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Dripping behavior of burning polymers under UL94 vertical test conditions

Yong Wang[1,2], Jinder Jow[3], Kenny Su[4] and Jun Zhang[1,2]

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Abstract

This article studied the dripping behavior of eight polymers under UL94 vertical test conditions. The results suggested two different dripping behaviors: Type I, dripping with uniform- and small-sized drops with the short first dripping time, and Type II, dripping with irregular- and large-sized drops with the long first dripping time. Polymers of Type I dripping had dominant decomposition mechanism of random-chain scission, low activation energy of viscous flow, and high ratio of effective heat of combustion to heat of gasification. Otherwise, Type II dripping dominates. The surface tension at ambient temperature and the melt flow index at processing temperatures were not as important to dripping as expected. It was found that talc could convert the dripping of low-density polyethylene from Type I to Type II at a critical talc loading level of 20 wt%, which was ascribed to the reduction in the burning rate and the formation of an integral residue. Finally, a generalized model was presented, and a derived correlation showed that the drop mass was a power law function of the dripping time.

Keywords

UL94, dripping, vertical burning, polyethylene, talc

Introduction

The UL94 vertical burning test[1] is widely employed in industry and fire research. In this test, the 20-mm-high UL94 flame is applied to the small bar specimen from the bottom end for

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[1]Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, Qingdao University of Science & Technology, Qingdao, P. R. China
[2]College of Environment and Safety Engineering, Qingdao University of Science & Technology, Qingdao, P. R. China
[3]The Dow Chemical Company, Freeport, TX, USA
[4]Taiwan Styron Ltd, Hsinchu Industrial Park, Hsinchu, Taiwan

Corresponding author:
Jun Zhang, Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, Qingdao University of Science & Technology, 53 Zhengzhou Road, Qingdao 266042, P. R. China.
Email: safetyqust@163.com

10 s and then removed. If the bar is not ignited or its burning ceases, the UL94 flame is applied soon for an additional 10 s. After each flame application, the burning time of the test specimen is recorded. During the test, it needs to be observed that whether or not the specimen drips and, if any, whether or not the drops are flaming. The rating of a polymeric product in the UL94 vertical burning test depends on the burning time and the dripping phenomena. The burning time after removal of the ignition source determines whether the polymer is V0, V1, or no grade. The dripping phenomena discriminate between the V2 grade and the V1 grade. If the flaming material drips and ignites the cotton placed under the test specimen, the grade of the polymeric product will be rated as V2. Clearly, the dripping phenomena are important to the UL94 vertical test. However, the fundamental aspects of the dripping behavior of polymeric materials in this type of testing burning mode have been seldom investigated. Wang et al.[2] qualitatively described the dripping of flame-retarded poly (ethylene terephthalate) in the UL94 test as "heavy," "slow," "slight," and "scarce." Zhang et al.[3] reported the diameter and the first drop mass of flame-retarded polyamide 6 (PA6) specimens. Their descriptions on the dripping phenomena are additional to the results of standard UL94 test, helpful for screening formulations but not involving physical and chemical mechanisms of dripping.

Dripping is a great threat in polymer fires. It can accelerate fire growth and spread fires between nonadjacent objects. For example, a pool fire will appear when a polymer product mounted on the wall melts, flows down, and burns. It has been reported that interactions between the burning polymer and the pool fire promote fire growth and increase fire hazards, such as raising the burning rate and the heat release rate.[4–9] The burning of a plastic lampshade at the ceiling might lead to the jump of fire from the ceiling to the floor when the burning plastic drips to the wooden floor.[10] However, there has been little research on dripping in fire because of significant difficulties involved, including lack of knowledge of the effect of melting on material properties, and no proper standard tests for measuring any of the melt properties affecting fire behavior.[8] Fortunately, a few studies conducted using a cone calorimeter and larger scale experimental apparatuses[8,9] show some progress. It has been found that for thermoplastics, there are two controlling mechanisms to fuel pool fire, surface melting and bulk softening leading to structural collapse. These two types of dripping can be qualitatively related to the decomposition mechanisms. The end-chain scission decomposition mechanism corresponds to the bulk softening dripping type, while the random-chain scission decomposition mechanism tends to result in surface melting dripping. But it has been found impossible to separate the two dripping types experimentally. A thick sheet of plastic with surface melting will eventually succumb to a slumping collapse.[8]

In our previous study[11] on the dripping behavior of materials under UL94 test conditions, the dripping is grouped into two types, small-sized dripping and large-sized dripping, according to the measured mass data of the first drop. The first drop of PA6, low-density polyethylene (LDPE), and polypropylene (PP) has relatively small size and appears spherical. Poly(acrylonitrile-butadiene-styrene) (ABS), high-impact poly(styrene-butadiene) (HIPS), polycarbonate (PC), and polymethylmethacrylate (PMMA) generate larger drop size.

In this study, the dripping behavior of polymers under the UL94 vertical burning test conditions was further investigated. Eight polymers of various chemical structures, including ABS, HIPS, PC, PMMA, polyethylenevinylacetate (EVA), PA6, LDPE, and PP, were tested. During the experiments, the times and masses of multiple drops were recorded in order to analyze the dripping behavior, although the rating of a product in the UL94 test depends on occurrence of the first drop rather than the subsequent drops. The key factors influencing dripping were analyzed. The effects of talc and melt flow index (MFI) on the dripping behavior of LDPE were also studied.

Experiments

Pellets of the polymers listed in Table 1 were dried in an oven at 80°C for 24 h and mold pressed or injected into plates. Then the plates were cut into 100 mm × 10 mm × 2 mm specimens for the dripping experiments. To study the effects of talc on the dripping behavior of LDPE specimens, LDPE pellets were plasticized and mixed with dry talc powder (purchased from Dongfang Fine Talc Powder Company, Yantai, China; whiteness: 85%–96%, median diameter: 12 μm, density: 2.78 g/cm^3) in a lab two-roll mill. The pellets of LDPE with and without talc were mold pressed into 100 mm × 100 mm × 4 mm plates. Some of these plates were tested in a standard FTT cone calorimeter (Fire Testing Technology Ltd, West Sussex, UK) under 50 kW/m^2 heat flux, and others were cut into 100 mm × 10 mm × 4 mm specimens for the dripping experiments. Similarly, to study the effects of MFI on the dripping behavior of PE, high-density polyethylene (HDPE, trade mark: DMDY 1158, density: 0.952 g/cm^3, purchased from SINOPEC Qilu Company Ltd, China) was blended with the LDPE polymer listed in Table 1 to prepare 100 mm × 10 mm × 4 mm PE specimens with different melt flow indices for the dripping experiments.

The prepared specimens were put into the melt indexer (GT-T100-MI; Gotech Testing Machines Inc., Taiwan) for measuring MFI, which is the melt flow rates of the polymer melt at a specified temperature and under a given pressure provided by a load. These specimens were also tested under UL94 vertical burning conditions for observations of the dripping phenomena. In the dripping experiments, the UL94 flame was applied to each specimen for 10 s and then removed. The time when each dripping occurred was recorded by a timer, with the time at the beginning of the flame application set to zero. The test station was open, and each drop was collected by a pan below the specimen. The catch pan was an iron pan coated with a layer of enamel. Each drop could be scraped by a blade and completely separated from the pan. If the drop was still burning in the pan, the drop fire was extinguished immediately by covering with an aluminum lid about 100 mm long, 100 mm wide, and 50 mm deep. The extinguishing operation might disturb the air flow field and subsequently influence the

Table 1. Descriptions of polymeric materials

Polymers	Trademark	Manufacturer
ABS	PA-747S	Chi Mei Corporation, China
HIPS	PH88HT	Zhenjiang Chi Mei Corporation, China
PC	N/A	GE Corporation, USA
PMMA	N/A	Mitsubishi Rayon Polymer Nantong Co., Ltd
EVA18	EVA18-3	Beijing Eastern Petrochemical Co., Ltd, China
PA6	N/A	Shijiazhuang Fibre Co., Ltd, China
LDPE	LDPE 18D	Daqing Petrochemical Company, China
PP	EPS30R	SINOPEC Qilu Company Ltd, China

ABS: poly(acrylonitrile-butadiene-styrene); HIPS: high-impact poly(styrene-butadiene); PC: polycarbonate; PMMA: polymethylmethacrylate; EVA: polyethylenevinylacetate; PA6: polyamide 6; LDPE: low-density polyethylene; PP: polypropylene; N/A: not available.

burning and dripping, but in our experiments, only a few drops of ABS, HIPS, and PMMA needed to be extinguished manually. Finally, the drops were collected, and the mass of each drop was measured using an analytical balance with an accuracy of 0.0001 g. In cases where the drop was difficult to collect separately and the size of each drop looked similar, the mass of multiple drops was measured and divided by the number of drops to obtain the average mass of a single drop.

