

C H A P T E R 1

INTRODUCTION AND SCOPE

Nowadays the polymeric materials are used in a lot of applications due to their interesting properties. However, they present some limitations, such as their high flammability and the shrinkage upon polymerization and polymer curing.

This chapter discusses the contribution in the recent years to improve the two limitations above mentioned, and explains the aims of this thesis.

- 1.1.** Introduction
- 1.2.** Scope and Purpose of this thesis

1.1 INTRODUCTION

Over the last few decades the replacement of conventional materials by synthetic polymeric materials has increased dramatically owing to the versatility, low density, and sometimes novel properties of the latter. Although the polymers have become widely accepted in a lot of applications, many of them are extremely flammable and, in presence of sufficient heat and oxygen, burn easily and rapidly. The problem is not only the destruction of the material but the smoke and toxic gases generated which are the main causes of hazards in a fire. This has led to the introduction of stricter legislation and safety standards concerning flammability in the plastics industry and on the fire resistant materials market.

To find methods to minimise polymer flammability it is important to understand the thermal decomposition processes of polymeric materials. The combustion of a polymer is a complex process involving a series of interrelated and/or independent stages which take place in the condensed phase and the vapour phase, and at the interface between these two phases. The most important step in the burning of a polymer is the fuel production stage, in which an external heat source causes an increase in temperature, resulting in the dissociation of chemical bonds and the evolution of volatile fragments. These volatiles diffuse into the air to create a flammable mixture, which starts the combustion when this mixture reaches the ignition temperature. Flaming combustion is exothermic and generates energy, in the form of heat transferred back to the material, to decompose the polymer further thus producing more fuel and so maintaining the combustion cycle (Figure 1.1).¹

Successful strategies to reduce the flammability of a material involve breaking one or more stages of the combustion cycle to reduce the rate or change the mechanism of combustion. All flame retardants act in the vapour

¹ Ebdon, J. R.; Jones, M. S. Flame Retardants. *Polymeric Materials Encyclopedia*; J.C. Salomone, Ed., CRC Press, Boca Raton, 1996, Vol 3, p. 2397.

phase and/or the condensed phase through a physical or chemical mechanism², which are described below:

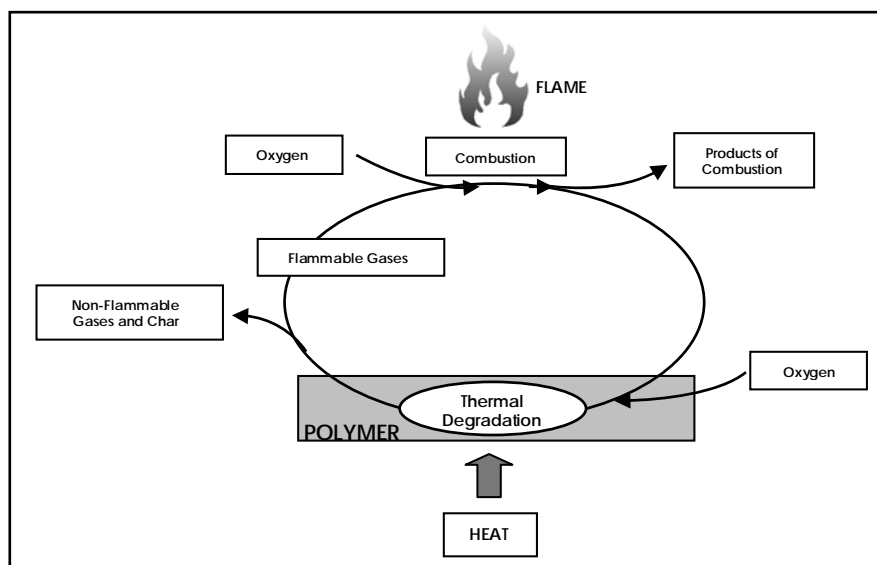


Figure 1.1. Combustion cycle of a polymer.

(a) Char formation: Some flame retardants act in the condensed phase promoting char formation on the surface, which acts as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air.

(b) Intumescent layer: In this case, the flame retardants swell when exposed to fire or heat to form a porous foamed mass, which acts as a barrier to heat, air and pyrolysis products.^{3,4}

² Lu, S.-Y.; Hamerton, I. *Prog Polym Sci* 2002, 27, 1661.

³ Camino, G.; Costa, L.; Luda, M. P. *Macromol Symp* 1993, 74, 71.

⁴ Le Bras, M.; Bourbigot, S.; Revel, B. *J Mater Sci* 1999, 34, 5777.

