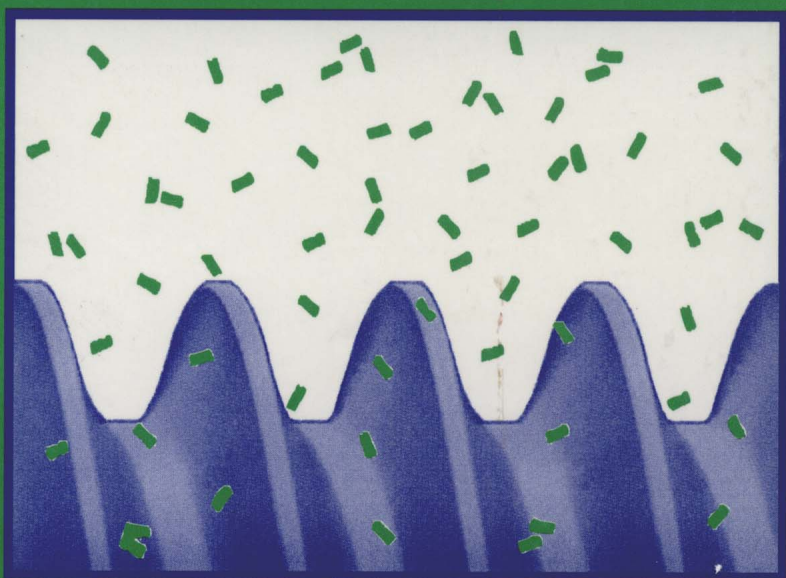


SOLID-STATE SHEAR PULVERIZATION

*A New Polymer Processing
and Powder Technology*



KLEMENTINA KHAIT
STEPHEN H. CARR

Solid-State Shear Pulverization

a **TECHNOMIC**[®] publication


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I dedicate my book chapters to the loving memory of my late husband, Ekhiel F. Khait, M.D., and to my children Irene and Alexander.

Klementina Khait

I dedicate my contributions in this book to my wife, Virginia McMillan Carr, and my daughters, Rosamond and Louisa.

Stephen H. Carr

Preface

This book is the first extended look at a new and multifaceted polymer processing technology that has already been discussed in numerous journal articles. Called Solid-State Shear Pulverization (S^3P), this innovative process produces polymeric powders with unique physical properties not found in the output of conventional size-reduction methods such as ambient or cryogenic grinding. This technology, which utilizes a pulverizer based on a modified co-rotating twin-screw extruder made by the German manufacturer Berstorff, has profound implications for both the creation of new polymer blends and the recycling of plastic and rubber waste.

Some principles of S^3P have their origins in work by Percy Bridgman at Harvard University in 1935. Bridgman studied the transformation of solid substances under simultaneous action of high shear and compression. Following up on his research on solids, scientists in Europe, the former Soviet Union, the United States, and Japan studied chemical reactions in polymers induced by the application of mechanical energy. They termed this new field of science “mechanochemistry.”

Excellent books in the field of polymer mechanochemistry have been published by Baramboim in the former Soviet Union [1], Simionescu and Oprea in Romania [2], and Porter and Casale in the United States [3]. These authors provide comprehensive reviews of topics including polymer stress reactions, methods for characterization of these reactions induced by stress, and mechanical synthesis of block and graft copolymers due to the formation of a chemically reactive species that they called mechanoradicals. Subsequently, Sohma in Japan reviewed methods for producing mechanoradicals in the solid state and molecular approaches to fracture of polymers [4].

Extensive research was conducted by Enikolopyan and co-workers since the early 1970s at the Russian Academy of Sciences, which resulted in the development of Elastic Deformation Grinding (EDG) of polymers. This was a new method of producing powder in a batch mixer or an extruder by first melting a polymer and then grinding it to powder. Despite numerous publications during the past 30 years by the Russian researchers, however, the mechanism of powder formation via EDG is not yet fully understood. These workers eventually came to refer to EDG as “Solid-State Shear Extrusion” (SSSE).