Results and discussions

Effect of polymers with various chemical structures on dripping behaviors

The photos of drops collected from eight polymers with the catch pan under UL94 vertical burning test conditions are shown in Figure 1. It can be seen that the drops of EVA18, PA6, LDPE, and PP are relatively uniform. The size difference among these drops is minor. The collected drops look like thin disks with diameters in the range of 5–10 mm. For PA6 and PP, most drops collected in the pan have branches at edges of thin disks, which should be ascribed to the splash of drops at the moment of falling onto the pan, implying that the viscosity of these drops at that moment was low. On the other hand, the drops of ABS, PC, PMMA, and HIPS are not uniform. For HIPS and PMMA, in particular, the difference among drop sizes is significant. The shapes of these drops are not similar. The PMMA drops tend to be round, while the ABS drops are irregular. The first drop of ABS is actually a folded long molten bar because the break position was close to the clamp. The maximum dimension of these drops ranges from 2 to 30 mm, and the drop of ABS is the biggest. In fact, during experiments, it was observed that during dripping, the length of ABS specimen shortened rapidly with the specimen bottom approaching the clamp. The collected drop of PMMA was hard after being cooled down and was filled with bubbles, most likely due to its

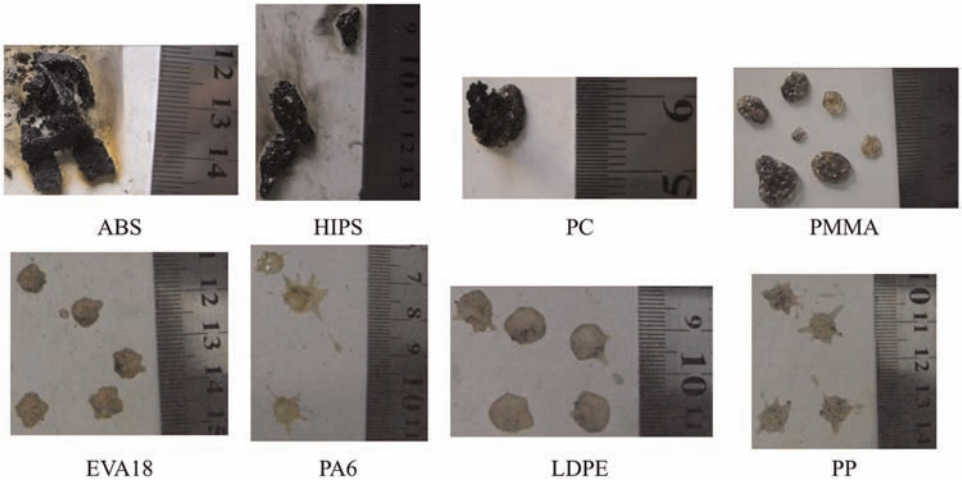

Figure 1. Photographs of collected drops of neat polymers.
ABS: poly(acrylonitrile-butadiene-styrene); HIPS: high-impact poly(styrene-butadiene); PC: polycarbonate; PMMA: polymethylmethacrylate; EVA: polyethylenevinylacetate; PA6: polyamide 6; LDPE: low-density polyethylene; PP: polypropylene.

end-chain scission, which produced the monomer at each decomposition step and reduced its molecular weight (MW) relatively slowly.

The time when dripping appears and the mass of each drop in three repeat tests are listed in Table 2. The order of the first dripping times is ABS > (PC, HIPS) > PMMA > (EVA18, LDPE, PA6) > PP. The order of the first drop mass is (ABS, HIPS) > PC > PMMA > PA6 > (EVA18, LDPE, PP). For ABS, the flame reached the clamp and wrapped around the whole specimen bar at about 20 s. In most ABS tests, the break position of the first molten drop was close to the clamp. After the first dripping, there was only a small part of the

Table 2. Dripping time and drop mass data for drops of neat polymers

Polymers	Drops	Test_1		Test_2		Test_3		Average	
		t_d (s)	m_d (g)	t_d (s)	m_d (g)	t_d (s)	m_d (g)	t_d (s)	m_d (g)
ABS	1	66.19	0.0659	58.36	0.3408	54.66	0.3939	59.74	0.2669
	2	72.37	0.0042	67.96	0.0054	62.06	0.0023	67.46	0.0040
	3	73.58	0.0036	68.33	0.0041	62.75	0.0028	68.22	0.0035
	4	74.69	0.0202	N/A	N/A	63.46	0.0024	69.08	0.0113
	5	75.72	0.0031	N/A	N/A	64.11	0.0023	69.92	0.0027
HIPS	1	24.21	0.2604	24.77	0.2507	19.11	0.3445	22.70	0.2852
	2	26.90	0.1037	28.62	0.1316	23.64	0.0531	26.39	0.0961
	3	31.17	0.0408	35.46	0.1569	24.17	0.0690	30.27	0.0889
	4	31.42	0.0089	38.62	0.1489	25.09	0.0303	31.71	0.0627
	5	31.80	0.0803	38.99	0.0600	25.68	0.0582	32.16	0.0662
PC	1	26.90	0.0694	23.42	0.0322	24.08	0.0731	24.80	0.0582
PMMA	1	17.50	0.0116	17.16	0.0145	15.74	0.0087	16.80	0.0116
	2	17.96	0.1675	17.62	0.1625	16.51	0.0145	17.36	0.1148
	3	18.55	0.0664	18.20	0.0893	16.94	0.0680	17.90	0.0746
	4	19.39	0.0378	18.78	0.0967	17.51	0.0430	18.56	0.0592
	5	20.06	0.0039	19.44	0.0800	18.19	0.0180	19.23	0.0340
EVA18	1	12.08	0.0030[a]	13.22	0.0039	11.95	0.0036	12.42	0.0035
	2	13.49		15.09	0.0026	12.88	0.0032	13.82	0.0029
	3	14.62		16.47	0.0022	13.72	0.0023	14.94	0.0023
	4	15.86		17.48	0.0019	14.60	0.0022	15.98	0.0021
	5	16.84		18.58	0.0015	15.57	0.0019	17.00	0.0017
PA6	1	10.61	0.0097[a]	N/A	N/A	N/A	N/A	10.61	0.0097[a]
	2	11.46		N/A	N/A	N/A	N/A	11.46	
LDPE	1	11.24	0.0036[a]	11.06	0.0034[a]	10.76	0.0037[a]	11.02	0.0035[a]
	2	12.76		12.51		12.32		12.53	
	3	13.97		13.76		13.56		13.76	
	4	14.88		14.76		14.69		14.78	
	5	15.60		15.66		15.69		15.65	
PP	1	9.87	0.0024[a]	8.99	0.0024[a]	8.76	0.0025[a]	9.21	0.0024[a]
	2	10.85		10.62		10.07		10.51	
	3	11.59		11.46		11.14		11.40	
	4	12.71		12.39		11.99		12.36	
	5	13.58		13.16		12.86		13.20	

ABS: poly(acrylonitrile-butadiene-styrene); HIPS: high-impact poly(styrene-butadiene); PC: polycarbonate; PMMA: polymethylmethacrylate; EVA: polyethylenevinylacetate; PA6: polyamide 6; LDPE: low-density polyethylene; PP: polypropylene; N/A: not available; t_d: time when dripping occurs; m_d: mass of the drop.

[a] Average mass.

specimen hanging below the clamp. Hence, the subsequent drops were small. This was especially true in Test_2, in which the specimen bottom approached the clamp after three drips. Both PA6 and PC specimens were extinguished when the flaming material dripped away, and their flaming drops were also extinct immediately after falling on the pan. The specimen of PA6 was ignited after the 10-s flame application period in only one test. For PC, the specimens in three tests were extinguished after the first dripping. Regarding the drop mass, the listed data for PA6 in the first test were the average mass of the two drops because the drops of PA6 were brittle and were broken when scraped from the pan. Drops of LDPE and PP were also relatively brittle and could not be easily collected. Although drops of EVA18 were tough, these collected thin disks tended to aggregate together if they were not scraped one by one and immediately separated. For LDPE and PP in three tests, and EVA18 in the first test, the listed drop mass data were the average values of five drops.

Statistical data, including the average, minimum, and maximum drop mass values for each polymer, are shown in Table 3. From the data shown in Tables 2 and 3, the following findings can be obtained.

- For ABS, HIPS, PC, and PMMA, the average mass of the drops is relatively large and greater than 0.01 g. Hence, the large-sized dripping seems to play an important role in the dripping behaviors of these polymers. Furthermore, the drop mass data of these polymers are widely distributed.
- For EVA18, PA6, LDPE, and PP, the average mass of the drops is less than 0.01 g, indicating that the small-sized dripping dominates their dripping behaviors. It can be seen that for EVA18, the drop mass data are narrowly distributed and the mass values slightly decrease sequentially with time.
- The first dripping time for large-sized dripping is usually longer than that for small-sized dripping, implying that longer first dripping times generally correspond to the larger drop size. EVA18, PA6, LDPE, and PP had first dripping times of less than 15 s, shorter than ABS, HIPS, PC, and PMMA.

The results suggested for the thermoplastics in the UL94 vertical burning test, dripping behaviors can be categorized into two types, that is, Type I: small and uniform drop size with

Table 3. Masses of drops and surface energies of polymers

Polymers	ABS	HIPS	PC	PMMA	EVA18	PA6	LDPE	PP
Average m_d (g)	0.0655	0.1198	0.0582	0.0588	0.0026	0.0097	0.0035	0.0024
Minimum m_d (g)	0.0023	0.0089	0.0322	0.0039	0.0015	N/A	N/A	N/A
Maximum m_d (g)	0.3939	0.3445	0.0731	0.1675	0.0039	N/A	N/A	N/A
Surface tension[a] (dynes/cm)	38.5	34[b]	44	37.5	N/A	43.9	31.6	30.5
MFI (g/10 min)	0.9	7.0	2.5	10.2	8.6	15.8	5.9	2.1

ABS: poly(acrylonitrile-butadiene-styrene); HIPS: high-impact poly(styrene-butadiene); PC: polycarbonate; PMMA: polymethylmethacrylate; EVA: polyethylenevinylacetate; PA6: polyamide 6; LDPE: low-density polyethylene; PP: polypropylene; m_d: mass of the drop; N/A, not available.

