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RAPID CURE COMPOSITES MATERIALS, PROCESSING AND MANUFACTURING



Edited by NISHAR HAMEED MAZHAR PEERZADA NISA SALIM JYOTISHKUMAR PARAMESWARANPILLAI

Rapid Cure Composites

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Woodhead Publishing Series in Composites Science and Engineering

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Materials, Processing and Manufacturing

Edited by

Nishar Hameed

Mazhar Peerzada

Nisa Salim

Jyotishkumar Parameswaranpillai

Editor-in-Chief

Constantinos Soutis

Series Editor

Suresh G. Advani

Ing. Habil. Bodo Fiedler





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List of contributors

Sadaf Abbasi Department of Mechanical and Product Design Engineering, Swinburne University of Technology, Hawthorn, VIC, Australia

Lucas Dall Agnol Postgraduate Program in Materials Science and Engineering (PGMAT), University of Caxias do Sul (UCS), Caxias do Sul, Rio Grande do Sul, Brazil

Ahmed Al-Qatatsheh School of Engineering, Swinburne University of Technology, Hawthorn, VIC, Australia

Muhammad Kashif Bangash School of Engineering and Technology, National Textile University, Faisalabad, Pakistan

Sanjay R. Dhakate Advanced Carbon Products Section, Advanced Materials and Devices Division, CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi, India

Hema Garg School of Interdisciplinary Research, Indian Institute of Technology Delhi, New Delhi, India

Nishar Hameed School of Engineering, Swinburne University of Technology, Hawthorn, VIC, Australia

Madeha Jabbar School of Engineering and Technology, National Textile University, Faisalabad, Pakistan

Hyun-Joong Kim Lab. of Adhesion & Bio-Composites, Department of Agriculture, Forestry and Bioresources, College of Agriculture and Life Sciences, Seoul National University, Seoul, Republic of Korea

Raghu Raja Pandiyan Kuppusamy Department of Chemical Engineering, National Institute of Technology, Warangal, Telangana, India

Abdul Sattar Larik Department of Electrical Engineering, Mehran University of Engineering & Technology, Jamshoro, Sindh, Pakistan

Thomas D. Lazzara Meissner Filtration Products Inc., Camarillo, CA, United States

Seong-Ju Lee Lab. of Adhesion & Bio-Composites, Department of Agriculture, Forestry and Bioresources, College of Agriculture and Life Sciences, Seoul National University, Seoul, Republic of Korea

Paul Liddel Enhanced Composites and Structures Centre, School of Aerospace, Transport and Manufacturing, Cranfield, United Kingdom

Francisco Maciel Monticeli Department of Materials and Technology, School of Engineering, São Paulo State University (Unesp), Guaratinguetá, São Paulo, Brazil

Yasir Nawab School of Engineering and Technology, National Textile University, Faisalabad, Pakistan

Swati Neogi Department of Chemical Engineering, Indian Institute of Technology, Kharagpur, West Bengal, India

Roberta Motta Neves Postgraduate Program in Mining, Metallurgical and Materials Engineering, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, Rio Grande do Sul, Brazil

Heitor Luiz Ornaghi Jr Mantova Indústria de Tubos Plásticos Ltda., Caxias do Sul, Rio Grande do Sul, Brazil

Yashwanth Padarthi Department of Chemical Engineering, Indian Institute of Technology, Kharagpur, West Bengal, India

Jyotishkumar Parameswaranpillai Department of Science, Faculty of Science & Technology, Alliance University, Bengaluru, Karnataka, India

Abhishek K. Pathak Department of Aeronautics and Astronautics, The University of Tokyo, Bunkyo city, Japan

Mazhar Peerzada Centre for Future Materials, Institute of Advanced Engineering and Space Sciences, University of Southern Queensland, Toowoomba, QLD, Australia

Sukanya Pradhan SARP-LARPM, Central Institute of Petrochemicals Engineering and Technology, Bhubaneswar, Odisha, India

Iftikhar Ali Sahito Department of Textile Engineering, Mehran University of Engineering & Technology, Jamshoro, Sindh, Pakistan

Nisa Salim School of Engineering, Swinburne University of Technology, Hawthorn, VIC, Australia

Noor Ahmed Sanbhal Department of Textile Engineering, Mehran University of Engineering & Technology, Jamshoro, Sindh, Pakistan

Khubab Shaker School of Engineering and Technology, National Textile University, Faisalabad, Pakistan

Jae-Ho Shin Lab. of Adhesion & Bio-Composites, Department of Agriculture, Forestry and Bioresources, College of Agriculture and Life Sciences, Seoul National University, Seoul, Republic of Korea

Kiersten M. Smith Meissner Filtration Products Inc., Camarillo, CA, United States

Zheming Tong Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College of Chemical and Biological Engineering, Zhejiang University, Zhejiang, Hangzhou, P.R. China

Hamed Yazdani Nezhad Advanced Composites Research Focused Group, School of Science and Technology, University of London, London, United Kingdom; Enhanced Composites and Structures Centre, School of Aerospace, Transport and Manufacturing, Cranfield, United Kingdom

Mo-Beom Yi Lab. of Adhesion & Bio-Composites, Department of Agriculture, Forestry and Bioresources, College of Agriculture and Life Sciences, Seoul National University, Seoul, Republic of Korea

Tomohiro Yokozeki Department of Aeronautics and Astronautics, The University of Tokyo, Bunkyo city, Japan

Xiaoli Zhan Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College of Chemical and Biological Engineering, Zhejiang University, Zhejiang, Hangzhou, P.R. China; Quzhou Research Institute, Zhejiang University, Zhejiang, Quzhou, P.R. China

Qinghua Zhang Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College of Chemical and Biological Engineering, Zhejiang University, Zhejiang, Hangzhou, P.R. China; Quzhou Research Institute, Zhejiang University, Zhejiang, Quzhou, P.R. China

Shen Zhang Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College of Chemical and Biological Engineering, Zhejiang University, Zhejiang, Hangzhou, P.R. China; Quzhou Research Institute, Zhejiang University, Zhejiang, Quzhou, P.R. China This page intentionally left blank

About the editors

Dr. Nishar Hameed is a group leader of Smart Materials Lab and associate professor at the Swinburne University of Technology, Australia. He completed his PhD in 2011 at the Deakin University, Australia followed by Alfred Deakin and Australian Research Council DECRA Fellowships. His research is mainly focused on the novel and faster processing of next-generation "smart" polymers and composite materials.

Dr. Mazhar Peerzada is a senior research technical officer at the Centre for Future Materials, the University of Southern Queensland, Australia. He completed his PhD in polymer composite materials from the University of Manchester, United Kingdom. He has a broad range of teaching experience and research experience. He has published more than 40 research papers, 4 book chapters, and 1 patent application.

Dr. Nisa Salim is a Vice Chancellor's Initiative Senior Research Fellow at the Swinburne University of Technology Australia. She received her PhD from the Deakin University with a highly prestigious Gold Medal for Research Excellence from AINSE. She has published more than 60 high-impact journal papers, 4 edited books, 5 book chapters, and 1 patent application. She won many awards in her research career, including the Smart Geelong Early Researcher award, Victoria Fellowship, Endeavour Fellowship, and many more despite a career break of over 2 years.

Dr. Jyotishkumar Parameswaranpillai is an associate professor at the Alliance University, Bangalore, India. He is a prolific editor and researcher who has published more than 30 edited books, 140 high-quality international research articles, and 65 book chapters. He has received numerous awards and recognitions, including prestigious KMUTNB best researcher award 2019 and INSPIRE Faculty Award 2011.

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Preface

Polymer composites are considered a highly desired material in manufacturing industries due to their lightweight, superior strength, design flexibility, and durability. According to Grand View Research, the global market for composites is expected to grow exponentially to USD 160 billion by 2027. The key challenge for these materials is achieving cost-effective high rates of production (parts per minute) without sacrificing the structural integrity and performance of composites. The current generation of resin matrices for polymer composites such as epoxy resins generally consolidates at a long curing cycle. Hence, the composite part production rate is slow. In the past, different approaches such as multidisciplinary technologies, advancement in resin chemistry, reduced processing routes, and multiingredient curing agents are adopted to improve the production rate. Rapidly processed materials together with automated manufacturing provide state-of-the-art approaches for the production of composites in critical applications. Over the past two decades, the composite manufacturing sector has transformed into widely employed automated tape laying and automated fiber placement processes.

The purpose of this book is to provide up-to-date information on materials, processing, and manufacturing of rapid cure composites. This book focuses on choosing the right methodology for synthesizing rapid curing matrices, choosing the correct resin for different applications, and enhancing the functional properties without compromising the efficiency of production and challenges of existing technology and future trends. This book is intended for engineers from industries, scientists from R&D centers, research scholars, and undergraduate and postgraduate students who are studying composite materials.

Chapter 1 begins with the introduction of thermoset and thermoplastic and the synthesis of epoxy resins. It further discusses the rapidly cured epoxy resin composites, their characterization, modeling, application, and current challenges.

Chapter 2 focuses on the advancement in curing processes such as microwave curing, UV curing, latent heat curing, photo/gamma rays curing, and electron beam curing. It begins with an overview of the synthesis of some novel rapid cure systems. Furthermore, a small portion of this chapter discusses the prospects in the area of rapid curing resin systems.

Chapter 3 is devoted to a systematic review of curing agents applied for the rapid curing of thermosetting polymers, focusing on the main findings in the last 10 years. The search was done based on the PRISMA protocol and elaborated as a systematic review focusing on a predefined primary search, avoiding bias in selecting studies. The primary focus is on the curing agent type, processing, resin, and

characterizations. This chapter provides the readers for an easy identification of the main trends and gaps in the field as well as future perspectives.

Chapter 4 provides great details of rapid cure composite manufacturing techniques including thermal and radiation curing. It further emphasizes the importance of rapid curing, types of thermal and radiation curing techniques, their curing process, and their advantages.

