

Handbook of
**Advanced Composite
and Polymers
Manufacturing**

Techniques, Processes and Applications

Gerrard Brison
Editor

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POLYMERS MANUFACTURING**
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Preface

Composite materials, in most cases fibre reinforced polymers, are nowadays used in many applications in which light weight and high specific modulus and strength are critical issues. The constituents of these materials and their special advantages relative to traditional materials are described in this paper. Further details are outlined regarding the present markets of polymer composites in Europe, and their special application in the automotive industry. In particular, the manufacturing of parts from thermoplastic as well as thermosetting, short and continuous fibre reinforced composites is emphasized. Composite material, in its basic form, is a heterogeneous combination of two or more materials, differing in form or composition. The structural strength of composites greatly depends on the nature of the bonding at the interface, the mechanical load transfer from the matrix (polymer) to the CNTs and the yielding of the interface. If the interface is weak, a crack formed at the interface will cause fracture and result in failure of the composite. In this aspect, CNTs are better than traditional macro-fibres due to their ability to inhibit nano and micro cracks.

Composites are made up of individual materials referred to as constituent materials. There are two main categories of constituent materials: matrix and reinforcement. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination. Engineered composite materials must be formed to shape. The matrix material can be introduced to the reinforcement before or after the reinforcement material is placed into the mould cavity or onto the mould surface. The matrix material experiences a melding event,

after which the part shape is essentially set. Depending upon the nature of the matrix material, this melding event can occur in various ways such as chemical polymerization or solidification from the melted state. A variety of moulding methods can be used according to the end-item design requirements. The principal factors impacting the methodology are the natures of the chosen matrix and reinforcement materials. Another important factor is the gross quantity of material to be produced. Large quantities can be used to justify high capital expenditures for rapid and automated manufacturing technology. Small production quantities are accommodated with lower capital expenditures but higher labour and tooling costs at a correspondingly slower rate.

Many commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, PEEK, and others. The reinforcement materials are often fibres but also commonly ground minerals. The various methods described below have been developed to reduce the resin content of the final product, or the fibre content is increased. As a rule of thumb, lay up results in a product containing 60% resin and 40% fibre, whereas vacuum infusion gives a final product with 40% resin and 60% fibre content. The strength of the product is greatly dependent on this ratio.

This book offers a comprehensive description of the applications of various fields in this subject. The book will be appropriate as a guide for students.

—*Editor*

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Chapter 1

Polymer Chemistry

In polymer chemistry, branching occurs by the replacement of a substituent, e.g., a hydrogen atom, on a monomer subunit, by another covalently bonded chain of that polymer; or, in the case of a graft copolymer, by a chain of another type.

