

## Thermal Decomposition Behaviour of Mixtures of Two Plastics

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When a mixture of two polymers is thermally decomposed, the behaviour of the component polymers may be different from that when degraded alone, whether in temperature range or in the pattern of decomposition, as a result of some form of interaction. Most polyblends are heterogeneous and the types of interaction which can occur strongly reflect this character: thus the commonest effects in decomposition of these systems involve migration of some mobile species from one phase into the other where it reacts with the polymer or interferes with its pattern of breakdown. In some cases stabilisation is observed, in others destabilisation. These effects are illustrated using examples taken from studies of systems involving several commercially important polymers.

### Introduction

The thermal decomposition behaviour of most of the commercially important polymers is now quite well understood in terms of the temperatures required for breakdown and the nature of the decomposition products, although in a few cases there remain areas of uncertainty or controversy regarding mechanism. It does not follow, however, that when two or more polymers are subjected to heat when mixed together, the component polymers will behave in the same way as when they are degraded alone. Many such systems have been studied in these laboratories and it has been found that some form of interaction often occurs, which may be reflected in a decrease or increase in stability, and changes in product composition may also be observed in some cases. Such changes in behaviour are of major importance in relation to recycling operations or to incineration of plastics waste. The purpose of this contribution is to illustrate typical effects in the decomposition of mixtures of two plastics and show why and how such behaviour occurs.

### Experimental

The results shown for illustration were obtained using thermal analysis and product analysis techniques. Thermogravimetry (TG) was carried out using a Du Pont 990 thermoanalyser at a heating rate of 10°/min in dynamic nitrogen. Thermal volatilisation analysis (TVA), a method developed in our laboratories based on measurements of pressure of evolved decomposition products in a continuously evacuated system [1], was also carried out at 10°/min. Studies using the latter approach were accompanied by separation and identification of the degradation products. The most volatile products were separated on the basis of their volatility [2], and the others mainly by GC-MS. Identification was based on IR spectroscopy and mass spectrometry.

The TVA method also allowed the effect of mixing to be detected very graphically in pairs of experiments making use of twin-limbed reaction tubes. The two polymers were degraded together. In the first experiment, each limb contained a single polymer so that although degraded together they were not in contact. This situation is referred to subsequently as "unmixed". In the second, a mixture of the two polymers was placed in each limb: this situation is referred to as "mixed". All other conditions in the two experiments (sample size,

heating rate, etc) were kept the same. Any observed differences in the TVA curves (or in the subsequent product separation and investigation) must therefore be due to the effect of mixing.

### **The Influence of Heterogeneity**

For thermodynamic reasons, most mixtures of two polymers are heterogeneous, involving a continuous phase of one polymer and a dispersed phase of the other. Such polyblends are quite often described as “incompatible”. As a consequence of this physical state, direct interaction between the two component polymers is only possible at the phase boundaries and such behaviour is in general only to be expected in certain cases involving mixtures of step-growth polymers which contain specific functional groups capable of coupling.

Small molecule decomposition products, or radical species which may be involved in the decomposition mechanism of one of the polymers, are free to migrate across the phase boundaries before they escape into the gas phase and these may induce reactions or interfere with reactions in the polymer other than the one from which they were produced. A range of possible effects may therefore result in decomposition of a two-phase polymer system. These divide into two groups: interactions involving small product molecules, and those involving small product radicals.

Small product molecules can interact by (a) reacting with the second polymer to alter one part of its chain structure; (b) reacting with an intermediate such as a macroradical involved in its decomposition. Such interactions will be reflected in some change in the pattern of breakdown of the second polymer.

Small product radicals can interact by reacting with the second polymer. These radicals, being highly reactive species, will seek to achieve stability by abstraction of hydrogen or other easily abstracted atom. This produces a macroradical of the polymer involved, which will then undergo further change.

Although radical intermediates, whether small or macroradical, are by their nature present in low concentration in any degrading polymer, their effects are of major importance in relation to observed behaviour.

### **Decomposition Behaviour of Single Polymers**

The following polymers have been selected for purposes of illustration: poly(vinyl chloride), polystyrene, polybutadiene, polyisoprene, poly(methyl methacrylate) and bisphenol A polycarbonate. After brief consideration of the thermal decomposition behaviour of these polymers when alone, under temperature programmed conditions, the behaviour of various two-component mixtures will be examined.