[a] Critical surface tension at 23°C determined by ASTM D2578.

[b] For PS.

short first dripping time, such as EVA18, PA6, LDPE, and PP, and Type II: large and irregular drop size with long first dripping time, such as ABS, HIPS, PC, and PMMA.

This division of dripping types might be attributed to the variation of MW due to decomposition of polymers during burning. The dominant decomposition mechanism for each polymer used in this study is listed in Table 4.[8,12] Random-chain scission causes a dramatic drop in MW. As the temperature rises, the viscosity is decreased by both the increased mobility of the polymer molecules and the degradation of the polymer as bonds break and leave shorter polymer chains.[13] Thus, polymers with random-chain scission as dominant decomposition mechanism, such as EVA, PA6, LDPE, and PP, result in rapid decrease in viscosity due to decomposition. Depolymerization, which is the process of converting a polymer into a monomer or a mixture of monomers, reduces MW step by step at a slower rate than random-chain scission. PMMA undergo mainly "unzipping" or end-chain scission, which is depolymerization occurring by a sequence of reactions, progressing along a macromolecule and yielding products, usually monomer molecules at each reaction step, from which macromolecules similar to the original can be regenerated.[14] So, the viscosity of PMMA slightly decreases due to decomposition. The side-chain stripping and the intra-aminolysis/acidolysis release small molecules at each reaction step, which also slightly decreases MW. Intramolecular cyclization also only slightly decreases MW and intermolecular cyclization can increase MW. Hence, ABS and HIPS, which decompose via depolymerization and cyclization, have slow MW reduction rate during burning. However, cross-linking can increase MW. For PCs, the decomposition mechanism seems to be a mixture of random-chain scission and cross-linking, initiated intramolecularly. If volatile products are not removed (the abnormal situation), no cross-linking is observed due to competition between condensation and hydrolysis reactions.[12] Normally, PCs yield substantial amounts of char, which enhances viscosity and melt strength (MS), and produce noncombustible gases such as carbon dioxide. The cross-linking increases MW, while the gas production process decreases MW slightly. As a whole, in this study, if MW is decreased significantly due to decomposition, the polymers including EVA18, PA6, LDPE, and PP form the Type I dripping. Otherwise, the Type II dripping dominates for ABS, HIPS, PC, and PMMA because the decomposition changes MW slightly.

Table 4. Dominant decomposition mechanism of polymers

Polymers	Main decomposition mechanism
ABS	Cyclization of polyacrylonitrile, cyclization of polybutadiene, and depolymerization of polystyrene
HIPS	Depolymerization and cyclization
PC	Random-chain scission and cross-linking
PMMA	End-chain scission
EVA	Side-chain stripping followed by random-chain scission
PA6	Intra-aminolysis/acidolysis, random-chain scission
LDPE	Random-chain scission
PP	Random-chain scission

ABS: poly(acrylonitrile-butadiene-styrene); HIPS: high-impact poly(styrene-butadiene); PC: polycarbonate; PMMA: polymethylmethacrylate; EVA: polyethylenevinylacetate; PA6: polyamide 6; LDPE: low-density polyethylene; PP: polypropylene.

The dripping time and the drop mass also seem to have something to do with the ability of the decomposition to decrease MW. Simply, we define the extent of decreasing MW with numbers as follows:

Random-chain scission: −2;
Depolymerization, end-chain scission, side-chain stripping, and intra-aminolysis/acidolysis: −1;
Cyclization: 0;
Cross-linking: +1.

where a negative represents the reduction in MW and a positive represents the increase in MW. The extent of changing MW by the decomposition is proportional to the absolute value of the number.

Thus, according to the dominant decomposition mechanisms of polymers during burning the extent of MW reduction can be theoretically ranked as: LDPE(−2), PP(−2), PA6(−1.5), EVA(−1.5), PMMA(−1), HIPS(−0.5), ABS(−0.3), and PC(+1). From the experimental results, the order of polymers by the first dripping time from the longest to the shortest time is ABS > (PC, HIPS) > PMMA > (EVA18, LDPE, PA6) > PP and the order of the first drop mass from the highest to the lowest is (ABS, HIPS) > PC > PMMA > PA6 > (EVA18, LDPE, PP). It is found that PMMA always locates between (ABS, HIPS, PC) and (EVA18, LDPE, PA6, PP), indicating that the theoretical order based on the decomposition mechanisms is agreeable with the experiments to a certain extent.

Combined with the research of Sherratt,[8] it can be found that the random-chain scission decomposition mechanism relates to the small-sized dripping and the surface melting, and the end-chain scission decomposition mechanism relates to the large-sized dripping and the bulk softening. This indicates that the dripping behavior in the UL94 test should be consistent with that found in the larger scale experiments to a certain extent. The small-sized dripping and the large-sized dripping correspond to the surface melting and the bulk softening, respectively. Furthermore, in our previous study,[11] it was found that for the large-sized dripping, the molten polymer broke at the cross section and the mass of first drop increased with the thickness of test specimens, implying that it was related with bulk softening. On the contrary, for the small-sized dripping, the mass of the first drop was independent on the thickness, namely, the cross-section area of the specimen, implying that it had relationships with surface melting. However, in our studies, the dripping behaviors were subdivided by the drop size rather than by the mechanisms to fuel pool fire because the small-sized specimen in the UL94 test was three dimensional. The dripping of polymer melt formed at lateral surfaces could be determined as surface melting. It was difficult to determine whether the dripping of polymer melt formed at the bottom surface was surface melting, except that the break position of molten polymer was far away from the bottom surface, which should be bulk softening.

It is well known that a liquid drop may form when liquid accumulates at the lower end of a surface boundary, producing a hanging drop called a pendant drop. The pendant drop is in balance between the gravity force and the component of the surface tension in the vertical direction. When the drop exceeds a certain size, it is no longer stable and detaches itself.[15] Therefore, it is possible that the mass or size of the drop of polymer melt during burning is also related to the surface tension. The surface tension data at 23°C determined by the contact angle between a drop of liquid and the solid polymer are listed in Table 3.[16] The polymers with the lowest surface tension (LDPE and PP) have small-sized drops, and high surface tension corresponds to a large drop size except for PA6. However, correlations between the surface tension and the drop size are not good enough to explain the results. The surface tension is in the following order: (PP, LDPE) < (PMMA, ABS) < (PA6, PC), whereas the average first drop mass is in the following order: (PP, LDPE) < PA6 < (PC, PMMA, ABS). The difference in ordering might be attributed to three aspects. First, values of surface tension for burning polymers at high temperatures are unavailable. Second, some polymers such as PC have special burning behaviors, including charring. For these polymers, the composition of the drops is no longer the same as that of the original polymer. Third, the shape of drops may be irregular and varies with different polymers. Drops of LDPE and PP are roughly spherical, while those of ABS are bars broken off from the original object.

Effect of talc on dripping behaviors of LDPE

In practical applications, thermoplastics are often added with fillers to reduce product costs and improve their properties. Therefore, a talc filler was selected to examine the effect on dripping behavior. The photos of drops of LDPE with and without talc collected on the pan are shown in Figure 2. It can be seen that the drop shape is circular, and the size of drops is relatively uniform when the mass fraction of talc is less than 20%. The diameter of these disks is about 5–8 mm. When the mass fraction of talc is 20%, the size of drops is not uniform. The differences in size and shape among the drops become more evident when the mass fraction of talc is higher than 20%. The drops are no longer a thin layer adhered to the pan. It was observed that the drops are lumpish when the mass fraction of talc is 40%. When the mass fraction of talc is 60%, the drops are large and rectangular, with length exceeding 40 mm.

The dripping time and mass data for drops of LDPE with and without talc are listed in Table 5. The average first dripping time and the average mass of first drop are plotted versus

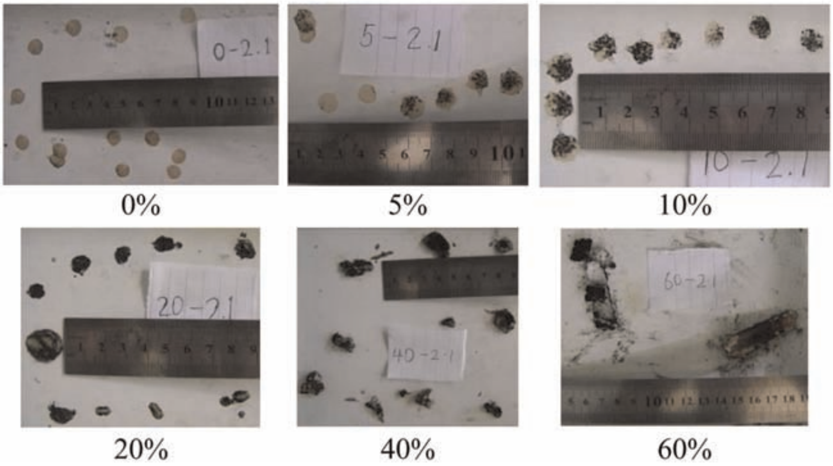

Figure 2. Photographs of drops of LDPE with and without talc.
LDPE: low-density polyethylene.

