Engineering Materials

Abhijit Bandyopadhyay Poulomi Dasgupta Sayan Basak

Engineering of Thermoplastic Elastomer with Graphene and Other Anisotropic Nanofillers



Engineering Materials

This series provides topical information on innovative, structural and functional materials and composites with applications in optical, electrical, mechanical, civil, aeronautical, medical, bio- and nano-engineering. The individual volumes are complete, comprehensive monographs covering the structure, properties, manufacturing process and applications of these materials. This multidisciplinary series is devoted to professionals, students and all those interested in the latest developments in the Materials Science field, that look for a carefully selected collection of high quality review articles on their respective field of expertise.

More information about this series at http://www.springer.com/series/4288

Abhijit Bandyopadhyay · Poulomi Dasgupta · Sayan Basak

Engineering of Thermoplastic Elastomer with Graphene and Other Anisotropic Nanofillers



Abhijit Bandyopadhyay Department of Polymer Science and Technology University of Calcutta Kolkata, West Bengal, India

Sayan Basak Department of Polymer Science and Technology University of Calcutta Kolkata, West Bengal, India Poulomi Dasgupta Department of Polymer Science and Technology University of Calcutta Kolkata, West Bengal, India

 ISSN 1612-1317
 ISSN 1868-1212 (electronic)

 Engineering Materials
 ISBN 978-981-15-9084-9
 ISBN 978-981-15-9085-6 (eBook)

 https://doi.org/10.1007/978-981-15-9085-6
 ISBN 978-981-15-9085-6
 ISBN 978-981-15-9085-6

© Springer Nature Singapore Pte Ltd. 2020

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd. The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Foreword

My whole career has been dedicated to pursuing the development of various types of functional nanoparticles and their nanoscale dispersion across multiple polymer matrices, from engineering to bio-based polymers. So, the content of this book is very close to my expertise.

The group, leading by Prof. Abhijit Bandyopadhyay, is well known to me through their high-quality work on processing and development of new generation engineering thermoplastic elastomers. Over the years, this group used various types of advanced nanofillers to modify the inherent properties of different types of elastomers using polymer nanocomposite technology.

Over the last few years, nanocarbons and related nanoparticles are becoming emerging fillers for the development of next-generation engineering polymer materials for a wide range of applications, from construction to biomedical. Therefore, this book has immediate relevance, interest, and importance owing to the trend in the plastic industry.

In this book, the authors tried to cover various characteristics of nanofillers and several types of processing techniques to disperse them in thermoplastic elastomers. The key to manufacturing a useful engineering thermoplastic elastomer nanocomposite for practical applications is to achieve the desired degree of dispersion of filler particles in a polymer matrix and tune the obtained composite properties as per the product requirement. I am thrilled to say that the authors very meticulously cover this aspect in this book.

Based on my knowledge in this field and going through the content of this book, I must say that this is an ideal book for postgraduate students, researchers, and polymer processing technologists who are interested in engineering thermoplastic elastomers in general. I also believe this book will be beneficial for industry-based scientists and engineering, including product development managers who want to bring advanced elastomer-based products in the market.

Congratulations and all the best!

Professor Suprakas Sinha Ray Chief Researcher and Manager Centre for Nanostructures and Advanced Materials Council for Scientific and Industrial Research Pretoria, South Africa

> Distinguished Visiting Professor Department of Chemical Sciences University of Johannesburg Johannesburg, South Africa

Preface

Rubber is a unique class of polymer pact with some uncanny properties like high shock absorption, compressibility resistance, resilience, recoverable deformability along with low modulus and strength. High molecular weight, high chain entanglement density, and extremely low cohesive force of attraction among the segments are the keys to form a rubber, which during processing is mixed with several other ingredients (at least 10-12) to achieve the strange combination of properties. Vulcanization or chemical crosslinking (either sulphur- or non-sulphur-based) between the molecules of a rubber is thought to be the key that confers the true rubberiness, and once that is achieved, the rubber becomes a thermoset. However, in an era of sustainable development, a thermosetting polymer with zero recyclability and complex formulation is not a preferred choice indeed. The world is obsessed for polymers with "zero waste" technology—conventional rubber, being unfit to that, makes a way for the relatively new thermoplastic elastomers or TPE which by virtue of its inimitable molecular design has got the immense potential to replace conventional rubbers in many of its applications. Believing to that, the world has seen a steep rise in consumption of TPE of late and is also predicted to hold an even stronger ground in future. The exclusive molecular design of tri- or di-blocking of homopolymers developed though special living anionic polymerization imparts the essence of both thermoplastic and elastomeric properties combining both melt recyclability and recoverable elongation once the stress is lifted. TPE, representing a unique combination of hard and soft polymer segments alluring with high and low Tg s, respectively, inherits high cohesive strength, thus could avoid nearly all additional ingredients unlike rubbers, and emerges as an ideal "zero waste" future elastomer material. The good part is this elastomer could be tailor-made as and when, driven by the application demand.

Of late, the world has seen the development of many new TPEs with different monomers, block length, etc., befitting new as well as conventional applications. Alongside, nanotechnology has emerged as a promising new material technology for serving the human kind. Both isotropic and anisotropic nanomaterials have shown remarkable properties that could revolutionize the material world with advanced applications in optical, optoelectrical, and other relevant fields. The first revolutionary work on polymer nanotechnology was reported by the Toyota Research Group in Japan nearly 30 years back, and since then different nanomaterials have been explored in a variety of thermoplastics and elastomers and yielded some good to exciting results in many of the cases. However, on critical review, anisotropic nanomaterials were found more effective on thermoplastics than on elastomers largely due to the inherent viscoelasticity and presence of huge number of ingredients in the latter. TPE, on the other hand, has been able to derive greater benefit of the anisotropic nanomaterials and, thus of late, has been considered as a better matrix than the conventional elastomer for exploration. The combination of TPE and anisotropic nanomaterials like clay, carbon materials, and graphene has yielded many exciting properties, befitting conventional as well as advanced applications. Acknowledging the progress of this important hybrid material technology for the past seven to ten years, an attempt has been made to tot up important outcomes, and analyse and predict the future applications. We believe this book would serve as an important document for the readers for awareness and knowledge enhancement.