Chapter 5 reviews a range of monitoring techniques to measure the rapid curing of polymer composites, their working principle, advantages, and challenges of the techniques such as differential scanning calorimetry, Fourier-transform infrared spectroscopy spectroscopy, dynamic mechanical, thermal analysis, near-infrared spectroscopy, Raman spectroscopy, ultrasonic dynamic analysis, laser ultrasonic system, sensor-based methods (in situ flexible sensors and optoelectronic sensors), and infrared thermography.

Chapter 6 gives an overview of composite materials' conventional joining techniques and the most common adhesive systems. The major techniques used to join reinforced plastic composite materials to themselves and dissimilar materials using rapid curing resin systems including microwave irradiation, UV, and induction heating are discussed in detail.

Chapter 7 explains the classification of self-healing systems, intrinsic selfhealing, activation, and measurement of the self-healing process. It further discusses in detail the self-healing materials and their advanced applications in polymer composite industries.

Chapter 8 highlights the need for rapid material processing while achieving optimal bonding properties. It further discusses the successful composite preparation; the end user has to evaluate different considerations. The commonly used types of rapid cure adhesives and their benefits as well as limitations are explained in detail.

Chapter 9 provides a comprehensive overview of different characterization techniques for rapid cure resin systems and their composites. The review includes the characterization of the curing mechanism and the current application status of various curing processes for the fabrication of advanced polymer composites. Furthermore, the properties of rapid cure composites produced by each technique, composite production faults, and technological and material inadequacies are also reviewed.

Chapter 10 provides basic cure systems frequently used in the chip packaging process and assembly components that need a fast cure profile during manufacturing. The basic concept, processing condition, composition, and required properties of surface mount adhesive, dicing die attach film, underfill, electrically conductive adhesive, and glob-top encapsulants are addressed. Finally, the prioritized properties to which the rapid cure composites are obliged, in accordance with the RoHS green initiatives and the state-of-the-art technologies in chip packaging, such as system-on-integrated-chips, system-in-package, and heterogeneous packaging, are stated at the end of the chapter.

Chapter 11 discusses the technologies used to manufacture aerospace structures including heated tools and Quickstep. This chapter further provides information about the process evaluation including the challenges faced by the aerospace industry. Finally, the expectation of the aerospace industry in view of future trends is discussed.

Chapter 12 discusses the paint composition, preparation, and spraying processes in detail. It further focuses on the use of rapid cure resins and composites in the spray and paint industry.

Chapter 13 briefly identifies the ongoing challenges with the exploitation of rapid composite microwave cure and gathers information from state-of-the-art research across the globe for tackling such challenges.

Nishar Hameed Mazhar Peerzada Nisa Salim Jyotishkumar Parameswaranpillai This page intentionally left blank

Rapid cure composites in electronics industry



Jae-Ho Shin, Mo-Beom Yi, Seong-Ju Lee and Hyun-Joong Kim Lab. of Adhesion & Bio-Composites, Department of Agriculture, Forestry and Bioresources, College of Agriculture and Life Sciences, Seoul National University, Seoul, Republic of Korea

10.1 Introduction

10.1.1 Why the rapid cure matters in electrics industry

Among the so-called eight core processes in semiconductor manufacturing, the packaging is the final process for interconnecting the chip to internal components and protecting the chip from the external environment. Typically, the packaging process consists of five major steps; wafer dicing, die attaching, electrical interconnection, molding, and final package inspection. Through the die attaching to the molding process, each component mounted or applied inside the package, usually composed of polymeric materials, is to be cured by either heat or ultraviolet (UV). The cure process turns flowable adhesives and films into a firm composite (chipfilm-substrate) and provides the "green" strength to withstand shock and vibrations during the remaining processes and eventually the adhesion or cohesion strength to the system. The throughput of the packaging process is governed by the time required to cure adhesives, encapsulants, and molding compounds and any loading and unloading time according to the optimized cure schedule. Therefore, the cure procedure is the most decisive step that controls manufacturability (throughput and capacity) and achieves the final product's performance and reliability. Conventionally the packaging process used the large benchtop, and convection oven as an electric fan to distribute heat within the chamber, queuing downstream according to the programmed cure profile. Nowadays, the factory is equipped with an automated inline cure system, integrating the cure and dispensing process together and minimizing the queue time. Still, the cure process inevitably takes a large amount of time and energy and seizes the manufacturing's ankle, dragging down the overall productivity. That is why rapid cure strategies are desired from the beginning step of the packaging process and should be concerned and optimized in multiple aspects, including material selection, product recipe, cure equipment, and assembly flow.

The cure schedule of the semiconductor package is a sum of the required cure time/temperature for all the components included in the assembly. A separate vendor used to provide the postcured subpackaging products before, however, the chip

makers have become endured a total package solution on account of the expanded usage of ASIC and the provider-dependent design/architecture of equipment, interposer, and substrates. Followed lists are the typical heating steps performed in the chip packaging. Generally, the cure processes are performed by hot-air convection or heating plate conduction at varying temperature ranges, from 100°C to 180°C for periods ranging from 1 to 6 hours [1]. For sensitive components, a two-step cure profile is favored.

- **1.** *Substrate Bake-Out*: The prior stage of semiconductor packaging to bake-out residual moisture in the organic substrates for pin grid array, ball grid array (BGA), and chip scale packages (CSPs).
- 2. Adhesive/Encapsulant/Potting/Seal Material Cure: The essential accessories that integrate, hold and wrap the chip and substrate into a single package are mainly made of polymeric materials and supplied in an individual product. The detailed cure schedules for the product are described in Section 14.3.
- **3.** *Heatsink Cure*: The highly thermal conductive adhesives are applied within the interface between the package and heat sink. With higher filler loading, the system provides a uniform heat dissipation across the heterogeneous materials (polymer-metal).
- **4.** *Die Attaching Cure*: For attaching an IC die to either a metal lead frame or laminate substrate, the electrically conductive or insulative adhesive or film is directly dispensed onto the chip. In the case of multichip and stacked-die packaging, the die-attaching and curing operations could be repeated multiple times.
- **5.** *Protective Coating Cure*: For increasing adhesion to epoxy molding compound (EMC) or providing protection to fragile bonding wire, often a thin film of a polymeric material is spin-coated onto the targeted component. The conformal coating is usually UV-cured and postcured by heat for homogeneous film formation.
- **6.** *Postmolding cure:* The pelletized EMC flows into a hot mold die, enclosing the single IC and being cured at above 170°C for a short period of time (1–2 minutes). The prepackage is then ejected from the mold, should be further cured for a prolonged schedule often over 1 or 2 days, which is called postmold cure, to complete the vitrification for the solid package.
- 7. *Marking Cure*: For accurate dicing and chipping of the molded package, there should be a mark somewhere. In flip-chip applications, the coating tapes or marking inks were applied onto the backside of the bare chip and either cured with UV or heat. Once removed from the chip, the mark endows the part identity and trace code to each package, enabling post-saw singulation.
- **8.** *Dry Pack Bake-Out*: After the packaging process, the final products should be prepared for storage and shipping. To rid moisture from the package, one additional bake-out process is required before being sealed in air-tight bags during an operation.

It is not an exaggeration to say that there exist as many cure processes as the number of subpackaging components. Here we focus on the cure process that participates in chip assembly and protection and highly requires time and energy reduction in the act. Packaging manufacturers optimize the cure process to their own processing facilities and control the cure profile of adhesives or encapsulants by mixing many species of raw materials, usually provided by separate vendors.

The global suppliers of semiconductor packaging material are Henkel (Adhesive and Sealant), Showa Denko (Coating, EMC), Sumitomo Chemical (Photoresist), Kyocera (Package), Mitsui Chemical (Polymer and Monomer), Toray Industries (PPS), Evonik (Plastic), LG Chem (Tape and Plastic), Dupont (Adhesive and Resin), BASF SE (Chemical). However, the semiconductor packaging material industry is not solely controlled by the big players, but rather is very finely fragmented by local, and regional vendors. The packaging materials are generally stored at very low temperatures, used in a small quantities at one time, tailored to the packaging facility, and required various processing properties and performance according to the kaleidoscopic needs of the package manufacturer, usually the final vendor. Local suppliers are much better fitted for coping with innovative solutions at reasonable prices than international vendors. Also, the acute international competition in the electronics industry has impacted even the packaging material sector, making the big chip makers reluctant to rely on foreign subcontractors. Currently, the Asia Pacific holds the highest rank in the worldwide semiconductor packaging material market, especially the Japanese suppliers, trading in adhesives, cure agents, photoresists, dielectrics, bonding or insulating films, etc. The market is also expected to have high expansion due to the tremendous need for the IC chip, ignited by Industry 4.0, 5 G, and internet of thing applications. According to the report, the market constantly proliferates at 5% compound annual growth rate (CAGR) between 2020 and 2027 [2]. As an essential component in the packaging process, adhesive resin and cure agents are highly used in the electronics manufacturing industry. Thanks to the properties and process advantages, which suit the picky requirements which are hard to meet on many fronts including versatile applicability to each facility of vendors, design-specification, lost cost, and manufacturing throughput and reliability. Since adhesive and cure agents are the forefront building blocks, the customers depend heavily on few reliable conventional manufacturers and generally refrain from changing the supplier group traded with. The key players in the market are H.B. Fuller (general), Henkel Adhesives (Epoxy), Sika AG (Epoxy), Kukdo (Epoxy), 3 M (Acrylate), Dymax (Acrylate), Permabond (Cyanoacrylate), Bostik (Urethane), DELO (Urethane), Wacker AG (Thermoplastic), Dow (Silicone), and Shinetsu (Silicone), etc. Along with the resin production, the manufacturer provides a cure agent or hardener as if it's a tagalong, with recommended mix ratio. In contrast to the case of resin, there are some needs for a special type of cure agents such as rapid cure, latent cure, UV or LED cure, and dark or humid cure, which can be the subject of regional suppliers. Vendors must offer cost-effective, environment-friendly, and high-quality products that adhere to the international quality standards of the industry as well as meet the environmental norms to compete in the market. Market Research Future reported forecasts for the market's expansion with 7.76% of CAGR from 2021 to 2028 and 10,800 million of the market size in 2028 [3].