(c) Reactions in the vapour phase: Vapour-phase retardants act interfering with the free radical reactions involved in flame propagation.⁵⁻⁷

(d) Cooling: The cooling happens when the flame retardant decomposes endothermically to cool the pyrolysis zone at the combustion surface.^{8,9}

(e) Dilution: The dilution could take place in the solid or vapour phase. In the former, the flame retardant acts to dilute the polymer and reduce the concentration of decomposition gases. In the latter, the flame retardant decomposes to inert gases, which act to dilute the flammable gases.

There exist two different approaches to achieve flame retardancy in polymeric materials; these are known as the additive type and reactive type. Additive type flame retardants are incorporated into the polymer by physical means, generally during processing. This obviously provides the most economical way to achieve flame retardancy. Nevertheless, they have several disadvantages, such as poor compatibility, leaching from the polymer, particularly if used for external applications and they may even volatilize during use. They also have to be used in significantly high concentrations in order to be effective, which may in turn affect the physical and mechanical properties of the polymer.^{2,10} On the other hand, the reactive flame retardants involve a covalently bond with the flame-retardant unit and the polymer. The reactive strategy may be achieved in two ways: by simple copolymerization of monomers containing flame-retardant groups and by modification of the existing polymers.^{11,12} The relatively low loadings required to achieve sufficient flame retardancy to a large extent maintain the original physical and

⁵ Camino, G.; Costa, L. *Polym Degrad Stab* 1988, 20, 271.

⁶ Gann, R. G.; Dipert, R. A.; Drews, M. J. *Encyclopedia of Polymer Science and Engineering* 2nd ed.; Wiley-Interscience: New York, 1987, Vol. 7, p. 154.

⁷ Rosser, W. A.; Inami, S. H.; Wise, H. *Combust Flame* 1966, 10, 287.

⁸ Vandersall, H. L. *J Fire Flamm* 1971, 2, 97.

⁹ Papa, A. J. *Flame Retardancy of Polymeric Materials*. Kuryla, W. C.; Papa A. J. Eds., Marcel Deker: New York, 1975, Vol 3.

¹⁰ Cullis, C. F.; Hirschler, M. M. *The Combustion of Organic Polymers*. Clarendon Press, Oxford, 1981.

¹¹ Price, D.; Pyrah, K.; Hull, R.; Milnes, G. J.; Ebon, J. R.; Hunt, B. J.; Joseph, P.; Konkel, C. S. *Polym Degrad Stab* 2001, 74, 441.

¹² Ebdon, J. R.; Hunt, B. J.; Jones, M. S.; Thorpe, F. G. *Polym Degrad Stab* 1996, 54, 395.

mechanical properties of the polymer. Furthermore, the flame retardant is thus not easily lost from the polymer, eliminating one of the major problems associated with the additive approach.^{13,14}

Although in the last few years there has been an increase of heteroelements used in flame retardants, the commercial market is still dominated by compounds based on halogens, notably bromine and chlorine. They present exceptional efficiency, acting basically in the vapour-phase by reacting with HO[•] and H[•] radicals⁵⁻⁷, which are responsible for propagation of combustion via chain branching. However, they have some negative aspects, particularly their potential for releasing toxic and corrosive gases as well as carcinogenic chemicals during combustion.¹⁵ A growing demand for ecological and safe flame retardant systems, with the growing number of restrictions and recommendations from the European Community and the United States government, has promoted the development of nonhalogen-containing flame retardants.

Phosphorus-containing polymers are considered environmentally friendly flame retardants because they generate less toxic gas and smoke than halogen-containing compounds.¹⁶⁻¹⁹ Phosphorus-based flame retardants are mainly active in the condensed phase and arise as a consequence of thermal generation of phosphorus acids (Figure 1.2). These acids change the thermal degradation mechanism of the polymer, promoting esterification and dehydration of the polymer to give a carbonaceous char layer, which insulates the material from the flame and also acts as a barrier to fuel transfer.^{1,20}

¹³ Matheu, D.; Nair, C. P. R.; Ninan, K. N. *Polym Int* 2000, 49, 48.

¹⁴ Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S.; Jeng, R. J.; Ma, C. *J Appl Polym Sci* 1996, 59, 1619.

¹⁵ Nelson, G. L. *The future of fire retarded materials: applications and regulations*. FRCA; 1994, p. 135.

¹⁶ Kishore, K.; Annakutty, K. S.; Mallick, M. *Polymer*, 1988, 29, 762.