Poly(vinyl chloride), PVC. PVC is a polymer of quite low thermal stability. It breaks down in two stages, the first of which gives mainly hydrogen chloride in near quantitative yield relative to the initial chlorine content of the polymer. The loss of HCl occurs sequentially along the chain to give conjugation, so discoloration of the polymer is observed. In the higher temperature stage, chain fragmentation occurs to give coloured tars and a range of more volatile products. The dehydrochlorination probably proceeds by a radical chain mechanism although other routes may also contribute.

Polystyrene, PS. PS has moderate thermal stability. It degrades in a single stage to give

up to 50% of styrene monomer, together with smaller amounts of dimer, trimer, etc. and some tar and wax products. The molecular weight of the polymer falls sharply during depolymerisation. The mechanism involves initial backbone homolysis followed by depropagation and inter- and intramolecular transfer reactions of the macroradicals initially formed.

Polybutadiene, PB, and Polyisoprene, PI. PI is moderately stable and PB is of somewhat higher stability. PI breaks down in a single stage, but PB shows some initial weight loss before the main stage of decomposition. Both give both volatile and tar/wax products, the former in greater amount. The main volatile products are monomer and 4-vinylcyclohexene (cyclic dimer) from PB and monomer and dipentene (cyclic dimer) from PI. The less volatile fraction in both cases comprises mainly oligomers. The mechanism involves chain homolysis followed by depropagation and transfer reactions.

Poly(methyl methacrylate), PMMA. PMMA has fairly low thermal stability. Polymer made by the normal radical route shows two stages of breakdown unless the molecular weight is very high, but polymer made by the anionic route shows only a single stage of breakdown. If the polymer is pure, the sole product of breakdown is monomer. The mechanism involves chain homolysis near unsaturated chain ends, if present (as in PMMA made by the radical route), then at random at higher temperatures, followed in each case by depropagation to monomer with long "zip" length.

Bisphenol A Polycarbonate, PC. PC has high thermal stability and shows a single stage of breakdown, giving cyclic oligomers plus a diverse range of minor products. Some workers claim that the mechanism consists of ester interchange, but the products and temperatures at which they are formed are also explicable by homolytic routes: some minor products are only satisfactorily explained by the latter. Possibly both types of mechanism are involved.

The decomposition behaviour of these addition polymers [3] and of PC [4,5] has been discussed elsewhere by the author.

### **Decomposition Behaviour of Mixtures**

The behaviour of various pairs of these polymers when thermally degraded together will now be considered. Unless otherwise stated, mixtures of equal weights of the two polymers were used in each case. These studies included thermal analysis by TG and TVA and product separation and analysis, although only selected data for illustration and the overall conclusions regarding mechanism are presented here.

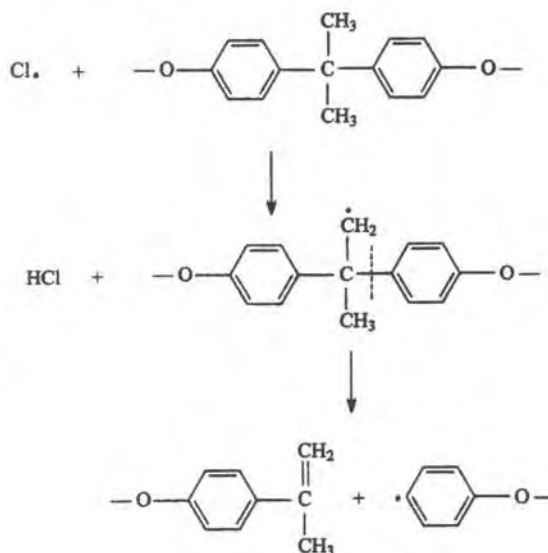
PS, PMMA mixtures. This pair illustrates the fact that mixing does not invariably lead to some form of interaction during thermal decomposition. When the TVA behaviour of 1:1 and 1:4 PS/PMMA mixtures is compared with that of the polymers alone (Fig.1), it is evident that the behaviour is simply additive [6].

