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

© 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

vi Foreword

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 T_g 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

viii Preface

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	Grow	th and Development of TPE	1
	1.2	Break	through Developments in Commercialization of TPE	2
	1.3	TPE:	A Sustainable Elastomer Composition	2
	1.4		Based on Rubber—Plastic Blends	- 7
	1.5		s/Nanofillers for TPE: Isotropic and Anisotropic Fillers	9
	1.6	Concl	usion	13
	Refe	erences		14
2	Anis	sotropi	c Nanofillers in TPE	1′
	2.1	Introd	luction	1'
	2.2	Nanof	fillers and Its Advantages	1
	2.3	Layer	ed Double Hydroxide (LDH)	2
		2.3.1	Structure of LDH	2
		2.3.2	Organophilisation of LDH	2
		2.3.3	Strategies to Fabricate the Layered Double Hydroxide	2
		2.3.4	Synthesis of Polymer/LDH Nanocomposites	2
		2.3.5	Properties and the Recent Trends in the Areas	
			of Application	3
	2.4	Nano	clay	3
		2.4.1	Structure of Nanoclay	3
		2.4.2	Organomodification of Nanoclay	3
		2.4.3	Factors Affecting the Organoclay Hybrid Formed	3
		2.4.4	Modification of Nanoclay	3
		2.4.5	Properties and Applications	4
	2.5	Carbo	on Nanotube (CNT)	4
		2.5.1	Structure and General Properties of Carbon	
			Nanotubes	4
		2.5.2	Synthesis Routes to Fabricate Carbon Nanotubes	5
		2.5.3	Purification and Dispersion of Carbon Nanotubes	5

x Contents

		2.5.4	Functionalization of Carbon Nanotubes	55
		2.5.5	Applications	61
	2.6	-	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		usion	84
	Refe	erences		84
3	Pre	paratio	n of Graphene Based Nanocomposite Based on TPE	101
	3.1	Introd	uction	101
		3.1.1	Trends in Graphene Research	103
	3.2	Differe	ent Methods of Preparation	106
		3.2.1	Intercalation	106
		3.2.2	In-situ Polymerization	112
		3.2.3	Shear Mixing	115
	3.3	Chara	cterization of Graphene/TPE Nanocomposites	115
	3.4	Applic	cation of Graphene/TPE Nanocomposites	121
	3.5	Concl	usion	123
	Refe	erences		123
4	Stru	cture—	-Property Co-relation of Graphene/Graphene	
			Based TPE	127
	4.1	Introd	uction	127
	4.2		Specialized Properties of Graphene and Its Derivative	
			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 O	verview on the Fabrication of the Graphene Sheet	
		Deriva	ates	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	

Contents xi

		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	Concl	usions	173
				174
5	Doto	ntial A	unlication of Cranhona TDE Nanacampacita	183
3			pplication of Graphene-TPE Nanocomposite	
	5.1	Introd	uction	183
	5.2	Sensin	g and Actuation	184
	5.3	Shape	Memory	199
	5.4	Self-h	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, xiv About the Authors

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.

List of Figures

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. Source: 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	
J	permission from [51]	13