10.1.2 Cautions and technical challenges in designing cure strategies

In a typical chip assembly and packaging procedure, both sides of the adherend are heterogeneous materials, silicon chip and organic substrates (polyimide or cured

epoxy-based composite, FR4), with different properties of coefficient of thermal expansion (CTE), modulus, and glass transition temperatures. As a third component, when the adhesive is included in the system, a high degree of stress gradient results, which later can cause interfacial delamination and damage to sensitive IC chip. The main cause of residual stress is the CTE mismatch between the adjoint materials, experiencing recurrent local interfacial failure, and eventually crack propagation. The abovementioned packaging downstream with successive heating and cooling loads often exerts excessive force, especially on polymeric components, leading to misalignment of the cured adhesive or even vast dimensional deformation, called warpage. Warpage is the out-of-plane bending deformation, persistently encountered in many packaging approaches, such as fine-pitch BGA, flip-chip BGA, package-on-package memory, and system-in-package. Warpage modes can be concave, convex, and mixed, threatening the coplanarity within the package and frustrating the subsequent assembly/packaging processes. The stress level is proportional to the dimension of chip size and becomes a critical issue with the trends of thinner and larger wafers in wafer-level packaging [4]. The encapsulant materials, including EMCs, the primary packaging material, are usually applied onto only the top front, which unbalances the stress dissipation within the system during molding and postmold curing. During cure, the viscous resin is deprived of its free volume because of crosslinking, and hence volumetric retraction occurs, which is called chemical shrinkage. Once the material is fully cured after postmold curing, it shows a lower CTE value than one of the resins, resulting in a smaller dimensional change during cooling, which leads to cold shrinkage and an irreversible deformation in size during the curing process (Fig. 10.1).



Figure 10.1 Cure-driven shrinkages during heating and cooling process.

Warpage control should be approached on many fronts, including the resin backbone, curing agent selection, the heating equipment and its way of conduction, filler loading, and changing the cure profile for the encapsulant or adhesive material. The easiest way to effectively reduce warpage is to use a two-step cure profile with very thorough heating and cooling rate control according to the premeasured gelpoint temperature and CTE values of the material. The cure-induced stress and CTE values can be lowered by pregelation at a temperature far below the maximum cure temperature. The pregelation step provides the polymer chains with enough time to anneal [1]. Therefore, the step cure tactics are often adopted for flip-chip underfill where the solder ball interconnection cannot endure stress propagation across the solder joint with pads or bumps. In the light of productivity, however, the step cure adds queueing time and space and hence is meant to circumvent remedy at best. The already-used adhesive or encapsulant products are a composite whose components play each part to satisfy the grand purpose. The approaches to change their cure and thermomechanical properties should address the trade-off parameters; otherwise, the nearsighted solution can be faced with unexpected failures during the long journey of packaging. The viscosity, flow property, gel time, and glass transition temperature are the essential processing parameters for resins, which control the processability and throughput of the packaging process. Filler settling and resin bleed may occur if the gelation starts too early or too late. The hot-hardness, a minimum stiffness for handling cured material, is also an important factor in the determination of curing and postcuring time and temperature required. Justly, it's no use when the configuration changes compromise the final product's performance. Any rapid cure strategy is viable only after the cured composite satisfies the features required for packaging material, covering all aspects of mechanical properties (flexural modulus and strength), electrical properties (dielectric constant and dissipation factor), and hygroscopic properties (ion concentration, moisture absorption, and diffusion coefficient) [5]. A deviser of a rapid cure strategy, whether they belong to resin vendor or heating equipment vendor, or packaging management, should seriously take into account the respective possibility of improper or incomplete cure in each manufacturing step involved. Only then, the total solution with detailed individual efforts from each supplier for rapid cure makes an actual contribution to the chip package industry.

10.2 The resins used in rapid cure packaging materials and their curing mechanisms

10.2.1 Ероху

Epoxy is the most widely used resin in electronics and semiconductor packaging. There are three types of widely used epoxy resins: diglycidyl ethers (bisphenol A and F), phenolic and cresol novolacs, and cycloaliphatic epoxides. The diglycidyl ethers of bisphenol A (DGEBA) are obtained from petrochemical derivatives and have low viscosity and good adhesion performance. The phenolic and novolacs exhibit superior thermal resistance and are used for molding compounds. The cycloaliphatic epoxides provide outstanding electrical properties. In addition, multifunctional and biphenyl resins are used for their high glass-transition temperature, low stress, and low shrinkage. The polymerization of epoxy resin is obtained by the reaction of the glycidyl ether (epoxy) group with a curing agent (hardener). Epoxy resins are cured by curing agents with labile hydrogen atoms such as amine and acid anhydride molecules. The labile hydrogen attacks the oxirane group of epoxy molecules, opening the ring structure to form dangling hydroxyl groups, consecutively reacting with neighbor epoxides until the epoxy resin is fully polymerized (cured or crosslinked).

Amines and acid anhydrides are the most widely used curing agents. Aliphatic amines react fast at a lower temperature, and aromatic amines provide higher chemical and thermal resistance. As the reaction is quantitative, the resins and curing agents should be mixed with an equimolar ratio (one labile hydrogen to one epoxide). Amines may have primary, secondary, or tertiary nitrogen atoms. The primary amine has two hydrogens, which can react with two epoxides. After curing of primary amine, tertiary amine and hydroxyl groups are produced. The hydroxyl group in the epoxy resin can increase adhesion performance and further react with other epoxides. Often, a latent curing agent is required for epoxy film adhesives and B-staged composite. Dicyandiamide (DICY) is one of the most common anionic latent curing agents. DICY does not react with epoxide at low temperatures (under room temperature), but it cures the epoxy resins at 150°C-180°C [6]. With different latency mechanisms from the anionic cure agents, a complex of Lewis acids and bases are also good alternatives with low out-gassing. Boron trifluoride-amine complex, hexafluoroantimonate-imidazole complex, hexafluorophosphate salts, and organic acid hydrazide are excellent examples of cationic cure agents. The latency benefits one-component adhesives with a long pot life under ambient or relatively high storage temperatures ($\sim 4^{\circ}$ C). They are stable before heat is applied. After a heating process, the complex dissociated into the reactive agents, resulting in cured epoxy resins.

In some cases, the appropriate addition of a curing accelerator is required to achieve a faster cure profile. Tertiary amines, phenols, resorcinol, and triphenylphosphine are the representatives. Accelerators pump the curing reaction of epoxy resins by adding hydroxyl groups or additional reactivity to cure agents, resulting in increased heat generation in the system. Plus, the properly chosen accelerators can tune the properties of the cured epoxy resin, such as glass transition temperature (T_g) , elastic modulus, chemical resistance, and so on. Occasionally, inorganic fillers are added to a composite to achieve specific characteristics required for packaging material, such as low CTE, high thermal conductivity, low moisture absorption, etc. Fused silica has a CTE of 0.5 ppm/°C, while a CTE of a typical epoxy resin is about 50–70 ppm/°C. The addition of fused silica fillers can reduce the CTE of composite even below 20 ppm/°C [7]. Thermal conductivity can be improved by adding aluminum nitride (AlN, ~285 W/mK) and silicon carbide (SiC, ~360 W/mK). The thermal conductivity of composites can be more than ten times that of a typical base

epoxy resin (0.2 W/mK) [8]. In the meantime, extra care should be considered in selecting cure agents and additives, which are usually hygroscopic, and hence the dose in the recipe should be limited.

10.2.2 Silicone

Silicone material has multiple silicone-to-oxygen bonds in its backbone structure instead of the carbon-to-carbon structure of other polymers. Silicone has many advantages due to its unique molecular structure. Examples are the thermal stability (up to 300° C), flexibility even at low temperatures (down to -80° C), and outstanding electrical insulation properties. It is cured by condensation or addition polymerization with catalysts. For condensation polymerization, chloro-silanes (mono-, di-, and tri-) are hydrolyzed by water, and then condensation occurs with the elimination of water, producing alkyl polysiloxanes. Addition polymerization occurs by vinyl and another unsaturated group in silicones. The catalyst such as platinum decomposes by heating and produces active species. Then, a rapid polymerization occurs between the vinyl group and silicon atom by exchanging hydrogen atoms [9]. Moisture-curing types are widely used for adhesives in electronics. They are typically cured at room temperature in 30%-80% relative humidity. After 1-3 days, final mechanical and electrical properties are fully obtained. Alkoxy and acetoxy groups are applied to block the undesired polymerization reaction by the residual hydroxyl groups in the composite. However, silicone suffered from a relatively high vulnerability to moisture by nature, and hence its usage is restricted to moisture-free conditions.

10.2.3 Acrylic

Acrylic materials are used not so frequently as epoxy but have an enormous advantage in rapid curing by UV or visible light. Acrylic becomes gel to film through crosslinking, but the curing mechanism is different from that of typical thermosets. A radical initiator initiates acrylic adhesive curing. When exposed to UV, the initiator is decomposed to form radicals, and curing proceeds as the radical attacks monomers, propagating the chain. Either by bond cleavage of the initiator or the bimolecular reaction induced by the excited initiator, the free radical species initiate, propagate, and finally terminate the cure reaction. Equipment and process conditions should be considered when selecting an initiator, and prepolymer composition since the concentration of radicals and their potential to attack a specific acrylic monomer varies depending on the light source's wavelength. Because acrylic adhesives must be exposed to UV for curing, acrylic adhesives cannot be applied to all components in packaging. Due to these limitations, it is mainly used in optical parts and optoelectronics, where transmittance and refractive index characteristics are important. When the UV cure is not strong enough to fully cure the material, the additional thermal cure method can be utilized to complete curing.

10.2.4 Cyanoacrylates

Cyanoacrylates are a one-component adhesive that can be adhered to a substrate instantly. They are cured by moisture present on most surfaces without the need for heat or UV irradiation. Cyanoacrylate is not widely used in packaging manufacture, and the biggest reason is that it cannot withstand the solder flow process because of its poor heat resistance. In addition, if the curing speed is too fast, there is a disadvantage in that the curing may proceed before the adhesive is applied and the component is positioned for assembly.

