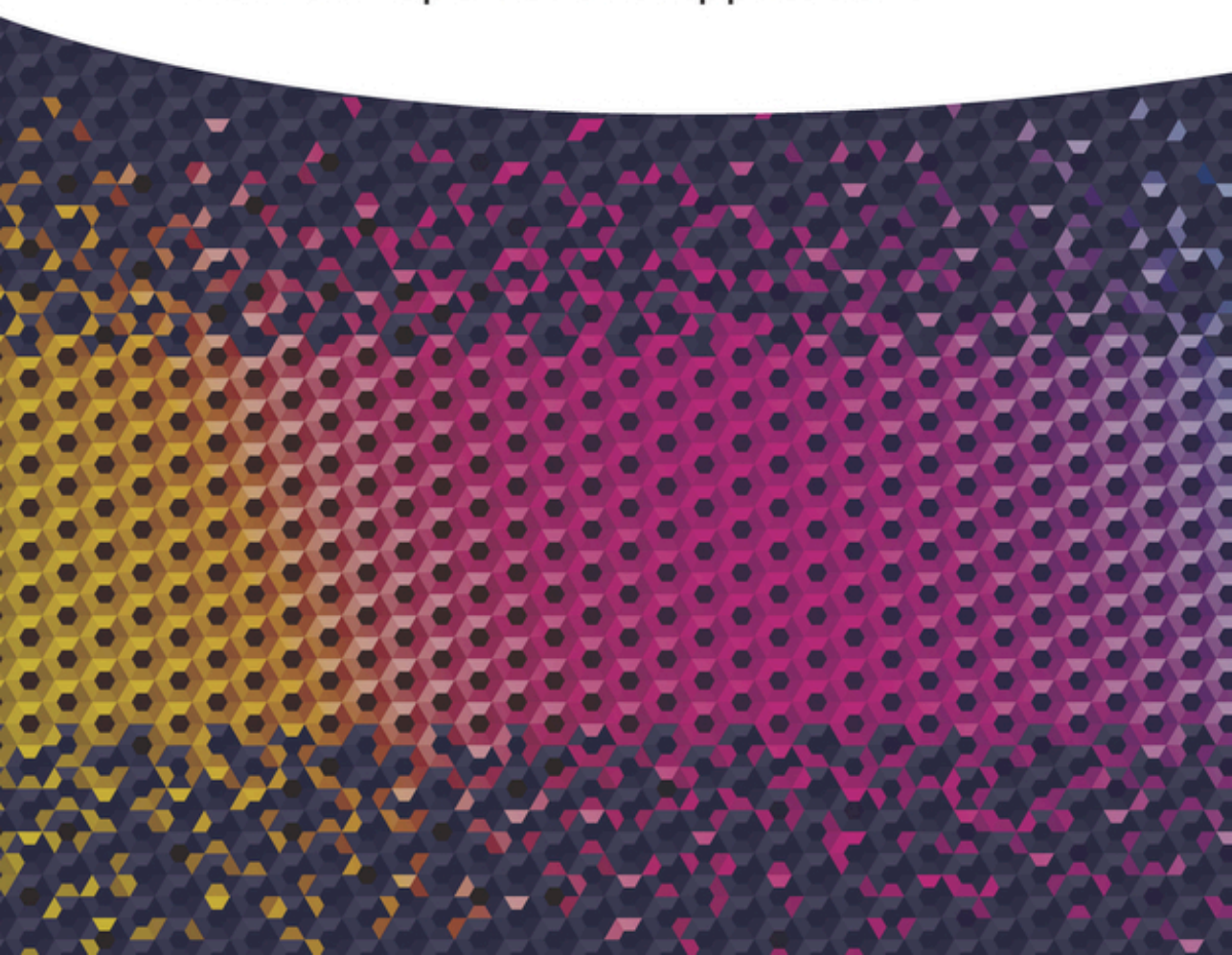


Edited by Senthilkumar Krishnasamy, Senthil Muthu Kumar Thiagamani,  
Chandrasekar Muthukumar, Rajini Nagarajan, and Suchart Siengchin

# 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:** © derrrek/Getty Images

■ All books published by **WILEY-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

**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>>.

© 2022 WILEY-VCH GmbH, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

**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** *xiii*

<b>1</b>	<b>Thermal Characterization of the Natural Fiber-Based Hybrid Composites: An Overview</b>	<b>1</b>
	<i>Chandrasekar Muthukumar, Senthilkumar Krishnasamy, Senthil Muthu Kumar Thiagamani, Rajini Nagarajan, and Suchart Siengchin</i>	
1.1	Introduction	1
1.2	Thermal Characterization	3
1.2.1	DMA	3
1.2.2	TMA	5
1.2.3	DSC	6
1.2.4	TGA	6
1.3	Conclusion	10
	Acknowledgment	11
	References	11
<b>2</b>	<b>Thermal Properties of Hybrid Natural Fiber-Reinforced Thermoplastic Composites</b>	<b>17</b>
	<i>A. Vinod, Yashas Gowda, Senthilkumar Krishnasamy, M.R Sanjay, and Suchart Siengchin</i>	
2.1	Introduction	17
2.2	Thermal Properties	18
2.2.1	Thermogravimetric Analysis (TGA)	18
2.2.2	Differential Scanning Calorimetry (DSC)	20
2.2.3	Thermomechanical Analysis (TMA)	21
2.2.4	Dynamic Mechanical Analysis (DMA)	23
2.2.5	Melt Flow Index (MFI)	24
2.3	Conclusions	25
	References	26