xvi List of Figures

Fig. 2.1	Top: A snapshot of the articles (including patents) published in the respective subject domains till date, Bottom: The number of manuscript share with reference to the TPE based on the nanofillers, Data source- SciFinder, Chemical Abstracts	
	Service (Plotted with the accessed data on 24/05/2020)	18
Fig. 2.2	Illustrative representation of a Layered Double Hydroxide.	
	Reproduced with permission from [59]	21
Fig. 2.3	The Ion exchangeable double layered hydroxide developed by increasing the gallery height. Reproduced with permission	
	from [66]	22
Fig. 2.4	Illustration of the process of anion exchange for the synthesis	
	of double layered hydroxides. Reproduced with permission	
F: 0.5	from [85]	24
Fig. 2.5	SEM images showing the microstructure of the Zn-Al/LDH	
	composite for an excellent photocatalytic activity a Zn–Al-	
	LDH-(3 h of reaction time), b Zn-Al-LDH-(6 h of reaction	
	time), c Zn–Al-LDH-(9 h of reaction time), d Zn–Al-LDH-(12	26
Eig 26	h of reaction time). Reproduced with permission from [101]	20
Fig. 2.6	A comprehensive overview of the fabricating techniques of the double-layered hydroxides. Reproduced with permission	
	from [115]	27
Fig. 2.7	Pathway of nanocomposite preparation by a monomer	21
11g. 2.7	exchange and in situ polymerization, b direct polymer	
	exchange, and c restacking of the exfoliated layers over the	
	polymer. Reproduced with permission from reference [130]	29
Fig. 2.8	The TEM images of thermoplastic polyester elastomer	
118. 2.0	reinforced with zinc hydroxide nitrate and sodium benzoate	
	nanoparticle (a low magnification, b enhanced magnification).	
	Reproduced with permission from [75]	33
Fig. 2.9	Crystal structures of clay minerals: a Type 1:1; b Type 2:1.	
8	Reproduced with permission from [167]	34
Fig. 2.10	Classification of silicates based on their physicochemical	
Ü	nature	35
Fig. 2.11	The layered structure of kaolinite clay. Source http://jan.ucc.	
	nau.edu/doetqp/courses/env440/env440_2/lectures/lec19/Fig.	
	9_3.gif, accessed on 10.05.2020	35
Fig. 2.12	The smectite clay structure. Source http://www.pslc.ws/	
	macrog/mpm/composit/nano/struct3_1.htm, accessed	
	on 11.05.2020	36
Fig. 2.13	TEM images of the polymer/clay nanocomposites using a	
	combination of nitroxide-mediated radical polymerization and	
	solution are blending methods. Reproduced with permission	
	from [202]	40

List of Figures xvii

Fig. 2.14	Visualization of the use of montmorillonite-intercalated metallocene catalyst to reinforce ethylene and 10-undecen-1-ol	42
Fig. 2.15	matrix. Reproduced with permission from [210] Surface modification and the possible mechanism of the exfoliation for the butadiene-based rubbers and the thiological attenuation. Permission	42
	modified attapulgite. Reproduced with permission from [225]	44
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. 2.17	Illustrative representation of the different types of carbon nanotubes, accessed from [236] on 30/01/2020	43 47
Fig. 2.18	Visual representation of the different conformation of carbon nanotubes, accessed from [251] on 30/01/2020	49
Fig. 2.19	The chemical vapor deposition to fabricate carbon nanotubes a tip growth model, b base growth model. Reproduced with	
Fig. 2.20	permission from [173]	51
Fig. 2.21	images. Reproduced with permission from [263] Layout of the second-generation high pressure CO	53
	disproportionation producing the single walled carbon nanotubes. Reproduced with permission from [265]	53
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	
Fig. 2.26	with permission from [288]. The thermoplastic polyurethane matrix reinforced with carbon nanotubes a wound on a reel; b sewn into the fabric; c , d ironed	62
Fig. 2.27	onto the fabric. Reproduced with permission from [292] The microscopic stricture of graphene layers. Reproduced with	65
Fig. 2.28	permission from [304, 305]	68
	30-04-2020	72

xviii List of Figures

Fig. 2.29	The cryogenic-TEM images of graphene flakes dispersed in chlorosulphonic acid. Reproduced with permissions from [327]	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]	75
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 from [347]	83
Fig. 3.1	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 permission from [7]	102
Fig. 3.2	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].	103
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
	· ·	