PVC, PC mixture. The mixture is heterogeneous. The degradation temperature ranges of the constituent polymers are well separated (unmixed situation, Fig.2), the first stage being due to PVC breakdown and the second mainly to that of the PC. The evolution of HCl has been distinguished by shading. In the mixture, the HCl evolution stage of PVC breakdown

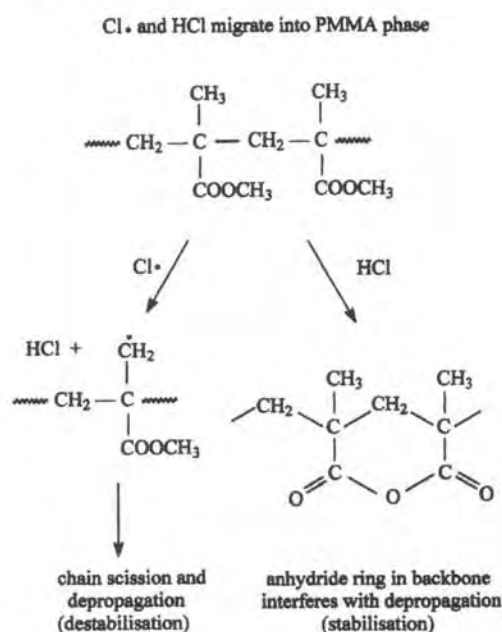
is not much affected, but the higher temperature breakdown of the PC is considerably shifted to lower temperature (mixed situation, Fig.2). Product analysis over the whole temperature range of the decomposition shows no new degradation products. The proposed mechanism has to reflect the fact that the PC is stabilised but no new products are formed. It is believed that the interaction effect involves chlorine radical migration across the phase boundary and attack on the PC (Scheme 1), which leads to reduction of molecular weight. The PC degrades mainly to chain fragments and the reduction in MW of the PC at dehydrochlorination temperature facilitates early volatilisation [7].

#### PVC, PMMA mixture.

The mixture is heterogeneous. The sample of PMMA used was of very high MW so that essentially single stage decomposition occurs at 300-400°C. The TVA behaviour for the unmixed situation (Fig.3) shows that the regions of decomposition of the two polymers are quite well separated, with HCl evolution from the PVC (distinguished by shading) largely preceding MMA monomer evolution. The effect of mixing on degradation behaviour in this case is dramatic. As soon as PVC decomposition begins, MMA monomer is evolved, but a second stage of MMA formation (showing also new minor products methanol and CO<sub>2</sub>) occurs at a higher temperature than for pure MMA. The PVC dehydrochlorination is slightly retarded. The interactions in this polymer mixture are quite complex, involving the migration of two different species from the PVC phase into the PMMA phase. A few chlorine radicals, chain carrier intermediates in the PVC dehydrochlorination, on entering the PMMA phase immediately attack the chains by H-atom abstraction, resulting in initiation of PMMA breakdown at abnormally low temperature. Thus the PMMA is initially destabilised, and the PVC is partly stabilised by loss of some of the chain carriers. Hydrogen chloride from the PVC also enters the PMMA phase and (more slowly) interacts with the PMMA to convert a few of the MMA chain units to cyclic anhydride structures. These interfere with the depropagation to monomer. This effect is responsible for the shift in temperature range of the second stage of MMA evolution in the blend and for the presence of methanol and CO<sub>2</sub> as minor products. The two mechanisms of interaction are shown in Scheme 2 [8,9].