10.3 The electronic packaging products of highly requires rapid cure

10.3.1 Surface mount adhesive

10.3.1.1 Basic concept and application

Surface mount technology mounts a component on the board surface by using adhesives. The main advantages of surface mount technology are saving space and enabling efficient automation processes. Surface-mounted components can be mounted on both sides of the board and are smaller in size than conventional components, reducing the assembly's weight and lowering the internal stress and vibration within the system. Regarding the automation process, through-hole mounting requires different autoinsertion equipment depending on the component size. On the other hand, all components can be mounted with a single type of equipment by surface mounting. This system utilizes adhesives called surface mount adhesive. Surface mount adhesives perform two functions during mounting. They temporarily hold the parts until they can be permanently attached by soldering. They can also provide stress relief to the soldering connection to prevent failure of the electrical connections (Fig. 10.2).

10.3.1.2 Process

There are numerous types of SMT processes. In the general process, the solder paste is printed after washing and drying the board. Adhesives are dispensed between solder pads, and electronic components are placed on wet adhesives. The adhesives may be cured to sufficiently hold the components before the solder reflow or wave soldering step. Even if the board is shaken by acceleration and deacceleration during the process, the displacement of the components should not occur. The process may be shortened by curing the adhesive in the solder reflow step. As a result, surface mount adhesives physically supplement the permanent binding by the solder.



Figure 10.2 Process for applying surface mount adhesive [1].

10.3.1.3 Materials composition and properties

Most surface mount adhesives are made of epoxy adhesives. Acrylic, silicone, or polyurethane adhesives are often used. The adhesive is generally based on base resin and curing agent. Since the curing mechanism varies depending on the type of base resin, the curing agent varies. Furthermore, sometimes, catalysts are used for curing. Many additives are used to modify properties and impart functionality. The filler controls flowability, thermal expansion, and shrinkage during curing processes and imparts electrical or thermal conductivity to the adhesive. It is also used to color the adhesives. In addition to fillers, reactive diluent for viscosity control and elastomeric polymers for toughness control are sometimes added to the adhesive. Also, pigments are added to the adhesive to easily detect the shape or amount of the dispensed adhesive. Most surface mount adhesives have similar basic compositions, but the type or content of the constituent material varies to exhibit performance suitable for their application.

Several properties are required for the adhesives for the surface mount technology. The required properties of the adhesive are classified into precure properties, cure properties, and postcure properties. Before curing, the adhesive must have a long shelf life (storage) and pot life (processing). A one-component adhesive has a short shelf life but a long pot life. Moreover, it is efficient because it can eliminate the blending process during manufacture. The occurrence of a blending error may be excluded. On the other hand, multicomponent adhesives may cause viscosity changes in the dispensing process due to their short pot life; hence one-component adhesives are preferred.

During the process, the components must be fixed well before curing. Wet strength (green strength) should be high enough. Because the board moves due to a change in speed in the automation process, it is necessary to prevent the bonded passive and active components from shifting. In general, high-viscosity adhesives have high green strength. In addition to viscosity, the adherend surface and dot profile also affect green strength. The adhesive dot dispensed on the board surface must meet the appropriate geometric needs because many problems are encountered in the adhesive dispensing process. The shape, size, and volume of the adhesive need consistency in the dispensing process. Too much adhesive pollutes the pad, causing the solder joint to fail. Too few adhesives fail to cover the component on the board. The adhesive should have a sufficient volume to fill the gap while at the same time having a volume not overflowing. It is very important to dispense quantitative and repetitive adhesive dots. At the end of the step, adhesives should be easily released from dispensing tips with no tailing or stringing. The thixotropic properties of the adhesive, surface conditions and nozzle size should be appropriately controlled [10].

For SMA, the curing temperature should be low enough not to warpage or damage the assembled electronic components or boards. The shorter the curing time, the better to protect board materials. In addition, shrinkage should be small to minimize the internal stress caused by curing. Generally, epoxy surface mount adhesives are appropriate to cure within 3 minutes at a temperature of 150°C or less. There should be no outgassing during curing to prevent voids. After curing, the adhesives hold the component in place in the solder flow process. The postcure properties of the adhesive should not impair the system's reliability as the adhesive remains on the board even after the adhesive is completely cured after the solder reflow process. The modulus and thermal expansion coefficient of the adhesive affect the reliability of the device. Since the device is exposed to various temperature and humidity changes, the thermal expansion coefficient must be low, and the resulting stress must be relieved to avoid failure of solder joints. Too stiff, high modulus adhesives have poor stress relief ability. The expansion coefficient suitable for surface mount adhesive is 45-100 ppm/°C below the glass transition temperature and 150-190 ppm/°C above the glass transition temperature [11]. Other required properties for reliability should be low moisture absorption and not corroding. Reworkability is also an important postcure property of adhesives. For rework, the adhesive must have a low glass transition temperature. An adhesive having a T_g of $75^{\circ}C-95^{\circ}C$ is suitable for a rework process.

10.3.1.4 Rapid cure type products

Refer Table 10.1.

10.3.2 Dicing die attach film

10.3.2.1 Basic concept and application

With the recent development in the packaging industry, all components used in semiconductor assembly are miniaturized and integrated. CSP is a mounting technology developed for miniaturization and high semiconductor chip integration. The chip size is almost the same as the package size in the CSP. The package size is less than 1.5 times the die area. As part of this current package trend, one of the more advanced packages is the multichip package (MCP) [12]. The MCP is a technology for mounting a chip on a chip and has much more capacity than single-chip packages. The MCP method of stacking chips increases memory density effectively.

Product name	Supplier	Cure type	Resin type	Viscosity [mPa · s]	Thixotropic Index	T _g (cured) [°C]	CTE1 [°C/ ppm]	CTE2 [°C/ ppm]	Shelf life	Cure schedule
Loctite 3609	Henkel	Heat	Epoxy	160-2000 ^a	3.3-12	73	N.A.	145	n.d.	90-120 s @ 150°C
Loctite 3629 C	Henkel	Heat	Epoxy	n.d.	n.d.	118	45	144	n.d.	90 s @ 150°C
Loctite D125F	Henkel	Heat	Ероху	350,000 ^b	n.d.	85	n.d.	58	183 days @ 0°C-8°C	90 s @ 150°C
KokiJU-90LT-3	Koki	Heat	Epoxy	65,000	n.d.	n.d.	n.d.	n.d.	6 months @ 0°C-10°C	90 s @ 90°C-100°C
AlphaSM42-120P	MacDermid Alpha	Heat	Ероху	5,500-7,000	3.0	110	65	190	6 months @ 10°C	80 s @ 150°C
AlphaSM42-1311	MacDermid Alpha	Heat	Epoxy	35,000-55,000	5.0	90	60	190	6 months @ 10°C	80 s @ 150°C
HeraeusPD955M	Heraeus	Heat	Epoxy	10,000-50,000	n.d.	n.d.	n.d.	n.d.	6 months @ 5°C-12°C	90 s @ 150°C
HeraeusPD955M	Heraeus	Heat	Epoxy	10,000-50,000	n.d.	n.d.	n.d.	n.d.	6 months @ 5°C-12°C	90 s @ 150°C
Vitralit6104VT	Panacol	UV/ Heat	Acrylic	80,000–90,000°	n.d.	65-90	71	238	6–12 months @ 0°C–10°C	15 s, 60 mW/cm ² (UV) 15 min @ 120°C (Heat)
Structalit3060	Panacol	Heat	Epoxy	30,000-40,000 ^d	n.d.	40-50	30	247	4.5–9 months @ 0°C–10°C	90 s @ 120°C
Seal-GloNE8800T	Fuji	Heat	Epoxy	300,000 ^e	n.d.	n.d.	n.d.	n.d.	n.d.	60 s @ 120°C

Table 10.1 Rapid cure type products of commercial surface mount adhesives.

^aCasson viscosity. ^bBrookfield 10 rpm. ^cBrookfield 6 rpm. ^dBrookfield 5 rpm. ^eBrookfield 5 rpm.

In conventional chip packages, paste-type adhesives have been used. Individual chips have adhered to a substrate or lead frame by paste. However, production costs increase because dispensing processes are added when using paste. In addition, it is not easy to control the dispensing amount and uniform thickness. When an excessive amount of paste is dispensed, a bleeding problem occurs in which the adhesive flows out of the adhesion area. Film-type adhesives called die attach film (DAF) are used in a stacked chip package to overcome the disadvantage of paste adhesives. DAF has a constant thickness without excessive adhesive flowing out like pastes and can improve processability by simplifying the process. Films with a thickness of $10 \sim 25$ microns are used for die stacks. Recently, an adhesive film in which a DAF for die adhesion and a dicing tape for cutting wafers are integrated has been used (Fig. 10.3).

10.3.2.2 Process

Semiconductor packaging is carried out after transistors are engraved on the wafer's front during the semiconductor process. The dicing DAF is laminated to the wafer before the dicing process. The wafer is preheated to $60^{\circ}C-80^{\circ}C$ to ensure the adhesion between the wafer and the film. The dicing die attach holds the wafer during the dicing process. After sawing the wafer, UV is irradiated to the film to reduce the adhesion of the dicing tape and pick up the die. After dicing is completed, to remove hundreds of chips attached to the dicing tape individually, the tack of the dicing tape must be lowered. In general, the adhesion of the dicing process is separated individually and weakly attached to the dicing tape. To pick up the chip, apply physical force to the chip with an ejector to give it a slight gap with other chips, and pick up the chip with a plunger and place it onto the packaging substrate. Die adhesion is directly carried out without a dispensing process since there is a DAF under the chip from which the dicing tape has been removed (Fig. 10.4).



Figure 10.3 Comparison of processes for chip attaching with (A) paste and (B) die attach film.



Figure 10.4 (Upper) Structure of dicing-die attach film and (lower) process for dicing-die bonding.

10.3.2.3 Materials composition and properties

Most DAFs are epoxy-based adhesives. Acrylic, polyimide, and silicone resins are also used. The DAF should have both fluidities for laminating and heat resistance that can withstand solder reflow. Therefore, an epoxy resin and a low T_g polymer may be mixed and used. In addition, inorganic fillers such as silica are used to suppress thermal expansion. Bisphenol-based or novolac resin is widely used as the base resin of epoxy adhesive. A latent curing agent is mainly used to prevent curing during storage or in the process. In the dicing film part, an acrylic polymer is mainly used. Blowing agents or a photoinitiator are used according to a mechanism for reducing adhesion force. In the industry, debonding by UV is more widely used. Since the adhesive force is reduced by chemical crosslinking, materials capable of forming additional chemical bonds should be included in the composition.