<b>3</b>	<b>Thermal Properties of the Natural Fiber-Reinforced Hybrid Polymer Composites: An Overview</b>	<b>31</b>
	<i>Jyotishkumar Parameswaranpillai, Senthilkumar Krishnasamy, Suchart Siengchin, Sabarish Radoor, Roshny Joy, Jinu Jacob George, Chandrasekar Muthukumar, Senthil Muthu Kumar Thiagamani, Nisa V. Salim, and Nishar Hameed</i>	
3.1	Introduction	31
3.2	Thermal Properties of Natural Fiber Composites	33
3.2.1	Thermogravimetric Analysis (TGA)	33
3.2.2	Differential Scanning Calorimetry (DSC)	38
3.2.3	Dynamic Mechanical Analysis (DMA)	41
3.3	Conclusion	45
	Acknowledgment	45
	References	46
<b>4</b>	<b>Thermal Properties of Sugar Palm Fiber-Based Hybrid Composites</b>	<b>53</b>
	<i>R.A. Ilyas, S.M. Sapuan, A. Atiqah, M.R.M. Asyraf, N.M. Nurazzi, Mohd N. F. Norrrahim, Mohd A. Jenol, M.M. Harussani, R. Ibrahim, M.S.N. Atikah, and Chandrasekar Muthukumar</i>	
4.1	Introduction	53
4.2	Thermal Analysis of Sugar Palm Fiber-Based Hybrid Composites	58
4.2.1	TGA Properties of Sugar Palm Composites	58
4.2.2	TGA Properties of Sugar Palm Hybrid Composites	60
4.3	Dynamic Mechanical Properties of Sugar Palm Fiber-Based Hybrid Composites	63
4.3.1	Sugar Palm/Glass Fiber	63
4.3.2	Sugar Palm/Cassava Bagasse	66
4.3.3	Sugar Palm/Flax	66
4.4	Potential Applications	66
4.5	Conclusions	72
	Acknowledgment	72
	References	72
<b>5</b>	<b>Thermal Properties of Sisal Fiber-Based Hybrid Composites</b>	<b>85</b>
	<i>Tamil Moli Loganathan, Jesuarockiam Naveen, Koduri Naga Ganapathi Lakshmi Reshwanth, Kandasamy Jayakrishna, and Chandrasekar Muthukumar</i>	
5.1	Introduction	85
5.2	Thermal Properties of Sisal Fiber-Reinforced Polymeric Composites	87
5.3	Thermal Properties of Hybrid Sisal Fiber/Synthetic Fiber-Reinforced Polymeric Composites	88
5.4	Thermal Properties of Sisal/Other Natural Fiber-Reinforced Polymeric Composites	89
5.5	Conclusions	91
	References	91

<b>6</b>	<b>Thermal Properties of Flax Fiber Hybrid Composites</b>	<b>93</b>
	<i>Carlo Santulli</i>	
6.1	Introduction	93
6.2	Techniques for Thermal Analysis of Natural Fiber Composites	95
6.3	General Properties and Composition of Flax Fibers	97
6.4	Thermal Analysis of Flax Fibers	98
6.5	Thermal Analysis of Flax Fiber Composites	99
6.6	Conclusions	100
	References	101
<b>7</b>	<b>Thermal Properties of the Pineapple Leaf Fiber-Based Hybrid Composites</b>	<b>107</b>
	<i>Bheemappa Suresha, Rajashekaraiah Hemanth, and Gurumurthy Hemanth</i>	
7.1	Introduction	107
7.2	Thermal Properties of Polymers	108
7.2.1	The Hypothesis of Thermal Conductivity	108
7.2.2	Factors Influencing Thermal Conductivity of Composite Materials	109
7.2.2.1	Fibers	109
7.2.2.2	Resins	111
7.2.2.3	Fillers	112
7.2.2.4	Additives	112
7.2.2.5	Thermal Conductivity of the Composites	113
7.3	Improving the Thermal Properties of Epoxies	114
7.3.1	Modification of Epoxies with Other Polymers or Additives	114
7.3.2	Modification of Epoxies by Reinforcing Fibers	115
7.3.3	Modification of Epoxies by Micron-sized Particulate Fillers	115
7.3.4	Modification of Epoxies by Filling Nano-Sized Particulate Fillers	116
7.3.5	Modification of Epoxies by Hybridization	116
7.4	The Thermal Properties of PALF Composites	116
7.4.1	Thermogravimetric Analysis of PALF Composites	116
7.4.2	Dynamic Mechanical Analysis of PALF Composites	120
7.4.3	Differential Scanning Calorimetric Analysis of PALF Composites	124
7.4.4	Thermal Conductivity of PALF Composites	126
7.5	Concluding Remarks	127
	References	129
<b>8</b>	<b>Thermal Properties of the Grass/Cane Fiber-Based Hybrid Composites</b>	<b>135</b>
	<i>Manickam Ramesh, Jaganathan Maniraj, and Sengottuvelu Ramesh</i>	
8.1	Introduction	135
8.2	Hybrid Composite Materials	137
8.3	Cane/Grass Fiber Hybrid Composites	138
8.4	Properties of Cane/Grass Fiber Hybrid Composites	140
8.5	Thermal Properties	140
8.5.1	Thermal Conductivity	141

- 8.5.2 Thermogravimetric Analysis 142
- 8.5.3 Differential Scanning Calorimetry Analysis 142
- 8.5.4 Flammability Test 142
- 8.5.5 Heat Deflection Temperature Test 143
- 8.5.6 Specific Heat Capacity Measurement 143
- 8.5.7 Thermal Diffusivity 143
- 8.6 Applications of Grass/Cane Hybrid Composites 144
- 8.7 Conclusion 145
- References 145