List of Figures xix

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	
	applications [31], and thermal interface materials [32].	
	Reproduced with permission from [21]	105
Fig. 3.6	Process flow diagram (a) and Schematic representation	
	(b) of the melt intercalation method. Reproduced with	
	permission from [44]	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]	108
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]	109
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	
	technique. Reproduced with permission from [55]	112
Fig. 3.12	Process flow diagram (a) and Schematic representation	
	(b) of the in-situ polymerization process. Reproduced with	
	permission from [60]	113
Fig. 3.13	Schematic representation explaining the synergetic effect of	
	SWCNT and GNP in PTT-PTMO based nanocomposites.	
	Reproduced with permission from [61]	114
Fig. 3.14	Synthetic route of PU-GNS nanocomposite. Reproduced with	
	permission from [62]	115
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]	116
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	

xx List of Figures

	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	110
11g. 3.17	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 SEBS with 5 wt% xGnPs, d SEBS with 10 wt%	
	xGnPs, and e SEBS with 20 wt% xGnPs. Reproduced	110
F: 2.10	with permission from [47]	119
Fig. 3.18	Depiction of i combined small- and wide-angle X-ray	
	diffractograms of graphite, GO Ph-iGO, and TRG. Profiles	
	were vertically shifted for clarity. Scattering reflections from	
	the layered spacing of graphitic carbons are marked by arrows.	
	ii Contact-mode AFM scans of GO and TRG on mica	
	substrates, and their height profiles (insets) along the straight	
	white lines. iii WAXD profiles of TPU composites. The inserts	
	are WAXD patterns in $2\theta = 3.5-13^{\circ}$ for melt-blended TRG,	
	solvent-blended PhiGO, AcPh-iGO, and in situ polymerized	
	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 \sim 3 wt % (1.6 vol %) TRG, g solvent-	
	mixed 3 wt% (1.6 vol%) Ph-iGO, h AcPh-iGO, and 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- <i>ter</i> -1-hexene- <i>ter</i> -	
	divinylbenzene), b thermoplastic elastomer poly	
	(ethylene- <i>ter</i> -1-hexene- <i>ter</i> -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- <i>ter</i> -1-hexene- <i>ter</i> -divinylbenzene)	
	with 5% graphene. Reproduced with permission from [71]	122
Fig. 4.1	Graphene—the breakthrough material (https://www.autocar.	1 44
115. 7.1	co.uk/car-news/industry/graphene-breakthrough-material-	
	could-transform-cars, accessed on 12/07/2019)	128
	COURT-HARSTOFFIT-CAIS, ACCESSED OIL 12/07/20191	-148

List of Figures xxi

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	
	24/05/2020)	129
Fig. 4.3	Comparison of analysis of Graphene and its derived researchers. Reproduced with permission from [4] and	
T. 4.4	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	
E: 4.5	permission from [7] and accessed on 12/07/2019	130
Fig. 4.5	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	
	building block. Reproduced with permission from [8]	131
Fig. 4.6	SEM image of graphene layers on SiC. Reproduced with	
	permission from [14]	132
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	
	[15]	133
Fig. 4.8	Three different stackings for trilayer graphene (Simple	
	hexagonal, Bernal, and Rhombohedral) and the corresponding	
	calculated electronic structures. Reproduced with permissions	
	from [20]	135
Fig. 4.9	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	

xxii List of Figures

	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.	
	Reproduced with permission from [1]	136
Fig. 4.10	A piece of graphene aerogel, which weighs only 0.16	
	milligrams per cubic centimeter—is placed on a flower.	
	Reproduced with permission from [42]	138
Fig. 4.11	Representative images of a Hexagonal honeycomb lattice of	
	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	
T. 440	[46]	139
Fig. 4.12	Prospects of Graphene paper. Reproduced with permission	1.40
E'. 4.12	from [49]	140
Fig. 4.13	A visualization of the thermal properties of graphene and	
	nanostructured carbon materials. Reproduced with permission	142
Fig. 4.14	from [53]	142
Fig. 4.14	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]	144
Fig. 4.15	Pictorial representation of the atomic structure of a carbon	
<i>6</i> , , , , ,	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	

