

Extract from PhD thesis by
Jo Sherratt B Eng, MSc

The effect of thermoplastic melt flow behaviour on the dynamics of fire growth

This extract from the full thesis covers only the introduction, larger scale experimental work, and conclusions. Additional experimental work was carried out using a cone calorimeter, and there is a substantial section describing theoretical approaches to the melting of a large block of material exposed to radiant heat, the polymer properties at temperatures at which it starts to melt and flow, and the variation of the polymer viscosity as it starts to degrade. There is also a discussion of existing standardised fire tests, and why these offer no assistance with the current problem.

The full thesis is available, either from HSE, or by application to the University of Edinburgh, contact, Professor Drysdale.

1.1 Introduction

According to the UK Fire Statistics over the last five years unwanted fires have caused an average of 697 deaths each year and approximately 10,000 injuries (HMSO, 1998). Each year ~ 110,000 indoor fires are reported, 60 – 65% of which occur in dwellings. Associated with these fires is a cost, including building damage and loss of stock, estimated to be between £0.5 and 1 billion. To attempt to reduce these losses, researchers have been investigating fire growth and spread mechanisms to provide a scientific basis for the progression of fire safety engineering. Research has shown that rapid fire growth is dominated by upward flame spread. Further work found this growth rate is exponential for vertical surfaces of combustible materials of semi-infinite thickness. Unfortunately, this [worst case] orientation is commonly encountered in warehouses and storage facilities. Storage presents particular challenges to fire safety because large quantities of combustible stock are often stored in vertical configurations separated by narrow aisles and pathways. This is widely recognised as a ‘high risk’ arrangement in terms of fire escalation potential.

There are several published studies looking at the hazards associated with storage fires, including problems related to vertical flame spread. The studies provide a basis for semi-empirical mathematical models. The models are used to develop

more accurate methods of predicting material behaviour in a fire scenario, providing data for use in risk assessment.

This approach is increasing in significance as the legislature moves away from the traditional prescriptive approach, towards goal setting and performance based codes. A UK framework for performance based fire safety is contained within Draft Document DD 240 (BSI, 1997), the basis of forthcoming BS 7974. When performance based codes are eventually fully adopted, complete risk assessments incorporating fire safety will be required for every project. Risk assessments are formulated by combining hazard identification with the probability of occurrence and severity of potential outcome.

The project sponsor, the UK Health & Safety Executive, (HSE), is concerned with assessing and reducing risks in the workplace to an acceptable level. A previous HSE funded study identified that a particular material behaviour, thermoplastic melt-flow, had been largely overlooked by previous research. Understanding how melt-flow effects fire growth will greatly help in assessing the fire hazard posed by many thermoplastics.

1.2 Materials Which Exhibit Melt-flow Behaviour

There are three main polymer classifications; *thermoplastics*, *thermosets* and *elastomers (synthetic rubbers)*. All three types consist of small molecules, formed into larger repeating structural units of the original molecules during polymerisation reactions. If the polymerisation process produces a cross-linked structure, the result is a thermoset, which decomposes rather than melting when heated. If the molecular structure is not cross linked, the result is a thermoplastic which when heated will soften and perhaps start to melt and flow. It is the tendency to melt-flow when heated that results in this fire spread mechanism, which by definition only involves thermoplastics.

Heating above a particular temperature will cause polymers to decompose, evolving smaller volatile species. Due to the structural difference, this occurs at higher temperatures for thermosets than thermoplastics. The actual combustion of polymers is a complex process, with the possible routes illustrated in Figure 1-1.

Pyrolysis is an endothermic reaction requiring sufficient energy input to dissociate the molecular bonds. Therefore, molecular composition dictates both the decomposition temperature range and mechanism.

The melt-flow behaviour is often complicated by the incorporation of various additives¹ during processing. This implies published material properties are either

¹ **Additive** – any material mixed with a polymer to modify processing or end use properties. The resulting mixture is usually called a 'plastic' to distinguish it from the base polymer.

Common additives – dye, pigments, fillers, plasticisers, lubricants, UV stabilisers, anti-oxidants, flame retardants, fibres, mould release agents.

Product *and* manufacturer specific, or else related to a pure polymer rather than a commercial material.