¹⁷ Horrocks, A. R.; Zhang, J.; Hall, M. E. *Polym Int* 1994, 33, 3470.

¹⁸ Liou, G. S.; Hsiao, S. H. *J Polym Sci Part A: Polym Chem* 2001, 39, 1786.

¹⁹ Sato, M.; Yokohama, M. *J Polym Sci Part A: Polym Chem* 1980, 18, 2751.

²⁰ Camino, G.; Costa, L.; Luda, M. P. *Polym Degrad Stab* 1991, 33, 131.

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As an alternative to the use of phosphorus compounds as environmentally friendly flame retardants, silicon compounds can also be used. The flame retardancy arises partly from the property that such compounds have in diluting the combustible organic gases and partly from the barrier that siliceous residues can form to an advancing flame.²¹⁻²³

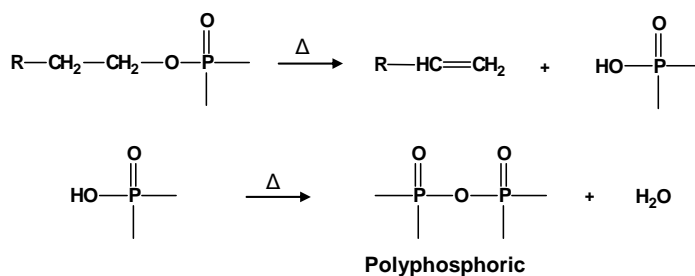


Figure 1.2. Thermal degradation of a phosphorus-containing polymer.

As mentioned above, phosphorus or silicon compounds can be used alone as environmentally friendly flame-retardant elements, and moreover, it has been described a synergistic effect when both elements are present in the material.²⁴⁻²⁸ This means that the resulting flame retardance effect is greater than the predicted on the basis of the additivity effect of the individual elements. The reason for the synergistic effect is that phosphorus offers the tendency of char formation, and silicon provides the thermal stability of the forming char during fire.²⁸⁻³⁰

²¹ Lomakin, S. M.; Artois, M. I.; Zaikov, G. E. *Flamability of polymeric materials*. New York: Nova Science, 1996, p. 139.

²² Wu, C. S.; Liu, Y. L.; Shun, Y. *Polymer* 2002, 43, 4277.

²³ Ebdon, J. R.; Hunt, J. B.; Joseph, P. *Polym Degrad Stab* 2003, 83, 181.

²⁴ Liu, Y. L.; Chou, C. I. *Polym Degrad Stab* 2005, 90, 515.

²⁵ Chiang, C. L.; Ma C. C. M. *Polym Degrad Stab* 2004, 83, 207.

²⁶ Liu, Y. L.; Chiu, Y. C.; Wu, C. S. *J Appl Polym Sci* 2003, 87, 404.

²⁷ Hsiue, G. H.; Liu, Y. L.; Tsiao, J. *J Polym Sci Part A: Polym Chem* 2001, 39, 986.

²⁸ Hsiue, G. H.; Liu, Y. L.; Tsiao, J. *J Appl Polym Sci* 2000, 78, 1.

²⁹ Li, Q.; Jiang, P.; Su, Z.; Wei, P.; Wang, G.; Tang, X. *J Appl Polym Sci* 2005, 96, 854.

³⁰ Liu, Y. L.; Wu, C. S.; Chiu, Y. S.; Ho, W. H. *J Polym Sci Part A: Polym Chem* 2003, 41, 2354.

Another problem, often overlooked, that affects the polymeric materials is the shrinkage during polymerization and polymer curing, and the consequences can be presented in many different forms (Figure 1.3). For example, in cast electrical insulators, polymerization shrinkage can produce internal stress in the polymer, which can reduce the durability of the material as a consequence of the appearance of microvoids and microcracks. In molding applications, polymer shrinkage results in incomplete filling of the mold and poor replication of the mold surface. In polymeric coatings poor adhesion of the coating to the substrate can be observed.³¹



Figure 1.3. Typical polymer shrinkage problems.

The most common way in the industry of reducing the shrinkage during polymerization and polymer curing is through a physical approach, using inert fillers such as silica, mica, quartz, etc., and passive fillers such as polyvinylchloride powders, polystyrene beads, etc.^{31,32} It does mean that the dimensionally unstable polymer is replaced by fillers, which exhibit no dimensional change during the polymerization and cure processes. However, this method is not applicable in many encapsulating, potting, and impregnating applications due to the significant increase of the viscosity, which restricts

³¹ Sadhir, R. K.; Luck, R. M. Ed. Expanding Monomers. Synthesis, Characterization and Applications. CRC Press, Boca Raton, 1992.