Kolkata, India

Abhijit Bandyopadhyay Poulomi Dasgupta Sayan Basak

Contents

1	Intr	oductio	n	1
	1.1	Growt	h and Development of TPE	1
	1.2	Break	through Developments in Commercialization of TPE	2
	1.3	TPE:	A Sustainable Elastomer Composition	4
	1.4	TPE E	Based on Rubber—Plastic Blends	7
	1.5	Fillers	/Nanofillers for TPE: Isotropic and Anisotropic Fillers	9
	1.6	Concl	usion	13
	Refe	erences		14
2	Anis	otropi	c Nanofillers in TPE	17
	2.1	Introd	uction	17
	2.2	Nanof	illers and Its Advantages	17
	2.3	Layer	ed Double Hydroxide (LDH)	20
		2.3.1	Structure of LDH	20
		2.3.2	Organophilisation of LDH	22
		2.3.3	Strategies to Fabricate the Layered Double Hydroxide	23
		2.3.4	Synthesis of Polymer/LDH Nanocomposites	27
		2.3.5	Properties and the Recent Trends in the Areas	
			of Application	31
	2.4	Nanoc	elay	32
		2.4.1	Structure of Nanoclay	34
		2.4.2	Organomodification of Nanoclay	37
		2.4.3	Factors Affecting the Organoclay Hybrid Formed	38
		2.4.4	Modification of Nanoclay	38
		2.4.5	Properties and Applications	44
	2.5	Carbo	n Nanotube (CNT)	47
		2.5.1	Structure and General Properties of Carbon	
			Nanotubes	48
		2.5.2	Synthesis Routes to Fabricate Carbon Nanotubes	50
		2.5.3	Purification and Dispersion of Carbon Nanotubes	54

		2.5.4	Functionalization of Carbon Nanotubes	55
		2.5.5	Applications	61
	2.6	Graph	ene	65
		2.6.1	Structure and General Properties of Graphene	67
		2.6.2	Synthesis Strategy of Graphene	70
		2.6.3	Application and Recent Trends	82
	2.7	Concl	usion	84
	Refe	erences		84
3	Prei	naratio	n of Granhene Based Nanocomposite Based on TPE	101
•	3.1	Introd	uction	101
	5.1	311	Trends in Granhene Research	101
	32	Differ	ent Methods of Preparation	105
	5.2	3 2 1		106
		3.2.1	In situ Polymerization	112
		3.2.2	Shoer Mixing	112
	22	Choros	stical Mixing	115
	5.5 2.4		action of Graphene/TPE Nanocomposites	121
	5.4 2.5	Applic		121
	3.3 D.f.	Conci	usion	123
	Refe	rences	• • • • • • • • • • • • • • • • • • • •	123
4	Stru	cture-	-Property Co-relation of Graphene/Graphene	
	Der	vative	Based TPE	127
	4.1	Introd	uction	127
	4.2	Some	Specialized Properties of Graphene and Its Derivative	
		Releva	ant to New Age Application	128
		4.2.1	A Succinct Update on the Quantum Perspective	
			of the Graphene	134
		4.2.2	Dipping into the Chemistry	137
		4.2.3	The Hidden Beauty	141
	4.3	An Ov	verview on the Fabrication of the Graphene Sheet	
		Deriva	ites	153
		4.3.1	Fabrication of the Graphene and Graphene Derived	
			Elastomeric Nanocomposites	155
	4.4	Chara	cterization Techniques for the Graphene/Graphene	
		Deriva	ates and Elastomeric Nanocomposites	158
		4.4.1	Studying the Cure Behavior	158
		4.4.2	Analyzing the Antioxidant Effect of the Graphene	
			Derivatives in Elastomeric Nanocomposites	160
		4.4.3	Morphology and Detailing the Dispersion of the	
			Graphene and Its Derivative in the Elastomeric	
			Nanocomposites	165
		4.4.4	The Effect of Wrinkling of the Graphene Derivates	100
			on the Elastomeric Nanocomposites	166
				-00

Contents

		4.4.5	Predicting the Consequences of Modified and Hybrid	
			Graphene Derivates on the Mechanical Properties	
			of the Nanocomposite Elastomers	169
		4.4.6	Analyzing the Dynamic Mechanical Behavior Along with	
			Barrier Properties of the Graphene Derived Elastomeric	
			Nanocomposites	171
	4.5	Conclu	usions	173
	Refe	erences		174
5	Pote	ential A	pplication of Graphene-TPE Nanocomposite	183
	5.1	Introdu	uction	183
	5.2	Sensin	g and Actuation	184
	5.3	Shape	Memory	199
	5.4	Self-he	ealing	206
	5.5	Biome	edical	212
	5.6	Conclu	usion and Future Outlook	218
	Refe	erences		218
6	Con	clusion		223
	Refe	erences		226

About the Authors



Dr. Abhijit Bandyopadhyay is presently working as Full Professor in the Department of Polymer Science and Technology, University of Calcutta, along with as Technical Director in South Asia Rubber and Polymers Park (SARPOL), West Bengal. He did his B.Sc. (Chem. Hons.) from the University of Calcutta securing first class in the year 1997 followed by B.Tech. and M.Tech. in polymer science and technology from the University of Calcutta in the years 2000 and 2002, respectively, with first class, and subsequently completed Ph.D. in the year 2005 in polymer nanocomposites from Rubber Technology Centre, IIT Kharagpur. Before joining the University of Calcutta in November 2008, he worked as Assistant Professor in Rubber Technology Centre, IIT Kharagpur, during 2007–2008. He has published 90 papers in high-impact international journals and 3 books and has filed two Indian patents so far. He has successfully handled many funded research projects and did consultancies for renowned companies like Exide Industries Ltd., Phillips Carbon Black Ltd., etc. He is Fellow of the International Congress for Environmental Research (since 2010), Associate Member of Indian Institute of Chemical Engineers and Life Member of Society for Polymer Science, Kolkata Chapter, and Indian Rubber Institute, respectively. He is Editorial Board Member of two international journals. He has more than 12 years of teaching and research experience. He has been awarded Young Scientist Award by Materials Research Society of India, Kolkata Chapter, in 2005 and Career Award for Young Teachers by All India Council for Technical Education, Government of India, in 2010. His research areas include polymer nanocomposites, reactive blending, adhesion, polymer hydrogel in drug delivery, waste polymer composites, green polymer composites, and hyperbranched polymers. He has successfully supervised 11 research students for their doctorate degree so far, and 4 more are presently working under him.