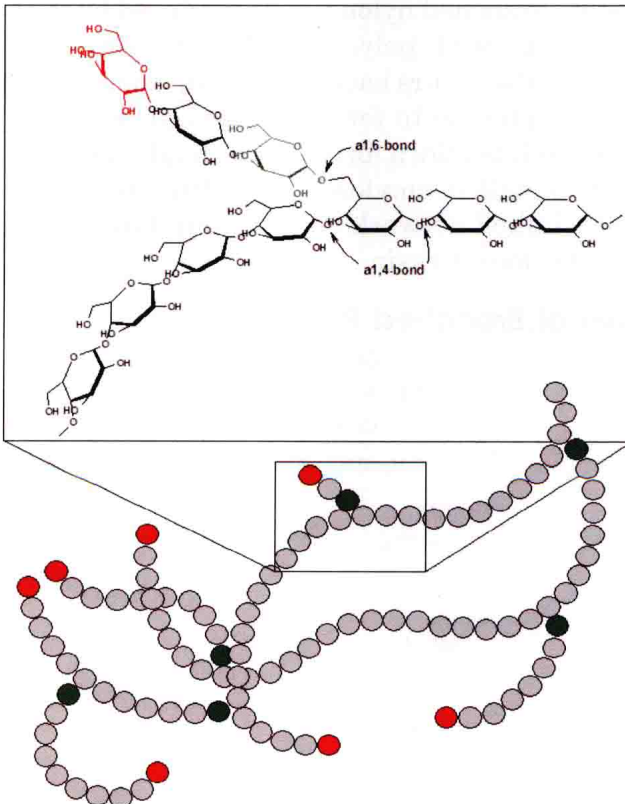


Figure: Glycogen, a branched polysaccharide

In crosslinking rubber by vulcanisation, short sulfur branches link polyisoprene chains (or a synthetic variant) into a multiply branched thermosetting elastomer. Rubber can also be so completely vulcanised that it becomes a rigid solid, so hard it can be used as the bit in a smoking pipe. Polycarbonate chains can be crosslinked to form the hardest, most impact-resistant thermosetting plastic, used in safety glasses.

Branching may result from the formation of carbon-carbon or various other types of covalent bonds. Branching by ester and amide bonds is typically by a condensation reaction, producing one molecule of water (or HCl) for each bond formed.

Polymers which are branched but not crosslinked are generally thermoplastic. Branching sometimes occurs spontaneously during synthesis of polymers; e.g., by free-radical polymerisation of ethylene to form polyethylene. In fact, preventing branching to produce linear polyethylene requires special methods. Because of the way polyamides are formed, nylon would seem to be limited to unbranched, straight chains. But “star” branched nylon can be produced by the condensation of dicarboxylic acids with polyamines having three or more amino groups. Branching also occurs naturally during enzymatically-catalysed polymerisation of glucose to form polysaccharides such as glycogen (animals), and amylopectin, a form of starch (plants). The unbranched form of starch is called amylose. The ultimate in branching is a completely crosslinked network such as found in Bakelite, a phenol-formaldehyde thermoset resin.

Special types of Branched Polymer

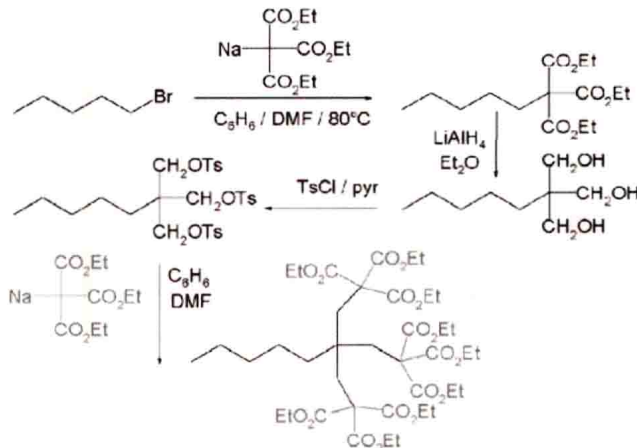


Figure: Dendrimer synthesis first generation Newkome 1985

- A graft polymer molecule is a branched polymer molecule in which one or more the side chains are different, structurally or configurationally, from the main chain.
- A star polymer molecule is a branched polymer molecule in which a single branch point gives rise to multiple linear chains or arms. If the arms are identical the star polymer molecule is said to be regular. If adjacent arms are composed of different repeating subunits, the star polymer molecule is said to be variegated.
- A comb polymer molecule consists of a main chain with two or more three-way branch points and linear side chains. If the arms are identical the comb polymer molecule is said to be regular.
- A brush polymer molecule consists of a main chain with linear, unbranched side chains and where one or more of the branch points has four-way functionality or larger.
- A polymer network is a network in which all polymer chains are interconnected to form a single macroscopic entity by many crosslinks.
- A dendrimer is a repetitively branched compound.

