

Polymer Science and Technology Series

Particulate-Filled Polymer Composites

颗粒充填型聚合物复合材料

Editor: Roger Rothon

Addison Wesley Longman

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POLYMER SCIENCE AND TECHNOLOGY SERIES

PARTICULATE-FILLED POLYMER COMPOSITES

Editor: ROGER ROTHON

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Preface

When David Briggs asked me if I would put together a book on particulate-filled polymer composites, I was delighted to accept, and hence this work was started on its long journey from concept to publication.

In my career I have been involved in many aspects of the subject, from new filler production, through the design of novel surface modifiers to the development of new filled composites, and also in the setting up and running of the ICI Fillers Club. As a result I had long felt the need for a work that dealt with the fundamentals in a way that was accessible to the many people from different industries and disciplines who, often temporarily, find themselves involved with, and bewildered by, the subject. I also wanted to address the unfair, but widely held view, that the area of particulate-filled composites is mundane compared to the glamorous area of fibre-filled ones. Having experience of both fields, it is my firm belief that particulate systems offer equally rewarding intellectual challenges and opportunities for product differentiation. Moreover, the variety of materials and of effects being sought is probably greater.

Just like the subject itself, the topic is a truly composite one. It brings together many scientific and technological disciplines. This is well illustrated by the scope of the references in the present work, which are drawn from many fields including mineralogy, crystallography, precipitation and crystal growth, powder technology, surface and colloid science, organic and organometallic chemistry, optics, materials science, and polymer science and technology. It also brings together people from different industries such as filler producers, machinery manufacturers, polymer compounders, and suppliers of processing aids and of surface modifiers.

As with any composite, there are complex interfacial problems which create a great deal of misunderstanding between the various groups involved, and this leads to inefficiency in developing and introducing new products. Some specialist works do exist, but these concentrate very much on specific aspects and are usually technological and written from the perspective of one industry.

This then has been the central theme of my approach to this book. Together with my co-authors, all chosen for their long and deep association

with the topic and the esteem with which they are regarded within the industry, I have set out to describe the fundamentals involved in producing, characterizing and using particulate fillers in as clear and concise a way as possible. The authors have been encouraged to pay particular attention to those areas of their subject which experience shows them to cause the most confusion or are poorly treated elsewhere. Furthermore, where a subject is controversial or poorly understood they have been encouraged to interpret the existing literature, not merely to quote opposing views, as so often happens. Where possible, use has been made of previously unpublished work to illustrate key points and extensive literature references are provided so that any subject can be followed up in depth if needed.

Chapter 4 on surface modification is a good example of the approach. In most works this subject is dominated by organosilanes. While they are still treated in detail here, a similar amount of space is given to fatty acids and to organotitanates. Fatty acids are of great commercial use, and can exhibit complexities that can cause problems for the unwary. Considerable controversy exists about the mode of action of organotitanates, which is usually glossed over in favour of reporting of effects. The available scientific literature on the subject is critically reviewed here, probably for the first time.

As with any editor, I am very much indebted to my co-authors for their hard work. I am also indebted to staff at Longmans for their support and encouragement, and to all those involved in turning our amateurish copy into a professional product. I should also like to express my particular thanks to Professor Derek Birchall, FRS, who first aroused my interest in this subject and has given me great support over many years.

In addition to the colleagues specifically acknowledged in the text, I should like to acknowledge the helpful discussions with my former colleagues in ICI, especially in the Fillers Club, and particularly Reg Ashley and Martin Evans who have worked with me for many years. I also want to thank my present colleagues in the Manchester Metropolitan University and in the CSIRO Division of Minerals. I also express special thanks to several friends and colleagues who have helped me to maintain an interest in the industrial development of particulate fillers since leaving ICI, especially Adrian Ryder of Premier Periclase Limited, Yves Horel of Mines de la Lucette and last, but certainly not least, Ian Howard-Smith of Queensland Metals Corporation Limited.

Finally, I must express my thanks to my wife Pamela and to my children for their tolerance and understanding while I have been engaged in this labour of love. They may find it hard to adjust now that I am free for conversation and wanting to watch my choice of television programmes!

R N ROTHON

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General principles guiding selection and use of particulate materials

R N ROTHON AND M HANCOCK

1.1 Introduction

Particulate-filled polymer composites have a long history and newcomers to the field usually expect to find an area of well-understood science with few intellectual challenges remaining. Unfortunately they are usually amazed to find that this is far from the truth with few reliable generalizations (but several unreliable ones) available and much basic information yet to be established.

The main reason for this is that, in the early composites such as clay-filled rubber, the filler was added primarily to reduce price, although other properties such as hardness and tack were changed. Any physical effects of filler changes were minimized (see Chapter 7) because natural rubber was the only one available, and indeed there was little interest in understanding what was happening or even in differentiating between filler types. This attitude has been carried through the years and it is still possible to find in a treatise on plastics that fillers are characterized simply as 'inert' and 'reinforcing'; clays are still referred to as 'soft' and 'hard'; and the authors have frequently heard any white powder called 'chalk' whether it is clay, talc or calcium carbonate. This lack of knowledge or even interest has been aided by the fact that there are many mineral producers around the world who still simply extract a material from the ground and sell it with very little beneficiation, few specifications or attempts at categorization. A consequence of the above is that much work – fundamental research, technical development and even commercialization – has been and is being done on poorly defined 'fillers'.