Ms. Poulomi Dasgupta completed her graduation with Chemistry (Hons.) from Vidyasagar College, Kolkata, in 2013. She subsequently received her B.Tech. (2016) and M.Tech. (2019) degrees at the Department of Polymer Science and Technology at the University of Calcutta. She was awarded gold medal from the University of Calcutta (during B.Tech.). She was a recipient of GATE fellowship, AICTE, Government of India, during M.Tech. Prior to joining M.Tech., she worked with Indag Rubber, Himachal Pradesh, as R&D Executive. Currently, she is associated with TCG Lifesciences (Chembiotek Research International) as Research Chemist. Her area of research was based on "development of thermoresponsive self-healable elastomeric compound and its characterization".



Mr. Sayan Basak has completed his B.Tech. from the Department of Polymer Science and Technology, University of Calcutta, India (2015–2019), and is currently pursuing his Ph.D. from the School of Polymer Science and Engineering, University of Akron, USA (2019–2024). His undergraduate research interest, along with his present research domain, revolves working with thermoplastic elastomers and multi-component polymer systems, thereby prospecting into new materials to develop smart polymer materials for new-age applications. Apart from being a budding technologist, he loves to spend his time creating content, which is supported by the Society of Plastic Engineers, The Times of India, and Medium on sustainability, recyclability, and green chemistry.



Fig. 1.1	Market Trend of TPEs since 2012 and projection until 2022.	
-	Source Asia Pacific Thermoplastic Elastomers (TPE) Market	
	Analysis By Product (Styrenic Block Copolymers (SBC, SBS,	
	SIS, HSBC), Thermoplastic Polyurethanes (TPU),	
	Thermoplastic Polyolefins (TPO), Thermoplastic Vulcanizates	
	(TPV), Copolyester Elastomers (COPE)), By Application	
	(Automotive, Footwear, Construction, Medical, Electronics,	
	Industrial, Advanced Materials) And Segment Forecasts To	
	2022 Published: April 2016 180 Pages Format: PDF Report	
	ID: 978-1-68038-625-7. http://www.grandviewresearch.com/	
	industry-analysis/asia-pacific-thermoplastic-elastomers-tpe-	
	market accessed on 14.02.2018	2
Fig. 1.2	Block copolymer morphology—illustration of hard blocks	
	crystallized into domains with soft, rubber block regions	
	between them. Reproduced with permission from [4]	6
Fig. 1.3	Chemical structure of block copolymeric TPEs; i styrenic,	
	ii COPE, iii thermoplastic polyurethane, and iv thermoplastic	
	polyamide	7
Fig. 1.4	TPO rubber/plastic blend morphology. Reproduced with	
	permission from [4]	8
Fig. 1.5	Thermoplastic vulcanisate morphology with a continuous	
	plastic phase and discrete rubber particles. Reproduced with	
	permission from [4]	8
Fig. 1.6	TOT structure of Nanoclay. Reproduced with permission from	
	[25]	10
Fig. 1.7	Layered structure of LDH. <i>Source</i> : http://www.scielo.br/scielo.	
	php?script=sci_arttext&pid=S0100-06832015000100001,	
	accessed on 24.04.2018	12
Fig. 1.8	Allotropes of carbon popular as nanofillers. Reproduced with	
	permission from [51]	13

Fig. 2.1	Top: A snapshot of the articles (including patents) published in the respective subject domains till date, Bottom: The number of menuscript share with reference to the TDE based on the	
	nanofillers. Data source, SciEinder, Chemical Abstracts	
	Service (Plotted with the accessed data on 24/05/2020)	18
Fig 2.2	Illustrative representation of a Lavered Double Hydroxide	10
1 15. 2.2	Reproduced with permission from [59]	21
Fig 23	The Ion exchangeable double layered hydroxide developed	21
116. 2.5	by increasing the gallery height Reproduced with permission	
	from [66]	22
Fig 24	Illustration of the process of anion exchange for the synthesis	22
1 lg. 2. 4	of double layered hydroxides. Reproduced with permission	
	from [85]	24
Fig 2.5	SEM images showing the microstructure of the 7n A1/I DH	24
11g. 2.5	composite for an excellent photocatalytic activity a Zn. Al	
	$LDH_{-}(3 h of reaction time) h Zn_Al_LDH_{-}(6 h of reaction$	
	time) $c_{7n-A1-I}DH_{-}(9 h of reaction time) d_{7n-A1-I}DH_{-}(12)$	
	h of reaction time). Reproduced with permission from [101]	26
Fig 26	A comprehensive overview of the fabricating techniques of the	20
1 lg. 2.0	double-layered hydroxides. Reproduced with permission	
	from [115]	27
Fig 27	Pathway of nanocomposite preparation by a monomer	21
11g. 2.7	exchange and in situ polymerization b direct polymer	
	exchange and a restacking of the exploited layers over the	
	polymer. Reproduced with permission from reference [130]	20
Fig 28	The TEM images of thermonlastic polyester elastomer	2)
1 lg. 2.0	reinforced with zinc hydroxide nitrate and sodium benzoate	
	nanoparticle (a low magnification b enhanced magnification)	
	Reproduced with permission from [75]	33
Fig 20	Crystal structures of clay minerals: a Type 1:1: h Type 2:1	55
1 lg. 2.)	Reproduced with permission from [167]	34
Fig. 2.10	Classification of silicates based on their physicochemical	54
1 lg. 2.10	nature	35
Fig. 2.11	The layered structure of kaolinite clay. Source http://ian.ucc	55
1 lg. 2.11	nau edu/doetan/courses/env/40/env/40/2/lectures/lec19/Fig	
	9.3 gif accessed on 10.05.2020	35
Fig. 2.12	The smeetite clay structure Source http://www.pslc.ws/	55
115. 2.12	macrog/mpm/composit/nano/struct3_1_htm_accessed	
	on 11.05.2020	36
Fig. 2.13	TEM images of the polymer/clay papocomposites using a	50
1 1g. 2.13	combination of nitrovide-mediated radical polymerization and	
	solution are blending methods. Reproduced with permission	
	from [202]	40
	nom [sos]	ru

