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Developments in Plastics Technology – 3

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DEVELOPMENTS IN PLASTICS TECHNOLOGY—3

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CONTENTS OF VOLUMES 1 AND 2

Volume 1

Volume 2

PREFACE

Because of the sheer size of the plastics industry, the title *Developments in Plastics Technology* now covers an incredibly wide range of subjects or topics. No single volume can survey the whole field in any depth and so what follows is therefore a series of chapters on selected topics. The topics were selected by us, the editors, because of their immediate relevance to the plastics industry.

When one considers the materials produced and used by the modern plastics industry, there is a tendency to think of the commodity thermoplastics (such as poly(vinyl chloride) or polyethylene); the thermosetting materials are largely ignored. Because of this attitude we are very pleased to include in this volume a chapter which deals with the processing of a thermosetting material, i.e. the pultrusion of glass reinforced polyester.

The extrusion of plastics is, of course, a very important subject but an aspect which is often overlooked is the need to remove volatile matter during processing: for this reason we have included a chapter on devolatilisation. Current industrial practice is towards materials modification and this attitude is reflected in the chapters on the transformation of ethylene vinyl acetate polymers and the use of wollastonite in two important thermoplastics. When assessing the performance of materials, there is a tendency to concentrate on short-term mechanical tests and ignore such topics as fatigue and longer-term testing. We are therefore very pleased to include a chapter on this subject.

Over the past few years, since the advent of cheap computing power, there has been a tremendous growth in the science of computer modelling of processes such as injection moulding and extrusion. This interest is reflected in what is the longest chapter in the book and which is devoted to computer-aided analysis of some thermoplastic processing operations. Alternative methods of polymer processing are always being sought in an effort to reduce costs, save energy or to obtain unusual properties in selected components. One such technique is solid phase compaction and a review of this interesting technique is presented.

Each of the contributions was written by a specialist in that field and to them all, we, the editors, extend our heartfelt thanks, as writing a contribution for a book such as this, whilst doing a full-time job, is no easy task.

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CONTENTS

Chapter 1

PULTRUSION

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1. INTRODUCTION

The pultrusion technique is a closed mould system for the manufacture of fibre/matrix composites. It is one of the few fully automated continuous processes used in the reinforced plastics industry. The technique is finding increasing application in industries that range from the manufacture of domestic products to aircraft construction.

The technique is a process whereby constant section shapes are produced by pulling fibre filaments through a heated die, the filament having been previously impregnated with resin. The actual processes are described in Section 3.

The products are generally straight and can take most geometrical cross-sectional shapes, although recently some products which are curved in the longitudinal direction have been manufactured.

In all processes the production procedure can essentially be divided into three steps which are assigned to corresponding parts of the production line. These are:

(a) feed-in and impregnation;
(b) shaping and curving;
(c) pulling and cut-off.

The greatest technical problems appear in steps (a) and (b) above. The first processing section is an important part because the final product depends upon the care with which the reinforcement material is fed in and impregnated. For economic reasons the highest possible operating speed is desired.

2. CHARACTERISTICS OF THE CONSTITUENT COMPONENTS OF PULTRUSION

2.1. Basic Constituents

The pultrusion composite is manufactured basically from the components:

(a) the polymer;
(b) the fibre reinforcement.

A third component, the filler, may be incorporated into the composite to either impart a specific inservice property or to displace the polymer for economy reasons.

All types of filamentary reinforcements can be utilised in the pultrusion process. These reinforcements would generally be in the form of rovings, tows, mat, cloth or any combination of these fibres. The majority of the products available commercially use E-glass filaments in their various forms but high modulus fibres, such as carbon, may also be used.

The resin systems utilised include polyesters, which constitute about 85% of the annual volume of pultrusion stock, and epoxides.

2.2. The Polymerisation Process for Polyesters

The unsaturated polyesters generally used in reinforced plastics consist of an unsaturated ester dissolved in a vinyl monomer which is able to be polymerised and which provides three-dimensional chain cross-linking. Such resins are not materially different from those used in hand lay-up processes. The solution is then polymerised under the influence of heat and/or a peroxide catalyst to provide an infusible thermoset. Polymerisation is initiated as the catalyst breaks down into free radicals under the influence of the energy derived from the heat. A chain reaction then occurs, causing the molecules to react and unite; the rate of catalyst decomposition is dependent upon the temperature. Consequently, the rate of polymerisation can be controlled by regulating the temperature and the amount of catalyst used. Catalysts for pultrusion processes are commonly based on benzoyl peroxide.