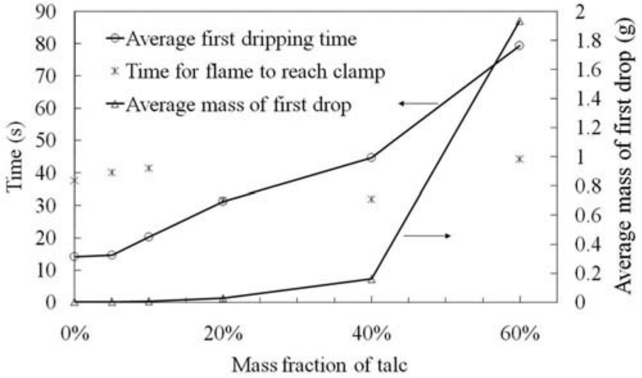

Figure 3. Effects of talc on the first dripping of LDPE.
LDPE: low-density polyethylene.

the mass fraction of talc in Figure 3. From Figure 3, it is seen that both the first dripping time and the mass of the first drop increase with the mass fraction of talc. The first dripping time increases nearly linearly with the mass fraction of talc. When the mass fraction of talc is 20%, the first drop mass is in the order of magnitude of 0.01 g. When the mass fraction of talc increases from 40% to 60%, the first drop mass increases dramatically. Figure 3 also shows the time for the flame to reach the clamp, indicating that all these LDPE/talc samples have no ratings in the UL94 test conditions.

From the data listed in Table 5, it is also found that when talc is added into LDPE not only is the first dripping time delayed but also the dripping frequency is lowered. The dripping times of successive drops are shown in Figure 4, illustrating that the time interval between two successive drippings is about 1 s for the neat LDPE and the 5 wt% talc-filled LDPE, while the time interval approaches as much as 3 s for 20 wt% talc-filled LDPE and 7 s for 40 wt% talc-filled LDPE.

The statistical mass data of drops are listed in Table 6. From Table 6, it can be found that the average drop mass exceeds 0.01 g when the mass fraction of talc is greater than 20%. Although the maximum drop mass of LDPE with 10 wt% talc can reach 0.0 1 g, the average drop mass for LDPE with the talc content less than 20 wt% is in the order of magnitude of 0.001 g. When the mass fraction of talc is 20% and 40%, the distribution of the drop masses is wide and the maximum drop mass is 30–40 times the minimum drop mass. The results suggest that dripping behavior can be shifted from the shorter first dripping time and smaller drop size to the longer time and larger drop size by adding a sufficient amount of noncombustible filler. Combined with the appearance changes of collected drops shown in Figure 2, it is considered that the dripping type of LDPE may convert from small-sized dripping to large-sized dripping as the mass fraction of talc increases, with the dripping type transition point for the mass fraction of talc in LDPE at about 20 wt%. When the mass fraction of talc is lower than 20 wt%, the drops are uniform and small size with short first dripping time, while when the mass fraction is higher than 20 wt%, the drops are irregular and relatively large size with relatively long first dripping time.

The transition in the dripping type of LDPE due to the addition of talc at the higher loading level might be attributed to the flame retardancy of talc and the amount of talc particles

Table 5. Effects of talc on multiple drops of LDPE

Mass fraction	Drops	Test_1		Test_2		Average	
		t_d (s)	m_d (g)	t_d (s)	m_d (g)	t_d (s)	m_d (g)
0%	1	13.77	0.0048	14.44	0.0043	14.11	0.0046
	2	15.99	0.0041	16.33	0.0052	16.16	0.0047
	3	17.93	0.0044	17.99	0.0044	17.96	0.0044
	4	19.40	0.0046	19.35	0.0045	19.38	0.0046
	5	20.50	0.0045	20.42	0.0040	20.46	0.0043
	6	21.62	0.0040	21.46	0.0043	21.54	0.0042
	7	22.59	0.0035	22.58	0.0039	22.59	0.0037
	8	23.50	0.0038	23.49	0.0028	23.50	0.0033
	9	24.24	0.0034	24.29	0.0034	24.27	0.0034
	10	24.48	0.0025	24.99	0.0035	24.74	0.0030
5%	1	14.66	0.0026	14.42	0.0033	14.04	0.0030
	2	17.09	0.0025	16.20	0.0038	16.65	0.0032
	3	18.89	0.0045	18.44	0.0045	18.67	0.0045
	4	20.15	0.0041	20.19	0.0062	20.17	0.0052
	5	21.42	0.0051	21.64	0.0035	21.53	0.0043
	6	22.82	0.0065	22.79	0.0059	22.81	0.0062
	7	23.96	0.0026	23.88	0.0022	23.92	0.0024
	8	24.89	0.0033	24.95	0.0033	24.92	0.0033
	9	25.58	0.0071	25.42	0.0022	25.50	0.0047
	10	26.31	0.0038	26.28	0.0030	26.30	0.0034
10%	1	20.88	0.0082	20.44	0.0064	20.66	0.0073
	2	21.86	0.0078	21.76	0.0074	21.81	0.0076
	3	22.86	0.0032	23.11	0.0095	22.99	0.0064
	4	23.62	0.0039	24.92	0.0097	24.27	0.0068
	5	24.44	0.0055	26.26	0.0093	25.35	0.0074
	6	25.74	0.0070	27.96	0.0107	26.85	0.0089
	7	26.91	0.0091	28.84	0.0091	27.88	0.0091
	8	28.06	0.0098	29.94	0.0078	29.00	0.0088
	9	29.35	0.0102	31.90	0.0068	30.63	0.0085
	10	30.35	0.0093	33.01	0.0069	31.68	0.0081
20%	1	31.58	0.0320	30.93	0.0246	31.26	0.0283
	2	35.87	0.0236	33.52	0.0166	34.70	0.0201
	3	38.22	0.0168	36.28	0.0211	37.25	0.0190
	4	40.34	0.0196	38.78	0.0232	39.56	0.0214
	5	42.30	0.0180	41.06	0.0155	41.68	0.0168
	6	42.87	0.3141	41.91	0.2781	42.39	0.2961
	7	44.63	0.0586	43.09	0.0901	43.86	0.0744
	8	46.77	0.0852	44.48	0.0355	45.63	0.0604
	9	47.96	0.0402	45.95	0.0700	46.96	0.0551
	10	49.18	0.0189	47.52	0.0230	48.35	0.0210
40%	1	43.60	0.0736	45.66	0.2473	44.63	0.1605
	2	45.55	0.3335	48.22	0.1304	46.89	0.2320
	3	46.53	0.3264	53.28	0.1840	49.91	0.2552
	4	52.40	0.2583	54.48	0.2002	53.44	0.2293
	5	54.15	0.0378	61.26	0.3220	57.71	0.1799
	6	57.32	0.3390	68.60	0.0574	62.96	0.1982
	7	59.12	0.1177	71.94	0.2431	65.53	0.1804
	8	63.87	0.2156	79.08	0.4541	71.48	0.3349

(continued)

Table 5. (continued)

Mass fraction	Drops	Test_1		Test_2		Average	
		t_d (s)	m_d (g)	t_d (s)	m_d (g)	t_d (s)	m_d (g)
	9	68.78	0.0203	80.25	0.0122	74.52	0.0163
	10	78.38	0.1214	85.75	0.0637	82.07	0.0926
60%	1	82.11	1.9233	76.84	1.9507	79.48	1.9370
	2	138.58	1.1347	N/A	N/A	N/A	N/A

LDPE: low-density polyethylene; t_d: time when dripping occurs; m_d: mass of the drop; N/A: not available.

present in the polymer melt during burning. The heat release rate curves of LDPE specimens in the cone calorimeter test at 50 kW/m^2 radiation heat flux are shown in Figure 5. It can be seen that when the mass fraction of talc is 20%, the heat release rate during the cone test is significantly reduced, which will decrease the heat feedback to the specimen and lower the rate of temperature rise within the specimen. The decrease in the specimen temperature definitely reduces the melt flow tendency and delays the first dripping time. The reduction of burning rate by introduction of talc should be ascribed to the formation of the integral non-combustible residues. The digital photos of residues of the talc-filled LDPE specimens in the cone calorimeter test at 50 kW/m^2 radiation heat flux are shown in Figure 6. In Figure 6, it is seen that when talc is at 5 and 10 wt%, the residue consists of talc flakes. When the mass

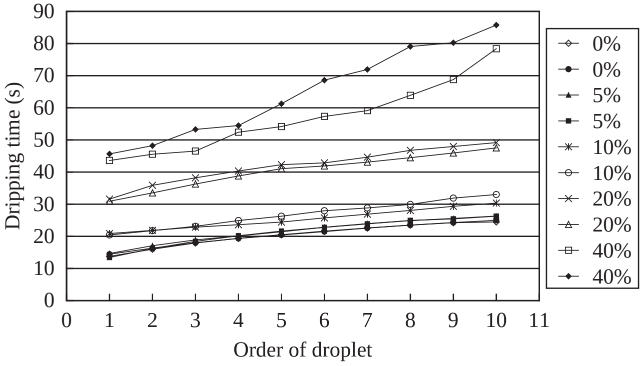

Figure 4. Dripping times of drops in two tests of LDPE with and without talc.
LDPE: low-density polyethylene.