 Fig. 2.15 Surface modification and the possible mechanism of the exfoliation for the butadiene-based rubbers and the thiol-modified attapulgite. Reproduced with permission from [225]	Fig. 2.14	Visualization of the use of montmorillonite-intercalated metallocene catalyst to reinforce ethylene and 10-undecen-1-ol matrix. Reproduced with permission from [210]	42
 another in the builder outer with permission from [225]	Fig. 2.15	Surface modification and the possible mechanism of the exfoliation for the butadiene-based rubbers and the thiol-	42
 Fig. 2.16 TEM images of the nanofiller incorporated into the thermoplastic elastomer matrix, while a represents the solid section, whereas, b-d represents the transverse sections. Reproduced with permission from [228]		modified attapulgite. Reproduced with permission	11
 Fig. 2.17 Illustrative representation of the different types of carbon nanotubes, accessed from [236] on 30/01/2020	Fig. 2.16	TEM images of the nanofiller incorporated into the thermoplastic elastomer matrix, while a represents the solid section, whereas, b–d represents the transverse sections. Reproduced with permission from [228]	45
 Fig. 2.18 Visual representation of the different conformation of carbon nanotubes, accessed from [251] on 30/01/2020	Fig. 2.17	Illustrative representation of the different types of carbon nanotubes, accessed from [236] on 30/01/2020	47
 Fig. 2.19 The chemical vapor deposition to fabricate carbon nanotubes a tip growth model, b base growth model. Reproduced with permission from [173]	Fig. 2.18	Visual representation of the different conformation of carbon nanotubes, accessed from [251] on 30/01/2020	49
permission from [173]. 5 Fig. 2.20 TEM profiles of typical carbon nanotubes produced by hydrothermal treatment of polyethylene at 800 °C for 2 h in the presence of 3% Ni powder. The PE/H2O ratio was 1.6. 5 a End of the nanotubes, b the graphite fringes c,d lattice fringe images. Reproduced with permission from [263] 5 Fig. 2.21 Layout of the second-generation high pressure CO disproportionation producing the single walled carbon nanotubes. Reproduced with permission from [265] 5 Fig. 2.22 A concise representative image of the functionalization of carbon nanotubes. Reproduced with permission [280] 58 Fig. 2.23 Green Functionalization of single-walled nanotubes in ionic liquid. Reproduced with permission from [283] 60 Fig. 2.24 Green functionalization of multi-walled nanotubes with poly (ε-caprolactone). Reproduced with permission from [284] 60 Fig. 2.25 Non-covalent functionalization of carbon nanotubes (CNTs) a with a surfactant and b with a polymeric agent. Reproduced with permission from [288]. 60 Fig. 2.26 The thermoplastic polyurethane matrix reinforced with carbon nanotubes a wound on a reel; b sewn into the fabric; c,d ironed onto the fabric. Reproduced with permission from [292] 60 Fig. 2.27 The microscopic stricture of graphene layers. Reproduced with permission from [304, 305]. 60 Fig. 2.28 The AFM image of exfoliated GO sheets with three height profiles acq	Fig. 2.19	The chemical vapor deposition to fabricate carbon nanotubes a tip growth model, b base growth model. Reproduced with	
 images. Reproduced with permission from [263]	Fig. 2.20	permission from [173] TEM profiles of typical carbon nanotubes produced by hydrothermal treatment of polyethylene at 800 °C for 2 h in the presence of 3% Ni powder. The PE/H2O ratio was 1.6. a End of the nanotubes, b the graphite fringes c,d lattice fringe	51
 Fig. 2.22 A concise representative image of the functionalization of carbon nanotubes. Reproduced with permission [280]	Fig. 2.21	images. Reproduced with permission from [263] Layout of the second-generation high pressure CO disproportionation producing the single walled carbon	53
 Fig. 2.23 Green Functionalization of single-walled nanotubes in ionic liquid. Reproduced with permission from [283]	Fig. 2.22	A concise representative image of the functionalization of carbon nanotubes. Reproduced with permission [280]	53
 Fig. 2.24 Green functionalization of multi-walled nanotubes with poly (ε-caprolactone). Reproduced with permission from [284] 60 Fig. 2.25 Non-covalent functionalization of carbon nanotubes (CNTs) a with a surfactant and b with a polymeric agent. Reproduced with permission from [288]	Fig. 2.23	Green Functionalization of single-walled nanotubes in ionic liquid. Reproduced with permission from [283]	60
 Fig. 2.25 Non-covalent functionalization of carbon nanotubes (CNTs) a with a surfactant and b with a polymeric agent. Reproduced with permission from [288]	Fig. 2.24	Green functionalization of multi-walled nanotubes with poly (ε-caprolactone). Reproduced with permission from [284]	60
 Fig. 2.26 The thermoplastic polyurethane matrix reinforced with carbon nanotubes a wound on a reel; b sewn into the fabric; c,d ironed onto the fabric. Reproduced with permission from [292] 65 Fig. 2.27 The microscopic stricture of graphene layers. Reproduced with permission from [304, 305]	Fig. 2.25	Non-covalent functionalization of carbon nanotubes (CNTs) a with a surfactant and b with a polymeric agent. Reproduced with permission from [288].	62
 Fig. 2.27 The microscopic stricture of graphene layers. Reproduced with permission from [304, 305]	Fig. 2.26	The thermoplastic polyurethane matrix reinforced with carbon nanotubes a wound on a reel; b sewn into the fabric; c , d ironed onto the fabric. Reproduced with permission from [292]	65
Fig. 2.28 The AFM image of exfoliated GO sheets with three height profiles acquired in different locations, accessed from https://www.hielscher.com/ultrasonic-graphene-preparation.htm on 30-04-2020.	Fig. 2.27	The microscopic stricture of graphene layers. Reproduced with permission from [304, 305].	68
	Fig. 2.28	The AFM image of exfoliated GO sheets with three height profiles acquired in different locations, accessed from https:// www.hielscher.com/ultrasonic-graphene-preparation.htm on 30-04-2020	72