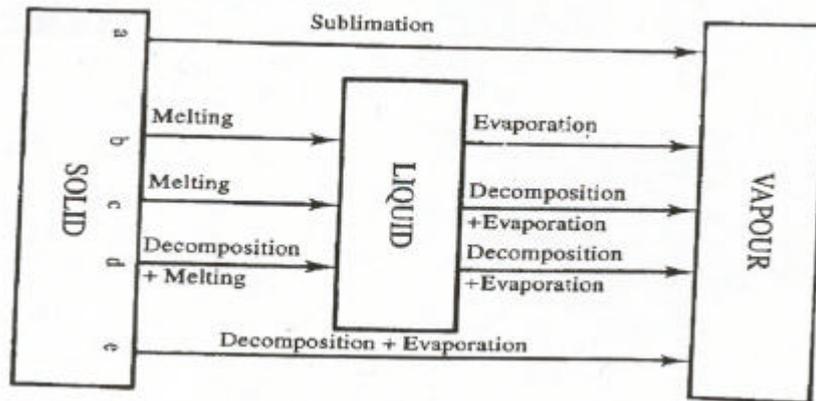


Figure 1-1. Modes of plastic thermal decomposition (Drysdale, 1999)

The thermal decomposition routes are shown in Figure 1-1. From this, route 'e' is mainly applicable to thermosets, leaving four main decomposition mechanisms for thermoplastics, listed in Table 1-A. Some polymers such as Polymethyl methacrylate undergo mainly 'unzipping' or end chain scission, (route 'a' in Figure 1-1), reversing the polymerisation process giving high yields of the original monomer. Others exhibit a mixed decomposition behaviour. The decomposition process is determined by molecular structure, but the decomposition rate is a function of other parameters including molecular weight, degree of crystallinity, amount of surface oxygen present and temperature. A polymer will generally undergo the predicted route of decomposition in a fire, although some low molecular weight polymers may melt as well as unzip.

Generally, polymers which chain strip or cross-link upon heating will form a char, and those that unzip will volatilise. Therefore the only polymers which are prone to exhibit melt-flow are those which randomly decompose, or exhibit a mixed decomposition behaviour, following routes b, c, or d in Figure 1-1.

Table 1-A. Mechanisms of Thermal Decomposition of Organic Polymers (Cullis & Hirschler, 1981)

Mechanism	Polymer (examples)	Products
Random Scission	Polyethylene, Polypropylene	Alkanes, alkenes, very little monomer
	Polystyrene	Styrene monomer, dimer, and trimer
End Chain Scission	PMMA Polymethacrylonitrile PTFE	90-100% monomer
Chain Stripping	Poly(vinyl chloride) Poly(vinylidene chloride)	Hydrogen chloride, aromatic hydrocarbons and char
Cross linking	Polyacrylonitrile Poly (oxy-m-xylene)	Char

1.3 Thermoplastics which pose the greatest risk

The thermoplastics representing the greatest melt-flow fire spread risk are the most widely available. In Western Europe, the quantity and type of thermoplastics consumed are shown in Table 1-B. This clearly shows the most widely encountered commercial thermoplastics are polyethylene, polypropylene, poly (vinyl chloride) (PVC), and polystyrene.

PVC decomposes by chain stripping, and is inherently flame retarded by its halogenated molecular structure. In contrast, polyethylene, polypropylene and polystyrene all undergo random scission, which will result in melt-flow behaviour.

Thermoplastics are increasingly encountered inside dwellings, industrial and retail premises as well as recycling depots, as both products and packaging. The kaleidoscopic range of thermoplastic applications ensures some level of thermoplastic contribution to the fuel load of most unwanted fires. The main thermoplastic applications are illustrated in Figure 1-2, and show 35% of thermoplastics produced to be used for packaging, 23% in building construction and 11% in electric / electronic applications.