List of Figures xxiii

	bond and pi bond formed by sp ² hybridization. Reproduced	1.47
Dia 4.16	with permission from [66]	147
Fig. 4.16	elastomeric matrices and their hybrid nanocomposites during	
	the last ten years. Reproduced with permission from [78]	149
Dia 4.17	To visualize the versatility of graphene based thermoplastic	149
Fig. 4.17		
	elastomers—I (Subject Category-Technology). Source	
	SciFinder, Chemical Abstracts Service, Plotted with the	1.40
E' 4.10	accessed data on 24/05/2020.	149
Fig. 4.18	To visualize the versatility of graphene based thermoplastic	
	elastomers—II (Subject Category-Polymer Chemistry).	
	Source SciFinder, Chemical Abstracts Service, Plotted with the	
	accessed data on 24/05/2020.	150
Fig. 4.19	To visualize the versatility of graphene based thermoplastic	
	elastomers—III (Subject Category-Physical chemistry).	
	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).	
	Source SciFinder, Chemical Abstracts Service, Plotted with the	
	accessed data on 24/05/2020.	151
Fig. 4.21	To visualize the versatility of graphene based thermoplastic	
	elastomers—V (Subject Category-Biotechnology). Source	
	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).	
	Source 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). Source	
	SciFinder, Chemical Abstracts Service, Plotted with the	
	accessed data on 24/05/2020	152
Fig. 4.24	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	
	formation of reduced graphene oxide. Reproduced with	
	permission from [78]	153
Fig. 4.25	The most prevalent nanofiller mixing methods used in the	
_	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

xxiv List of Figures

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, g 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	1.50
E: 4.20	permission from [106]	158
Fig. 4.28	Rheological curves showing time dependant torque for NBR	
	and its Nanocomposites at 160 °C. Reproduced with	
	permission from [114]	159
Fig. 4.29	Rheographic profile of a NBR-OM15 at four different	
	temperatures, b cure conversion versus time of NBR-OM15	
	at four different temperatures. Reproduced with permission	
	from [114]	161
Fig. 4.30	SEM images of a SBR, b SBR/GO-RT(1)%,	
	c SBR/GO-RT(2)%, d SBR/GO-RT(3)%, e SBR/GO-RT(4)%,	
	f SBR/GO(4) control. Reproduced with permission	
	from [119]	162
Fig. 4.31	The reported data of the modification of the dynamic mechanic	
	properties with the oxidative thermal aging. Reproduced with	
	permission from [120]	164
Fig. 4.32	The reported TEM images illustrating the wrinkling	
	phenomenon of the graphene derivates when incorporated into	
	an elastomeric matrix. Reproduced with permission	
	from [78]	167
Fig. 4.33	Graphical representation of a Tensile and tear strength of SBR/	
	CNTs and SBR/rGO-CNTs composites as a function of CNTs	
	content. b 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	Graphical representation of a Storage modulus (E'), b loss	
U	modulus (E"), and \mathbf{c} loss tangent (tan (δ)) versus frequency for	
	the TPU-based nanocomposites. Reproduced with permission	
	from [145]	172
Fig. 5.1	Graphical representation of i Resistance-strain behavior of	
8	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	
	the stand are stand face of our mine, during the	

List of Figures xxv

	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 φ - φ _c (φ and φ _c being the	
	filler content and percolation threshold, respectively).	
	Reproduced with permission from [28]	186
Fig. 5.3	Graphical representation of i Piezoresistive behavior of a TPU/	
U	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	
	structures. Reproduced with permission from [29]	187
Fig. 5.4	Depiction of i Responsivity of TPU-based CPCs containing	
6 , 5,	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	
	temperatures. Reproduced with permission from [30]	188
Fig. 5.5	I-V curves of SEBS and rGO/SEBS composites up to 6 wt%	100
116. 5.5	(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%	
	ractor of GO/SEDS and IGO/SEDS composites with 4 wt%	