Branching in Radical Polymerisation

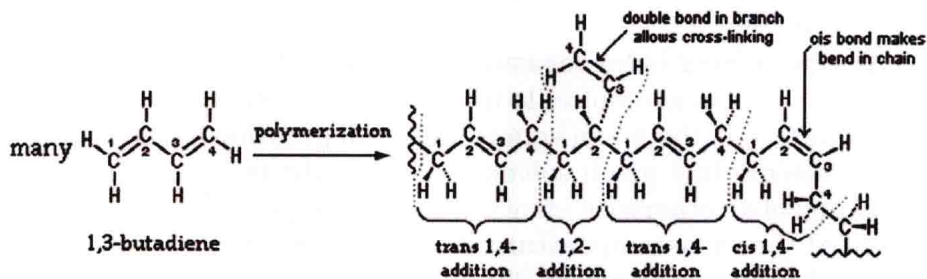


Figure: Polymerisation of 1,3-butadiene

In free radical polymerisation, branching occurs when a chain curls back and bonds to an earlier part of the chain. When this curl breaks, it leaves small chains sprouting from the main carbon backbone. Branched carbon chains cannot line up as close to each other as unbranched chains can. This causes less contact between atoms of different chains, and fewer opportunities for induced or permanent dipoles to occur. A low density results from the chains being further apart. Lower melting points and tensile strengths are evident, because the intermolecular bonds are weaker and require less energy to break.

The problem of branching occurs during propagation, when a chain curls back on itself and breaks - leaving irregular chains sprouting

from the main carbon backbone. Branching makes the polymers less dense and results in low tensile strength and melting points. Developed by Karl Ziegler and Giulio Natta in the 1950s, Ziegler-Natta catalysts (triethylaluminium in the presence of a metal (IV) chloride) largely solved this problem. Instead of a free radical reaction, the initial ethene monomer inserts between the aluminium atom and one of the ethyl groups in the catalyst. The polymer is then able to grow out from the aluminium atom and results in almost totally unbranched chains. With the new catalysts, the tacticity of the polypropene chain, the alignment of alkyl groups, was also able to be controlled. Different metal chlorides allowed the selective production of each form i.e., syndiotactic, isotactic and atactic polymer chains could be selectively created.

However there were further complications to be solved. If the Ziegler-Natta catalyst was poisoned or damaged then the chain stopped growing. Also, Ziegler-Natta monomers have to be small, and it was still impossible to control the molecular mass of the polymer chains. Again new catalysts, the metallocenes, were developed to tackle these problems. Due to their structure they have less premature chain termination and branching.

Branching Index

The branching index measures the effect of long-chain branches on the size of a macromolecule in solution. It is defined as $g = \langle s_b^2 \rangle / \langle s_l^2 \rangle$, where s_b is the mean square radius of gyration of the branched macromolecule in a given solvent, and s_l is the mean square radius of gyration of an otherwise identical linear macromolecule in the same solvent at the same temperature. A value greater than 1 indicates an increased radius of gyration due to branching.

Polymer Brush

Brush polymers are a class of polymers that are adhered to a solid surface. The polymer that is adhered to the solid substrate must be dense enough so that there is crowding among the polymers which then, forces the polymers to stretch away from the surface to avoid overlapping.

The stretched form of the polymers adhered to the solid surface often have different properties than the polymer chains in solution and therefore, often affects the behaviour and results in the novel properties of several brush polymers. Brush Polymers are formed by an assembly of polymer chains adhered by one end to a surface or an

interface. The assembly of polymer brushes allows for tailor-made surfaces for various applications.

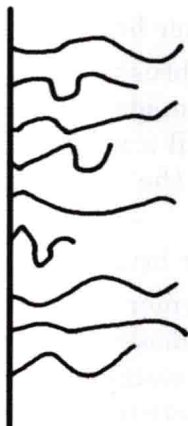


Figure: Depiction of Polymer Brush Classifications

The diverse applications of brush polymers on solid surfaces and at liquid interfaces allows for several applications including new adhesive materials, protein-resistant biosurfaces, chromatographic devices, lubricants, polymer surfactants and polymer compatibilizers. Polymer brush structures have existed in nature for quite some time. Examples of naturally occurring polymer brushes include extracellular polysaccharides on bacterial surfaces, neurofilaments and microtubules with associated proteins in neuritis, and the proteoglycans of cartilage. In particular, ultrathin polymer coatings are of particular interest for the surface modification of small (nano) particles. Some of these applications include antithrombogenic and anti-inflammatory which can allow for enhanced compatibility of biomaterials.