I first became interested in EDG (or SSSE) technology in the late 1980s. Initially, I was intrigued by the idea of applying mechanochemistry to the in-situ compatibilization of mixed plastics from the waste stream. Unlike SSSE, where polymers are melted prior to pulverization, I proposed pulverizing mixtures of polymers with the S³P process, which does not involve melting. By contrast, S³P maintains polymers in the solid state and avoids the additional heat history that occurs during the SSSE process, which can be detrimental to the physical properties of pulverized materials. The research and development of the S³P technology at the Polymer Technology Center at Northwestern University has grown significantly since 1990 from the development of a new plastics recycling process to a much broader polymer processing method that allows intimate mixing of polymers with very different viscosities, solid-state dispersion of additives, including pigments, and continuous production of powder with unique shapes and large surface areas. Polymeric powders are of growing importance to plastics processors due to the increased use of plastics in various applications, such as rotational molding, powder coatings, and compounding, which require powder as the feedstock.

In more recent years, it has become clear that this process allows for in-situ compatibilization of dissimilar polymers by applying mechanical energy to cause chemical reactions. This aspect of the S³P technology that we describe in this book should interest those individuals who are developing new polymer blends with the use of pre-made compatibilizing agents. In addition, it has been discovered that S³P efficiently mixes polymer blends with different component viscosities, resulting in the elimination of phase inversion. The S³P process directly produces blends with matrix and dispersed phase morphology like those obtained after phase inversion during a long melt-mixing process. This phenomenon is of practical importance because a long processing time is required by conventional melt-mixing to produce a stable blend morphology. S³P is also advantageous for producing thermoplastic or thermoset powder-coating compounds in a one-step process as opposed to a conventional multi-step operation that involves melt extrusion followed by batch grinding. The major capabilities of this new process can be summarized as follows:

- continuous powder production from plastics or rubber feedstocks
- blending of immiscible polymers

- efficient mixing of polymers with unmatched viscosities
- environmentally friendly recycling of multicolored, commingled plastics waste
- solid-state dispersion of heat-sensitive additives
- engineered plastic/rubber blends

It is hoped that this book will be of use both as a general technical resource and as a class text for undergraduate or graduate courses centered on polymeric powder production, polymer blends, efficient mixing of polymers, and dispersion of additives in plastics. The book should also be of interest to scientists, engineers, and processors, including those involved in the recycling of both pre- and post-consumer plastic and rubber waste. Because the S³P process allows economical recovery of mixed plastics without sorting by type or by color, diverse markets should emerge for utilizing S³P-made powders in creating many new value-added consumer products from recycled waste.

KLEMENTINA KHAIT

DEVELOPING novel methods for processing polymeric materials has been a large and crucial field of opportunity for over a century, and the S³P process, with which this book is largely concerned, seems likely to become a significant technology in this area. The compelling advantages of the S³P process include its ability to make fine powders of polymeric materials (plastics as well as elastomers), its ability to create intimate mixtures from very heterogeneous feeds, and its ability to alter physical properties—often making improvements over those of the constituents themselves—in the resulting blends. This latter effect is due, in part, to the mechanochemistry that occurs to the material undergoing S³P processing. When I first learned of the S³P process from Dr. Khait about a decade ago, it was immediately clear to me that this was a technology for which I would want to make a contribution, and it has been a pleasure to do so over that period of time. I sincerely wish to express my appreciation to her for letting me become a research collaborator in the advancement of this technology. Furthermore, the intellectual challenges associated with trying to understand its fundamental aspects are substantial—just as a professor would wish!

STEPHEN H. CARR

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Overview of Polymer Powders

POLYMER powders are desired for a host of purposes, some of which relate to processing advantages but others of which relate to the nature of the final form. The nearly ubiquitous form of industrial polymers, molding pellets, offers many advantages such as near fluid-like handling characteristics without the risk of dust formation and an ability to be stirred for good mixing or heat transfer. Processing methods, including common extrusion and injection molding, have been optimized over the past decades for the efficient use of molding pellets [1].

Other techniques, however, such as rotational molding and metal coating, cannot be performed well with molding pellets [2]. Here, polymer powders offer the distinct advantage of uniform deposition of the in-process material and its nearly instantaneous fusion rate. Molding pellets lack these characteristics because their discrete, fraction-of-a-gram particles have relatively high thermal masses and, therefore, exhibit a sluggish tendency to stick together when heat is applied. Achieving thin, uniform polymer coatings by depositing polymer solutions works well but requires the management of large amounts of solvent (with its attendant cost penalty). Powders, on the other hand, lack these drawbacks altogether.

