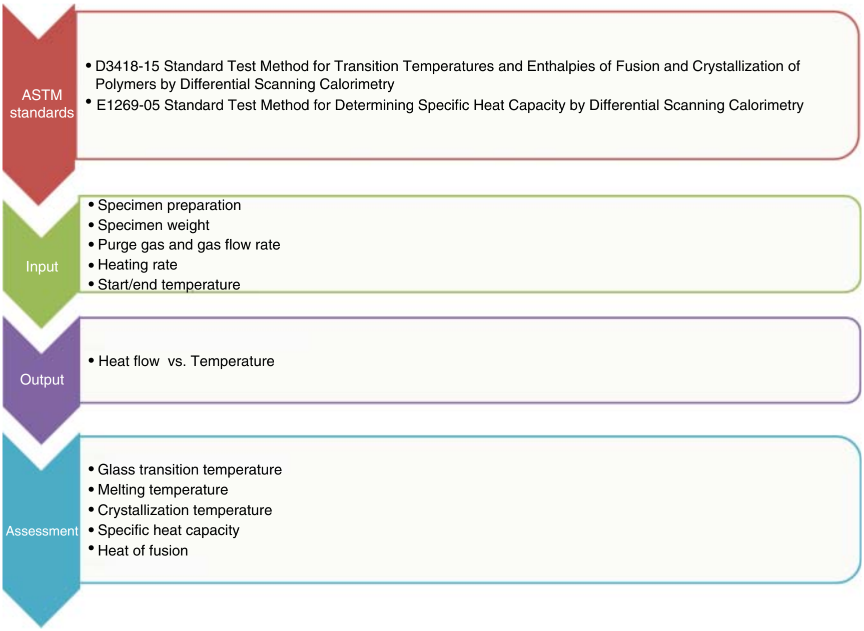


Figure 1.6 T_g measured from the various thermal characterization techniques: (a) TMA, (b) DSC, and (c) DMA. Source: Saba and Jawaid [54].


ASTM standards

- D3418-15 Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry
- E1269-05 Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry

Input

- Specimen preparation
- Specimen weight
- Purge gas and gas flow rate
- Heating rate
- Start/end temperature

Output

- Heat flow vs. Temperature

Assessment

- Glass transition temperature
- Melting temperature
- Crystallization temperature
- Specific heat capacity
- Heat of fusion

Figure 1.7 Thermal characterizations of the polymer and polymer-based composite through DSC, step-by-step process.

A few milligram of sample is placed in the TGA chamber and heated from room temperature to as high as 700 °C at a defined ramp rate in the presence of nitrogen to prevent oxidation inside the chamber. The thermal stability of a polymer-based composite is usually assessed from the thermogram (TG curve) and the derivative thermogram (DTG curve) obtained from the TGA, as shown in Figure 1.10. Parameters

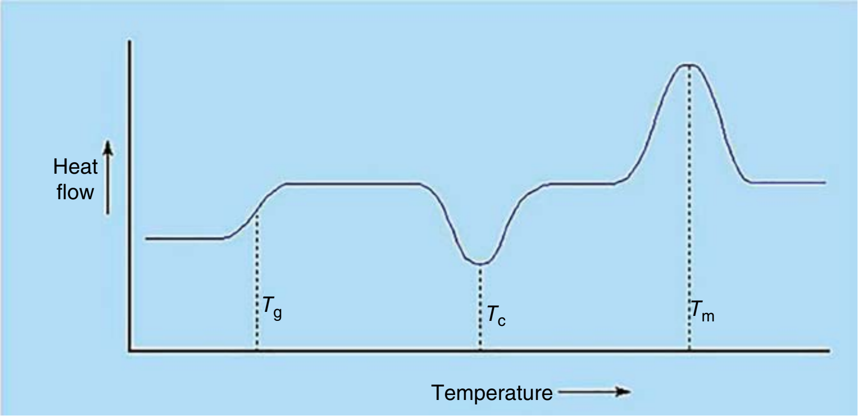


Figure 1.8 Thermogram from the DSC. Source: Chandrasekar et al. [55].