History

Interest in brush polymers was gained in the 1950s when it was discovered that the aggregation of colloidal particles can be prevented by grafting polymer molecules to them. Van der Waarden found that by grafting hydrocarbon chains to carbon black particles, aggregation could be inhibited and thus, founded a new movement in polymer science. In 1975, S. J. Alexander began focusing on theoretical study of polymer brushes. He noted the distinctive properties of polymer brushes through theoretical analysis of adsorption of functionalised polymers on flat surfaces. The theoretical work started by Alexander was later elaborated on by de Gennes and by Cantor which stressed the application of tethered polymers in defining brush polymers.

Classifications of Linear Brush Polymers

There are several various types of brush polymers including:

- Flexible homopolymer brush
 - A homopolymer brush refers to an assemblage of tethered polymer chains made up of a single type of repeat unit. This would entail a polymer solely made up of monomer A resulting in the polymer (-A-A-A-A-A-A-A...) after polymerisation.
- Mixed homopolymer brush
 - Mixed homopolymer brushes refer to an assemblage of tethered chains made up of two or more different types of repeat unit. For example, in a mixed homopolymer brush system where there are only two different polymer chains, each chain would be made up of a single monomer repeat unit. Also, each of these polymers would be made up of a different repeat unit thus, conferring different physical properties to a brush polymer. Two possible polymers in a mixed homopolymer system could be made up of a monomer A and a monomer B leading to the polymerisation of the polymers (-A-A-A-A-A-A-A...) and (-B-B-B-B-B-B-B...).
- Random copolymer brush
 - Random copolymer brushes refer to an assemblage of tethered polymer chains consisting of two different repeat units which are randomly distributed along the polymer chain. In a random copolymer system with the monomer A and monomer B, the resulting polymer would be completely random with no patterned distribution along the chain. An example of a resulting polymer could be (-A-B-A-A-B-A-B...).
- Block copolymer brush
 - Block copolymer brushes refer to an assemblage of tethered polymer chains consisting of two or more homopolymer chains covalently connected to each other at the ends. In a block copolymer system, “blocks” of single repeat units would be repeated along the polymer chain that is subsequently attached or polymerised from the target polymer or solid substrate. An example of a block copolymer brush with the monomers A and B could yield the resulting polymer, (-A-A-A-B-B-B...).

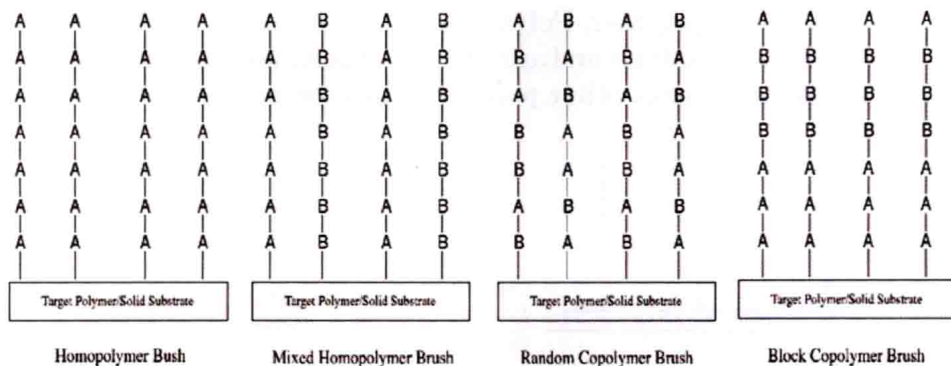


Figure: *Depiction of Polymer Brush Classifications*

Synthesis

There are several strategies that have been employed to synthesize brush polymers thus, increasing interest in their various possible applications. Brush polymers can be synthesized using any of the various polymerisation techniques available including: cationic, anionic, radical, ring-opening metathesis, photochemical, and electrochemical polymerisation. There have also been recent advances using controlled radical polymerisation (CRP) techniques such as atom transfer radical polymerisation (ATRP), reversible addition-fragmentation chain transfer polymerisation (RAFT (chemistry)), and nitroxide mediated polymerisation (NMP). These techniques have emerged as powerful synthesis techniques due to their ability to control polymer growth. Although there are several techniques for brush polymer synthesis, most people outline their synthesis strategy around the “grafting from” and “grafting to” approach and then decide which polymerisation tools to employ based on their specific needs.