Fig. 2.29	The cryogenic-TEM images of graphene flakes dispersed in chlorosulphonic acid. Reproduced with permissions from	74
Fig. 2.30	The tapping-mode AFM topography image visualizing particles obtained by thermal exfoliation of graphite oxide along with the height of the derived sheets. Reproduced with permissions from [329]	74
Fig. 2.31	HRTEM images of nanosheets grown under 40% CH ₄ for 20 min on a tungsten substrate. Reproduced with permission from [339]	78
Fig. 2.32	The arc discharge method of preparing graphene sheets under various atmospheres. Reproduced with permission from [340]	79
Fig. 2.33	The possible mechanism of developing chemically reduced graphene using moieties having sulfur groups. Reproduced with permission from [342].	81
Fig. 2.34	Representation of a stress versus strain, b strain at break, and c stress at break values for pure thermoplastic elastomer, carbon black reinforced thermoplastic elastomer, modified carbon black reinforced thermoplastic elastomer, and exfoliated graphene reinforced thermoplastic elastomer obtained from tensile test results. Reproduced with permissions	
Fig. 3.1	from [347] Representative example of a The two-dimensional honeycomb structure of carbon atoms in graphene under high-resolution transmission electron microscopic (TEM) image. Reproduced with permission from [6] on 24.03.2020, b three-dimensional single graphite sheet consisting of a honeycomb lattice structure of sp^2 bonded carbon atoms. Reproduced with	83
Fig. 3.2	permission from [7] Graphene (top) and related structures: fullerene (bottom left); carbon nanotubes (bottom centre); and graphite (bottom right). Reproduced with permission from [8]	102
Fig. 3.3	Graphical representation of a number of publications/year on the graphene materials. The inset is the distribution of the document type, where only 2.7% of the publications are related to review work, b Delivery of the publications by subject area. Reproduced with permission from [18].	102
Fig. 3.4	Graphical representation of a number of the review publications/year on the graphene materials, b distribution of the review publications per subject area. Reproduced with permission from [18]	104

xviii

Fig. 3.5	Graphene derivatives show promising results for various fields, including energy conversion [25], energy storage [26], electronic materials [27], quantum effects [28], low density structural materials [29], sensors [30], chemical screening	
	Reproduced with permission from [21]	105
Fig. 3.6	Process flow diagram (a) and Schematic representation (b) of the melt intercalation method. Reproduced with	107
Fig. 3.7	FESEM images of a the fractured surface of the SEBS/xGnPs nanocomposites containing five wt% xGnPs, b the same image at higher magnification. Reproduced with permission from [47]	107
Fig. 3.8	SEM micrographs of the fractured surface of the TPE/GNP nanocomposites containing: a 5 wt% GNP, b 7 wt% GNP. Reproduced with permission from [49]	100
Fig. 3.9	Process flow diagram (a) and Schematic representation (b) of the solution intercalation method. Reproduced with permission from [51]	110
Fig. 3.10	Schematic representation of the preparation of functionalized graphene and it's composite with ethylene-vinyl acetate copolymer. Reproduced with permission from [53]	111
Fig. 3.11	Schematic representation of the fabrication of graphene/TPU nanocomposite by co-coagulation plus compression molding	112
Fig. 3.12	Process flow diagram (a) and Schematic representation (b) of the in-situ polymerization process. Reproduced with permission from [60]	112
Fig. 3.13	Schematic representation explaining the synergetic effect of SWCNT and GNP in PTT-PTMO based nanocomposites.	113
Fig. 3.14	Synthetic route of PU-GNS nanocomposite. Reproduced with permission from [62]	114
Fig. 3.15	Representation of i XRD patterns of GO, Gr, AlOOH, and AlOOH–Gr. ii TGA curves of EVA and its composites in air atmospheres. iii TEM images of a GO, b Gr, c AlOOH, and d AlOOH–Gr, e SEM image of AlOOH–Gr. iv TEM micrographs of EVA composites: a 2.0 Gr/EVA, b 2.0 AlOOH/EVA, and c 2.0 AlOOH–Gr/EVA. Reproduced with permission from [66]	115
Fig. 3.16	Illustration of a X-ray diffraction patterns of synthesized materials, b Fourier transform infrared spectroscopy spectra of graphene oxide (GO) and reduced graphene oxide (RGO), c attenuated total reflection Fourier transform infrared	110