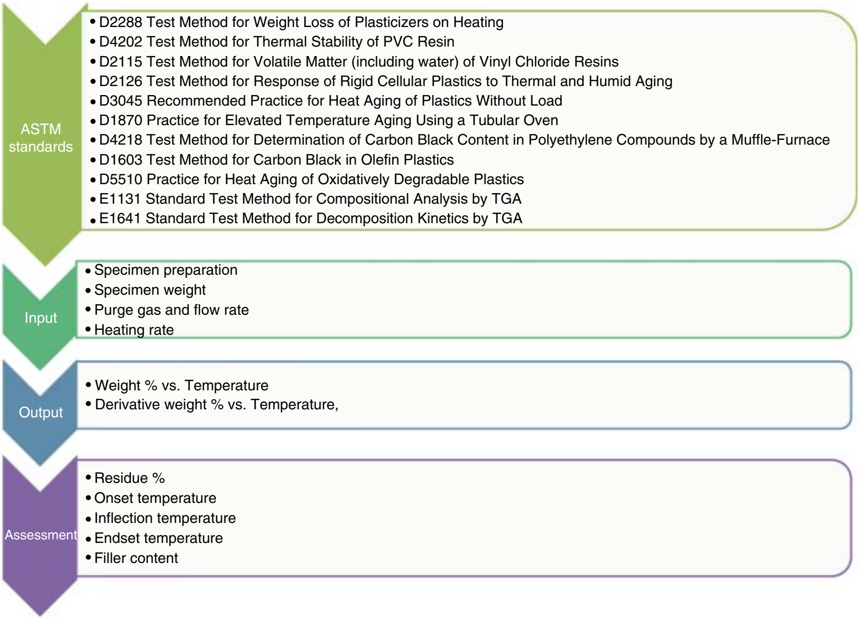


Figure 1.9 Thermal characterizations of polymer and polymer-based composites through TGA, step-by-step process.

such as the onset, endset, inflection temperature, and residue percentage at the end of the heating process in the TGA chamber are usually compared to identify changes due to the reinforcement percentage and type of fiber. Degradation temperature at 5%, 10%, 20%, 40%, and 80% weight loss along with the residue can also be discussed.

In the case of a polymer, thermal decomposition usually occurs in single stage, whereas, for the natural fiber, thermal decomposition occurs in two or three stages

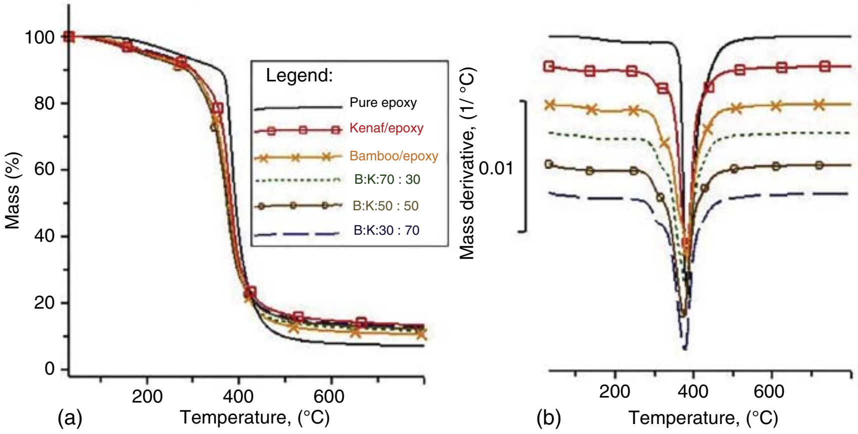


Figure 1.10 A typical TGA curve of the hybrid composite with kenaf and bamboo fibers. (a) Thermogram. (b) Derivative thermogram. Source: Chee et al. [41].

depending on the fiber constituents. Initial mass loss between 50 and 150 °C is due to the evaporation of moisture in the fiber. The weight loss at a temperature range between 150 and 300 °C is associated with the decomposition of hemicellulose and lignin. The final weight loss between 300 and 700 °C is attributed to the decomposition of cellulose. Since the fiber constituents vary from one fiber to another, TGA has proved to be an excellent tool for determining the changes in thermal decomposition characteristics of the hybrid polymer composite reinforced with two or more natural fibers. Thermal stability is also evaluated by residue percentage at the end of the heating process. The higher the residues, the better the thermal stability of the composite.

1.3 Conclusion

Thermal characterization of the hybrid composites using various commercially available techniques such as DMA, TMA, DSC, and TGA has been discussed. The following are the conclusions:

- DMA is useful in determining the creep properties and interfacial interactions of the composites and measuring their stiffness, material behavior with respect to the phase transitions, damping, and relaxation processes in a range of frequencies and temperatures.
- TMA helps in defining the material structure with respect to the dimensional and volumetric change, surface roughness, molecular structure, cure, and cross-linking polymerization under both static and dynamic loads.
- DSC is considered as one of the primary tools for thermodynamic analysis and cure kinetics. It gives useful information on the phase transitions upon heating and quantifies the glass transition temperature, melting temperature, and crystallization temperature related to the polymers and polymer-based biocomposites.