Scheme 1



Scheme 2



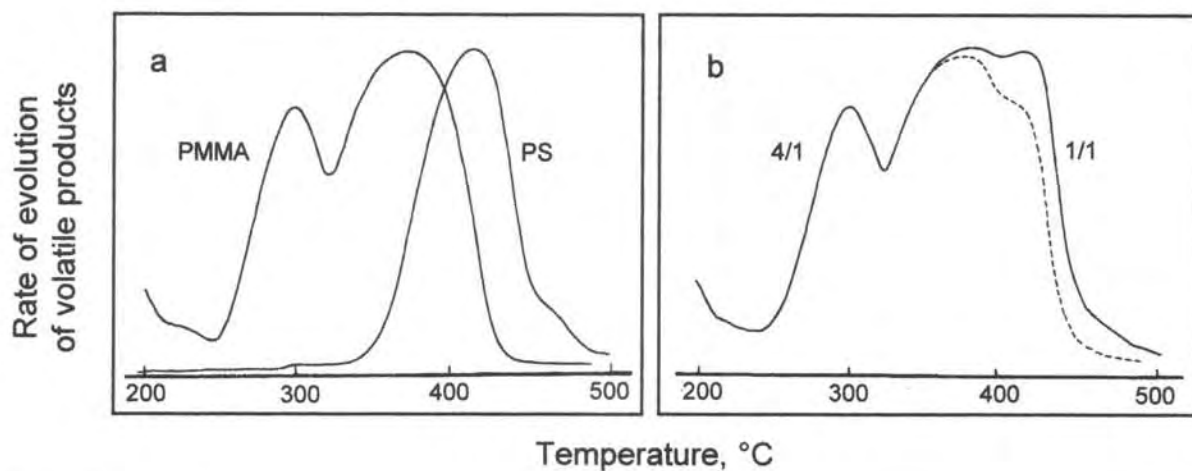


Figure 1  
TVA curves for PMMA, PS,  
4/1 PMMA/PS and 1/1  
PMMA/PS mixtures (heating  
rate 10°/min).

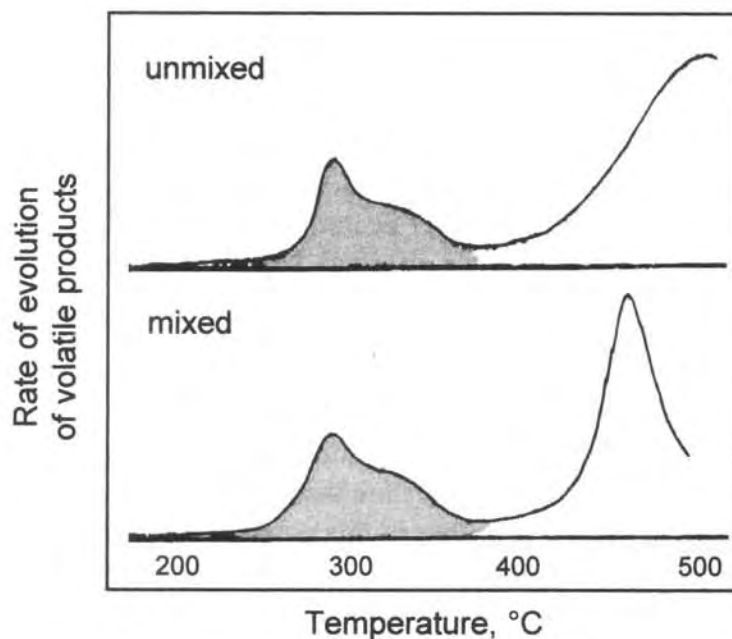


Figure 2  
Comparison of TVA curves  
for thermal decomposition of  
PVC/PC in unmixed and  
mixed conditions (heating rate  
10°/min).