Since the dicing DAF is directly attached to adhesives that function differently, the interface's adhesion properties are very important. The adhesion of the interface should not be too low. Water is injected into the wafer at high pressure to cool the frictional heat generated between the blade and the semiconductor wafer in the dicing process. If the adhesion between the dicing adhesive and the die attach adhesive is weak, there is a problem peeling off without enduring the pressure caused by the water jet. The peeled film can cause contamination of the wafer. On the contrary, if the two adhesive layers are too strongly attached, a problem occurs in removing the dipping film. When the dicing DAF is stored for a long period than required, or excessive heat/pressure is applied, the fusion of the two adhesive layers occurs. Thereby the dicing tape does not peel off, or residue remains. In this case, the die is not picked off, and the performance of the DAF is degraded. The properties required for the dicing DAF during the assembly process are as follows [13]:

- Temperature for temporary laminating to wafer should be below 80°C.
- No damage to chips or films during the dicing process.

- The adhesion should be sufficiently lowered after UV irradiation so that the die is well picked off.
- Chip warpage should be prevented by relieving stress.
- The difference in CTE between the substrate and the chips should be buffered.
- Package cracks should not occur in the solder reflow process.
- Low moisture absorption

10.3.2.4 Rapid cure type products

Refer Table 10.2.

10.3.3 Underfill

10.3.3.1 Basic concept and application

The integrated circuit (IC) on a semiconductor chip is essential in modern electronics. The IC chip should be interconnected to other electronic parts to make the electronics work. There are three major interconnection techniques: wire bonding, tapeautomated bonding, and flip-chip. In the wire-bonding system, the chip is attached to a substrate with a die-attach adhesive, and a wire (gold or aluminum) is then bonded between the substrate and chip to provide electricity. Tape automated bonding uses a lead frame carrier with polymer tape to provide electricity to the IC chip. Both wire-bonding and tape-automated bonding required delicate processing. However, a flip-chip, an IC chip with an active side faced down, has solder bumps onto the chip-pad. After mounting the chip on a substrate, a heating process (solder-reflow) is applied, and interconnections are obtained between the chip and the substrate. This flip-chip technique offers many advantages, including short interconnections, simple processes, high input/output density, etc. However, the flip-chip process could make some voids between the chip and a substrate. Thus, underfill is applied to fill the voids and reinforce the connections. Underfill is electrically insulated composites, which contain epoxy resin, hardener, inorganic fillers, etc. The underfill protects the connection between the chip and the substrate from dust and moisture, improving the reliability of the devices (Fig. 10.5).

10.3.3.2 Process

Conventional underfill is applied after the formation of a connection between flipchip and substrate. The dispensed underfill flows into the connection gap owing to a capillary force, called "capillary underfill." After the underfill flow, a heating process is needed to cure the epoxy resin for a permanent bonding between the chip and substrate. However, the size and pitch of the bump get smaller, and chip size becomes larger as the semiconductor technology develops. Therefore, the capillary underfill exhibited some limitations (voids, long waiting time, etc.). Besides, the capillary underfill needs an additional heating process for curing. The other processes (dispensing, curing, etc.) for capillary underfill hinder an efficient process for semiconductor packaging. No-flow underfills, as an alternative approach, have

Product name	Supplier	Cure type (DAF)	Resin type (DAF)	Adhesive thickness (µm)	<i>T_g</i> (cured) [°C]	Shelf life	Cure schedule	Cure type (dicing tape)	Curing condition (dicing tape)	Application
FH-900	Showa denko	Heat	Silica filled epoxy	10-40	180	n.d.	n.d.	UV	150-400 mJ/ cm ²	
Loctite ABLESTIK ATB 100 series	Henkel	Heat	Silica filled epoxy	15-30	n.d.	n.d.	n.d.	Non-UV	n.d.	Cu or Au wire packages Stealth dicing before grinding
Loctite ABLESTIK ATB 100HA series	Henkel	Heat	Silica filled epoxy	5-30	n.d.	n.d.	n.d.	UV/non-UV	n.d.	Large die application Stealth dicing before grinding
Loctite ABLESTIK ATB 100U series	Henkel	Heat	Silica filled epoxy	5-30	n.d.	n.d.	n.d.	Non-UV	n.d.	Cu or Au wire packages Stealth dicing before grinding
AFN301	Furukawa	Heat	Ероху	20	125	1 year @-5°C -10°C	60 min @ 150°C	UV	200 mJ/cm ²	Die to substrate
AFN303	Furukawa	Heat	Ероху	10	120	1 year @-5°C- 10°C	60 min @ 150°C	UV	200 mJ/cm ²	Die to die
AFN601	Furukawa	Heat	Ероху	50-80	156	1 year @-5°C -10°C	60 min @ 150°C	UV	200 mJ/cm ²	Film over Wire (FoW)

 Table 10.2 Rapid cure type products of commercial dicing die attach films.



Figure 10.5 Process of capillary underfill.



Figure 10.6 Process of no-flow underfill.

been developed. A preapplied underfill on a chip spread fills the gap during the solder reflow process. With this approach, standing time for capillary flow and another curing process could be eliminated. However, there are some challenges for noflow underfill to achieve high-volume production. In a rapid curing process, voids could be trapped in the gap because of the short time for spreading of underfill. Another point is a restriction of fillers, which can hinder the connection between the solder balls and the bumps (Fig. 10.6).

If no-flow underfill is applied, time-consuming oven curing processes ($\sim 150^{\circ}$ C, 30 minutes) can be passed, and underfill curing occurs at the solder-reflow process. The temperature of the solder reflow process is shown in Fig. 10.7. The chip and substrate are preheated to 150°C for minutes, and the temperature is raised to 220°C to make solder reflow for a minute [14]. The no-flow underfill must be cured completely during the solder reflow process, much shorter than the previous oven curing process for capillary underfill. In addition, there is a demand for replacing lead (Pb) in solder alloy (with Sn), which is toxic to the human body, with a silver (Ag), copper (Cu), bismuth (Bi), and indium (In). Among the substitutes, Sn–Bi and Sn–In alloys show low reflow temperature ($\sim 140^{\circ}$ C) [13]. This lower reflow temperature would be desirable in the point of productivity and reliability of devices, as the glass transition temperature of the substrate (FR4) is around 125°C. A rapid-curing composite is required to obtain a completely cured underfill for the low-temperature and large-volume process.



Figure 10.7 Comparison between the heating profile of capillary and no-flow underfill.

10.3.3.3 Materials composition and properties

Underfill is commonly composed of liquid epoxy resin, hardeners, and inorganic fillers. Hardeners (amine, anhydride, etc.) are used to make a cross-linked structure with epoxy resins. In addition, latent curing agents are used to give a long pot life with fast curing. Inorganic fillers, mainly micron-sized silica, are added to enhance the mechanical properties of the final product (low CTE, high modulus, moisture and dust barrio, etc.). Other additives could be incorporated in an underfill formation, such as dispersing agents, elastomers, and adhesion promoters.

Many kinds of properties need to be considered to make outstanding underfill. Long pot life is required for large-volume production, and reliability must be provided to remain stable during usage. Size and amount of filler are other important factors to balance lower CTE and sufficient capillary flow. The lower CTE relieves the stress accumulation resulting from the mismatches in the CTE among the chip, the substrate, and the solder (chip: 3 ppm/°C, substrate (epoxy + glass fiber): 20 ppm/°C, epoxy: 70 ppm/°C). Relieving a shear strain on bumps, which could cause creep during thermal cycling, increases the lifetime of devices 5–20 times compared to devices without underfill [15]. Material properties such as elastic modulus, tensile strength, glass transition temperature, and moisture resistance are important for reliability. In addition, proper adhesion strength must be obtained. The low adhesive strength of cured underfill could result in cracks and delamination.

10.3.3.4 Rapid cure type products

Refer to Table 10.3.

10.3.4 Electrically conductive adhesives

10.3.4.1 Basic concept and application

Electrically conductive adhesives (ECAs), which contain dispersed conductive fillers and polymer resin (conductive or nonconductive), are widely utilized in PCBs

Product name	Supplier	Viscosity (cps)	Cure schedule	Shelf Life (-40°C) /Pot Life (25°C)	Bond strength (psi)	MOE (MPa)	T _g (Cured) (°C)	CTE1 (°C/ppm)	CTE2 (°C/ppm)	Description
Stacychip3082	Cookson	4,000	20 min @ 165°C	6 months/32 h	10,821	4,800	125-136	38	141	Silica-filled epoxy anhydride underfill
NUF 2078E	Cookson	500-1,500	PCB solder- reflow profile	6 months/24 h	n.d.	1,800	130	65	222	Epoxy-anhydride underfill (rubber modified)
FP 4549	Loctite	2,300	30 min @ 165°C	9 months/24 h	11,000	5,600	140	45	143	Fast-flow underfill
FP 3568	Loctite	30,000-300,000	30 min @ 150°C	n.d. /30 h	8,900	2,053	116	24	110	Epoxy
UF-3400	3 M	1.9 × 10 ⁶	Temp. plateau 135°C - 165°C Ramp to reflow temp.	4–6 months/5 h	9,509	2,200	> 150	55	157	Ероху
X6-82-5	Zymet	< 3,000	30 min @ 150°C or 5 min @ 165°C	n.d.	n.d.	4,000	120	31	n.d.	Ероху
FF7673	AI Technology	n.d.	30 min @ 150°C	n.d.	2,000	n.d.	170	26	n.d.	Quartz-filled epoxy

 Table 10.3 Rapid cure type products of commercial underfill materials.

and electronics for their conductivity of electric current and adhesion between various substrates. ECAs replace solder alloy in electronics assembly with advantages like low processing temperature, simple process, low toxicity (lead-free), etc. In addition, ECAs exhibit high chemical and thermal resistance, adhesion performance, outstanding mechanical properties, and low shrinkage. According to conductive directions, ECAs are classified as isotropic conductive adhesives (ICAs) and anisotropic conductive adhesives (ACAs). ICAs conduct the electric current in all directions. However, ACAs are conducted only for Z-direction via a specific alignment of fillers. ICAs can be applied for chip joining and conductive interconnections between substrates (ceramics, plastics, etc.). ACAs have applications with a fine pitch, such as flat panel displays, flip-chip attachments, and smart cards, thanks to their anisotropic nature (Fig. 10.8).