## **9 Thermal Properties of the Banana Fiber-Based Hybrid Composites 153**

*Nasmi Herlina Sari and Senthil Muthu Kumar Thiagamani*

- 9.1 Introduction 153
- 9.2 Fabrication of Banana Fiber-Based Hybrid Composite 154
  - 9.2.1 Hand Layup 154
  - 9.2.2 Vacuum Bag-Assisted Resin Infusion Technique 155
- 9.3 Thermal Properties of Banana Fiber-Based Composites 155
  - 9.3.1 Thermal Stability 155
  - 9.3.2 Limiting Oxygen Index (LOI) 155
  - 9.3.3 Thermogravimetric Analysis (TGA) 156
    - 9.3.3.1 Jute and Banana Fiber Hybrid Composites 156
    - 9.3.3.2 Glass and Banana Fiber Hybrid Composites 157
    - 9.3.3.3 Banana/Flax-Based Glass Fiber Hybrid Composite 158
- 9.4 Specific Heat of Banana Fiber Hybrid Composites 159
  - 9.4.1 Banana and Pineapple Leaf Fiber Hybrid Composites 159
- 9.5 Thermal Conductivity of Banana Fiber Hybrid Composites 160
  - 9.5.1 The Pineapple Leaf and Banana Fiber Hybrid Composites 160
- 9.6 Thermal Diffusivity 160
- 9.7 Applications 162
- 9.8 Conclusions 162
- References 163

## **10 Thermal Properties of Kenaf Fiber-Based Hybrid Composites 167**

*Chinnaiyan Deepa, Lakshminarasimhan Rajeshkumar, and Manickam Ramesh*

- 10.1 Introduction 167
- 10.2 Hybrid Composites 168
- 10.3 Thermal Properties 169
  - 10.3.1 Thermogravimetric Analysis 169
  - 10.3.2 Dynamic Mechanical Analysis 172
  - 10.3.3 Derivative Thermogravimetric Analysis 174
  - 10.3.4 Differential Scanning Calorimetry 175
  - 10.3.5 Thermal Mechanical Analysis 176

- 10.3.6 Flammability Tests 177
- 10.3.7 Heat Deflection Temperature 178
- 10.4 Conclusion 178
- References 179
  
- 11 Thermal Properties of Hemp Fiber-Based Hybrid Composites 183**  
*Hom Nath Dhakal and Mohini Sain*
- 11.1 Introduction 183
- 11.2 Thermal Properties Measurements and Importance 185
- 11.2.1 Thermogravimetric Analysis (TGA) 185
- 11.2.2 Hybrid Approach for Thermal Properties Improvement 186
- 11.2.3 Differential Scanning Calorimetry (DSC) 189
- 11.2.4 Thermal Conductivity 190
- 11.2.5 Linear Coefficient of Thermal Expansion 192
- 11.2.6 Dynamic Mechanical Analysis (DMA) 193
- 11.3 Conclusions and Perspectives 197
- References 198
  
- 12 Thermal Properties of Cellulose Nanofibers and Their Composites 201**  
*Sadia Khalid, Tania Ali, Asiya Gul, and Sara Qaisar*
- 12.1 Introduction 201
- 12.2 Nanocellulose 202
- 12.3 Cellulose Nanofibers (CNFs) 202
- 12.4 CNF Preparation 203
- 12.5 Surface Functionalization of CNFs 203
- 12.6 CNF-Based Composites 205
- 12.7 Thermal Properties of CNF Composites 208
- 12.8 Current Status: CNF-Based Composites 209
- 12.9 Outlook and Future Perspective 212
- References 214
  
- 13 Influence of Graphene Nanoparticles on Thermal Properties of the Natural Fiber-Based Hybrid Composites 219**  
*Theivasanthi Thirugnanasambandan*
- 13.1 Introduction 219
- 13.2 Graphene 220
- 13.3 Polymer/Graphene Composites 220
- 13.4 Polymer/Natural Fiber Composites 223
- 13.5 Polymer/Natural Fiber/Graphene Composites 226
- 13.6 Conclusion 233
- Acknowledgments 233
- References 233

<b>14</b>	<b>Influence of Nanoclay on the Thermal Properties of the Natural Fiber-Based Hybrid Composites</b>	<b>239</b>
	<i>Sabarish Radoor, Jasila Karayil, Reshma Soman, Aswathy Jayakumar, Edayilveettill K. Radhakrishnan, Jyotishkumar Parameswaranpillai, and Suchart Siengchin</i>	
14.1	Introduction	239
14.2	Effect of Nanoclay on the Thermal Stability of Natural Fiber-Based Hybrid Composites	240
14.3	Effect of Nanoclay on the Inflammability of Natural Fiber-Based Hybrid Composites	244
14.4	Effect of Nanoclay on the Melting and Crystallization (DSC) of Natural Fiber-Based Hybrid Composites	246
14.5	Effect of Nanoclay on the Glass Transition Temperature of Natural Fiber-Based Hybrid Composites	247
14.6	Conclusion	248
	Acknowledgments	249
	References	249
<b>15</b>	<b>Effect of CNT Fillers on Thermal Properties of the Bamboo Fiber-Based Hybrid Composites</b>	<b>255</b>
	<i>Mohit Hemath, Babu V. Hemath, Hemath K. Govindarajulu, Sanjay M. Rangappa, Suchart Siengchin, and Suresh N. Sundaram</i>	
15.1	Introduction	255
15.2	Materials and Methods	257
15.2.1	Materials Used	257
15.2.2	Extraction of Bamboo Microfibers	258
15.2.3	Amino Functionalization of SWCNTs	258
15.2.4	Fabrication of SWCNT/Bamboo Fiber (BF)/Epoxy Hybrid Nanocomposites	258
15.2.5	Characterization	259
15.2.5.1	Thermal Properties	259
15.2.5.2	Fourier Transform Infrared (FTIR) Spectroscopy	259
15.2.5.3	Mechanical Properties of SWCNT/BF/Epoxy Composites	259
15.2.5.4	Morphological Characteristics	260
15.3	Results and Discussion	260
15.3.1	Effect on FTIR Spectra	260
15.3.2	Effect on Thermal Degradation Properties	260
15.3.3	Effect on Thermal Conductivity	262
15.3.4	Effect on Mechanical Characteristics	264
15.3.4.1	Flexural and Tensile Properties	264
15.3.5	Tensile Fracture	265
15.3.5.1	Impact Strength and Hardness	266
15.4	Conclusion	267
	Acknowledgment	267
	References	267