Theoretically, the reaction should proceed to the situation where all unbroken double bonds of the original unsaturated mixture have been reacted by the free radicals; however, in practice only about 92% of the unsaturated polyester is converted. When 35–40% of the unsaturated polyester is converted, gelation takes place and when about 80% is converted, an incomplete cure exists.

2.3. The Polymerisation Process for Epoxies

Epoxy resins are characterised by the presence of epoxide groupings which may exist in the raw materials or may be formed during the reaction. The curing process of the resins is achieved by using either hardeners or curing agents. The polymerisation process occurs by either:

(a) a catalytic reaction in which the epoxide groups or the resin molecules interact; or
(b) a cross-linking reaction in which copolymerising molecules unite with the epoxy resin molecules, so becoming a part of the cured resin network.

During the polymerisation of epoxies the exotherm begins before gelation commences; this is contrary to the sequence for the polyesters.

Frequently the epoxy polymers exhibit higher viscosities than the polyester polymers; consequently, the former require longer filament wet out times. In addition, it is more difficult to remove the entrapped air and to dissipate volatiles in the epoxy polymers. However, systems which are solventless are available and are particularly suited to pultrusion. In order to obtain high quality epoxy composites it is desirable to apply pressure to the system at approximately the time that gelation commences.

2.4. Comparison of Epoxy and Polyester Polymers in the Pultrusion Technique

Polyester and epoxy polymers exhibit a number of different characteristics, all of which lead to different levels of complexity in the pultrusion technique. The main differences are:

(a) the variation in the polymerisation shrinkage;
(b) the interface adhesion between the pultrusion section and the adjacent mould surface.

Referring to item (a), the volume reduction of polyesters varies between about 7 and 10% whereas the equivalent value for epoxies varies between about 1 and 2%; the majority of this volume reduction occurs at the time of gelation. As the resin cures and shrinks in the die, the stock surface separates from the die surface. The resulting decrease in frictional force allows for lower pull loads and possibly faster line speeds. The high degree of shrinkage of polyester resins can cause a problem when pultruding stock with a large cross-sectional area. In many cases, low profile additions (e.g. polyethylene) are needed to control the external cracks caused by this shrinkage. A major reason for polyester stock being capable of high speed and low full loads is the high degree of shrinkage associated with the material.

The frictional forces that accumulate due to the shear of the epoxy resin/die interface are considerably higher than those for polyester impregnated stock due to the longer period of cure and the lower shrinkage at gelation. Consequently, the epoxies are more difficult to pultrude than the polyesters and those which can be pultruded have line speeds considerably below those of the polyesters. The shrinkage characteristics of the epoxy affect the ease with which the pultruded section can be detached from the inside of the die. If, in addition, a mandrel is used to form a hollow closed section, attachment of the section to the die may take place.

With regard to (b), the epoxy resins produce higher adhesion forces during the pultrusion process than the polyesters because of the assimilation of hydrogen groups from amine curing agents and because of the effects of low surface tension.

The effects of shrinkage and internal adhesion and hence the interface traction may be minimised by techniques such as using slip sheets, waxing or plating the die, applying external die releases or using internally acting ones.

2.5. The Reinforcing Materials

There are four main types of fibres used in the pultrusion technique; these are:

(a) E-glass fibre;
(b) S-glass fibre;
(c) aramid fibre (based on aromatic polyamides);
(d) graphite (carbon) fibre.

The primary type of fibre used in the system is the E-glass; the other reinforcements are mainly for the aerospace industry and for the manufacture of advanced composites for space applications. It is possible to obtain greater stiffness from the pultruded section by replacing the E-glass fibre with a hybrid reinforcement consisting of glass and carbon fibre.

2.5.1. Glass Fibre Roving Reinforcement

Glass fibre rovings may be used in the pultrusion process to provide high longitudinal strength and stiffness. In addition, they provide the tensile strength required to pull the reinforcing fibre array through the die. The amount and location of these reinforcements are determined at the design stage.

2.5.2. Glass Fibre Mat Reinforcement

The continuous strand mat provides the most economical method of obtaining a high degree of transverse physical properties. The mats are layered with rovings and this combination forms the basic reinforcement composition for most pultruded products.