Changes started to occur with the reinforcement of synthetic rubbers by carbon black, which was followed by such developments as the modification of the electrical performance of PVC by calcined clay and the use of precipitated calcium carbonate to improve the impact properties of UPVC (unplasticized PVC). The understanding of properties of fillers and of filled composites has grown apace in recent years.

The purpose of this chapter is to prepare readers for this situation, and to give them sufficient background so that they may approach the subject with an open mind and see the whole area as one with stimulating intellectual challenges, not as an area of mystery and witchcraft.

The principal aims of this chapter are to show how fillers can be characterized and defined with the least ambiguity, how their behaviour in composites can be predicted, to highlight the principal sources of misunderstandings and limitations imposed by methods of measurement, and to explain why and where deviations from general rules are likely to occur.

1.2 Basic characteristics of particulate fillers

In developing a particulate-filled composite, the formulator needs to be able to answer the following questions:

1. What property benefits are being sought?
2. What deleterious changes may also occur and can they be tolerated?
3. How easy is the filler to handle and how might it affect processing?
4. Are special additives needed?
5. What is the true cost of using the filler, is it justifiable and are there more cost-effective alternatives?

Information in answer to the above has to be supplied by the filler producer and usually covers cost, purity, particle size and shape, density, hardness, optical and thermal properties, and chemistry, although frequently data may be sparse. A brief description of each factor and its measurement follows.

1.2.1 Cost

In theory this is a fairly simple topic but one that causes considerable problems for the unwary. It is widely assumed that polymers are expensive and fillers are cheap, and many articles on filled polymers start with the statement that fillers are used to cheapen. While this can sometimes be the case, these savings are frequently not as great as anticipated and, in quite a few instances, compound costs, even with the lowest cost filler, can be higher than the unmodified polymer. There are two principal reasons for this.

Firstly, the process of compounding filler into polymer costs money in the form of capital investment, manpower and energy:¹ more energy is often required to process the filled material than the virgin polymer. In cases where compounding is essential because other additives such as stabilizers or curatives have to be added to the polymer, then the cost of

incorporating a filler is markedly reduced. In these cases, exemplified by elastomers, PVC and thermosets, the use of fillers is the rule rather than the exception as is the case with, say, polyethylene.

Secondly, prices of fillers and polymers are usually quoted in weight terms, while the majority of their composites are used on a volume basis. The specific gravity of most fillers is 2–3 times that of most polymers and, while raw material savings may accrue on a weight basis, more of the final compound will have to be used than would be the case with the unfilled polymer. When looking at potential cost-savings comparison of polymer and filler costs must be made on a volume basis. On this basis one should generally regard the effective raw material costs of mineral fillers as 2–3 times their price (by weight). As a consequence many fillers will not give significant cost savings in the commodity plastics such as polypropylene and this explains why the emphasis today is on achieving specific effects. However, while fillers may not 'cheapen' a filled composite they may well produce a cost-property performance that allows the composite to compete against and often replace more expensive systems. This is discussed in Chapter 8.

1.2.2 Chemistry, composition and impurities

While the chemical nature of the filler is frequently of little direct importance to its use in composites, it plays two important roles (perhaps even the key roles) in that it determines the structure of the mineral, and also the nature of the interaction between polymer and filler. However, away from these *a priori* considerations, only chemically reactive fillers affect the properties of a composite.

1.2.2.1 Bulk chemistry

Intrinsically fillers can be divided into two types, reactive and non-reactive. Reactive fillers will react with their environment. A good example of this is gibbsite, alumina hydrate, which will react with both acidic and basic substances. Alumina hydrate also loses its water of crystallization at around 200°C. Other fillers exhibit similar behaviour to a greater or lesser extent.

The silicate minerals (kaolin, mica, talc, quartz, etc) are, in classical chemical terms, virtually inert, only being attacked by very strong acids and alkalis. The carbonate minerals and the hydroxide minerals are very reactive to acids.

The interactions between the constituent elements in a filler determine its crystallinity, which then dictates all the intrinsic properties of the filler.

Table 1.1. Surface energies of fillers and plastics

Filler	Surface energy (MJ m^{-2})
Diamond	10 000
Mica	2 400 500
Glass	1 200
Titanium dioxide	650
Kaolin	500–600
Calcium carbonate	65–70
Stearate-coated calcium carbonate	28
Talc	65–70
Polymers	15–60
Polypropylene	31

The genesis of the filler will dictate impurities present and these play an important role in determining the properties of the filler.