Table 6. Statistical mass data for drops of LDPE with and without talc

Talc content	0%	5%	10%	20%	40%	60%
Average m_d (g)	0.0040	0.0040	0.0079	0.0612	0.1879	1.9370
Minimum m_d (g)	0.0025	0.0022	0.0032	0.0155	0.0122	1.1347
Maximum m_d (g)	0.0052	0.0071	0.0107	0.3141	0.4541	1.9507

LDPE: low-density polyethylene; m_d: mass of the drop.

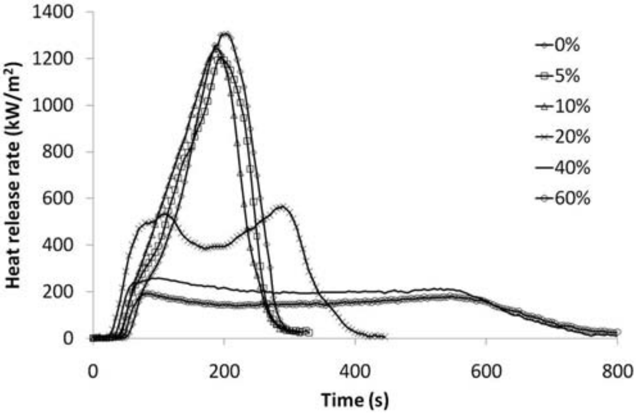

Figure 5. Heat release rate curves of the talc-filled LDPE at 50 kW/m^2 heat flux.
LDPE: low-density polyethylene.

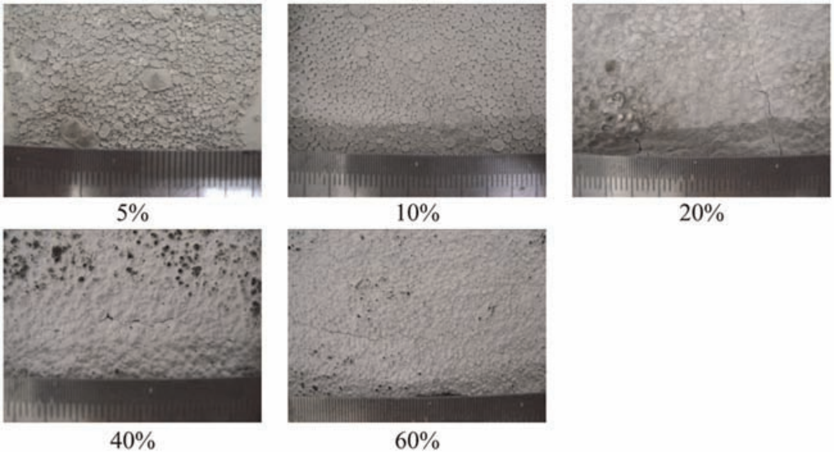

Figure 6. Digital photographs of the top surface for residues of the talc-filled LDPE after cone calorimeter testing at 50 kW/m^2 heat flux.
LDPE: low-density polyethylene.

fraction of talc is higher than 20%, an integral residue with cracks remain, and the residue becomes more and more compact as the talc content is increased. The integral residue formed by the talc particles may reduce the flow rate of polymer melt during burning and lead to large-sized dripping behavior by inhibiting small-sized dripping.

Effect of MFI on dripping behaviors

It is natural to presume that the dripping of polymers during burning could be correlated with the melt flow tendency. However, the melt flow indices of polymers at processing temperatures seem to have no direct relationship with the dripping behaviors in the UL94 fire test conditions. This can be seen through comparing the MFI data listed in Table 3 with the experimental data of dripping. From these data, it can be found that the melt flow tendency from high to low is in the following order: PA6 > PMMA > EVA18 > HIPS > LDPE > PC > PP > ABS. However, the order of polymers by the first dripping time from the shortest to the longest is PP < (EVA18, LDPE, PA6) < PMMA < (PC, HIPS) < ABS. Obviously, the polymer with high melt flow rate does not always correspond to short first dripping time as expected. For example, the MFI of PMMA is nearly five times that of PP, but the first dripping time of PMMA is nearly two times that of PP. This disagreement between the MFI data and the dripping time might be ascribed to the fact that the melt flow rate at processing temperatures could not reflect the real melt flow tendency of the polymers in fire because the MFI data shown in Table 3 were measured at 230°C with 2.16-kg load, both of which will affect the data.

To investigate the effect of MFI on dripping behavior, blended PE specimens with different melt flow indices were studied. In the blend, LDPE (trade mark: LDPE 18D) has MFI of 1.5 g/10 min at 190°C with a 2.16-kg load, while HDPE (trade mark: DMDY 1158) has weight average molecular weight (M_w) of 400,000 and MFI of 1.3–2.3 g/10 min at 190°C with a 21.6-kg load, which is much greater than that used for MFI measurement of LDPE. The MFI of blended PE specimens at 190°C with a 2.16-kg load is shown in Figure 7. In Figure 7, the MFI of the blend decreases significantly with increasing mass fraction of the additive. When the mass fraction of DMDY is higher than 25%, the melt could be barely squeezed out by the load and the MFI approaches zero.

The digital photos for drops of PE blends are shown in Figure 8. It can be seen that all drops have similar sizes and are thin disks with diameters of about 5 mm. The drop size does not vary with the mass fraction of DMDY, indicating that the MFI of the PE blend does not significantly affect the dripping behavior.

The first dripping time and first drop mass for PE blends are plotted in Figure 9. This shows that both the first dripping time and the first drop mass increase slowly with increasing mass fraction of DMDY, indicating that if the chemical structures of polymers in a blend are similar, the dripping may be delayed by decreasing the melt flow tendency. However, when

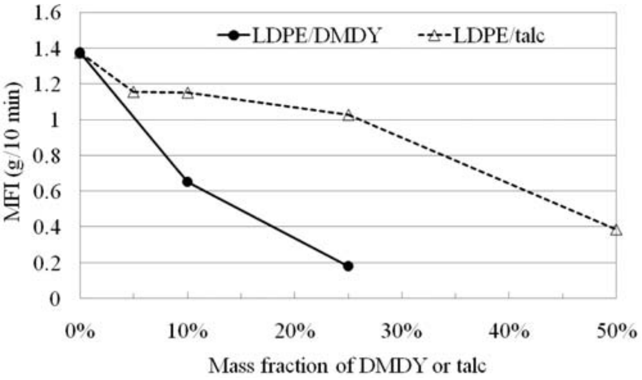

Figure 7. MFI of PE blends and the talc-filled PE at 190°C, 2.16 kg.
LDPE: low-density polyethylene; MFI: melt flow index; PE: polyethylene.

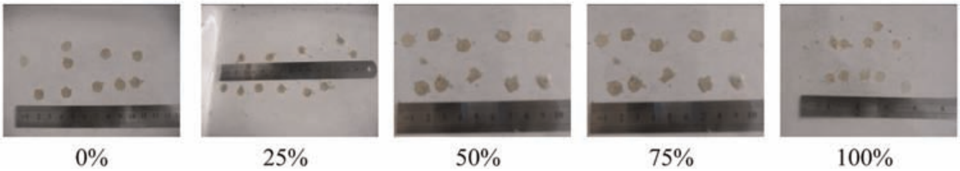

Figure 8. Digital photographs of drops of PE blends.
PE: polyethylene.

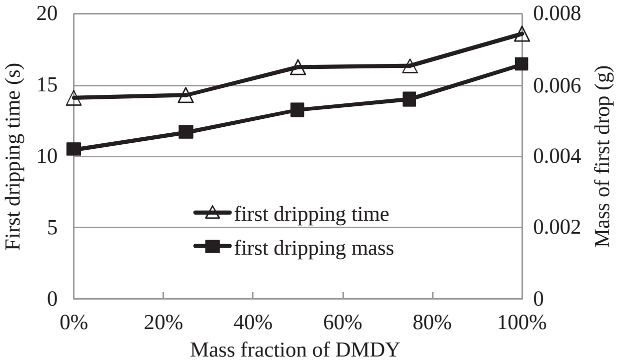

Figure 9. Average data of first dripping time and first drop mass plotted versus mass fraction of DMDY in blended PE.
PE: polyethylene.

the mass fraction of DMDY increases from 0% to 100%, the first dripping time increases by only about 5 s and the drop mass ranges from 0.004 to 0.007 g, corresponding to the small-sized dripping behavior. Compared with the talc-filled LDPE, the changes in the dripping behaviors of PE blends are minor. Combining Figures 3, 7, and 9, it can be found that adding 25% DMDY to reduce the MFI of LDPE 18D from 1.4 to 0.2 increases the first dripping time from 14 to 19 s, while a similar MFI reduction from 1.4 to 0.4 achieved by adding 50% talc significantly increases the first dripping time to 79 s. Since talc is noncombustible and forms a residue during burning, the flowability during the fire seems to be more critical than the initial MFI for the dripping phenomenon.