**Table 1-B, Polymer consumption in Western Europe, 1997 – 2002
(Duffon, 1998)**

Plastic Type	1997 '000 tonnes	Estimated Growth p.a.	*1999 '000 tonnes	*2002 '000 tonnes
LDPE/LLDPE	6200	1% LDPE 6 – 7% LLDPE	6500	6900
HDPE	3850	3%	4085	4460
Polypropylene	5800	6%	6520	7760
Polystyrene	2000	2%	2080	2200
EPS	720	0-2%	735	780
PVC	5575	3-4%	5945	6500
Acrylics	250	2-5%	265	290
ABS	655	2-3%	690	745
Polyamides	540	4-5%	590	670
Acetals	140	3-4%	150	165
Polycarbonate	500	7-8%	575	730
PC Blends	155	6-8%	170	220
PET	1100	15-20%	1520	2300
PBT & Blends	90	3% & 6%	100	115
Mod PPE	70	5-7%	80	92
High Performance (PPS, LCP etc)	45-50	2-4%	60	80
Polyurethanes	2050	2-4%	2150	2300
<i>Thermoset Resins</i>				
Polyesters	450	2-4%	475	515
Aminos	75		80	85
Phenolics	220		225	235
Epoxy	60		65	71

* *predicted volumes*

Further examination of the fire statistics (HMSO, 1998) shows an average of 323 fires annually over the past decade in premises involved in rubber and/or plastics processing, and ~110 fires per year in recycling plants. Reported fires involving plastic manufacturers are shown to be a daily event, whilst 2 or 3 fires will be expected weekly in recycling facilities across the UK. Although not comprehensive, these statistics seem to indicate the fire risk posed by thermoplastics is not constant through the product life cycle. There are further statistics (although not published) from the HSE, focusing on large fires, although the limited number investigated mean that few are of direct relevance to this study.

2 Large scale fire tests

2.1 Full Polyethylene Roll Test (The 'Kebab' Experiment)

A supply of 'polyethylene' sheet wound onto rolls, ~ 2m long was supplied by the Health and Safety Laboratory for testing. The rolls, total mass ~21.5 kg, have a PE bulk density of 887kg/m³. The 12µm thick PE sheet is wound around a cardboard core, inside which a scaffold pole welded to a supporting steel disk was inserted. The pole was suspended from a chain incorporating a tensile load cell, above a 25mm thick monolux tray, 2.4m x 1.2m, divided in the centre by an insulated ridge to form two square sections. The tray rested on a separate load cell rig, as shown in Figure 4-21.

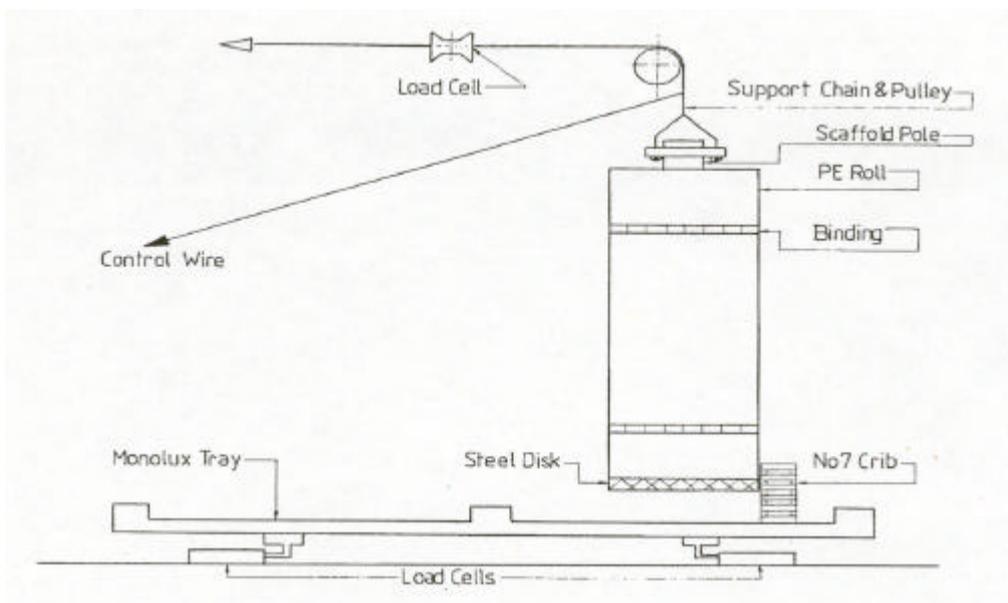


Figure 2-21. The 'Kebab' Experiment

As illustrated in Figure 2-21, the burning roll is suspended above the centre of the tray. A steel line attached above the roll on the supporting steel chain allowed the burning roll to be pulled across into the second area in order to observe the extent of vertical/horizontal burning interaction.