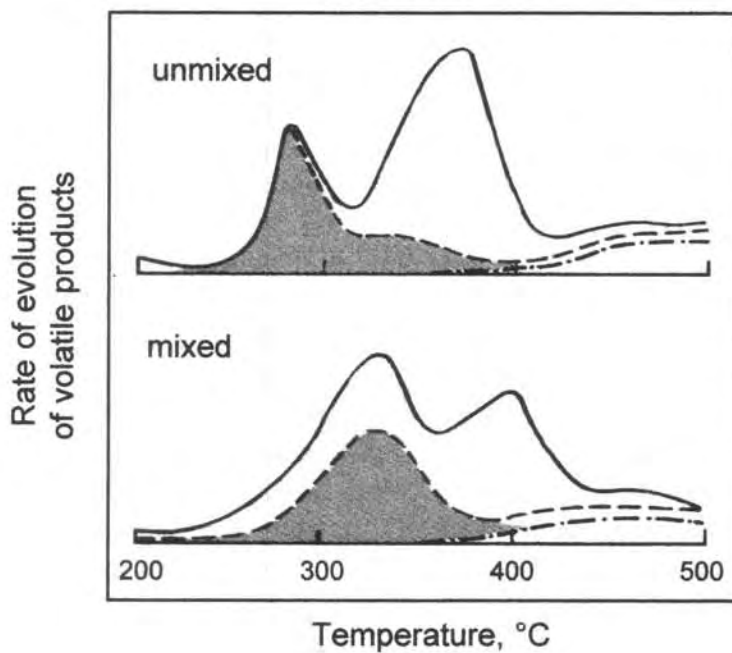
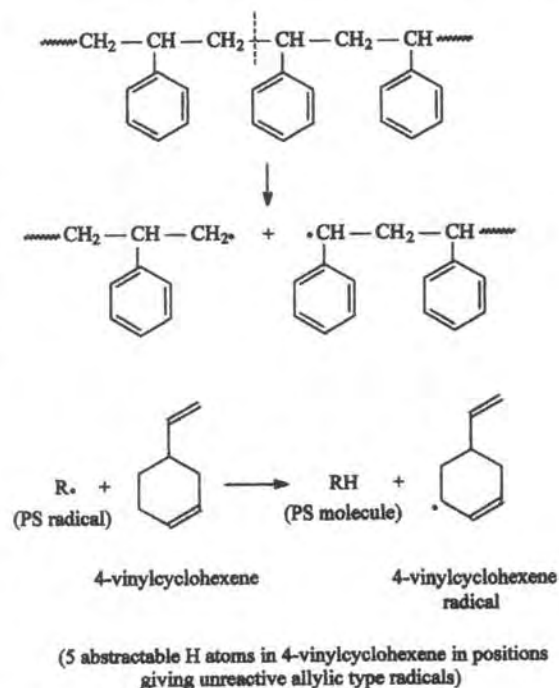


Figure 3  
Comparison of TVA curves  
for thermal decomposition of  
PVC/PMMA in unmixed and  
mixed conditions (high MW  
PMMA sample, heating rate  
10°/min).

**PS, PB mixture.** This mixture is also heterogeneous. The TVA curves (Fig.4) show clear evidence of stabilisation in the blend. Product analysis shows that the PB begins to degrade first in the mixture and while it does so the evolution of styrene from the PS is inhibited. In this mixture, therefore, one of the polymers is stabilised by the presence of the other, During the stabilisation period, the PB is evolving butadiene and 4-vinylcyclohexene (cyclic dimer). These volatile products are small molecules which can diffuse from the PB phase across the phase boundary into the PS phase. Thermal decomposition of PS begins by backbone scission to give macroradicals. Normally these can depropagate to monomer and take part in transfer reactions. The product 4-vinylcyclohexene, however, can act as a radical scavenger because H-abstraction by a PS radical gives a PS macromolecule and a relatively stable, unreactive 4-vinylcyclohexene radical, as shown in Scheme 3 [10].

**PS, PI mixture.** This mixture is also heterogeneous. The behaviour in this system closely parallels that in the case of PS, PB mixtures, except that PI is less stable than PS. In the mixture there is considerable stabilisation and little styrene is evolved until production of isoprene and dipentene from the PI has ceased. This behaviour can also be explained by a radical scavenging effect, in this case due to dipentene reacting with PS macroradicals and stabilising them as shown in Scheme 4 [11].



Scheme 3

**PC, PMMA mixture.** This polymer mixture is unusual in being homogeneous. The TG data shown (Fig.5) indicate that the polymers are well separated in temperature region of decomposition. The sample of PMMA used was a high MW sample giving a single stage of decomposition. In the presence of PC, there is some stabilisation of the PMMA and destabilisation of the PC. Because this mixed polymer system is homogeneous reactions of the type macroradical A plus macromolecule B become possible. It is believed that PMMA macroradicals abstract H atoms from PC macromolecules. This reduces the "zip length" of the depropagation, stabilising the PMMA. The PC radicals formed undergo chain scission: the reduction of molecular weight facilitates volatilisation of oligomeric species in the higher temperature region, so earlier PC breakdown is observed. The mechanism is shown in Scheme 5 [12].