Main factors related to dripping

The dripping is related to the viscosity and MS of the polymeric material at the rising temperatures in a fire. Small-sized dripping is hypothesized to result from melt flow over the surface of the specimen, similar to the drips from a candle. Large-sized dripping may be caused by temperature elevation of the inner specimen and the elongation of the molten specimen bar. If this is true, the small-sized dripping would depend primarily on the shear viscosity η or MFI of the polymer, while the large-sized dripping would be dominated by the MS or the extensional viscosity η_e. For uniaxial extension of Newtonian fluid, the extensional viscosity is three times the shear viscosity. For non-Newtonian fluid of polymer melts, the extensional viscosity is much higher than shear viscosity. Especially at high shear rate, the extensional viscosity is even two magnitudes higher than the shear viscosity.[17] Thus, it is reasonable that the extensional viscosity can support greater drop mass than the shear viscosity.

The key factors influencing viscosity and MS for dripping during a fire test include the original MW, the temperature T, and the decomposition mechanism related to chemical structure, as discussed individually below.

MW. Typically, the zero shear rate viscosity η_0 of polymers is related to MW. When MW is lower than a critical value M_c, η_0 is linear with the weight averaged molecular weight, M_w. When M_w is higher than the M_c, η_0 increases significantly with M_w in a power law of order 3.4 as described below[18]

$$\eta_0 = K_1 M_w (M_w < M_c) \tag{1}$$

$$\eta_0 = K_2 {M_w}^{3.4} (M_w > M_c) \tag{2}$$

where K_1 and K_2 are constants at a given temperature.

MFI is proportional to ${\eta_0}^{-1}$, and the relationship between MFI and MW is as follows[18]

$$\log(\mathrm{MFI}) = A - B \times \log(\mathrm{MW}) \tag{3}$$

where A and B are constants of polymers at a given temperature.

For a given polymer, MS increases with the melt viscosity[18] and is proportional to $(\mathrm{MFI})^{-1}$ for polymers such as PP,[19] implying that MS should be a power law function of MW.

Temperature. When the temperature ranges from the glass transition temperature T_g to (T_g + 100), the viscosity of the polymers comply with the following Williams–Landel–Ferry (WLF) equation[17,20]

$$\lg[\eta(T)/\eta(T_g)] = -17.44(T - T_g)/[51.6 + (T - T_g)] \tag{4}$$

For most amorphous polymers, $\eta(T_g)$ is 10^{12} Pa s.

When the temperature is much higher than T_g ($>T_g + 100$) and the melting temperature T_m, the dependence of viscosity on temperature can be expressed by the Arrhenius equation[17,20]

$$\ln\eta_0(T) = E_h/RT + \ln K_3 \tag{5}$$

where K_3 is constant for a given polymer and $K_3 = \eta_0(T \to \infty)$, E_η is the activation energy (in J/mol) for viscous flow, R is molar gas constant, and T is the absolute temperature.

The MS[19] decreases as the temperature increases.

$$\ln(\mathrm{MS}) = E_{\mathrm{MS}}/RT + \ln C \tag{6}$$

where C is constant for a given polymer and E_{MS} is the activation energy for the MS.

Decomposition. Decomposition is an important process affecting MW and is strongly related to the chemical structure. Decomposition also affects temperature significantly. The endothermic pyrolysis of the polymer and the vaporization of decomposition products exert cooling effects in the condensed phase of a burning polymer material. The heat flux heating the specimen no longer results in an increase in polymer temperature, but instead results in an increase in the consumption of the material. Indeed, for noncharring materials, the surface temperature is proposed to be equal to the pyrolysis temperature as a pyrolysis zone moves through the sample.[21] So the pyrolysis temperature should be the upper limit temperature of the polymer melt.

Comprehensively, the dripping of polymers during burning is attributed to both physical melting and chemical decomposition. Before decomposition, the viscosity of the polymer melt depends on the original MW, initial viscosity or MFI, E_η, and T. Polymers in a fire will soften and flow as their temperatures increase with time. Their temperatures are proportional to the heat flux characteristic of the test and are inversely proportional to the density, the heat capacity, and the latent heat of melting. For thermally thin materials, the following energy balance equation can be used to describe the polymer temperature

$$\dot{q}t = \rho V\left[C_p(T - T_0) + h_m\right] \tag{7}$$

where $\dot{q}$, t, ρ, V, C_p, T_0, and h_m are the heat flux, time, density, volume, heat capacity, initial temperature, and the heat of melting, respectively.

Based on equation (7), for a given polymer in the specified fire test conditions, its temperature increases with time almost linearly to successively surpass its glass transition temperature, melting point, or viscous flow temperature, which is illustrated in Figure 10. Thus, according to equation (5), the polymer's viscosity decreases exponentially with time as the temperature increases, which is also shown in Figure 10.

For physical melting, the melting point (or viscous flow temperature) and the decomposition temperature are important properties, which determine the lower limit and the upper limit of the temperatures, respectively. If the activation energy for viscous flow, the melting point, and the onset decomposition of a thermoplastic are 80 kJ/mol, 150°C, and 350°C, respectively, its viscosity approaching the decomposition temperature will decrease to 6.7×10^{-4} times its viscosity at the melting point according to equation (5). During the temperature rise period, if the viscosity is low enough, dripping due to physical melting will occur soon. Since the decomposition temperature is the upper limit, it determines the lowest viscosity of physical melting. If the viscosity at this temperature is low enough, physical melting and dripping will emerge before decomposition.

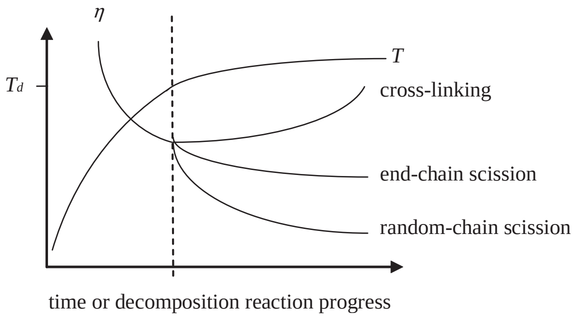

Figure 10. Schematic diagram for temperature history and viscosity variation.

However, for materials having the same chemical structure and close decomposition temperatures, the dripping depends on MW. The material with very low MW may melt and drip before decomposition, while the viscosity of the polymer with high MW might be too high to flow even if the decomposition temperature is approached. For example, MW of PE wax ranges from 1000 to 5000, while some PE products have MW over one million. Thus, according to equations (1) and (2), the viscosity of PE wax is about 10^{-3}– 10^{-10} times the viscosity of those high MW products at the same temperature. Such PE wax has so low viscosity that it will melt and drip before reaching its onset decomposition temperature. Actually, the MW of a polymer distributes widely. Thus, it is possible that some chains with low MW form drops before decomposition, while other chains do not form drops until decomposed, especially for the polymer with very wide MW distribution.

After ignition, the surface temperature of a noncharring thermoplastic is nearly kept at the pyrolysis temperature. Its viscosity mainly depends on the MW, which is changed by decomposition significantly. Ideally, for a polymer with end-chain scission decomposition mechanism, its MW decreases by the MW of a monomer at each reaction step. Simply, the following equation can be presumed

$$\mathrm{MW} = \mathrm{MW}_0 - n\mathrm{MW}_m \tag{8}$$

where MW_0 and MW_m are the original MW of the polymer and the MW of its monomer, respectively, and n denotes the decomposition reaction progress.

Thus, its viscosity will decrease slowly as the MW reduces slightly with the reaction progress. While, for a polymer with random-chain scission decomposition mechanism, if it is assumed that the chain scission always occurs at the midpoint of the main chain, its MW will decrease as the decomposition reaction progresses according to the following equation

$$\mathrm{MW} = (1/2)^n \mathrm{MW}_0 \tag{9}$$

According to equation (2) the viscosity will be $(1/2)^{3.4n}$ times the original viscosity of the polymer approaching its decomposition temperature, implying that the viscosity decreases as a power law function of the reaction steps.

For a polymer with original MW higher than 10,000 such as a PP product with 240 repeat units of propylene, it needs 6–7 reaction steps to decompose to a small molecule with three repeat units. If $n = 6$, the viscosity will decrease to 7×10^{-7} times the viscosity of the polymer melt approaching the decomposition temperature.

On the contrary, if the dominant decomposition mechanism is cross-linking which will increase the MW the viscosity increases as the reaction progresses. Ideally if two molecules are cross-linked at each reaction step the MW is doubled and the viscosity is a power law function of the reaction progress as shown in Figure 10.

Although the viscosity of a polymer after ignition is significantly affected by the decomposition mechanism with regard to molecular structure, it should also be significantly related with the kinetic parameters of the decomposition reaction, which determine the reaction progress.

All polymers used in this study were ignited before dripping, implying that the factors related to decomposition, including the decomposition temperature, the dominant decomposition mechanism, and the decomposition reaction kinetics, played an important role in dripping.

For the eight polymers used in this study, their properties are listed in Table 7, including the glass transition temperature T_g,[12] the melting temperature T_m,[12] E_η,[17,20] and the parameters obtained from the literature,[22] including the onset decomposition temperature T_d, the temperature at peak mass loss rate of the differential thermogravimetric curve T_p, the ignition temperature T_{ign}, the thermal conductivity k, the density ρ, the heat capacity C_p, the enthalpy of gasification of the polymers h_g, the char yield μ, the latent heat of gasification L_g, the heat of complete combustion H_c, the combustion efficiency χ, and the effective heat of combustion (EHC).