	spectroscopy spectra of low-density polyethylene (LDPE)/	
	ethylene vinyl acetate (EVA) and LDPE/EVA/GO 5 wt%, d C	
	1 s spectra of GO and RGO, e Raman spectra of as-prepared	
	materials, and f X-ray diffraction pattern of LDPE/EVA blend	
	and its nanocomposites with 1, 3, 5, and 7-wt% RGO.	
	Reproduced with permission from [67]	118
Fig. 3.17	Representation of i WAXD patterns of pure xGnPs and	
	SEBS/xGnPs nanocomposites. ii Raman spectra of the pristine	
	xGnPs and xGnPs/SEBS nanocomposites, iii FESEM images	
	of fractured surface of the SEBS/xGnPs nanocomposites	
	containing: a 1 wt% xGnPs, b 3 wt% xGnPs, c 5 wt% xGnPs.	
	d 10 wt% xGnPs e 20 wt% xGnPs and f 40 wt% xGnPs	
	iv SAXS profiles for: a neat SEBS b SEBS with 3 wt%	
	xGnPs c SERS with 5 wt% xGnPs d SERS with 10 wt%	
	xGnPs and e SERS with 20 wt% xGnPs Reproduced	
	with permission from [47]	110
Fig. 3.18	Depiction of i combined small- and wide-angle X-ray	11)
1 lg. 5.10	diffractograms of graphite, GO Ph iGO and TRG. Profiles	
	ware vertically shifted for clarity. Scattering reflections from	
	the layered spacing of graphitic carbons are marked by arrows	
	ii Contact mode AFM scens of CO and TPC on mice	
	substrates, and their height profiles (insets) along the straight	
	white lines iii WAXD profiles of TBU composites. The inserts	
	while lines. If wAAD profiles of 1FU composites. The line is $20 = 2.5$, 12° for mult blanded TPC	
	are wAAD patterns in $2\theta = 3.5 - 13^{\circ}$ for melt-blended TRG,	
	solvent-blended PhiGO, ACPh-IGO, and in slitt polymenzed	
	GO composites. IV TEM micrographs of TPU with a 5 wt %	
	(2.7 vol %) graphite, b , c melt-blended, d solvent-mixed,	
	e, f in situ polymerized ~ 3 wt % (1.6 vol %) TRG, g solvent-	
	mixed 3 wt% (1.6 vol%) Ph-iGO, \mathbf{h} AcPh-iGO, and \mathbf{i} in situ	
	polymerized 2.8 wt% (1.5 vol %) GO. Reproduced with	
	permission from [68]	120
Fig. 3.19	SEM images of graphene reinforced thermoplastic elastomer	
	poly (ethylene- <i>ter</i> -1-hexene- <i>ter</i> -divinylbenzene) a pristine	
	thermoplastic elastomer poly (ethylene-ter-1-hexene-ter-	
	divinylbenzene), b thermoplastic elastomer poly	
	(ethylene-ter-1-hexene-ter-divinylbenzene) with 1% graphene,	
	c thermoplastic elastomer poly (ethylene- <i>ter</i> -1-hexene- <i>ter</i> -	
	divinylbenzene) with 3% graphene and d thermoplastic	
	elastomer poly (ethylene-ter-1-hexene-ter-divinylbenzene)	
	with 5% graphene. Reproduced with permission from [71]	122
Fig. 4.1	Graphene-the breakthrough material (https://www.autocar.	
	co.uk/car-news/industry/graphene-breakthrough-material-	
	could-transform-cars, accessed on 12/07/2019)	128

Fig. 4.2	Top—trend analysis of Graphene researches. Reproduced with permission from [4] and accessed on 12/07/2019. Bottom—An illustrative pie chart along with a complimentary bar graph to visualize the categories of the manuscript with the index term 'graphene.' (<i>Source</i> Science Direct, Elsevier, with a sample size of 10971, Plotted with the accessed data on	
Fig. 4.3	24/05/2020)	129
	researchers. Reproduced with permission from [4] and accessed on 12/07/2019	130
Fig. 4.4	Comparison analysis of graphene and its derived researches as a function of the countries worldwide. Reproduced with	120
Fig. 4.5	 permission from [7] and accessed on 12/07/2019 Schematic illustration of the main graphene production techniques. a Micromechanical cleavage. b Anodic bonding. c Photoexfoliation. d Liquid phase exfoliation. e Growth on SiC. f Segregation/precipitation from the carbon-containing metal substrate. g Chemical vapor deposition. h Molecular Beam epitaxy. i Chemical synthesis using benzene as a 	130
	building block. Reproduced with permission from [8]	131
Fig. 4.6	SEM image of graphene layers on SiC. Reproduced with	120
Fig. 4.7	Epitaxial growth and functionalization of a graphene monolayer. a Clean Ni surface. b Graphene monolayer was grown by CVD. The unit cell with the nonequivalent A and B atoms is indicated. c Potassium atoms intercalate between the Ni and the graphene. The corresponding XPS spectra for d a clean Ni surface, e an epitaxially grown graphene monolayer on Ni, and f a potassium intercalated graphene monolayer with K/C = 0.69. Reproduced with permission from	152
Fig. 4.8	[15] Three different stackings for trilayer graphene (Simple hexagonal, Bernal, and Rhombohedral) and the corresponding calculated electronic structures. Reproduced with permissions	133
Fig. 4.9	from [20] Quasi-particle System. a Charge carriers in condensed matter physics are normally described by the Schrödinger equation with an effective mass m* different from the free electron mass (p is the momentum operator). b Relativistic particles in the limit of zero rest mass follow the Dirac equation, where c is the speed of light, and \rightarrow s is the Pauli matrix. c Charge carriers in graphene are called massless Dirac fermions and are described by a 2D analog of the Dirac equation, with the fermi velocity vF $\approx 1 \times 10^6$ m/s playing the role of the speed of light and a	135