<b>16</b>	<b>Effect of Metal Oxide Fillers on Thermal Properties of the Natural Fiber-Based Hybrid Composites</b>	<b>273</b>
	<i>Mohit Hemath, Hemath K. Govindarajulu, Sanjay M. Rangappa, Suchart Siengchin, Ruban Ramalingam, and Babu V. Hemath</i>	
16.1	Introduction	273
16.2	Materials and Methods	274
16.2.1	Materials	274
16.2.2	Extraction of Bamboo Nanocellulose Fiber (BNF)	275
16.2.3	Fabrication of Epoxy Hybrid Nanocomposites	275
16.2.4	Epoxy Hybrid Nanocomposite Characterization	275
16.2.4.1	Thermal Properties	275
16.2.4.2	Flame-Retardant Properties	275
16.2.4.3	Mechanical Properties	275
16.2.4.4	Morphological Properties	276
16.2.4.5	Fourier Transform Infrared (FTIR) Spectra	276
16.3	Results and Discussion	276
16.3.1	Effect on FTIR Spectra	276
16.3.2	Effect on Flammability	277
16.3.3	Effect on Thermal Stability	280
16.3.4	Effect on Mechanical Properties	280
16.3.4.1	Tensile Properties	280
16.3.4.2	Tensile Fracture	282
16.3.4.3	Flexural Properties	282
16.3.4.4	Compression Properties	283
16.3.4.5	Impact Strength	285
16.4	Conclusion	286
	References	286
<b>17</b>	<b>Influence of Chemical Treatments on the Thermal Properties of Natural Fiber-Reinforced Hybrid Composites (NFRHC)</b>	<b>291</b>
	<i>Rafael de Avila Delucis and José Humberto S. Almeida Jr</i>	
17.1	Introduction	291
17.2	Chemical Modifications for Natural Fibers Applied in Hybrid Composites	295
17.2.1	Chemical Treatments	295
17.2.1.1	Chemically Treated Natural Fibers in Hybrid Thermoset Composites	295
17.2.1.2	Chemically Treated Fibers in Hybrid Thermoplastic Composites	298
17.2.2	Chemical Coupling Agents	299
17.2.2.1	Maleic Anhydride	299
17.2.2.2	Silanization	300
17.2.3	Two-Step Treatments	301
17.3	Concluding Remarks	302
	References	303

<b>18</b>	<b>Physical, Mechanical, and Thermal Properties of Fiber-Reinforced Hybrid Polymer Composites</b>	<b>309</b>
	<i>Subramanian Ravichandran, Suresh Sagadevan, and Md Enamul Hoque</i>	
18.1	Introduction	309
18.2	Preparation of Composite Material	311
18.3	Characterization of Composite Material	312
18.3.1	Tensile Test	312
18.3.2	Flexural Test	312
18.3.3	Test of Water Absorption	312
18.4	Results and Discussion	313
18.4.1	Mechanical Properties	313
18.4.2	Water Absorption Studies	315
18.4.3	Thermal Properties	316
18.5	Conclusions	317
	Conflicts of Interest	318
	References	318
	<b>Index</b>	<b>321</b>

## 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<sup>1</sup>, Senthilkumar Krishnasamy<sup>2,3</sup>, Senthil Muthu Kumar Thiagamani<sup>3</sup>, Rajini Nagarajan<sup>3</sup>, and Suchart Siengchin<sup>4</sup>

<sup>1</sup>Hindustan Institute of Technology & Science, Department of Aeronautical Engineering, Kelambakkam, Chennai 603103, Tamilnadu, India

<sup>2</sup>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

<sup>3</sup>Kalasalingam Academy of Research and Education, Department of Mechanical Engineering, Krishnankoil 626126, Tamil Nadu, India

<sup>4</sup>King Mongkut's University of Technology North Bangkok, The Sirindhorn International Thai-German Graduate School of Engineering (TGGSE), 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

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	

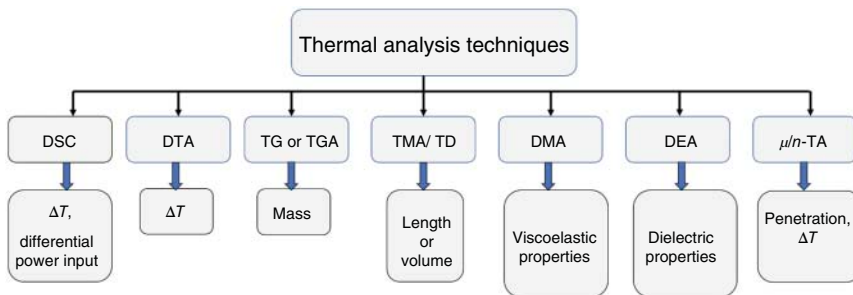
## 1.2 Thermal Characterization

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 ( $\tan \delta$ ) 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,