Ignition was achieved by means of a BS No 7 wooden crib, placed in the centre of one section of the monolux tray, contacting the perimeter at the base of the roll. The instrumentation consisted of the two load cell rigs, static DVD and Infra-Red (IR) cameras and a hand held DVD camera, in addition to a hand held thermocouple. The hand held equipment was used to monitor 'close up' behaviour until the burn

area became untenable due to the level of radiant heat. The static cameras were placed out with the burn area, and monitored through a hole in the shielding wall. All temperatures were recorded using the hand held thermocouple.

2.2 Observations

For the first test, the roll was suspended ~ 3cm above the base. This was found to be too close, as thermal expansion of the steel support chain led to contact between the roll and base during the test. A separation distance of 15cm was found satisfactory.

Initially, after ignition the fire growth rate was very slow. After 5 minutes a small fire was present around the base of the roll, with flames observed to wrap around the roll, and some white smoke was emitted. At 6 minutes, the total flame height reached around 15cm, and the crib had burned out. This flame height had doubled by 9 minutes, and by 12 minutes the thermocouple on the surface immediately behind the flaming area read 350°C, whilst when pushed into a softened bulk, read 280°C. Some slowly increasing surface distortion was apparent at this stage, evenly distributed across areas exposed to similar levels of heat. A circumferential 'diamond mesh' pattern, with diamonds 2cm wide x 1cm high, creating gentle surface contours, was observed at the upper roll area, away from direct flame exposure. Further down the roll, where the surface temperature was greater, the pattern was less ordered and distortion greater, producing surface protrusions which seemed to originate from swelling, (as illustrated in Figure 4-22) throughout the bulk thickness of the plastic. Some of the lower smoothly curved protrusions were 20 – 25mm proud of the original surface, and appeared opaque at depth, but transparent near the surface. The transparent surface layer was observed to flow downward.

A small non burning transparent brown liquid pool of approximately the same diameter as the roll started to form at 13 minutes, varying from 310°C in the centre to 190°C at the edge. The pool was fed by drips from the base of the roll, which had regressed to expose some of the steel disk. The liquid on the steel disk registered ~ 400°C on the thermocouple.

Some soot particles from the flame became absorbed in the molten surface layer, the (varying) downward velocity of which was at most 1 – 2 cm/s. The bulk of the roll was opaque, but the thin moving surface layer and drips had become transparent.

By 14 minutes, some burning was evident in the pool centre, but an outside 3 – 5 cm wide 'rim' of non burning material was also noted.

This rim was producing small bubbles of volatiles. The burning liquid pool varied between 340°C and 130°C at the outer edge, being 260°C just inside the edge. Pool depth varied between 3 – 5mm at the rim, and 1 – 2mm at the centre, covering an extent equivalent to around 60cm (not even). At this time, the flames from the pool were around 20 cm, with 50cm high flames attached to the roll. (This pool structure is consistent with the surface tension driven flow of the molten material).



Figure 2-22. PE roll surface distortion & drip site

By 18 minutes, the vertical flame height had reached 0.7m, the surface protrusions had increased and the smoke had turned black, rapidly increasing in volume. The temperature of the protrusions were found to be ~ 300°C for the main bulk, rising to 350°C for the upper surface, which was at most 2 – 3mm deep. A close up image from the hand held DVD is shown in Figure 2-22.

At 20 minutes, the pool covered around 1/5th of the tray area, with a total vertical flame height of around 1m, unevenly spread across the roll surface. It was noted that the pool depth never became greater than 3 or 4 mm.

At approximately 24 minutes, the area was evacuated due to the level of radiant heat present, and observation continued from the static camera location outside. With vertical flames over 2m in height, flickering up to 2.5 – 3m, the pool started to exhibit behaviour at 25 minutes. An area of pool would burn out completely, leading to flame extinction, and then a process of material accumulation, then the surface

would eventually re-ignite. This burn off – replenish – re-ignition cycle was unsteady in terms of time taken and also area covered, although it seemed to be within the ever present non flaming rim. By 26 minutes, the pool covered over half the tray area, although the above cycle made accurate estimation difficult. The roll was fully flame engulfed by 30 minutes, and was then temporarily physically removed from the pool. This clearly showed a large pool fire and a much smaller fire on the roll, proving the dominant fire to be from the pool (the roll flaming covered mainly the extent of roll surface).