xxvi List of Figures

	mm/min deformation speed (e). Reproduced with permission from [31]	189
Fig. 5.6	Graphical representation of i Histogram of conductivity of CNT, CNT/graphene and CNT/graphene/fullerene-based	10)
	sensor. ii GF and maximum strain range histogram	
	corresponding to sensors of different sensitive unit materials.	
	iii Human monitoring applications: a blowing air, b wrist	
	bending, and c finger bending. Reproduced with permission from [32]	190
Fig. 5.7	Representation of i IR absorption property of the three	
O	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	
	(1 wt%), sulfonated-graphene/TPU (0.1, 0.5, and 1 wt%),	
	and reduced-graphene/TPU (1 wt%). Reproduced with	
	permission from [33]	191
Fig. 5.8	Illustration of i Photocurrent switching response at 5 s	171
118. 5.0	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	
	transfer from porphyrin to graphene. Reproduced with	
	permission from [37]	193
Fig. 5.9	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 $(1 \times 10^{-7} \text{ mol L}^{-1})$ in the DMF solution of ZnS	
	$(1 \times 10^{\circ})$ mol L) in the DMF solution of ZnS	

List of Figures xxvii

	NPs-containing block copolymer-GO (a) and Stern–Volmer plots corresponding to the above graphs (b), Fluorescence quenching efficiency obtained for ZnS NPs-containing block copolymer-GO upon addition of 10 mM of different nitro	
	compounds $(1 \times 10^{-2} \text{mol L}^{-1})$ (c) and metal ions $(1 \times 10^{-2} \text{ mol L}^{-1})$ (d). iii Uv-vis absorption spectrum of MEA-TNT (blue) and PL emission spectrum of ZnS NPs-containing block copolymer-GO in DMF (red).	
Fig. 5.10	Reproduced with permission from [41]	194
	behavior of FGO2 in terms of PL quenching. Reproduced with permission from [42]	196
Fig. 5.11	Actuation performance: displacements at 0.5 V and 0.1 Hz under a square and b sine voltages; c displacements according to DC voltages; displacements according to d voltages and e frequencies, and f durability. (The free length of the actuator was 20 mm). Reproduced with permission from [43]	197
Fig. 5.12	Representation of a Maximum tip displacement of IPMCs based on SSPB/sGO/IL, SSPB/GO/IL, and Nafion/GO/IL with a series of filler content. b Bending deformation of an SSPB/sGO (0.5 wt%)/IL IPMC equilibrated under an applied potential of 2 V dc. c Comparison of bending strains of SSPB/sGO (0.5 wt%)/IL with those of top-ranked bending-type polymer actuators impregnated with ILs reported in the	
Fig. 5.13	literature. d Charge-specific displacement of SSPB-based membranes IPMCs. Reproduced with permission from [44] Pictorial representation of i NIR-triggered shape memory process for the ATA-POE/ODA-GO nanocomposites with a different weight content of ODA-GO loadings (i). ii NIR-controlled shape recovery of the APG-0.50 nanocomposite a original shape, b 100% elongated shape and gradually three-step recovered shapes: c left segment, d middle segment, and	198
Fig. 5.14	(e) right segment. iii Stress-strain curves of the APG-0.50 scratched samples a healed for various times under NIR irradiation and b comparison of NIR and thermal healed sample for 60 min. Reproduced with permission from [46] MW-induced shape recovery test of SMP/GNPs (2 GPU at 2.45 GHz) (i), Unconstrained MV-induced shape recovery behavior of SMP/GNPs (2 GPUat 2.45 GHz) (ii), Unconstrained MV-induced shape recovery behavior	200
	tested for 60 s (iii) Reproduced with permission from [50]	201