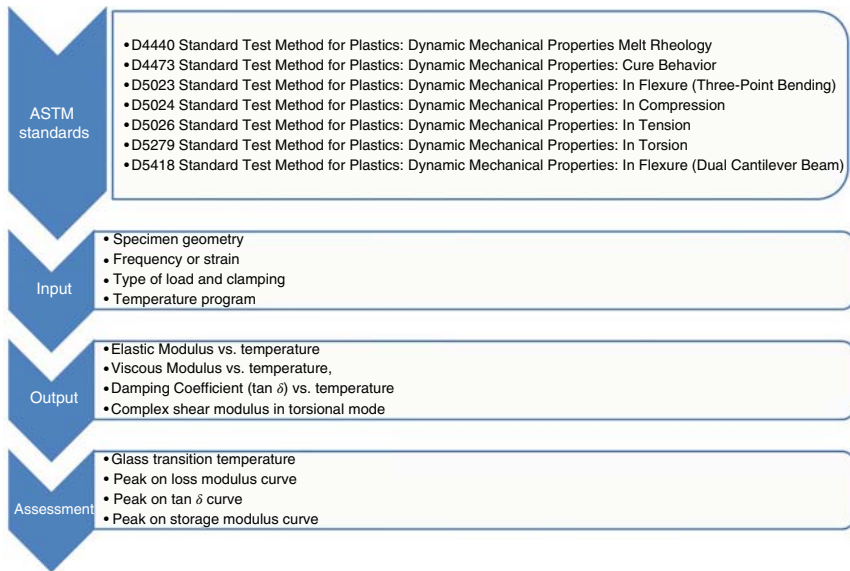


**Figure 1.1** Various thermal analysis techniques and their applications. DFA, dielectric analysis.

**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/ <i>Luffa cylindrica</i> /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.  $\tan \delta$  is a dimensionless number obtained through the ratio of loss modulus to the storage modulus. Lower  $\tan \delta$  indicates higher stiffness and better interfacial bonding between fiber and polymer matrix, which restricts the molecular mobility within the polymeric chains.



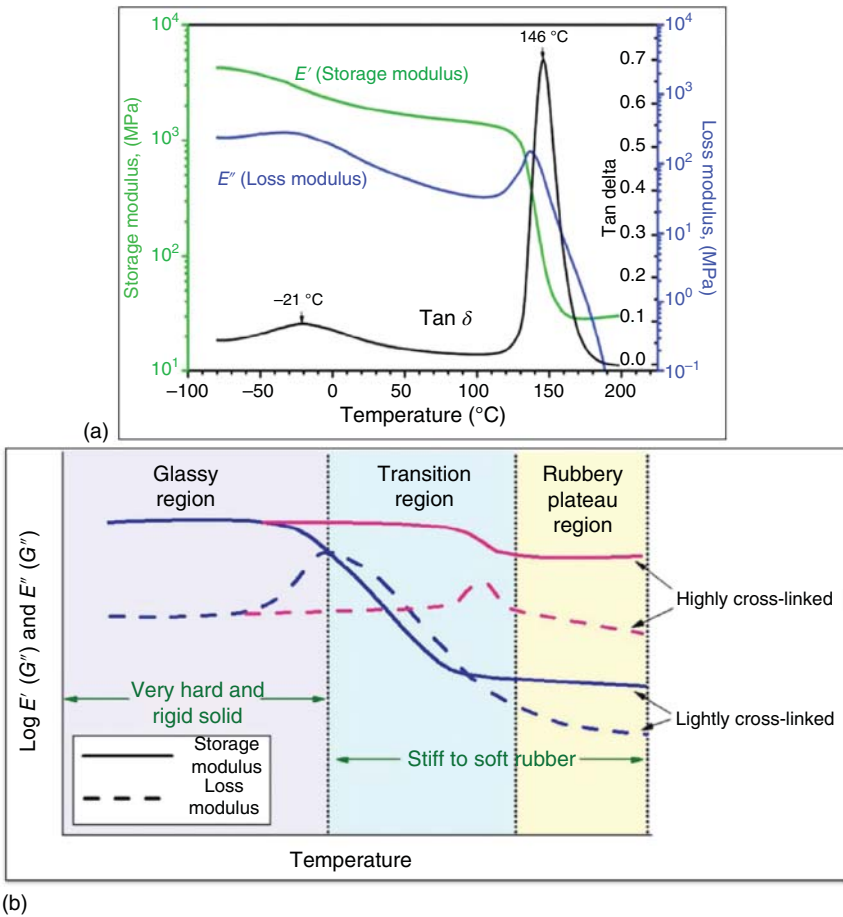
**Figure 1.2** Thermal characterizations of the polymer and polymer-based composite through DMA, step-by-step process.

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.



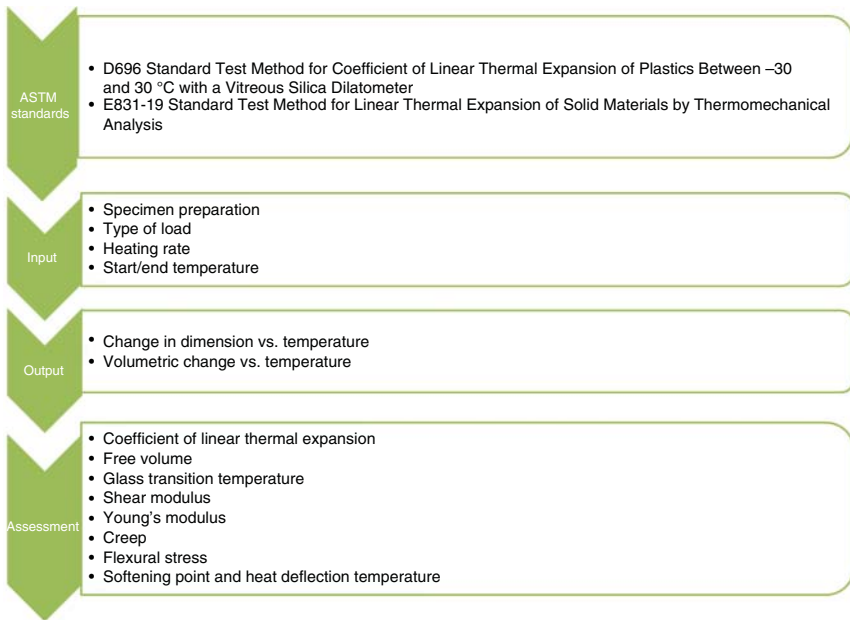
**Figure 1.3** Thermal characterization of polymer and polymer-based composite with DMA. (a) Typical curve. (b) Viscoelastic characteristics of the polymer. Source: Saba et al. [53].