There is a common set of general requirements for powders [1]. These include the following:

- (1) Non-sintering during storage
- (2) Low melt viscosity at low shear stresses
- (3) A wide range between melting and degradation temperatures
- (4) Good dry-flow characteristics, e.g., low tendency to bridge and a modest value of critical angle of repose

- (5) Low moisture sensitivity
- (6) No significant emission of volatiles during processing
- (7) Rapid cure after powder fuses, if a thermoset

The properties of the material undergoing pulverization relevant to selecting the appropriate size reduction strategy include the following:

- (1) Toughness/brittleness/hardness
- (2) Cohesivity of the particles/particle shape
- (3) Heat sensitivity
- (4) Toxicity
- (5) Potential for producing explosive dusts

The first two of these property groups are specific to the way particles break apart, and the last three deal with unavoidable considerations related to the size-reduction operation itself.

A further significant factor is the shape of particles produced during the formation of polymer powders. Equiaxed particles lead to the best behavior in a powder mass, especially in terms of flow characteristics, but elongated particles lead to the most rapid fusion characteristics. Semi-crystalline polymers, especially polyolefins, are usually highly ductile and are, therefore, more difficult to pulverize. During size reduction, these materials acquire high amounts of elastic strain energy and so will fracture according to the different energy release rates for energy accumulation and for particle cleavage. Cross-linking poly(ethylene) via irradiation or chemical means reduces this ductility and makes the material behave better in size reduction processes.

Polymers in the form of fine, free-flowing powders can be obtained by a variety of methods, including solution precipitation, isolation of nascent polymer directly from its synthesis reactor, and mechanical size reduction. This latter approach is by far the most commonly practiced. The fundamental considerations in the formation of polymer powders center on the simple idea of subjecting polymers to stresses sufficient to break pieces into successively smaller particles. In general, making powders is an act of size reduction, and the various strategies employed fall into these categories:

- (1) Crushing
- (2) Impacting
- (3) Cutting
- (4) Exploding
- (5) Solution Spraying

Machinery for doing this comes in all imaginable configurations, converting pellets or flakes into powder using cutting action or exploiting crushing forces. Some equipment is capable of varying temperature (especially to create cryogenic conditions) so as to modify the properties of the in-process material. Comminution is the generic term for these processes in which particulates are reduced in size by repetitive grinding via compression or impact. Mechanically ground powder typically has particles ranging from 10 to 40 mesh (2,000 to 420 μm) in diameter. Commonly, these methods produce particle size distributions that conform to the log-normal function. Interestingly, there is also a limited amount of particle enlargement that also occurs during pulverization processes. Particle enlargement is termed “granulation” or “cold welding.”

The energy consumed in pulverizing materials is exceptionally large, and most of that energy is dissipated in moving material within the equipment, rather than in the direct process of cleaving particles and making new surfaces. The fate of the energy distributes as follows:

Machine losses	13 percent
Heat dissipated in material	85 percent
Size reduction	<1 percent

Typically, only 30 percent of a material is size-reduced to the desired size in a single pass.

Of significant note, and of major concern in this book, is the novel process for producing polymer powders, Solid-State Shear Pulverization (S^3P). S^3P involves processing a feed stream of ground or shredded polymer fed into a modified co-rotating twin-screw extruder *with cooling applied along the barrel where heat is ordinarily applied*. The in-process material is not allowed to enter the molten state; otherwise, the process would fail to have the desired effect. Accordingly, the discharged material is the desired, free-flowing powder.

Feed materials may include any *or all* of plastics, fibers, rubbers, or any combination of them suitable for S^3P processing. The essential action responsible for the benefit of S^3P lies in the intense shear stresses to which in-process particles become subjected. This process not only performs size reduction very efficiently, but it also produces particles whose surfaces have been modified to be chemically reactive. Such reactivity created by a mechanical process is termed mechanochemistry, and it is well-known to occur in size reduction of many materials. S^3P represents the most controllable size-reduction process ever employed, and it can be put to good advantage for adding value to the material being put through it.

S^3P operates successfully on virtually all polymers, as Dr. Khait and her co-workers began learning during the 1990s. Some alterations are occasionally