### Predicting the Effect of Mixing

Not all mixtures, even of common polymers, have been studied. There are, however, some guidelines for predicting behaviour. To study behaviour experimentally, both thermal analysis and product analysis techniques are needed.

The following relevant questions need to be considered. How do the constituent polymers behave when degraded alone? Is the mixture compatible? This determines whether

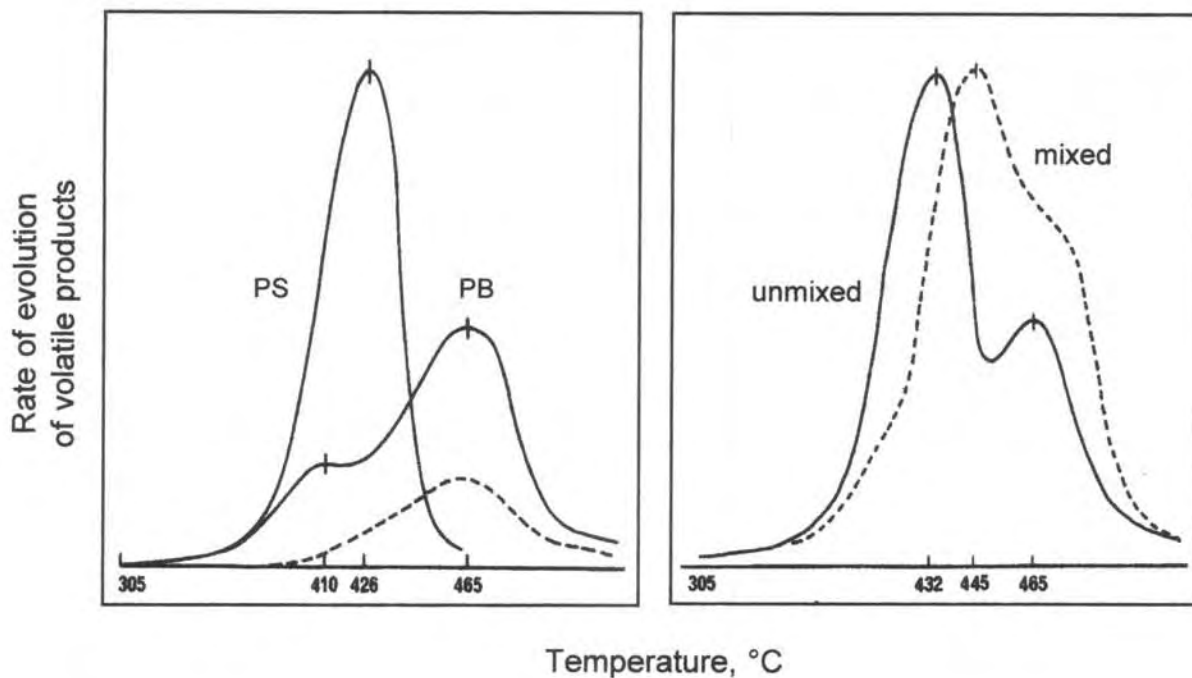


Figure 4.  
TVA curves for PS, PB and for PS + PB in unmixed and mixed situation (heating rate 10°/min).