### 1.2.3 DSC

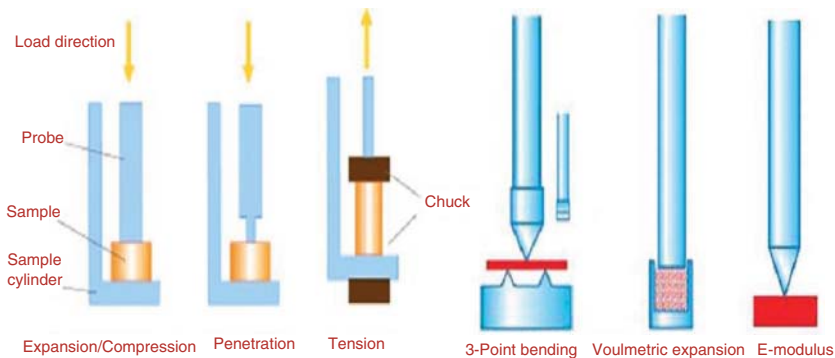
Figure 1.7 presents the step-by-step process involved in the DSC of the polymers and polymer-based composites. In DSC, the sample is heated around 30 to the elevated temperature beyond 300  $^{\circ}\text{C}$  with the constant supply of liquid nitrogen in a controlled chamber. Heat flow from the sample 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

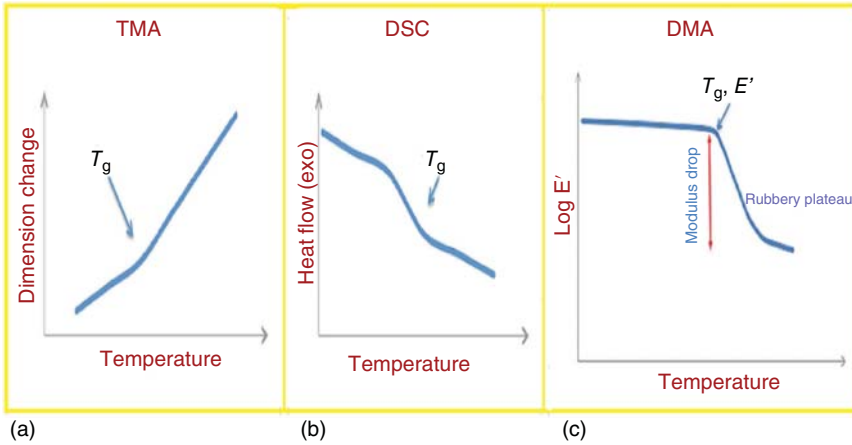


**Figure 1.4** Thermal characterizations of the polymer and polymer-based composite through TMA, step-by-step process.

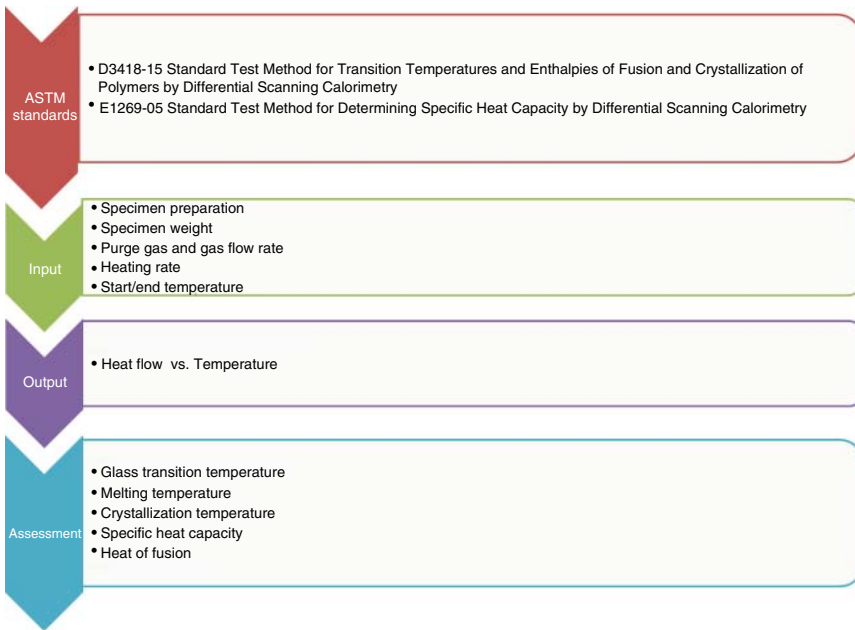


**Figure 1.5** Test modes in TMA. Source: Saba and Jawaid [54].

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.

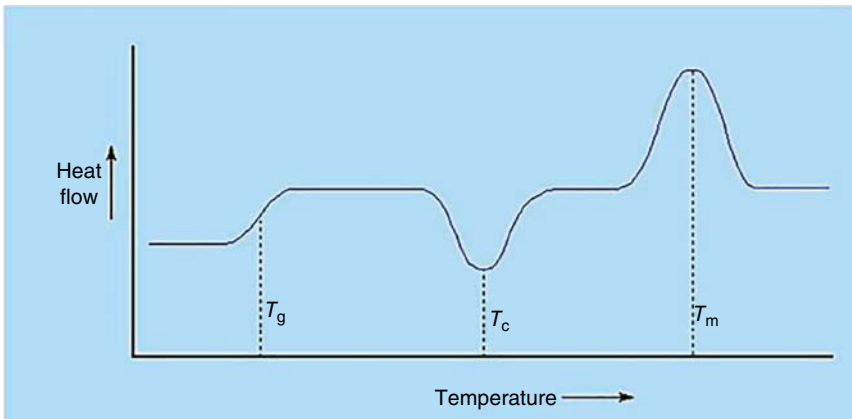


**Figure 1.6**  $T_g$  measured from the various thermal characterization techniques: (a) TMA, (b) DSC, and (c) DMA. Source: Saba and Jawaid [54].