2.5.3. Glass Fibre Veils

The pultrusion technique is a low pressure process and the glass fibre reinforcement tends to position itself close to the surface of the composite. This can affect the appearance, corrosion resistance and the handling of the products. Glass fibre and polymeric veils can be added to the laminate construction to depress the reinforcement from the surface, thus providing a polymer rich surface to the composite. The two most commonly used products are surface tissues of high alkali content glass (A-glass) or a chemical resistant glass (C-glass), and polymeric veils of polyester if this is the parent material.

2.5.4. Woven and Knitted Fabrics

If the mechanical properties of the pultruded composite cannot be satisfied by conventional mat/roving arrangements, then selected woven products can be utilised to meet the end-use requirements. These products can be used by themselves or in conjunction with the standard mat construction to obtain the required strength and stiffness. The woven glass fibre reinforcements are available in directions which are balanced, mainly longitudinal, mainly transverse or 45° ply construction. As these materials are more costly than those mentioned above, the composites which utilise them are more expensive than the standard construction pultrusions.

2.5.5. Other Reinforcing Fibres

Graphite (carbon) and aramid fibres are also used in the pultrusion technique in the form of roving and woven fabric. These fibres can be used separately or in conjunction with glass fibres and add considerable stiffness to the composite. As these fibre materials are very expensive the optimum cost performance must be borne in mind when designing with them.

3. THE PROCESSING TECHNIQUES

The processing techniques for producing pultrusion sections can be divided into three categories. These are:

(a) the horizontal pultrusion process;
(b) the vertical pultrusion process;
(c) the lamination process with film tapes.

Each of these processes has particular characteristics which make it more suitable for certain areas of application.

In all the above types of pultrusion processes the production procedure can be divided into three stages; these are:

(a) the insertion of the fibre and matrix and the impregnation of the component parts;
(b) the shaping and curing of the composite;
(c) the pulling of the components through the dies and the cut-off of the composite.

The first stage of manufacture is an important one as the final composite depends upon the care with which the reinforcement material is fed into the system and is impregnated. From an economic viewpoint, it is necessary to achieve the highest possible operating speed; consequently, the impregnation process must be consistent with this speed. However, pultrusion components usually have a high glass fibre content and, therefore, the penetration of the resin mixture through the glass is difficult to achieve with high operating speeds.

3.1. The Horizontal Pultrusion Process

The horizontal pultrusion equipment for production of simple rod stock existed in the early 1950s. Round, elliptical or square cross-sectional rods, reinforced with continuous fibres of high fibre content and tubular profiles of small diameter, are generally manufactured by this method. This is because this process was developed first and it is also more convenient to manufacture long sections horizontally. The horizontal pultrusion process can be divided into three types:

(a) the resin impregnation bath process with a steel die;
(b) the resin impregnation bath process with several short dies;
(c) the injection moulding process.

3.1.1. Resin Impregnation Bath Process with Steel Dies

The resin impregnation baths are used in most production lines. In order to facilitate the impregnation of the fibres, the strands are separated by rollers or bars which the fibres pass over and under, thereby achieving a certain milling effect which promotes the impregnation process. Before entering the die, the strands are combined together again. Strands in the form of rovings are generally used and may be combined with mat, cloth or other fibre arrangements, or the latter fibres may be used without rovings but care must be taken to ensure that sufficient fibre material in the longitudinal direction (the pull direction) is available to accommodate the pulling force.

The wetting speed of the fibres depends on their pre-treatment and on the resin mixture. Consequently, the type of sizing agent used and the type of binder play an important role, as does the length of wetting time. The length of the resin impregnation bath is limited only by practical considerations and the pot life of the resin mixture.

The shaping and the curing of the composite take place primarily in the steel dies, where the lengths vary from 500–2000 mm. The dies are generally heated electrically or they may be heated indirectly with oil as the heat carrier. The gelling and the curing of the composites takes place within the die.

The distance, the maximum temperature and the length of the gelling zone from the entrance to the die are dependent upon:

(a) the reactivity and the amount of resin;
(b) the peroxides used;
(c) the pulling speed;
(d) the thickness of the composite profile walls.

Figure 1 is a photograph of a horizontal pultrusion machine manufactured by Pultrex Ltd, Clacton, Essex, UK. Figure 2 is a typical diagrammatic view of a Pultrex machine which is a free