³² Lee, H.; Neville, K. Handbook of Epoxy Resins. McGraw-Hill, New York, 1982, Chap. 14.

material flow, and mold fill. Another problem in the use of fillers is their tendency to settle out, and this leads to inhomogeneous systems.

To find new methods to intrinsically solve the shrinkage problem, it is essential to discover what causes it. One of the main causes is the fact that the monomer molecules are located at a van der Waals distance from one another, whereas in the polymer the monomeric units move to within a covalent distance of each other³¹⁻³⁵ (Figure 1.4). Therefore, the atoms are much closer to one another in the polymer than they were in the original monomer.

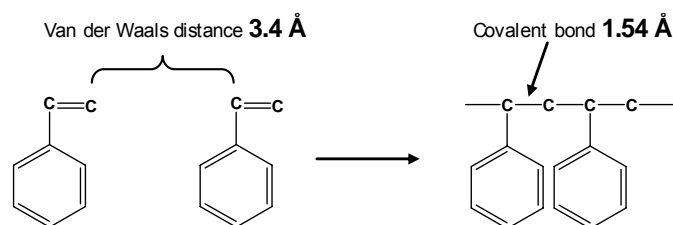


Figure 1.4. Bond changes which produce shrinkage during polymerization of styrene.

Another important factor that we have to take into consideration is the mechanism of the polymerization.^{33,34} In condensation polymerization, the shrinkage is also partially related to the small molecule which is eliminated during the formation of the new bond. Obviously, the shrinkage depends on the size and the amount of the eliminated molecules. During addition polymerization, even though there is no small molecule eliminated, there is still large shrinkage in many cases, because of the change in distance between atoms. In ring-opening polymerization, the shrinkage is less than in the other two cases just discussed. Not only is a small molecule not eliminated during the polymerization, but for every bond that undergoes a change from a van der

³³ Bailey, W. J.; *J Macromol Sci-Chem* 1975, A9(5), 849.

³⁴ Bailey, W. J.; Iwama, H.; Tsushima, R. *J Polym Sci. Polym Symp* 1976, 56, 117.

³⁵ Fukuda, F.; Hirota, M.; Endo, T.; Okawa, W.; Bailey, W. J. *J Polym Sci Part A: Polym Chem* 1982, 20, 2935.

Waals distance to a covalent distance, another bond goes from a covalent distance to a van der Waals distance.

In tables 1.1 to 1.3 some typical calculated shrinkages during polymerization of different monomers are listed. These are grouped under polymerization mechanism.

Table 1.1. Calculated shrinkage during condensation polymerization.

Monomer A	Monomer B	Shrinkage (%)
Diethyl adipate	Hexamethylenediamine	66
Dimethyl adipate	Hexamethylenediamine	31
Adipic acid	Hexamethylenediamine	22

Table 1.2. Calculated shrinkage for addition polymerization.

Monomer	Shrinkage (%)
Ethylene	66
Vinyl chloride	34.4
Styrene	14.5

Table 1.3. Calculated shrinkage during ring-opening polymerization.

Monomer	Shrinkage (%)
Ethylene oxide	23
Styrene oxide	9
Diglycidyl ether of Bisphenol A	5

To find monomers which would give near zero shrinkage or even expansion on polymerization, the most viable approach would be monomers which could polymerize under ring-opening polymerization. Above it was rationalized that the single ring-opening polymerization produces less shrinkage than any of the other forms of polymerization. Therefore, if monomers could polymerize under double ring-opening polymerization, less shrinkage or even some expansion could be expected. In 1973, William J. Bailey proposed that the compounds which fulfil this requirement are bicyclic compounds with fused rings. In the bicyclic monomer, for every bond that undergoes a shift from a van der Waals distance to a covalent distance, at least two other bonds shift from a covalent distance to a near van der Waals distance.^{31,36-38} These bond changes produce expansion as illustrated in Figure 1.5.