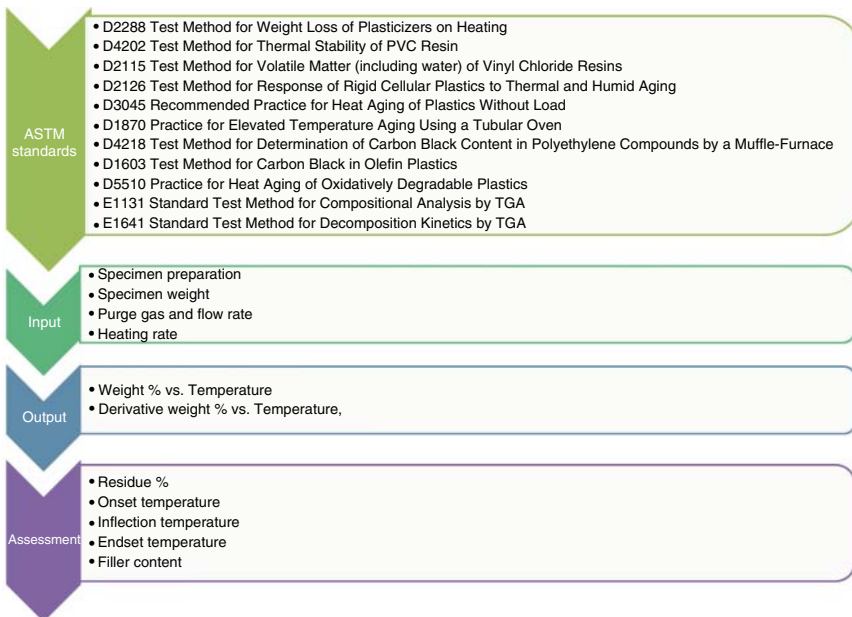


**Figure 1.7** Thermal characterizations of the polymer and polymer-based composite through DSC, step-by-step process.

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



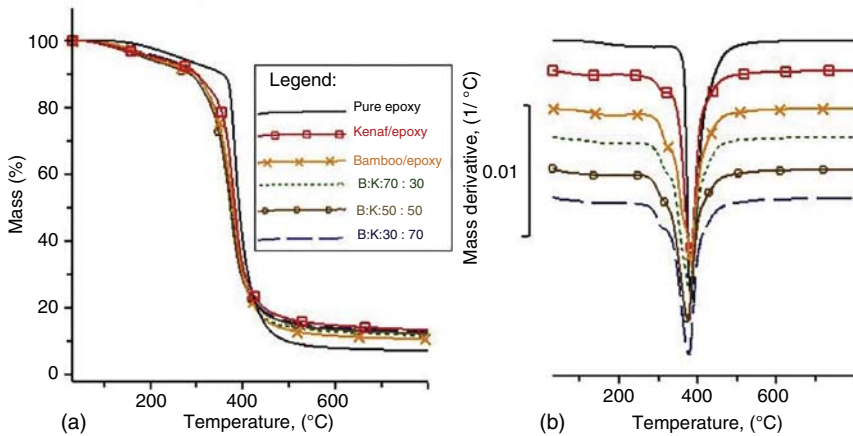
**Figure 1.8** Thermogram from the DSC. Source: Chandrasekar et al. [55].



**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.

- natural fiber composites (NFCs) 167–168
- natural fiber reinforced polymer composites (NFRPCs) 183
- natural fibers based composite 135
- N*-methylol dimethylphosphonopropionamide (MDPA) 210
- N,N*-di-methyl formamide (DMF) 221
- non-woven hemp mat 184
- o**
- oil palm empty fruit bunch (OPEFB) fibers 224
- oil palm fibers 72
- organoclay montmorillonite (OMMT) 240
- organosolv lignins 88
- oxidation onset temperature (OOT) 176
- p**
- PALF/GF/polyester hybrid composites 126
- PALF hybrid composites 157
- PALF/kenaf fiber composites 176
- PALF reinforced epoxy composites 115
- palmyra palm leaf stalk (PPLSF) 296
- PAN-based carbon fibers 110
- Parthenium Hysterophorus* 17
- peak heat release rate (PHRR) 210
- phenolic formaldehyde (PF) 22
- piassava fiber (PF) 226
- pineapple leaf fibers (PALF) 22, 45, 110, 159, 300
- pinneapple plant 110
- plant fibers 32
- PLA-TAF 242
- poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) 32
- poly(butylsuccinate) (PBS) 100
- poly( $\epsilon$ -caprolactone) (PCL) 293
- poly(glycolic acid) (PGA) 293
- poly(hydroxybutyrate) (PHB) 100
- poly(lactic acid) (PLA) 39, 99, 101
- polyacrylonitrile (PAN) 109
- polybutylene succinate (PBS) composites 22
- polycaprolactone (PCL) 32, 301
- polycarbonate (PC) 119, 293
- poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB) composites reinforced wood fiber 42
- polyether ether ketone (PEEK) 70
- polyethylene (PE) 293
- polyethylene glycol (PEG) 207
- polyhydroxy butyrate-co-valerate (PHBV) 20
- polylactic acid (PLA) 32
- polylactic acid polymer 126
- polymer-based composites 3, 6, 8
- polymer based nanocomposites 116, 255
- polymer-based nanolaminates 273
- polymer-based products 53
- polymer composites 153
- polymer/graphene composites 220–223
- polymeric composite materials 107
- polymerizable deep eutectic solvents (PDES) 206
- polymer/natural fiber composites 223–225
- polymer/natural fiber/graphene composites 226–232
- polymers
- additive materials 112
  - fibers 109–111
  - fillers 112
  - hypothesis of thermal conductivity 108–109
  - resins 111–112
  - thermal conductivity of composites 113
- polypropylene (PP) 38, 99, 101, 221, 226, 293
- polypropylene/PALF/nanoclay composites 120
- poly(hydroxybutyrate-co-valerate) resin 116