	2D pseudospin matrix \rightarrow s describing two sublattices of the honeycomb lattice (3). Similar to the real spin that can change its direction between, say, left, and right, the pseudospin is an index that indicates which of the two sublattices a quasi- particle is located. The pseudospin can be indicated by color (e.g., red and green). d Bilayer graphene provides us with yet another type of quasi-particles that have no analogies. They are massive Dirac fermions described by a rather bizarre	
	Hamiltonian that combines features of both Dirac and Schrödinger equations. The pseudospin changes its color index four times as it moves among four carbon sublattices.	
Fig. 4.10	Reproduced with permission from [1]	136
Fig. 4.11	milligrams per cubic centimeter—is placed on a flower. Reproduced with permission from [42]	138
н <u>е</u> , т .н	graphene with two carbon atoms (A and B) per unit cell. b Energy momentum dispersion in graphene. c Schematic illustration of the covalent chemistry of graphene. d Band structure change of single-layer graphene near the K point of the Brillouin zone before (left) and after (right) chemical modification. (a) and (b) Reproduced with permission from	
Fig. 4.12	[46] Prospects of Graphene paper. Reproduced with permission	139
Fig. 4.13	from [49] A visualization of the thermal properties of graphene and nanostructured carbon materials. Reproduced with permission	140
Fig. 4.14	Trom [53] Micrographs of a Graphene nanoribbons of sub-10-nm scale exhibit the transistor action with large on-off ratios b All the fundamentals are in place to make graphene-based HEMTs. This false-color micrograph shows the source and drains contacts in yellow, two top gates in light gray, and graphene underneath in green c Graphene-based NEMS. Shown is a drum resonator made from a 10-nm-thick film of reduced graphene oxide, which covers a recess in a Si wafer d Ready to use: Graphene membranes provide ideal support for TEM. Reproduced with permission from [1].	142
Fig. 4.15	Pictorial representation of the atomic structure of a carbon atom along with the Energy levels (a and b) of outer electrons in carbon atoms. c The formation of sp^2 hybrids. d The crystal lattice of graphene, where A and B are carbon atoms belonging to different sub-lattices, a_1 and a_2 are unit-cell vectors. e Sigma	

	bond and pi bond formed by sp ² hybridization. Reproduced with permission from [66]	147
Fig. 4.16	Survey of research publications on CNTs-/GSDs reinforced elastomeric matrices and their hybrid nanocomposites during	
Fig. 4.17	the last ten years. Reproduced with permission from [78] To visualize the versatility of graphene based thermoplastic elastomers—I (Subject Category-Technology). <i>Source</i>	149
	SciFinder, Chemical Abstracts Service, Plotted with the accessed data on 24/05/2020.	149
Fig. 4.18	To visualize the versatility of graphene based thermoplastic elastomers—II (Subject Category-Polymer Chemistry). <i>Source</i> SciFinder, Chemical Abstracts Service, Plotted with the	
Fig. 4.19	accessed data on 24/05/2020. To visualize the versatility of graphene based thermoplastic electomers (Subject Category Physical chemistry)	150
	Source SciFinder, Chemical Abstracts Service, Plotted with the accessed data on 24/05/2020.	150
Fig. 4.20	To visualize the versatility of graphene based thermoplastic elastomers—IV (Subject Category-Synthetic chemistry). <i>Source</i> SciFinder, Chemical Abstracts Service, Plotted with the	
Fig. 4.21	accessed data on 24/05/2020 To visualize the versatility of graphene based thermoplastic elastomers—V (Subject Category-Biotechnology). <i>Source</i>	151
	SciFinder, Chemical Abstracts Service, Plotted with the accessed data on 24/05/2020.	151
Fig. 4.22	To visualize the versatility of graphene based thermoplastic elastomers—VI (Subject Category-Environmental Chemistry). <i>Source</i> SciFinder, Chemical Abstracts Service, Plotted with the accessed data on 24/05/2020	152
Fig. 4.23	To visualize the versatility of graphene based thermoplastic elastomers—VII (Subject Category-Biology). <i>Source</i> SciFinder, Chemical Abstracts Service, Plotted with the	152
Fig. 4.24	accessed data on 24/05/2020 Illustration of the chemical modification of graphene to reduced graphene oxide a Graphene, b Oxidized graphite c Separation of oxidized graphite to graphene oxide sheets on sonication, d Hydrazine reduction of graphene oxide and	152
Fig. 4.25	permission from [78] The most prevalent nanofiller mixing methods used in the	153
0	fabrication of Graphene and its derived-elastomeric nanocomposites. Reproduced with permission from [78]	155
Fig. 4.26	SEM micrographs of CNTs: a purified CNTs; b ball-milled CNTs. Reproduced with permission from [103]	157

Fig. 4.27	TEM micrographs of Thermoplastic Polyurethane with a 5 wt% (2.7 vol %) graphite b c melt-blended d solvent-	
	mixed e f in situ polymerized with 3 wt% (1.6 vol %)	
	Thermally Reduced Graphene σ solvent-mixed 3 wt%	
	(1.6 vol %) Ph-iGO h AcPh-iGO and i in situ polymerized	
	2.8 wt% (1.5 vol %) Graphene Oxide Reproduced with	
	permission from [106]	158
Fig. 4.28	Rheological curves showing time dependant torque for NBR and its Nanocomposites at 160 °C. Reproduced with	150
	permission from [114]	159
Fig 1 20	Rheographic profile of a NBR-OM15 at four different	157
11g. 4.29	temperatures h cure conversion versus time of NBR-OM15	
	at four different temperatures. Reproduced with permission	
	from [114]	161
Eig 4 20	SEM images of a SBP b SBP/CO $PT(1)\%$	101
11g. 4.50	$c SBR/GO_RT(2)\% d SBR/GO_RT(3)\% e SBR/GO_RT(4)\%$	
	f SBR/GO(4) control Reproduced with permission	
	from [110]	162
\mathbf{Eig} 4.21	The reported data of the modification of the dynamic mechanic	102
11g. 4.51	properties with the ovidative thermal aging Reproduced with	
	properties with the oxidative thermal aging. Reproduced with	164
Fig 1 32	The reported TEM images illustrating the wrinkling	104
rig. 4.52	nbenomenon of the graphene derivates when incorporated into	
	an elastometric matrix. Reproduced with permission	
	from [78]	167
Eig 122	Graphical representation of a Tensile and tear strength of SBR/	107
115. 4.55	CNTs and SBR/rGO_CNTs composites as a function of CNTs	
	content h Typical stress-strain curves of blank SBR and SBR	
	composites with different filler systems c Typical stress-strain	
	curves of rGO_CNTs hybrid filled SBR composites with an	
	rGO/CNTs ratio of 2:1 d Relative Young's modulus of SBR	
	composites as a function of the filler volume fraction. The solid	
	lines are fitted by Guth-Gold-Smallwood equation	
	Reproduced with permission from [138]	170
Fig. 4.34 Fig. 5.1	Graphical representation of a Storage modulus (E'). b loss	170
	modulus (E''), and c loss tangent (tan (δ)) versus frequency for	
	the TPU-based nanocomposites. Reproduced with permission	
	from [145]	172
	Graphical representation of i Resistance-strain behavior of	
	composites with different graphene content, up to 5% strain at	
	the strain rate of 0.1 min ^{-1} during a cyclic loading and	
	b Resistance-strain behavior of TPU-0.2G for cycles 81–100	
	ii Resistance-strain behavior of TPU-0.2G. up to different	
	strain amplitude at the strain rate of 0.1 min ^{-1} , during the	