xxviii List of Figures

Fig. 5.15	Recovery photos at different times of LCPU at the first cycle (a), Stress-strain curves of the pristine LCPU, and its	
	composites at room temperature (b). Reproduced with permission from [51]	202
Fig. 5.16	Graphical representation of a Shape fixity and b shape	202
115. 5.10	recovery ratio of PU and its nanocomposites with GO under	
	cyclic loading at different temperatures of 298 K, 323 K and	
	348 K, c Correlation of shape recovery and temperature with	
	the crosslink density (fitted with the Maier and Göritz model)	
	for PU, PG0.5, PG1.5 and PG3 at 298 K, 323 K and 348 K.	
	Reproduced with permission from [45]	204
Fig. 5.17	Shape fixation and recovery of GO/SEBS-2 (a). The dashed	
U	line represents the temporal strain achieved by deformation.	
	Shape recovery of GO/SEBS as a function of time under the IR	
	light (b). L0 is the initial length of the cylindrical sample,	
	and L is the length after shape fixation or shape. Reproduced	
	with permission from [53]	205
Fig. 5.18	Electroactive shape-recovery behavior of graphene-crosslinked	
	PU composites. The samples undergo the transition from the	
	temporary shape (helix, left) to permanent (linear, right) within	
	10 s. Reproduced with permission from [54]	206
Fig. 5.19	The healing performances of the FG-TPU samples with	
	different FG loadings under the three healing processes. a The	
	IR light healing efficiencies of the pure TPU and the FG-TPU	
	samples with different FG loadings at the optimal healing time.	
	b The electrical healing efficiencies of the pure TPU and the	
	FG-TPU samples with different FG loadings at the optimal	
	healing time. c The electromagnetic wave healing efficiencies	
	of the pure TPU and the FG-TPU samples with different FG	
	loadings at the optimal healing time. d The optimal healing	
	time of the FG-TPU samples with different FG loadings. e The	
	relationship between the applied voltage and the healing time	
	for the FG-TPU samples with different FG loadings. f The	
	optimal healing time of the FG-TPU samples with different FG	207
F: 5.20	loadings. Reproduced with permission from [58]	207
Fig. 5.20	An overview of i Recipes for the preparation of the composites	
	with different contents of GO. ii Healing efficiency of PU-DA	
	and iGO-PU-DAs films determined by recovery of breaking	
	stress. iii Stress-strain curves of PU-DA and iGO-PU-DAs films before and after thermal healing: a PU-DA, b iGO-PU-	
	DA-1, c iGO-PUDA-2, and d iGO-PU-DA-3. iv Summary	
	DA^{-1} , C 100- C DA^{-2} , and C 100- C DA^{-3} . If Summary	

List of Figures xxix

	of the mechanical properties of the composite samples after the healing test. The average values were obtained from more than 3 samples. Reproduced with permission from [59]	209
Fig. 5.21	Tensile strength of G-TPU composite films before and after healed by electricity and IR light, respectively (i), SEM images	209
	of scratch samples healed at 130 °C for the different time using	
	electricity (ii), SEM images of scratch samples healed at	
	130 °C for the different time using IR light (iii). Reproduced	
F: 5.00	with permission from [60]	210
Fig. 5.22	Graphical representation of a Healing efficiency of the nanocomposites under sunlight, b repeatable healing efficiency	
	of the nanocomposites, c digital and optical microscopic	
	photographs of cracked and healed nanocomposite films and	
	d representative stress-strain profiles of HPU-T1RGO2, before	
	and after healing with different repeating cycles. Reproduced	211
Fig. 5.23	with permission from [61]	211
11g. 3.23	MW and sunlight (i). Stress-strain profile of HPU/Si-GO0.5	
	before and after healing (ii). Reproduced with permission	
	from [62]	212
Fig. 5.24	Demonstration of i The cellular viability detected by CCK-8	
	assay (OD450) at each set time point. The values are shown as	
	the means $\pm SD$ (n = 3). ii Antibacterial activity of	
	GO/MGO-TPU composite porous membrane with the ratio	
	between GO and MGO. a activation of <i>E. coli</i> ; b activation of	
	S. aureus. iii The long-lasting antibacterial activity of the	
	GO/MGO-TPU composite porous membrane was shaken and washed in PBS buffer for 0, 7, 30 days. a Inactivation of	
	E. coli; (b) Inactivation of S. aureus, iv a Representative	
	macroscopic appearance of the infected wounds, blank	
	(Wound without any treatment), Control (Sterile Vaseline	
	gauze covered wound), PHMG0.5-TPU, GO0.5-TPU, MGO0.	
	5-TPU; b Representative histological image of the length	
	of the newly formed epithelium tongue at day 9 post-surgery in	
	the Blank (Wound without any treatment), Control	
	(Sterile Vaseline gauze covered wound), PHMG0.5-TPU,	
	GO0.5-TPU, MGO0.5-TPU. c Wound healing curves;	
	d Wound closure time. The values are shown as the means	010
Fig. 5.25	±SD (n = 5). Reproduced with permission from [66] 96 h cell culture results of NIH3T3 cells on 3D printed TPU/	213
11g. 3.23	PLA with different GO loadings: a 0 wt % GO, b 0.5 wt %	
	GO, c) 2 wt % GO, d 5 wt % GO. Green color indicates live	
	cells. Reproduced with permission from [71]	215