- polystyrene-block-poly(ethylene-ranbutylene)-block-poly(styrene-graft-maleic anhydride) 120  
 poly-(styrene-co-maleic anhydride) 120  
 polyurethane (PU) 191, 294  
 pure LDPE-epoxy laminated composite 313
- R**
- raw jute 35  
 recycled polypropylene (RPP) composites 40  
 reduced graphene oxide (RGO) 221  
 reinforced sugar palm fiber polymer composite 61  
 reinforced sugar palm fiber with different polymer composites 57  
 residue 9, 10  
 resins 111, 139  
 resin transfer moulding (RTM) 139  
 rice husk biochar composites 310  
 roselle fiber/sugar palm fiber composites 63  
 roselle (RF)/sugar palm fiber (SPF) reinforced thermoplastic polyurethane (TPU) composites 33
- S**
- Saccharum Bengalense* 17  
 sago fiber-epoxy composites 115  
 Sansevieria fibers 141  
 scanning electron microscope (SEM) 257  
 seaweed/sugar palm fiber composites 62  
 self-hybridization 32  
 S3G3 310  
 S4G3 310  
 S glass 109  
 Shimadzu DTG-60H 55  
 silane treated sisal fibers 88  
 silanization 300–301  
 single-walled carbon nanotubes (SWCNT) 257  
     amino-functionalization 258  
     fabrication 258–259  
     mechanical properties 259  
 sisal (S) and kenaf (K) woven fabrics-based hybrid bioepoxy composites 37  
 sisal/banana (SB) 89  
 sisal/coir (SC) 89  
 sisal fiber (SF) 230  
 sisal fiber based hybrid composites 85–86  
 sisal fiber/organoclay reinforced PP composites 38  
 sisal fiber (mercerization and silane) reinforced epoxy composites 88  
 sisal fiber reinforced PLA composites 36  
 sisal fiber reinforced polymeric composites, thermal properties of 87  
 sisal/glass fiber reinforced epoxy composites 35  
 sisal/glyoxal-phenolic composite 88  
 sisal/jute based hybrid composites 90  
 sisal/nanoclay based composites 90  
 sisal/other natural fiber reinforced polymeric composites 89  
 sisal/propylene composites 90  
 sisal woven mat 42  
 smoke production rate (SPR) 245  
 SPF reinforced composites 55  
 storage modulus ( $E'$ ) 18, 86  
 sugar palm/cassava bagasse 66  
 sugar palm fiber (SPF) 20, 54  
     glass fiber (GF)-based TPU composites 34  
     hybrids 61  
     natural woven structure 56  
 sugar palm fiber based hybrid polymer composites  
     dynamic mechanical analysis (DMA) 63–66  
     potential applications 66–72  
     thermogravimetric analysis (TGA) 58–60  
 sugar palm/flax fibers 66  
 sugar palm/glass fiber 63–66

- sugar palm short fibers 56  
 sugar palm tree 56  
 surface-modified grass fibers 142  
 SWCNT/BF 262  
 synthetic fibers 89, 239  
 synthetic/natural hybrid composites 310
- t**
- TEMPO-oxidized cellulose nanofiber (TOCN) 207  
 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 204  
 thermal characterization 3  
   DMA 3–5  
   DSC 6  
   TGA 6–10  
   TMA 5–6  
 thermal conductivity 113, 141–142  
   banana fiber-based hybrid composites 160  
   of composites 113, 126–127  
   hemp fiber based hybrid composites 190–192  
   pineapple leaf and banana fiber hybrid composites 160  
   testing 107  
 thermal diffusivity 143–144, 160–162  
 thermal expansion coefficients (TEC) 208  
 thermal gravimetric analyzer (TGA) 11, 221, 262, 280  
 thermal property 18  
 thermal stability 8, 10, 141, 145, 155, 240–244  
 thermoanalytical technique 246  
 thermogravimetric analysis  
   bamboo fiber based hybrid composites 259  
   nanoclay 240  
 thermogravimetric analysis (TGA) 3, 95, 142, 154, 230  
   banana-flax based glass fiber hybrid composite 158  
   epoxy/pineapple fiber (PALF) 116–120  
   glass and banana fiber hybrid composites 157–158  
   heat of, pineapple leaf 159–160  
   hemp fiber based hybrid composites 185–186  
   jute and banana fiber hybrid composites 156  
   kenaf fiber based hybrid composites 169–172  
   natural fiber reinforced hybrid polymer composites 33–38  
   sisal fiber based hybrid composites 85–86  
   sugar palm fiber based hybrid polymer composites 58–63  
 thermo-mechanical analysis (TMA) 3, 5, 10, 21–22, 176–177  
 thermoplastic materials 111  
 thermoplastic polymers 18  
 thermoplastic polysulfone (PSF) 114  
 thermoplastic polyurethanes (TPU) 64  
 thermoplastic starch composites 42  
 thermoplastic sugar palm starch agar (TPSA) 62  
 thermoset polymers 294  
 thermoset resins 112  
 time to ignition (TTI) 210  
 time to peak heat release rate (TPHRR) 245  
 total time to ignite (TTI) 245  
 treated bamboo fibers (TBF) 224, 225  
 treated kenaf + epoxy single fiber composite 43  
 treated kenaf + glass + clay-based epoxy hybrid composites 43  
*Tridax procumbens* 17  
 Typha angustifolia grass fiber 141
- u**
- unsaturated polyester (UP) 45, 60, 112, 248  
 untreated bamboo fibers (UBF) 224, 225

untreated kenaf + epoxy single fiber composite 43  
untreated kenaf + glass + clay-based epoxy hybrid composites 43

**V**

vacuum bag assisted resin infusion technique 155  
vapor grown carbon fiber (VGN) 36  
vinyl ester 112  
viscoelastic characteristics, polymeric composites 86

**W**

water glass (WG) coated sisal fibers 90  
wood floor reinforced PLA composites 39

**X**

X-ray diffraction (XRD) 227

**Y**

Young's modulus 4, 22, 212

**Z**

zeolitic imidazolate framework-67 (ZIF-67) 207