	1st cycle (a) and cyclic loading (cycle 11–20) (b). iii Resistance-strain behavior of TPU-0.2G, up to 30% strain at different strain rates, during the 1st cycle (a) and cyclic loading (cycle 11–20) (b). iv Experimental (dots) and theoretical (solid lines) data of resistance as a function of strain. v Change of a conductive pathways (CP) and b tunneling distance (TD) as a function of strain. Reproduced with permission from [27]	185
Fig. 5.2	Electrical conductivity (σ_c) versus filler volume fraction (φ) for TPU/RGO/PVP nanocomposites. Insert is a log-log plot of the electrical conducting versus $\varphi - \varphi_c$ (φ and φ_c being the filler content and percolation threshold, respectively).	105
Fig. 5.3	Reproduced with permission from [28] Graphical representation of i Piezoresistive behavior of a TPU/ GE D40, b TPU/GE G40, and c TPU/GE S40 under cyclic compression, d Resistance ratio and gauge factor of TPU/GE porous structures at 8% compression strain. ii Variation of gauge factor as a function of compression strain for the TPU/GE porous structures with a Diamond, b Gyroid, and c Schwarz unit cells. iii a Piezoresistive behavior of TPU/GE S40 over 50-cycle compression test, and b resistance values at 8% strain as a function of time for all TPU/GE composite	186
Fig. 5.4	structures. Reproduced with permission from [29] Depiction of i Responsivity of TPU-based CPCs containing 0.4 wt% graphene towards saturated a cyclohexane and CCl4 and b ethylacetate and acetone as a function of time; c the maximum responsivity in saturated organic vapors and the residual responsivity in the air in a single IDR at 30 °C. ii Responsivity of TPU-based CPCs containing 0.4 wt% graphene towards saturated a cyclohexane & CCl4 and b ethylacetate and acetone vapors in five IDRs at 30 °C. iii Responsivity of TPU-based CPCs containing 0.4 wt% graphene towards saturated a cyclohexane, b CCl4, c ethyl acetate and d acetone vapors in a single IDR at different	187
Fig. 5.5	temperatures. Reproduced with permission from [30] I-V curves of SEBS and rGO/SEBS composites up to 6 wt% (a) and electrical conductivity of SEBS and GO, rGO and G-NPL composites with filler content up to 6 wt% (b), Gauge factor determination for samples up to 1, 5 to 10% of strain (c), Piezoresistive measurements for 1000 cycles at 5% strain and 5 mm/min for GO/SEBS composite (d) and Gauge Factor of GO/SEBS and rGO/SEBS composites with 4 wt%	188

	filler content for 1, 5 and 10% of maximum strain at 1 and 5 mm/min deformation speed (e). Reproduced with permission from [31]	190
Fig. 5.6	Graphical representation of i Histogram of conductivity of CNT, CNT/graphene and CNT/graphene/fullerene-based	109
	corresponding to sensors of different sensitive unit materials.	
	bending, and \mathbf{c} finger bending. Reproduced with permission from [32]	100
Fig. 5.7	Representation of i IR absorption property of the three graphene materials and their nanocomposites. a IR absorption properties of sulfonated-graphene and isocyanate-graphene solutions with a concentration of 0.05 mg/mL. Reduced- graphene being insoluble in DMF, its IR absorption spectrum is not shown here. b The TGA curves with a heating rate of 5 °C/min from room temperature to 400 °C under N ₂ for isocyanate-graphene, sulfonated-graphene, and reduced- graphene. c The normalized IR absorption of the films of pure TPU, isocyanate-graphene/TPU (1 wt %), sulfonated- graphene/TPU (1 wt%), and reduced-graphene/TPU (1 wt%) across a range of wavelength from 500 to 1100 nm. d Summary of the transmittance of IR light for the sample films at 850 nm: pure TPU, isocyanate-graphene/TPU	170
	and reduced-graphene/TPU (1 wt%). Reproduced with permission from [33]	191
Fig. 5.8	Illustration of i Photocurrent switching response at 5 s intervals in a 0.3 V 1 M NaOH aqueous solution under 500 W Xenon lamp illumination. a Photocurrent response of neat SEBS and Zn-PorSEBS elastomer with different porphyrin grafting ratio. b – d Photocurrent response of Zn- PorSEBS elastomer and G/Zn-PorSEBS with different graphene content at the same porphyrin grafting ratio, (e and f) Photographs giving the light on/light off process. ii a UV–vis spectra of Zn-PorSEBS matrix and G/Zn-PorSEBS composite. b Molecular orbital energy diagram of photo-induced electron transfor from northwrin to graphene. Banraduced with	
Fig. 5.9	permission from [37] Graphical representation of i PL spectra a and corresponding cycles of heating–cooling at above and below LCST b of ZnS NPs-containing block copolymer-GO nanocomposite. ii PL spectra with concentration increase of TNT	193
	$(1 \times 10^{-7} \text{ mol } \text{L}^{-1})$ in the DMF solution of ZnS	