- One particular method which is very common in brush polymer synthesis is the “grafting to” approach. The “grafting to” approach is advantageous for adding pre-synthesized polymers to a common polymer backbone. Pre-synthesized polymers can be purchased relatively cheaply and attached to a common polymer backbone with a variety of synthesis methods. Some of the common methods used to synthesize brush polymers include anionic and cationic polymerisation as well as adsorption methods such as chemisorption and physisorption. Although a wide variety of brush polymers can be quickly assembled using pre-synthesized polymers, a major disadvantage associated with brush polymer synthesis is that achieving high density polymer grafting becomes more difficult with increased

size of the polymer. Polymers tend to no longer remain linear with increased size and aggregation of polymers near the polymer backbone blocks other potential sites for polymerisation.

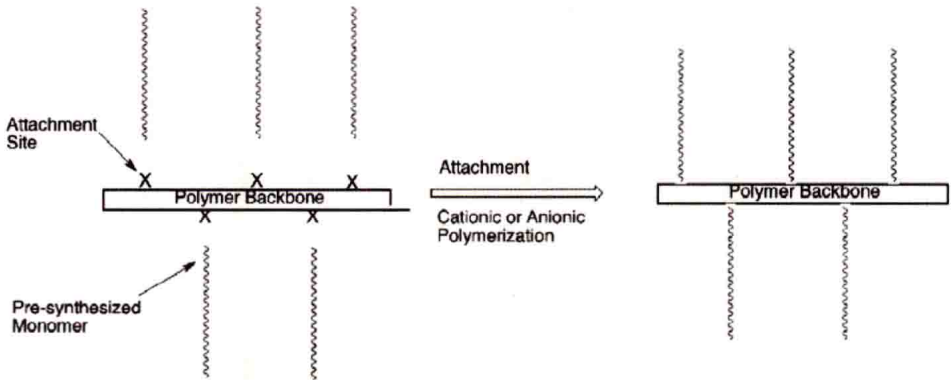


Figure: Example of “grafting to” synthesis for brush polymers”

- Another method for synthesis of brush polymers is the “grafting from” approach. The “grafting from” approach is advantageous because you can “grow” polymers from the common polymer backbone. In order to carry out the “grafting from” approach, the polymer backbone needs to have a radical initiator site which can supply the radical necessary for radical polymerisation or controlled radical polymerisation (CRP). Using the “grafting from” approach is extremely advantageous because it gives every radical site on the polymer backbone an equal chance for polymerisation. Therefore, much larger chains can be polymerised onto the polymer backbone without having to worry about the size of the polymer chain blocking other polymerisation sites.

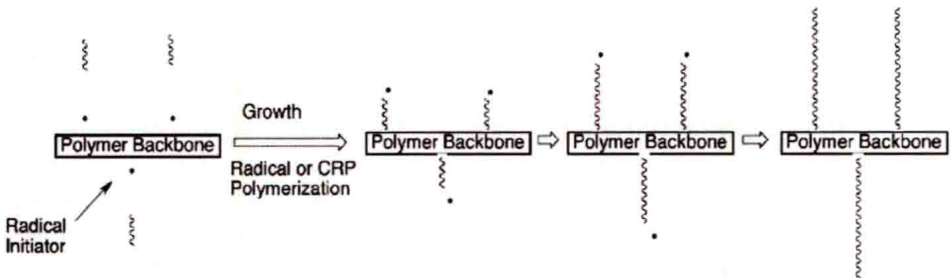


Figure: Example of “grafting from” synthesis for brush polymers”

- A hybrid approach to brush polymer synthesis is the “multi-step grafting approach”. This is mostly used to create surface-grafted or polymer-grafted hyperbranched polymers. The synthesis of hyperbranched polymers can be achieved through