Zhang et al.[5] reported that for PE, PP, PA6, and PC, the total mass of polymer melt collected from the vertically oriented burning specimens in the cone calorimeter is inversely proportional to T_g and T_m. From the data in Table 7, it can be seen that except PMMA, polymers with T_g lower than 80°C tend to form small-sized drops in the UL94 test, which is in agreeable with the report to certain extent. Since the melt flow of polymers depends on the sequential movement of the chain segments and above the glass transition temperature the polymer chain segments can move; it is reasonable that the glass transition temperature is important to the dripping. However, the relationship between the dripping type and T_m is not clear in the UL94 test. From Table 7, it is also found that the dripping type cannot be determined solely by typical burning parameters, including T_d, T_p, T_{ign}, h_g, μ, L_g, H_c, χ, and EHC, and thermophysical parameters, including k, ρ, C_p, thermal diffusivity $k/(\rho C_p)$, thermal inertia $(k\rho C_p)$.

Table 7. Properties of eight polymers

Polymers	ABS	HIPS	PC	PMMA	EVA	PA6	LDPE	PP
T_g (°C)	91–110	$>80^{a}$	145–150	50	N/A	75	−25	−20
T_m (°C)	110–125	230^{a}	215–230	90–105	65–110	215–220	109–125	170
T_d (°C)	390	327	476	354	448	424	399	354
T_p (°C)	461	430	550	383	473	454	453	424
T_{ign} (°C)	394	413	500	317	N/A	432	377	367
E_η (kJ/mol)	88–108	$92–96^{a}$	108–125	N/A	57.4^{b}	63.9	48.8	42–46
E_η/RT_m^c	30.2	22.5	28.2	N/A	19.2	15.1	15.1	11.9
E_η/RT_d^c	17.8	18.8	18.7	N/A	9.6	11.3	8.7	8.4
k (W/m K)	0.26	0.22	0.20	0.20	0.34	0.24	0.38	0.15
ρ (kg/m^3)	1050	1045	1200	1175	930	1130	925	880
C_p (J/g K)	1.50	1.40	1.22	1.40	1.37	1.55	1.55	1.88
$k/(\rho\ C_p)$ (m^2/s)	1.65E-7	1.54E-7	1.36E-7	1.19E-7	2.67E-7	1.37E-7	2.65E-7	0.89E-7
$k\rho\ C_p$ (J/m^4 K^2 s)	4.10E5	3.22E5	2.93E5	3.29E5	4.33E5	4.20E5	5.45E5	2.48E5
h_g (kJ/g)	2.3	2.0	1.8	1.7	N/A	1.5	1.9	1.9
μ	0	0	0.25	0	0	0.02	0	0
L_g (kJ/g)	2.3	2.0	2.4	1.7	N/A	1.5	1.9	1.9
H_c (kJ/g)	36.6	37.2	23.3	25.0	37.9	28.7	41.4	43.0
H_c/L_g	15.9	18.6	9.7	14.7	N/A	19.1	21.8	22.6
χ	0.79	0.76	0.91	0.99	0.81	0.90	0.97	0.97
EHC (kJ/g)	29.0	28.1	21.2	24.8	30.8	25.8	40.3	41.9
EHC/L_g	12.6	14.1	8.8	14.6	N/A	17.2	21.2	22.1

ABS: poly(acrylonitrile-butadiene-styrene); HIPS: high-impact poly(styrene-butadiene); PC: polycarbonate; PMMA: polymethylmethacrylate; EVA: polyethylenevinylacetate; PA6: polyamide 6; LDPE: low-density polyethylene; PP: polypropylene; N/A: not available; EHC: effective heat of combustion.

[a] Properties of polystyrene.

[b] The activation energy for viscous flow of polyvinylacetate is 250 kJ/mol. If EVA contains 18% polyvinylacetate and 82% polyethylene, we estimated the activation energy for viscous flow of EVA to be $250 \times 0.18 + 48.8 \times 0.82 = 57.4$ kJ/mol.

[c] The ratio of average activation energy to average melting temperature (in Kelvin) multiplied by gas constant.

Fortunately, distinct differences in E_η between small-sized and large-sized dripping types exist. Polymers with large-sized drops have E_η higher than 85 kJ/mol, while polymers with small-sized drops have E_η less than 65 kJ/mol. Even if at the temperatures T_m and T_d, E_η/RT_m, and E_η/RT_d for polymers of large-sized dripping are always greater than that for polymers of small-sized dripping. But the differences between E_η/RT_m and E_η/RT_d for ABS, HIPS, PC, EVA, PA6, LDPE, and PP are 12.4, 3.7, 9.5, 9.6, 3.8, 6.4, and 3.5, respectively, showing that this difference has no relationships with the dripping type. These values of the difference between E_η/RT_m and E_η/RT_d also demonstrate that the viscosity of these polymers will decrease to 1/exp(3.5)($= 3 \times 10^{-2}$) to 1/exp(12.4)($= 4 \times 10^{-6}$) times their viscosities at melting temperatures. E_η is the activation energy of viscous flow, and generally polymers with rigid chains or great intermolecular forces have great values of E_η. A polymer with low E_η is prone to form melt flow at low temperatures. So, E_η represents the physical melting to a certain extent, and it is reasonable that it could be used to discriminate the dripping types.

Furthermore, it seems that the dripping type can be related to H_c/L_g and EHC/L_g. Polymers of Type I dripping have H_c/L_g values greater than 19, while polymers of Type II dripping have H_c/L_g values less than 19. The relationships between EHC/L_g and the dripping types are clearer. EHC/L_g of polymers with large-sized drops is less than 15 while that of polymers with small-sized drops is more than 17. Generally, the heat release rate of a solid is estimated by the following equation[23]

$$\dot{Q}''_c = \dot{m}''\chi H_c = \left(\dot{Q}''_{net}/L_g\right)\chi H_c = \dot{Q}''_{net}\chi\left(H_c/L_g\right) = \dot{Q}''_{net}\left(\mathrm{EHC}/L_g\right) \tag{10}$$

where $\dot{Q}''_c$, $\dot{m}''$,$\dot{Q}''_{net}$, χ, and H_c are the heat release rate, the mass loss rate, the net heat flux into the solid surface, the combustion efficiency, and the heat of combustion, respectively, and H_c/L_g is a flammability parameter defined as "combustibility ratio."[23] From equation (10), it is known that EHC/L_g can be considered as the product of the combustion efficiency and the "combustibility ratio." Both H_c/L_g and EHC/L_g are intimately related with the heat release rate of a burning polymer. For free burning of the polymers in the UL94 test, the net heat flux is the heat feedback from the polymer flame, which relates to the heat release rate. Thus, the pyrolysis rate should be proportional to H_c/L_g and EHC/L_g. Both of them could reflect the chemical decomposition, especially EHC/L_g, which reflects the practical combustion efficiency. Since the chemical decomposition affects the dripping significantly, it is also reasonable that these two parameters have close relations with the dripping types.

It can be considered that the chemical structure is very important to the dripping behavior. The chemical structure not only significantly influences the glass transition temperature and the melting point or viscous flow temperature but also determines the decomposition temperature and the decomposition mechanism. Even the two key important parameters, the activation energy of the viscous flow and the combustibility ratio, which can be used to discriminate the dripping types, are also intimately related to the chemical structure. The activation energy of viscous flow is related with the rigidity and intermolecular force of polymer chain, and the heat of combustion can be estimated based on the stoichiometric reaction. The original MW is also important. It can influence the glass transition temperature and the melting point or viscous temperature, and the activation energy of viscous flow since it affects the intermolecular force of the polymer chain. But it should be mainly related to the dripping caused by physical melting and has little to do with the dripping due to chemical decomposition.

A model correlating the dripping time and the drop mass

From the simple hypothesis that the dripping time is proportional to the mass of the polymer melt and inversely proportional to the flow rate of the polymer melt, the following expression can be proposed

$$t = a\frac{m}{dm/dt} \tag{11}$$

where t, m, and a represent time, mass, and a coefficient, respectively (R.E. Lyon, 2012, personal communication). The term “dm/dt” is the melt flow rate, depending on the viscosity, which relates to physical melting and chemical decomposition.

The above equation can be modified through separating variables as follows

$$\frac{dm}{m} = a\frac{dt}{t} \tag{12}$$

Integrating the left-hand side from zero to the drop mass and the right-hand side from zero to the dripping time, the following power law function can be obtained

$$m_d = bt_d^a \tag{13}$$

where m_d, t_d, and b are the drop mass, the dripping time, and the coefficient, respectively.

The average mass of first drop plotted versus the average first dripping time was shown in Figure 11. In Figure 11, the data of eight polymers (2-mm-thick specimens) and LDPE/talc (4-mm-thick specimens) come from Tables 2 and 5, respectively. The data originated from the literature[11] are for 2, 4, 6, 8, and 10mm thick samples of ABS, HIPS, PC, PMMA, LDPE, and PP under UL94 vertical test conditions. The line in Figure 11 is equation (13) with coefficients $a = 2.3$ and $b = 2E\text{-}5$. From Figure 11, it is known that the average data for the first dripping of polymers under the UL94 test conditions comply with equation (13), great drop mass corresponding to relatively long dripping time.