A further, smaller pool was formed in the second area as liquid came off the roll, and some spitting of burning material from the roll surface was noted. When the roll was returned to its original position, it caught on the central ridge from where it had to be dislodged (again due to thermal expansion of the steel chain). However when the roll was put back over the pool, the fire grew in size and intensity before stabilising. By this stage, some pieces fell off the roll, landing in the pool to burn, but maintained the roll curvature on the outer surface. The pool shrunk back to around $\frac{1}{4}$ of the tray area by 32 minutes, increasing back to $\frac{1}{2}$ the area by 34 $\frac{1}{2}$ minutes.

The drips feeding the pool could clearly be seen to come from the mid-point of the curved protrusions at several locations, and were 2 –3mm diameter. The distortions maintained their geometry whilst losing the surface layer, which was continually replaced by the melting surface above. In addition to the surface drip points, there were occasional episodes during which a shower of flaming droplets was produced which burned out prior to reaching the floor.

By 40 minutes, most of the vertical surface had been consumed, larger pieces falling off due to the loss of surrounding plastic which they were previously attached to.

3 'Sedan Chair' Experiments

Following the kebab experiment, to allow more information to be gathered a new fire test rig was developed. A burn cage was supported on a metal frame supported on load cells. Below this was a pan filled with quenching oil, into which polymer which flowed from the fire could be collected, and prevented from burning further. This quench tank was also supported on load cells. The gaseous flow from the fire was drawn through ducting, and the rate of heat release measured using oxygen consumption calorimetry. Significant experimental difficulties had to be overcome,

particularly preventing fire within the quench tank, and temperature compensation for the load cells. The burn cage was large enough to accommodate beer and milk crates, of masses up to 3kg. These produced fires of up to 100kW output.

In further experiments on the same rig, the quench tank was replaced by different substrates, timber, steel and concrete to compare the effect of melting onto different types of floor. All these experiments showed an extended period of about 15 minutes, before the pool fire took over from the fire in the cage, as a significant factor in fire growth.

4 Conclusions & Recommendations for further work

4.1 Introduction & Main Problems For This Study

The objective of this research study was to investigate the effect of the melt flow process on fire growth. Foley pointed out that there had been little research on this topic, and it was discovered at an early stage that there were significant problems in three main areas;

- 1) Lack of knowledge of the effect of melting and burning processes on plastic material properties, which are the basic inputs for any model. Detailed published data does exist for a wide array of polymers as it is required for processing purposes. However, the data only applies to a relatively low temperature range, and does not account for thermal degradation of the polymer.
- 2) There are no published 'standard tests', experimental methods or industrial practices capable of measuring any of the melt properties affecting fire behaviour. It appears that melt-flow has been treated as a nuisance which can be ignored by various techniques, rather than an important material property. These 'avoidance techniques' include:
 - a) standard tests: for some tests, such as BS 476 Part 7, the minimum rating can be achieved by bonding the plastic to non-melting substrate, which stays in place during the test. The merit of

this approach was clearly demonstrated by Abbott with the agricultural EPS panels. Other tests, such as the SBI, accept that melting plastics cannot meet the test criteria, and so are listed as incapable of being tested. *(It should be emphasised, however, that even for geometrically stable materials, these tests suffer a large apparatus dependency, and the results from them are of little use in predicting actual fire behaviour).*

b) experimentalists & fire researchers: who circumvent the melt problem by the almost universal adoption of high MW PMMA which doesn't melt, for both testing and modelling purposes.

c) industry has considered melting, as it is a necessary property for moulding, and produced tests intended to measure a melt viscosity type parameter as a function of temperature (e.g. MFI). These tests are all apparatus dependent, generally involving pressure driven flow through a particular size, shape and temperature die, where if the apparatus is similar to processing equipment, the data is of use in that field.

- 3) The published properties of polymers differ from those of plastics, and commercial sensitivity prevents manufacturers disclosing the composition of their products. Therefore, it is possible that an effect may be due to an unspecified additive or degree of copolymerisation rather than the base polymer, but this is difficult to identify or quantify.

Despite the problems faced in this project, the work has produced some interesting results which lay the ground for further investigation.