10.3.4.2 Process

ECAs have been used widely and replaced soldering, which has environmental and health problems. Appropriate pressure, heat, and time are needed to make conductive and rigid bonding for ECAs. However, the processing temperature for ECAs is lower ($120^{\circ}C-200^{\circ}C$) than the solder reflow process ($220^{\circ}C-240^{\circ}C$). In the heating step, linear polymer chains in ECAs are cross-linked, making a three-dimensional network that enhances the mechanical properties. The curing ratio increases as the bonding temperature and time increase. However, the over-curing of ECAs causes degraded adhesion by thermal stress. With the development of industries, electronic devices require more fine pitches in chips and substrates. However, a high temperature in the bonding process causes a warpage of the chip and circuit, which results in a misalignment of electrodes. Thus, lower curing ECAs are needed to relieve the problem.

ICAs are used as die-attach adhesives and surface mount adhesives instead of the solder alloy. Generally, ICAs are cured at a lower temperature $(150^{\circ}C-170^{\circ}C)$ compared to that solder alloy $(220^{\circ}C-240^{\circ}C)$. The curing of ICAs is conducted by oven curing. However, ACAs require a thermos-compression bonding. The typical bonding condition is 180°C, 20 seconds, and 30 kg_f/cm² [16]. The conductive fillers in ACAs are deformed by the pressure and make the interconnection between the bump and electrode pad. Then, cured epoxy resins hold the interconnection, improving reliability.



Figure 10.8 Comparison of each direction of electrical conductivity between isotropic conductive adhesive and electrically conductive adhesive.

10.3.4.3 Materials composition and properties

ECAs are commonly composed of insulating adhesives resins (mainly epoxy resin) and conductive fillers. Typically used conductive fillers are metal, carbon, ceramic, and metal-coated fillers. Silver with a flake shape is the most widely used filler (60-80 wt.%) in ICAs for its high conductivity and simple processing. In the case of ACAs, filler concentration is around 5-20 wt.% to provide one-directional conductivity, obtained from a lower concentration than the percolation threshold. To provide Z-directional conductivity, spherical shape fillers are favored for ACAs. In addition, conductive polymers like polypyrroles, polythiophenes, polyacetylenes, etc., are used as conductive parts. The matrix could be thermoplastics or thermosets, which can make electrical and mechanical bonds with substrates. Polyvinyl acetate, polyvinyl ether, and acrylates are examples of thermoplastics. Thermosets include epoxy, silicone, cyanate ester, etc. Among the various polymer matrices, epoxies are the most favorable for their superior characteristics (adhesion strength, heat and chemical resistance, low cost, etc.) (Fig. 10.9).

The volume resistivity of ICAs $(5.0 \times 10^{-4} \,\Omega \cdot \text{cm})$ is somewhat higher than solder alloys $(1.5 \times 10^{-5} \,\Omega \cdot \text{cm})$. As the resistivity is affected by the cure shrinkage of polymer matrix and contacts of fillers, nano-sized Ag fillers with enhanced sintering and matrix with high shrinkage are preferred. However, the bond strength of ICAs (140 kg_f/cm²) is comparable to solder alloys (155 kg_f/cm²) despite the lower processing temperature [16]. The reliability of ICAs is determined by resistance to humidity, temperature cycling, etc. High humidity and temperature cause corrosion of metallic fillers in ICAs, deteriorating conductivity. Thus, resins with low moisture absorption, corrosion inhibitor, and oxygen scavengers are recommended for the reliability of ICAs.

As ACAs provide unidirectional conductivity in Z-axis, the conductive fillers can connect two-conductor surfaces with fine pitch. Thus, the size of conductive



Figure 10.9 Resistivity variance as a function of filler loading in electrically conductive adhesive.

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fillers should be limited according to the pitch of the circuit. In addition, the deformation of conductive fillers must occur in the thermos-compression bonding process (e.g., 180° C, 20 seconds, and $30 \text{ kg}_{\text{f}}/\text{cm}^2$). The bonding force in ACAs is a critical factor for electrical performance, as the contact of fillers determines the conductivity. The resistance to humidity and thermal cycling is important to ACAs to keep reliability with intact electrical and mechanical properties.

10.3.4.4 Rapid cure type products

Refer to Table 10.4 and Table 10.5.

10.3.5 Encapsulant materials: glob-top (dam-and-fill)

10.3.5.1 Basic concept and application

With the demand for compactness and multifunctions on the electric components, their footprint, or two-dimensional occupancy on any substrates, is to be reduced. A brilliant approach, a z-axis multiple stacks of chips easily alleviated the problem and as such widely acquired as bare die mounting or chip-on-board. By the process, however, the risk of exposure to moisture or contaminants increases accordingly, and hence the manufacturer should provide powerful but delicate protection for the components, including bare dies and bonding wires. Glob-top technology enables direct encapsulation for the stacked device with high I/O values, which normally comprises fragile dies or larger chips. In the process of flip-chip and chip-on-board, a glob top encapsulant, in the form of a viscous resin, is to be dispensed and applied onto the substrates (a printed circuit board or an interposer) and cured after hard as like an amber. In that way, the encapsulant provides a protective shell from the outer atmosphere without damaging the micro-sized component and the mechanical endurance required in other following packaging processes. The processing is apt for encapsulation areas under 2 mm × 2 mm, and another technique, called damand-fill, is needed for a larger protection area. Dam-and-fill is a much more selective process using two species of potting compounds speciated by viscosity; a higher one for dam material and a lower one for fill material. The dam material is first dispensed onto the targeted surface and demarcates the encapsulation area. The isolated void is then filled with the fill material with a slightly lower viscosity, which flows and forms a uniform thin layer covering the bonding wire and the chip beneath. The glob-top and dam-and-fill technologies can be co-used for an intricate design of substrate or chip, which requires more precise control over the protection area and height profile (Fig. 10.10).

For recent requirements in reduced substrate area and package height limit, the COB—direct chip mounting and interconnecting—technology is now widely used in mobile, power electronics, display, and customer products. Multichip module (MCM) with multiple stacked IC chips or other discrete components is representative and utilizes the glob top materials at the final protection process. A smart card, or IC card, also requires a package with a lower profile and thus receives benefits

Product name	Supplier	Viscosity (cps)	Cure schedule	Shelf life (-20°C) pot life (25°C)	Bond strength (psi)	Volume resistivity (ω·cm)	Thermal conductivity (W/mK)	Description
5132-CE	IQ- BOND	16,000	15 min @ 175°C or 60 min @ 150°C	6 months/12 h	> 2850	5.0×10^{-4}	4	Silver paste
5401 CE	IQ- BOND	15,000	5 min @ 150°C or 15 min @ 120°C	6 months/12 h	n.d.	5.0×10^{-4}	n.d.	Silver paste
Elecolit 323	Panacol	45,000	4 min @ 150°C	n.d./96 h	n.d.	2.0×10^{-4}	n.d.	Metallic fillers
Elecolit 336	Panacol	Paste-like	5 min @ 150°C	n.d.	n.d.	10.0×10^{-4}	n.d.	Metallic fillers
EL- TECH 235	Adhetron	n.d.	5 min @ 120°C or 30 min @ 95°C	n.d./12 h	n.d.	2.0×10^{-4}	7.8	Silver paste

 Table 10.4 Rapid cure type products of commercial electrically conductive adhesives.

Product name	Supplier	Viscosity (cps)	Cure schedule	Shelf life (-20°c) pot life (25°c)	Bond strength (psi)	Description
5970 ACE	IQ- BOND	6,000	60 s @ 170°C 3 min @ 150°C	3 months/12 h	> 2,850	Au-coated polymeric filler
5973 ACE	IQ- BOND	3,500	10 s @ 170°C 3 min @ 150°C	6 months/5 days	> 2,850	Conductive polymeric filler
MONOPOX AC268	DELO	28,000	8 s @ 170°C	6 months/72 h	n.d.	Nickel core filler
MONOPOX AC6530	DELO	20,000	1 s @ 230°C	6 months/72 h	n.d.	Nickel core filler
ACF 7303	3 M	Film	20 s @ 210°C	15 months (<2°C) 4 weeks (R.T.)	n.d.	Gold-coated Nickel

 Table 10.5
 Rapid cure type products of commercial anisotropic conductive adhesives.



Figure 10.10 Basic concept of glob-top (left) and dam-and-fill (right) material.

from the COB technology; it became a highly marketable application for the globtop (especially for dam-and-fill) materials. Moreover, in the display assembly manufacture, the dam-and-fill materials are used in optical bonding the gap between the cover glass and display module or touchscreen, where the special function of optical clarity is required for the encapsulants. As such, the applications for the glob-top materials gradually broadened, and their inherent shortcomings in the aspect of storage, manufacturing, and usage come up for air such as a long cycle time, dispensing time, voids, and especially the prolonged cure time and high cure temperature requirement. The time and energy input during the cure of the encapsulant is the main bottleneck of its manufacturing process, and even the additional postcure would be required to get rid of outgassing and enhance the coating surface completeness resulting in falling in productivity and attenuating the cost-saving advantage (Fig. 10.11).