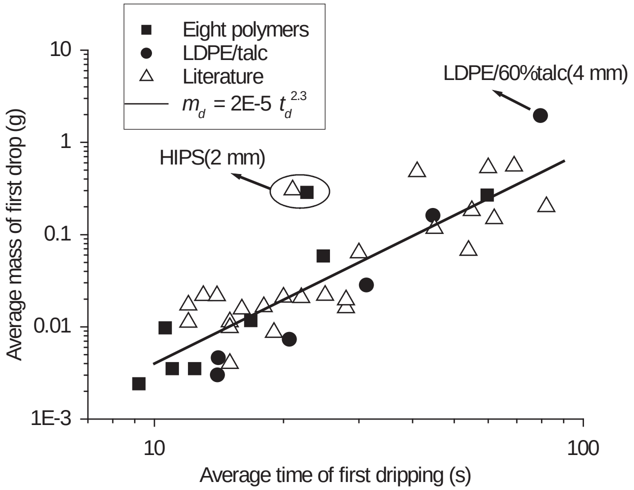

Figure 11. The correlation between first drop masses and first dripping times.
LDPE: low-density polyethylene.

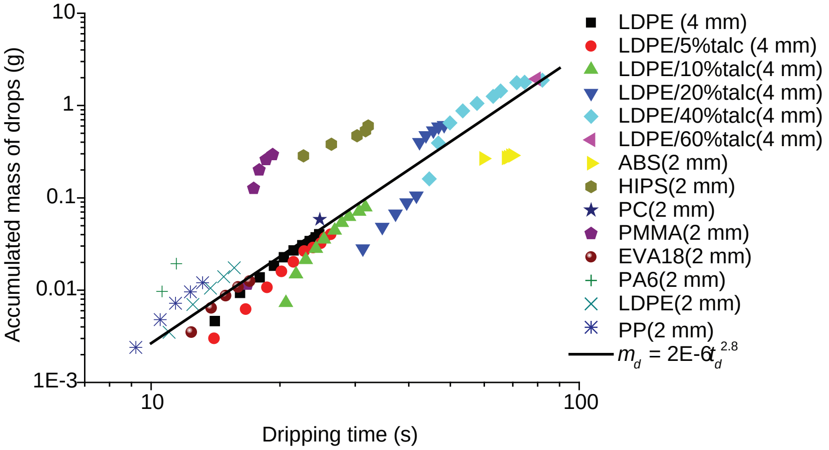

Figure 12. The correlation between accumulated mass of drops and dripping time.
ABS: poly(acrylonitrile-butadiene-styrene); HIPS: high-impact poly(styrene-butadiene); PC: polycarbonate; PMMA: polymethylmethacrylate; EVA: polyethylenevinylacetate; PA6: polyamide 6; LDPE: low-density polyethylene; PP: polypropylene.

The correlation between the accumulated mass of drops and the dripping time for the samples used in this study is illustrated in Figure 12. The accumulated mass is the total mass of all drops at that time. For 2-mm-thick PA6, LDPE, and PP samples, the average drop mass was measured. In such cases, we assumed that the mass of each drop equaled to the average value, and the accumulated drop mass was the number of drops multiplied by the average drop mass. From Figure 12, it seems that the power law function also works, with $a = 2.8$ and $b = 2E\text{-}6$.

However, from Figures 11 and 12, it can be found that some data points of large-sized dripping such as HIPS and LDPE/60% talc in Figure 11 and HIPS and PMMA in Figure 12 deviate from the equations. This might be ascribed to that the derivation of the model equation is based on the melt flow rate, which relates the viscosity more closely than the MS, implying that the model should be mainly applicable to the small-sized dripping.

Conclusions

This study investigated the dripping behaviors of eight polymers with different chemical structures (ABS, HIPS, PC, PMMA, EVA18, PA6, LDPE, and PP) and varied decomposition mechanisms under UL94 test conditions with a flame application time of 10 s. The order of polymers by the first dripping time from the longest to the shortest time was found to be ABS > (PC, HIPS) > PMMA > (EVA18, LDPE, PA6) > PP. The order of the first drop mass from the highest to the lowest was (ABS, HIPS) > PC > PMMA > PA6 > (EVA18, LDPE, PP). Drops collected in a pan from EVA18, PA6, LDPE, and PP were found to be uniform in size and shape, with disk diameters less than 10 mm (in the order of magnitude of 0.001 g) and first dripping times less than 15 s. ABS, HIPS, PC, and PMMA had irregular drop sizes larger than 0.01 g, and the first dripping times longer than 15 s. The results suggest two different types of dripping behaviors of burning polymers: Type I: dripping with small and uniform drop sizes with the short first dripping time and Type II: dripping with large and irregular drop sizes with the long first dripping time.

The dripping behaviors of Type I and Type II were hypothesized to correspond to the shear viscosity and the extensional viscosity, respectively, both of which were affected significantly by the factors such as the original MW, temperature, and the decomposition. It was found that the two dripping behaviors in this study could be discriminated by the dominant decomposition mechanisms related to chemical structures, the activation energy of viscous flow, the combustibility ratio, and the EHC/L_g. Polymers such as EVA18, PA6, LDPE, and PP tended to form Type I dripping due to a rapid reduction in MW caused by the random-chain scission decomposition, while polymers with the dominant decomposition mechanisms of slow reduction of MW tended to form Type II dripping such as ABS decomposed via cyclization, HIPS via cyclization and depolymerization, PC via random-chain scission and cross-linking, and PMMA via end-chain scission. Polymers of Type I dripping have the activation energy of viscous flow less than 65 kJ/mol, the combustibility ratio greater than 19, and the EHC/L_g values greater than 17. Polymers with the activation energy of viscous flow greater than 85 kJ/mol, the combustibility ratio less than 19, and the EHC/L_g values less than 15 tended to form Type II dripping. However, the surface tension at ambient temperature and the MFI at processing temperatures were not as important as expected. The surface tension at ambient temperature seemed to roughly relate to the order of drop mass. The MFI at processing temperatures could not be used to determine the dripping times of polymers and discriminate the dripping type.

The results of tests on dripping behavior for the talc-filled LDPE showed that increasing the talc level in LDPE to over 20% by weight would change Type I to Type II dripping behavior due to the reduction in burning rate and the significant flow reduction by talc. Although the dripping behavior of a burning polymer is dominated by its chemical structure–related decomposition mechanism, it can be modified by adding a sufficient amount of a noncombustible filler. In addition, it was found that although blending a high-MS polymer with the same dominant decomposition mechanism also reduces the initial melt flow tendency of PE, its effects on the dripping behavior were not as significant as adding talc.

Finally, a model was presented based on the dripping time being proportional to the mass of polymer melt and inversely proportional to the melt flow rate. This model is more applicable to Type I dripping than to Type II dripping, and the drop mass was derived to be a power law function of the dripping time. Comparing this function with experimental results for the mass of first drops and the accumulated mass of drops, it was found that the power law function was, to a certain extent, in agreement with experimental results, except for some data points of Type II dripping such as for HIPS and 60 wt% talc-filled LDPE.

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Author biographies

Yong Wang is a lecturer of Qingdao University of Science and Technology (QUST), China. He received his PhD degree in Materials Sciences from QUST in 2010. His research interests include fire dynamics, fire modeling, and flame-retardant polymers.

Jinder Jow received his PhD degree in Chemical Engineering from Michigan State University in 1988. He joined the wire and cable group at Union Carbide Corporation right after school. He spent first 15 years in wire and cable R&D in New Jersey and 4 years at the Dow Asia Pacific Technical Center in Singapore, and then joined the materials science group, Dow Core R&D at Freeport, Texas, in 2008. He received more than 12 patents and published more than 25 journal or conference papers. His research interests include nonhalogenated flame-retardant product development, electrical degradation for polymeric materials, cross-linking and scorch inhibition, polymer functionalization, scratch phenomenon, and self-healing materials development.

Kenny Su received his master's degree in chemistry in 1988. He spent 2 years with the engineering plastics department of Formosa in Taiwan to develop flame-retardant (FR) compounds based on polypropylene (PP), polybutylene terephthalate (PBT), nylon, and polycarbonate (PC). He worked for another 5 years at Plastic Industry Development Center (PIDC), funded by Taiwan government to help small- and medium-sized companies to advance their products development and manufacturing process. In PIDC, his research area was in FR, filled compounds, and new product and new processing development. He joined Application of Vacuum Coating Technology (AVCT) in Taiwan as a deputy manger to develop the plastic substrate sputtering coating for liquid crystal display (LCD) display applications. After AVCT, he joined Dow in 1999 and was responsible for ignition-resistance product development for poly(acrylonitrile-butadiene-styrene) (ABS), PC, and PC/ABS products and new market/application development as senior Technical Service and Development (TS&D) and technical partner for compound and blends business at Dow. From 2010, he has been working in Taiwan Styron Ltd.

Jun Zhang received his PhD degree from Bolton Institute, United Kingdom, in 1992, after which, he worked at the Fire Research Center of University of Ulster until 2001. He is now a full professor in polymer materials as well as in fire safety engineering for Qingdao University of Science and Technology and also for Shanghai Jiao Tong University in China. His main research interests include functional flame-retardant polymers, fire dynamics, and fire safety engineering. He has published more than 80 articles related to the areas of fire and polymer materials.