xxx List of Figures

Fig. 5.26	Images of i Day 3 3T3 fibroblast cell culture results of	
	freeze-dried TPU (a), TPU-GO1% (b), TPU-GO5% (c):	
	TPU-GO10% (d) scaffolds: (a-d) are fluorescence microscope	
	pictures (scale bar 5100 lm) where green indicates living cells.	
	ii Day 10 3T3 fibroblast cell culture results of freeze-dried TPU	
	(a), TPU-GO1% (b), TPU-GO5% (c): TPU-GO10% (d)	
	scaffolds: (a-d) are fluorescence microscope pictures (scale bar	
	5100 lm) where green indicates living cells and red indicates	
	dead cells. Reproduced with permission from [72]	216
Fig. 5.27	Micrographs of i cell morphology after a direct contact test:	
_	a negative control, b positive control and c PCU/GO	
	composite electrospun membrane. ii MTT assay representing	
	the cell viability (%) of the L-929 fibroblast cells on	
	electrospun membranes. iii Graphical representation of the	
	percentage of hemolysis of the PCURF (random fiber),	
	PCUAF, and composite electrospun membranes with	
	1, 1.5 and 3% loadings of GO. Reproduced with permission	
	from [73]	216
Fig. 5.28	Illustration of a Antibacterial activity of the prepared dressing	
	membranes against S. aureus, E. coli, and C. albicans.	
	b Wound healing process for 20 days, treated with gauze	
	(control), XSi-PU and XSi-PU/GO5%. c Representative	
	images of MT and H&E stained histological sections on day 20	
	after initial wounding, arrows indicated the blood vessels.	
	Reproduced with permission from [74]	217

List of Tables

Table 1.1	Breakthrough developments in commercialization of TPE	3
Table 1.2	Advantages of TPE over thermoset rubber processing	5
Table 1.3	A chart work showing subcategories of block copolymers	
	eligible as TPE	6
Table 2.1	General classification of nanoclays based on the charge	
	distribution	34
Table 2.2	A comprehensive overview of the various techniques	
	employed for the purification of carbon nanotubes	56
Table 2.3	The major functionalization strategies of carbon nanotubes	
	using non-covalent interactions [1]	61
Table 2.4	A comparative study to analyze the advantages and the	
	disadvantages of the functionalization methods of carbon	
	nanotubes [248–254, 256–288]	63
Table 2.5	The comprehensive review of the properties of carbon	
	nanotubes, reprinted with permission from [289]	64
Table 2.6	The glimpse of how graphene gradually evolved since its	
	inception in 1947 [298]	66
Table 2.7	A concise overview of the top down techniques [314–318]	76
Table 2.8	A concise overview of the bottom up techniques	81
Table 5.1	Value of shape fixity and shape recovery ratio of LCPU	
	and GO/LCPU nanocomposites [51]	203
Table 5.2	Average value of shape recovery rate of all the	
	samples [51]	-203