10.3.5.2 Process

In the glob-top process, an exact quantity of encapsulant is transferred from a reservoir or a prepacked dispenser through a pressure-controlled syringe valve onto the targeted area. During the dispensing, external heat can be applied to the dispenser part or the substrate part (60°C-110°C) to enhance flowability and reduce void formation caused by inconsistent flow. The required temperature during dispensing is mainly dependent on the type of material. Material quantity, viscosity, dispenser pressure, needle diameter, and the drop distance from the needle outlet to the surface are important processing parameters. On the other hand, the dam-and-fill materials are dispensed through two steps; a highly viscous material is deposited onto the substrate and solidified into a dam (wall), and then a lower viscous material fills the space within the dam at highspeed dispensing. The two-step process ensures faster and more compact filling under and around the bonding wires and achieves a lower height profile than the glob-top dispensing. New dispensers such as the rotary positive displacement valve or true positive displacement pump superseded the normal syringe-type pump to attain much more precise control over encapsulant flow. In the same vein, the dispense-in-vacuum technique can be applied to remove inconsistent material flow and void entrapment. In an attempt to increase productivity, stencil printing is utilized, and it covers several devices on a substrate simultaneously, and the resulting glob-top profile is ameliorated. The special formulation of stencil printable glob-top material is now developed and commercialized by several manufacturers.



Figure 10.11 Procedure of dam and fill encapsulation.

After the dispensing, the viscous liquid needs to be cured to fulfill its function to protect and provide mechanical support. A heat-assisted cure is usually conducted in a hot-air oven. A typical cure schedule requires heating around 150°C for 1-2 hours, and postcure with higher temperature and longer time might be needed in some cases. UV-light curable types show their merit of very low cure demand, 2-3 minutes of UV exposure (wavelength: 240-365 nm) with an intensity of over 100 mW/cm² and low to room temperature cure condition.

Note that any changes in material composition or mix ratio can seriously impact storage safety, processing viscosity, and phase separation. Plus, the large-scale industrial process completely relied on uniform processing parameters and an individual instrument. Hence, the rapid cure and processing strategy must consider the varying factors that conformed to the processing presets. The premature cure of the encapsulant is expected to induce an uprising in viscosity which deters the dispensing flow for the calculated quantity of the material. The thixotropy of the material during and postdispensing can also be negatively affected, which ultimately threatens the production streamline. For designing the proper rapid cure tactic, the impact of both the processing tools and the material itself should be thoroughly examined in advance.

10.3.5.3 Material composition and properties

Glob-top material comprises three types of resins; a typical thermoset epoxy, a thermoplastic acrylate, and a silicone-based. Usually, a mixture of thermoset and thermoplastic in a single component is preferred for complex material properties. A one-part epoxy encapsulant is supplied as a frozen mix in a dispenser and thus ready-to-use, that is, its working life is unlimited, and no mixing is required. A onepart type is preferred over a two-part type, which requires weighing, mixing, and defoaming before dispensing. The shelf-life of the one-part encapsulant is about three months, storage at -20° C or six months, storage at -40° C and can vary depending on the type of epoxy resin and hardener and its recipe. Most epoxybased encapsulant uses an anhydride as a hardener or an amine for a rapid cure at the cost of the shelf-life. The typical epoxy encapsulant cure at 125° C for an hour, some rapid cure types can cure at 80°C for 2-3 hours, and the postcure is also needed in some cases, at higher temperature and longer cure time. Recently developed acrylate or hybrid epoxy-based encapsulant utilizes UV light for a cure and offers the fastest cure time and minimized cure heat input where the material reliability has not been thoroughly confirmed yet in terms of published data. For applications with stress-sensitive components such as thinner bonding wire and chip, extra care must be taken during the curing process, and a softer silicone encapsulant can be optionally utilized for reduced stress development. The silicone-based encapsulant is cured by moisture, and this can be controlled by adding a platinum catalyst and additional heat. All types of glob-top and dam-and-fill material contain high contents of silica filler up to 80 wt.% to match a similar CTE to the commonly used FR4-based PCB substrate (less than 50 ppm) and to attain thixotropic property so that the encapsulant easily flows in response to dispensing pressure, but rapidly recovers its high viscosity after the deposition on the targeted area.

The composition (resin structures, hardener selection, etc.) for glob-top or damand-fill materials are designed to meet the properties both during and after the processing. The processing conditions and the required properties are already briefly abovementioned and thus omitted here. On the one hand, the performance requirements for the final encapsulated product deserve to be kept in mind. First, the globtop and dam-and-fill encapsulation are needed to be electrically insulative. Some level of electrical insulation is required for the encapsulated chip or device to function. The main factor for this is the electrical breakdown voltage of the encapsulant, which is normally not a problem at the typical voltage level of IC, 1-20 V. However when the encapsulant is applied in the SiC devices requiring 3-10 kV, much higher degree of the electrical breakdown voltage and hence the special formulation is required for glob-top resins in the case [17]. Second, encapsulation provides a high level of protection from moisture and chemicals to prevent the corrosion of encapsulated components. Since the metal and semiconductors are highly vulnerable to moisture-induced corrosion, care must be considered before resin and hardener selection. The glob-top materials should both have an extremely low mobile ion content (internal corrosion) and a lower rate of moisture permeability (external corrosion) so that the reactive oxidation within the ready-made encapsulant is suppressed. From a thermomechanical perspective, the encapsulant must induce minimum shrinkage and stress during the cure and heating & cooling process. The cure shrinkage leads to residual stress within the system where the molecular response is constrained, and the deformation is developed. The cureinduced volumetric shrinkage can occur from 1% to 3% for silicone and 2% to 5% epoxy-based encapsulant, depending on the resin structure and cure mechanism, and a far more serious result is expected for acrylate-based resin, which uses UV light to cure. After the cure procedure, the glob-top encapsulant and the surrounding devices are subjected to multiple thermal shocks from the subsequent soldering and packaging process. As a result, the material experiences repeated thermal shrinkage and expansion. Given this, the encapsulant should have a lower CTE value to reduce thermal stress on the interphase between the bare die (CTE of 3–4 ppm/°C) and a PCB (CTE of 4-6 ppm/°C, AIN-based or 14-20 ppm/°C, FR4-based). The glob-top and dam-and-fill encapsulants should have a thermal resistance to withstand temperatures from $-65^{\circ}C$ to $+180^{\circ}C$ (depending on the production). It is recommended the fully cured encapsulant has a higher glass transition temperature to reduce the stress during thermal cycling. For this, a large amount of inorganic particles (mostly silica) is added to reduce the CTE of the resin and the cured encapsulant (after gelation), and this also attributes to boosting the encapsulant's mechanical strength and elastic modulus, which enables the material to resist to heat distortion. The inclusion of inorganic filler into the glob-top resins offers another boon to the system, increasing thermal conductivity. As the encapsulant directly contacts the chip surface, bonding wires, and the other electric components, the heat generated should be effectively dissipated through the glob-top material. The increased thermal conductivity of the system attributes to lengthening the encapsulated device's life in usage.

10.3.5.4 Rapid cure type products

Refer to Table 10.6.

10.4 Trend shifting in packaging technology and strategies

10.4.1 Material regulation according to RoHS (lead, halogen, hazardous materials)

Now the world witnesses the plethora of materials. Exploding production of semiconductors, electronic devices, and components that are used in the conventional automotive, and mobile industry plus the newer, rapid growing industry such as IoT, smart house appliances, drones, and customized products, have pushed the planet's envelope and become the concern both for the suppliers and consumers. The global movement is proceeding to impinge on indiscreet production and irresponsible disposal, severely deteriorating human health and the environment. The most

Product name	Supplier	Encapsulant type	Cure type	Resin type	Hardener type	Viscosity [mPa · s]	T _g (cured) [°C]	CTE1 [°C/ppm]	CTE2 [°C/ppm]	Shelf life	Gel time	Cure schedule
Loctite EO7021	Henkel	Glob-top	Heat	Ероху	n.d.	17,000	125	67	187	9 Months @ 5°C	4 min @ 120°C	1 h @ 120°C (postcure needed)
Loctite ECCOBOND UV8800M	Henkel	Glob-top	UV	Ероху	n.d.	3,000	29	41	135	6 Months @ 5°C	n.d.	2 s @ 100 mW/cm ² (UVA)
Loctite ECCOBOND E1016	Henkel	Glob-top	Heat	Ероху	n.d.	58,000	126	46	140	1 Year @ -40°C	4.5 min @ 120°C	20 min @ 150°C
IQ-Bond 2280	IQ-Bond	Glob-top	Heat	Ероху	n.d.	13,000	n.d.	n.d.	n.d.	6 Months @ -20°C	n.d.	1 min @ 150°C or 60 min @ 80°C
IQ-Bond 7292 UV	IQ-Bond	Glob-top	UV	Ероху	n.d.	10,000	n.d.	n.d.	n.d.	6 Months @ 5°C	n.d.	30 s @ 120 mW/cm ²
EPM-2411-2	NuSil	Glob-top	Heat	Silicone	Platinum- catalyzed	300,000	n.d.	n.d.	n.d.	6 Months @ R.T.	n.d.	15 min @ 200°C
Hysol FP 4651	Henkel	Dam	Heat	Ероху	n.d.	130,000	150	11	50	9 Months @ -40°C	9 min @ 120°C	1 h @ 125°C + 1.5 h @ 165°C
Loctite ECCOBOND FP4451TD	Henkel	Dam	Heat	Ероху	Anhydride	300,000	150	21	65	9 Months @ -40°C	13 min @ 120°C	0.5 h @ 125°C+ 1.5 h @ 165°C
EPO-TEK OG116-31	Epoxy Technology	Dam	UV	Epoxy	n.d.	$20,000 \sim$ 30,000	115	41	170	1 Year @ R.T.	n.d.	30 s @ 100 mW/ cm ² , 1 day delay
Loctite STYCAST A316–48	Henkel	Fill	Heat	Ероху	Amine	50,000	145	55	155	6 Months @ 25°C	n.d.	1 min @ 160°C or 30 min @ 100°C
Loctite ECCOBOND EN 3838 T	Henkel	Fill	Heat	Ероху	n.d.	6,700	2	57	217	9 Months @ -20°C	n.d.	8 min @ 130°C
EPO-TEK 301	Epoxy Technology	Fill	Heat	Epoxy (2 K)	n.d.	100-200	65	39	98	1 Year @ R.T.	n.d.	1 h @ 60°C or 24 h @ R.T.