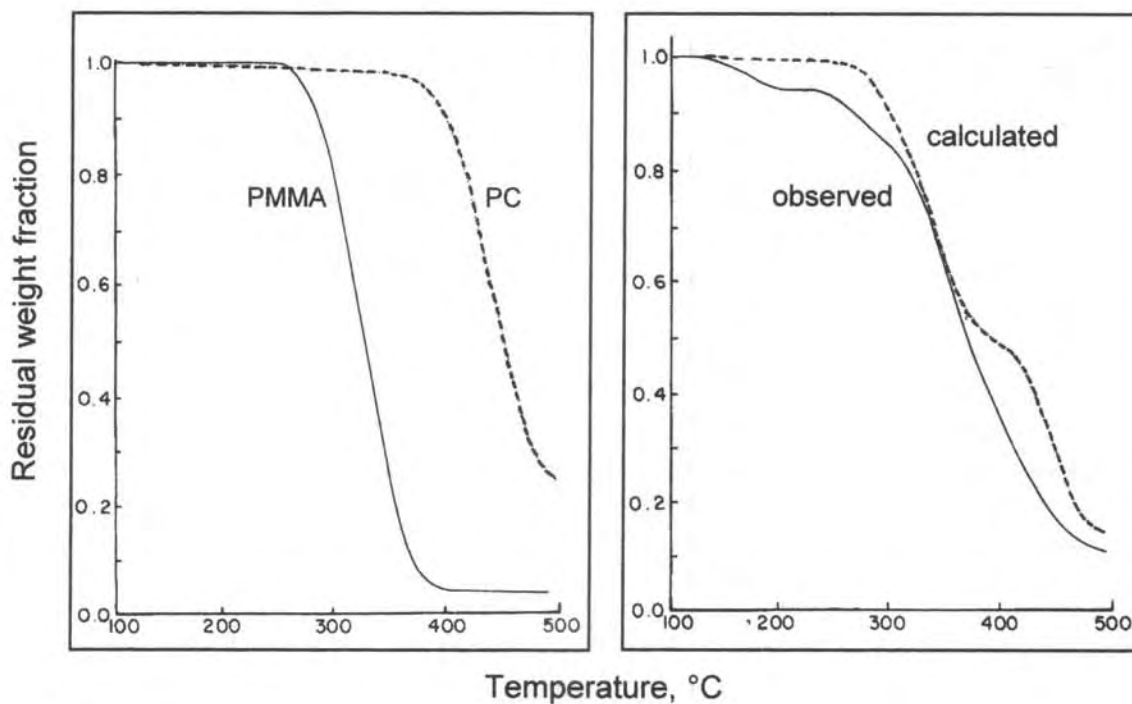
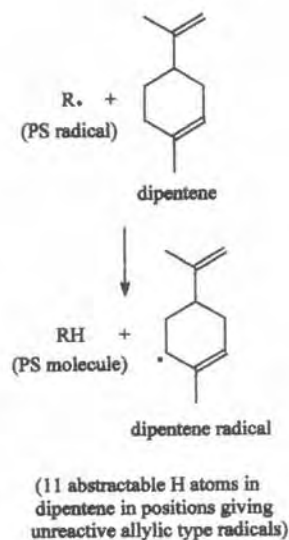
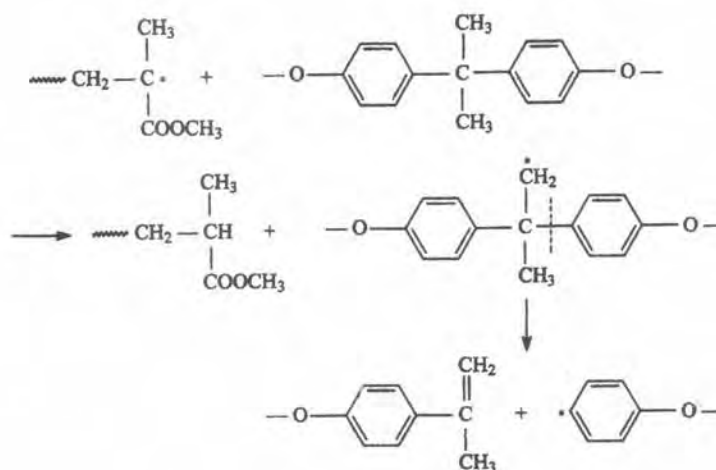


Figure 5.  
TG behaviour of PMMA and PC and comparison of calculated and observed TG behaviour for PMMA + PC mixture (heating rate 10°/min).



Scheme 4



Scheme 5

bulk or simply migration type interactions are feasible. Does either polymer break down to give small molecule reactive products or intermediates (e.g. small radicals)? This could result in either stabilisation or destabilisation. Does either polymer break down to give small molecule products which could act as radical scavengers? This could lead to stabilisation.

It is interesting to note that all polymer mixtures studied so far in which PVC is one component have shown some form of interaction effect. PMMA has also been found to be sensitive to the presence of reactive materials and modifications of the chain structure can prevent quantitative recovery of monomer on thermal decomposition as in pure PMMA.

### Acknowledgements

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