4.2 Conclusions

4.2.1.1 Small scale (Cone Calorimeter) Work

The previous research focused on PMMA has generally concentrated on thermally thick PMMA, thereby allowing steady state data to be obtained, but this not representative of commodity plastics.

This study has looked at commodity plastics, although small-scale work excludes any geometrical configuration effects, covering a range of common behaviour known to have caused problems in actual fire incidents. The results show a range of factors including molecular composition and weight, additives, orientation, ventilation conditions, material thickness and applied level of flux affect the small scale fire performance of thermoplastics. The effects of some of these variables can clearly be detected with Cone Colorimeter tests, but some, such as the effect of orientation, are apparatus dependent and not generally transferable. On the other hand, some larger scale problems such as thermal expansion, or loss of component rigidity due to softening are not apparent from a cone test.

The cone database indicates that all the plastics tested would begin to burn during flashover (defined by radiant flux in excess of 20 kW/m² received at floor level). In most cases it is possible to observe melting behaviour from a Cone Calorimeter test, particularly as if commonly occurred, the material overflows the sample holder. This may indicate a thermoplastic is capable of generating a pool fire in larger scale well-ventilated conditions. (This could also be observed from simply igniting a small specimen clamped in a retort stand).

4.2.1.2 Medium Scale work

To answer the problem of no appropriate measuring techniques, a method has been developed which is capable of assessing the influence of a melt on fire dynamics. The Sedan and Kebab rigs both operate on the principle of separating the mass flow components from vertical to horizontal. This technique seems to be moderately successful for medium scale tests.

It has been confirmed that increasing pool fire area increases overall rate of heat release, and therefore the radiant flux supplied to the material feeding the pool. This loop mechanism increases the flow rate into the pool and the burning rate of the pool. The Sedan and Kebab experiments show that for a thermoplastic exhibiting

melt-flow behaviour, the fire size and rate of growth are controlled by the pool fire formed at the base of the burning flowing material.

Results from the oil quenched experiments, show 70 – 80% of the mass loss from the array will enter the pool.

Flame deflection from the pool is a significant component of the level of flux received by the vertical wall, and when the wall is no longer physically present, this will influence the burning process.

All of the plastic fires studied during this project show an initial relatively long fire growth phase. It is not yet known if this is a function of the material properties, or whether a larger ignition source or different configuration would reduce this phase, increasing the level of hazard.

It has also been found that there are two controlling mechanisms influencing pool fire development. This project has focused on gravity driven surface melting, but it has also been observed that softening followed by geometrical slumping is an important pool feeding mechanism. This is harder to predict as it is only seen on larger scale tests. It appears to be driven partly by loss of the supporting base area combined with a moving centre of gravity. It has been found impossible to separate the two mechanisms experimentally, as even thick sheets of plastic will eventually succumb to a slumping collapse.

The material properties of the flooring substrate are a major influence parameter on the burning rate of the pool and therefore overall fire growth and development.

4.2.1.3 Modelling

Previous work by physicists and mathematicians has looked at melting ice. This has known properties, and is reversible (e.g. no chemical changes). Although burning plastic melts are not reversible, and the properties are largely uncertain beyond processing temperatures, this approach has been used as the basis for a model. Unfortunately, the only available flow data relates to a different flow mechanism to

that controlling melt-flow in a fire, and it is not certain that the extrapolation and assumptions are valid.

Despite these concerns, and although basic, the model reinforces the idea that initial MW, and type and rate of MW degradation are the most significant parameters influencing gravity driven flow. It has also been confirmed that the fire models in the literature, developed based on vertical flame spread mechanisms for PMMA and timber cannot be utilised to assess the potential fire hazards of melting plastics.

4.2.2 Overall Conclusion

If a plastic undergoes RCS, then the rate of MW degradation is rapid and there is a high probability of rapid fluid formation. The level of fire hazard is probably related to the rate of MW decrease. The formation of a pool fire seems to increase the duration of the fire growth phase, lowering the overall fire hazard in comparison to non pool forming materials, but after this phase fire growth is rapid and controlled by the pool. The pool is fuelled from the vertical array by two distinct mechanisms; melting and structural collapse. The burning rate of the pool is then partly determined by the nature of flooring substrate and also the level of radiant heat feedback from the vertical array.