 Table 10.6 Rapid cure type products of commercial glob-top and dam-and-fill materials.

famous action is RoHS, restricting hazardous substances, enacted in the 1980s in Europe; now expanded worldwide. RoHS urges to hinder using hazardous and unsafety materials used in electrical or electronic products, equipment, and small components. The restriction has kept pace with the demands of the times, and the updated RoHS 3 directive, by EU 2015/863 act, currently applies to 11 categories of products and bans the use of 10 substances of very high concern (SVHC): cadmium, lead, mercury, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers, bis(2-ethylhexyl) phthalate, butyl benzyl phthalate, dibutyl phthalate, diisobutyl phthalate. Greener initiative empowered by international organizations, each government, and huge global companies do not stop there and continues to expand the restrictions on the usage of hazardous but frequently used chemicals enlisted in the REACH SVHC list: halogens (fluorine, chlorine, bromine, iodine), aromatic compounds (benzene, anthracene, phenol), solvents (toluene, xylene, methanol, formamide), heavy metals (arsenate, antimony, chromate, cobalt, mercury, nickel compounds, etc.), carcino/mutagenic compounds (pyrroles, furan, sulfate, acetamides), and some epoxy ingredients (bisphenol A, ethylenediamine, 2methylimidazole), representatively [18].

These movements directly impacted the electronics manufacturers to procure alternative production lines, supply chains, and greener materials to substitute the enlisted chemicals, resulting in changes in processing conditions used for decades. The substitution of the previous eutectic Sn/Pb solder to Sn/Ag/Cu solder, derived from the leadfree act, brought forth the most striking changes across the board the semiconductor manufacturing; changes in (1) flux chemistry, (2) processing temperature during the solder reflow, requiring additional melting heat by 30°C-40°C (260°C), and (3) consequential the higher thermal reliability for the components (adhesives, encapsulants, organic substrates) at stake [19]. Nonhalogen-based flame-retardants, another big item of the greener initiative, also require the changes in (1) base resin structure, (2) resin composition, (3) filler type and content, and (4) consequential thermomechanical properties for the PCB and the peripheral components. The traditional strategies for rapid cure adhesives also confronted challenges where the material selection, recipe, adherend, surface, processing equipment, and conditions (temperature, pressure) are now replaced and revolutionized. For example, in the case of epoxy cure, the major process of packaging and encapsulating semiconductor production, the use of heavy metalbased latent cure agent, and the inclusion of imidazole, phenol, and thiol as cure accelerants should be cautiously considered in their dosage and the spreading effect on the final assembled product. Numerous studies about the rapid cure system are in progress, and they should walk in step with the green restrictions and the characteristic properties spinning off from the varying production line in the semiconductor industry.

10.4.2 New formulation conformed to an advanced packaging design

The famous Moore's law, which has been orthodox for semiconductor players, or a long-term target about scaling the IC density, pitch, nodes, and I/Os, is now reaching

the conceptual limitation as the world's best chip suppliers (IBM, TSMC, Intel and Samsung) unveiled their roadmap for process node, developing 2 nm EUV production by 2023 and 1.8 nm by 2025 [20]. They are now facing and building a new era of "More than Moore" which is not just about scaling but functional diversification. The paradigm of what value the future IT/electronics should focalize is shifted from offering uniform high-quality mass products to presenting a much-personalized experience (VR, big-data, metaverse) and comfortable interaction (wearable, smart appliances) to customers. These applications require massive data processing ability and functional versatility for the much thinner and more flexible device. Given the circumstance, the two-dimensional peripheral and area array of single-chip packaging on the substrate or wafer seems to unqualify the design and cost parameters presented by the stream of the miniaturization, high-speed manufacturing, and multifunctionality within the system. For the advanced design of semiconductor packaging, vertical die stacking (2.1D, 2.3D, 2.5D, 3D), package stacking, and multichip package technologies have been developed so far, and these are connected into a system with a higher level of integration, namely the system-on-integrated-chips (SoC), the system-in-package (SiP), and the heterogeneous integration.

As the name suggests, the SoC technology integrates different ICs into a single platform and makes the system function as a single component. To save up the spacing in a single processor and reduce power consumption, the vertical stack of multiple components like CPU, internal memory, I/O ports, etc., is performed on a microchip, which can later be placed on various targets platforms. The short interconnection between IC chips enables high-speed information processing and faster execution. With huge benefits of compactness and power efficiency, the SoC is recently treated as a breakthrough solution and the most important technique for packaging electronics. At this moment, its application has been expanded to powering desktop computers, exemplified by the MacBook powered by an ARM-based SoC, Apple's M1 chip, 2020 [19] (Fig. 10.12).



Figure 10.12 System-on-integrated chip die for AI application (left) and ultra-speed memory system-in-package (HBM2E, SK Hynix).

The SiP contains multiple IC chips stacked vertically using the flip-chip technique on the discrete carrier package, EMC-molded to a discrete module. The modules are combined horizontally with passive devices to a single substrate without causing low yield problems as in the MCM package. Multifunction is enabled by accommodating several specialized chips such as CPU, GPU, DRAM, flash memory, RF modules as separate components, similar to that of a motherboard-based PC. With the higher integration within the package, the system can achieve a much smaller form factor with multifunctions and flexibility in its design and size predetermined by various chip and substrate suppliers. By this virtue, the SiP integration technologies were rapidly adopted in mobile phones, GPS modules, and wireless Bluetooth applications. The heterogeneous integration is a more updated and compiled version of the SiP and SoC integration, where the separately produced modules are assembled into a much tighter level of aggregate so that the package can provide larger versatility in use and tailored characteristics cut out for each application.

Thanks to successful settlements of the 5 G network, the world begins to bask in system technologies, which enable various applications such as IoT, clouding computing, edge computing, supercomputing, wearable device, and AI. The 5 G broadband covers both the sub-6 GHz spectrum, where its frequency ranges from 900 MHz to 6 GHz, and the radio mmWave spectrum, where its frequency ranges from 24 to 100 GHz. The enhanced mobile broadband transmits data rates up to 10 Gbps and provides low communication latency down to 1 Ms. Industry 4.0, virtual reality (VR), augmented reality (AR), smart factory, and autonomous vehicles are suddenly rising applications by virtue of 5 G capability. In 2019, the US Federal Communications Commission opened up an experimental 6 G spectrum, covering 95 GHz to 3 THz. The forthcoming 6 G, by 2030, technology will offer ultra-high-speed data rate, low latency, precise localization, and sensing to cover the applications beyond the predecessor's capability, such as Industry 5.0, extreme reality (XR), metaverse, and space and deep-sea tourism [21].

To pace with the marvelous developments in network technology and the chip and device industry, advanced approaches in packaging design and materials should be followed. Especially with accompanying the integrated multichip technologies, the encapsulant materials are required to have electrical insulation performance with low loss dielectric constant (D_k) and dissipation factor (D_f) . To achieve a 5 G grade signal transmission rate and manage big data, a circuit's transmission loss must be avoided. Including Henkel, DuPont, Hitachi, Arakawa, the world's best resin and film supplier, devotes research and development for the materials with low D_k or low D_f properties by varying polymer chemistry or filler loading. In the same vein, thermomechanical properties such as CTE and the thermal dissipation ability of the composite become critical. With a much more crowded allocation for multiple chips and designs in a much smaller device or package, the number of interfaces between heterogeneous materials within a package drastically increases. The heat generated is prone to be trapped in thermal interfaces, resulting in the deterioration of the IC chips or devices. The polymeric adhesives are usually located in the place of the problem while their CTE value is too high (range $20-80 \text{ ppm/}^{\circ}\text{C}$) and thermal conductivity is too low (range 0.1-0.3 W/mK) to address the issue. To address heat management, many thermal interface materials are widely applied in heat sink bonding, encapsulating, BGA die heat spreader interface, and chip size packages in the forms of pastes, pads, and films. By filling up an inorganic particle that suits performance and cost, such as silica, alumina, boron nitride, graphite, carbon nanotube, silver, and metal carbide (MXenes), up to 80 wt.% in the composite effectively ameliorate the CTE and thermal dissipation properties within the system. Naturally, the filler-loaded composite won't be fully cured by UV and needs additional postcure by heat.

A rapid cure profile is the most wanted foundation technique for future packaging designs. A lower temperature cure can omit the need for step cure and reduce the cure-induced stress and heat generation inside the package. Simplified storage, dispensing, and pressing/molding process will ease the manufacturability and complexity, boosting throughput and yield, which is the greatest weakness of the heterogeneous packaging.

10.5 Summary

- Some important features and requirements for developing rapid cure composites in the semiconductor packaging are summarized as follows.
- Profound understanding of the material, process, cure equipment and parameters, and packaging design should be preceded.
- The rapid cure approach is highly differentiated according to the resin (epoxy, silicone, acrylate), cure agent, and cure type (UV or heat) and should consider cure profile preset, which is customized to each packaging manufacturer.
- During the cooling and heating procedure for a cure, hot and cool shrinkage can occur, distorting and warping the polymeric materials. A rapid cure strategy must include the remedy for relaxing cure-induced stress.
- Among the major semiconductor packaging products, SMA, dicing-DAF, underfill, ECA, and glob-top encapsulant highly demand a rapid cure strategy to reduce the long processing queue time. They usually consist of epoxy resin, latent cure agent, and high loading of filler whose composition can be altered by resin or film vendor for rapid cure.
- New RoHS 3 regulation and REACH list ban the use of lead-included material (solder) and some SVHC materials (epoxy and solvent involved). Antimonate-based or fluorineincluded cationic cure agents are awaiting their turns and need to be replaced soon. A new rapid cure strategy must conform to the worldwide and each regional green regulations.
- Advanced package design such as SoC, SiP, and heterogeneous packaging, is currently available or developed for the massive data processing imposed by near-future applications like IoT, VR, autonomous vehicles, and AI. The packaging materials, squished into more cramped chip or packaging, are required to have high electric insulation properties (low D_k and D_f), high thermal conductivity, extremely low hygroscopic (moisture absorption, diffusion), and low CTE. When an engineer adjusts the cure profile for a composite, those properties shall be considered so that they will not be compromised after the full cure.

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