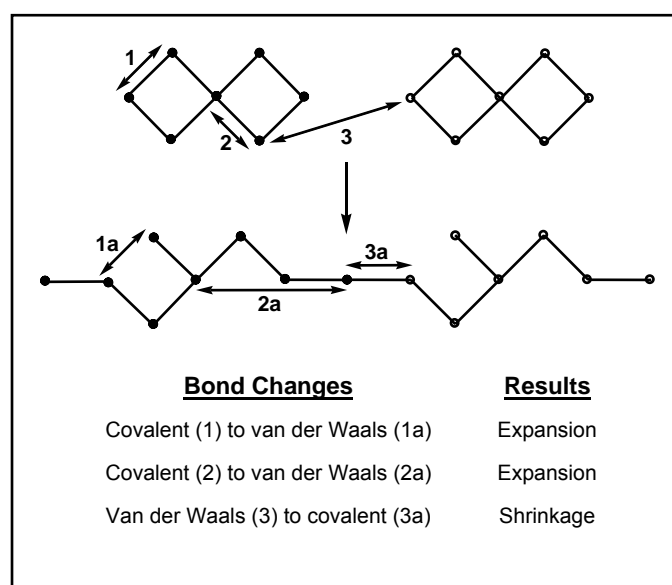


Figure 1.5. Bond transitions during the polymerization of a bicyclic compound.

³⁶ Bailey, W. J. *Elastoplast* 1973, 5, 142.

³⁷ Sanda, F.; Hitomi, M.; Endo, T. *J Polym Sci Part A: Polym Chem* 2001, 39, 3159.

³⁸ Nishida, H.; Sanda, F.; Endo, T.; Nakahara, T.; Ogata, K.; Kusumoto, K. *J Polym Sci Part A: Polym Chem* 1999, 37, 4502.

Furthermore, Bailey proposed two other requirements to get “expanding monomers”: (1) that each ring contain at least one heteroatom, so that the catalyst can be available for the polymerization (2) that the rings do not open in a symmetrical manner. For example, an oxygen atom in one ring may form a carbonyl group while the corresponding oxygen in the other ring would form an ether group.

There are several classes of compounds that fulfil all of the requirements. These include the spiroorthoesters (SOEs), the spiroorthocarbonates (SOCs) and the bicyclic orthoesters (BOEs).^{31,39-42} Their structure shown in Figure 1.6.

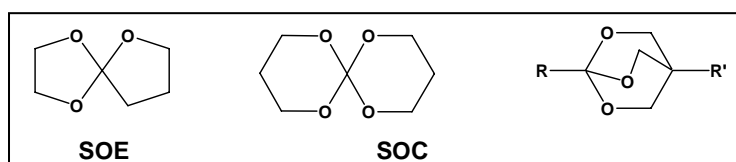


Figure 1.6. Expanding monomers.

Among them, SOEs are useful expanding monomers because they can be easily formed from epoxides and lactones. Thus, they have been chosen in this work to reduce the shrinkage.

1.2 SCOPE AND PURPOSE OF THIS THESIS

Until now there are not any approaches described in the literature that improve both the flame retardance and the shrinkage associated with the polymerization process. In some applications, like in the electronic industry, it is desirable to obtain materials that present these two properties. Thus, the purpose of the work reported in this thesis was to develop new materials which

³⁹ Takata, T.; Endo, T. *Prog Polym Sci* 1993, 18, 839.

⁴⁰ Cheng, K.; Takata, T.; Endo, T. *Macromolecules* 1995, 28, 3048.

⁴¹ Bailey, W. J.; Katsuki, H.; Endo, T. *J Am Chem Soc, Div Polym Chem* 1974, 155, 445.

⁴² Endo, T.; Okawara, M.; Saigo, K.; Bailey, W. J. *J Polym Sci Part C: Polym Lett* 1980, 18, 771.

combine flame retardancy properties and low shrinkage during polymerization and/or polymer curing. Several approaches have been developed to achieve these desired properties and are grouped in different chapters as follows:

Chapter 2 describes the synthesis and polymerization of novel phosphorus- and silicon-containing spiroorthoesters. Their application to modify epoxy resins, through the cationic copolymerization of these new spiroorthoesters with epoxy resins, and their properties were also evaluated. Moreover, the effect of combining phosphorus and silicon was also studied with the purpose of investigating the synergistic effect.

Chapter 3 describes the synthesis of new linear polymers that contain a spiroorthoester and phosphorus moieties in the side chain, obtained through a radical copolymerization of a spiroorthoester-containing acrylate with several phosphorus polymerizable monomers. In subsequent cationic ring-opening polymerization of the spiroorthoester moiety, the polymers were crosslinked with no accompanying volume shrinkage. Moreover, the application of the linear polymer containing SOE moieties in the side chain to modify epoxy resins was studied.

Finally, chapter 4 describes a new method of copolymerization of a spiroorthoester with epoxy resins using microwave irradiation and this system was then compared with conventional heating.