1.2.2.2 Surface chemistry

Surface chemistries are invariably different from bulk chemistry but, unfortunately, in general, are poorly understood. They do play a very important role in determining the nature of the interaction between mineral and polymer. Because of the interest in this very important topic, techniques for surface characterization are covered below and in detail in Chapter 3.

1.2.2.3 Surface interactions

Polymers have a very much higher (20–30 times) thermal expansion than mineral fillers and thus, in a well-dispersed composite, there will be an intimate interaction between matrix and filler. This results from a radial compressive stress developing on cooling, the value of which can be calculated, and which depends on both polymer and filler.² Because of this the interaction will at the very least be mechanical, but other types will exist depending on the surface chemistry of the filler and also the chemistry of the polymer.

Wettability of filler by polymer is an indication of compatibility between the two. This cannot be measured directly but the effect that the material has on surface tension of a liquid is a measure of its surface energy. Usually water is chosen as the medium. Schlumpf³ has reported surface energies for a variety of fillers (Table 1.1). There have been a wider number of claims that surface energies determine the forces between polymer chains and different phases, determining mechanical properties of the composite.

Adhesion at a polymer–filler interface has been shown to exert a considerable influence on mechanical responses, and a correlation between

acid-base characteristics of filler and polymer (determined by inverse gas chromatography) and properties has been established.⁴

Lewis acid-base interactions between filler and polymer are claimed to be the most important component in the adhesion of filler to polymer and thus in determining properties of the composite.⁵ For a given filler-polymer system, the strength of interfacial acid-base bonding may be appreciably enhanced by surface modification of the filler giving large increases in properties.

1.2.2.4 Spectroscopy

The ultraviolet and visible spectra of the common fillers are largely featureless unless there are significant levels of transition metal ions in the mineral, when strong absorptions will occur. However, the most important practical aspect is the infra-red (IR) spectrum of a filler. This arises from the nature of the chemical bonds present and will be unique for each filler type. A common use of IR spectroscopy is as an analytical tool to identify a filler. An important practical consequence of a filler's IR absorption is the use of certain fillers in horticultural and agricultural films (see Chapter 8). Spectra of some of the more common minerals incorporated in a low-density polyethylene film are shown in Fig. 1.1. Calcium carbonate shows only two strong absorption bands because the only energy absorptions occur in the CO_3^- ion (bending, stretching and deformation modes). Kaolin, a complex aluminosilicate, shows a much more complicated IR spectrum: after calcining, the —Al—O—Si— bonds rearrange and the resultant product has a very complex IR pattern with several broad, overlapping bands.

1.2.2.5 Chemical analysis

The purity of a filler is of importance both commercially and technically, i.e. the users need to know what they are buying, whether it contains materials that may be detrimental to their product properties and whether it will cause environmental problems. Impurities include trace elements that may be adsorbed on the filler surface or be in the structure of the filler and ancilliary minerals, which will have been formed at the same time as the main mineral (see Chapter 2). Frequently these impurities do not detract from the use of the filler. On the other hand, small traces of some impurities, if present on the surface in an active form, can seriously affect polymers. Examples are certain transition metals (e.g. iron, manganese, copper), which can seriously affect colour and thermal stability if present in an active form, even at levels of a few parts per million. Fillers are seldom analysed for such low-level impurities and it is a mistake to

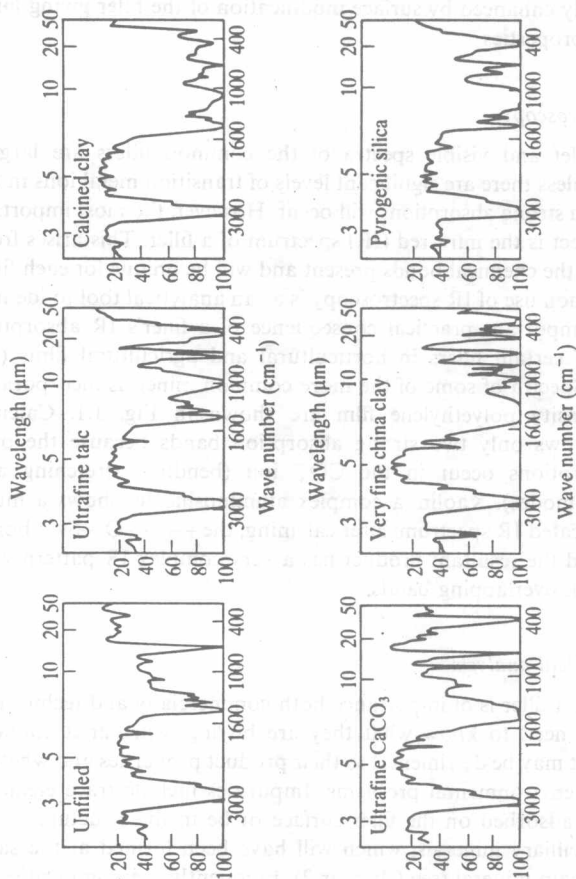


Figure 1.1 Infra-red spectra of mineral-filled polyethylene films.