

High temperature extensional rheology of commercially available polycarbonate mixed with flame retardant salts

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In this paper, we present a study of the dripping properties of polycarbonate (PC) modified with combinations of earth metal salts of inorganic sulfur, potassium perfluorobutane sulfonate (Rimar); non-halogenated flame retardant additives, potassium diphenyl sulfone-3-Sulfonate (KSS); and block co-polymers-polytetrafluoroethylene encapsulated with styrene acrylonitrile resin (T-SAN). Measurements of the extensional rheology of polycarbonate with different concentration of each flame retardant additive were performed using a custom-built high temperature Capillary Breakup Extensional Rheometer (CaBER) at temperatures up to $T = 400^\circ\text{C}$. From these measurements, the evolution of the apparent transient extensional viscosity was monitored as a function of time and strain both in air and in an inert nitrogen environment. The evolution of extensional viscosity has been shown to be an excellent tool for predicting the dripping behavior of polymers exposed to heat and a valuable tool for understanding the mechanism of polymer degradation which is typically dominated by either crosslinking or charring. We show that extensional rheology measurements are significantly more sensitive to temperature-induced changes to the polymer microstructure than shear rheology measurements. We have also performed systematic concentration of specific flame retardant salts and through variation in extensional rheology and investigated the optimum concentration required to achieve a V0 rating. Finally, we will show that extensional rheology is a powerful method for predicting the effect of flame retardant modifiers and optimizing their use in new flame resistant materials.

Keywords: polymer melt, extensional rheology, shear rheology, flame retardants additives

1. Introduction

Polymer combustion is driven by the thermally induced decomposition into smaller fragments, which then volatilize, mix with oxygen, and combust. This combustion releases more heat, which reradiates unto unburned polymer, thus continuing to drive pyrolysis and combustion until a lack of heat/fuel/oxygen causes the fire to extinguish. Thermoplastics polymers have a tendency to drip and flow under fire conditions, which can then lead to additional mechanism of flame spread or propagation. Thus, improving the fire-retardant behavior of polymers is a major challenge for extending the use of polymers to an ever increasing number of applications. The flame resistance of a polymer is often characterized by whether or not it drips when exposed to a high heat source. The melting and dripping drops can either remove the polymer fuel from the burning region, and hence stop further burning, or they can become a secondary source of ignition. If the melting and dripping drops further ignites the polymer or other materials in the vicinity, they can subsequently increase the intensity of the flame. As a result, the presence of polymer can become a serious fire hazard. Flame resistance can be improved through the addition of flame-

retardant additives to the polymer (Ban *et al.*, 2004, Horrocks *et al.*, 2005; Jenewein *et al.*, 2003; Laoutid *et al.*, 2009; Wu *et al.*, 2010). The addition of flame retardants can cause a disruption to the burning process so that the dripping of the molten polymer is terminated within an acceptable period of time, preferably before ignition of the polymer occurs (Hu *et al.*, 2011; Matzen *et al.*, 2015; Zhang *et al.*, 2015). In this way, flame retardants additives can help in the prevention of fires. In the event of a fire, the presences of flame retardant additives in the polymers act to give more escape time to the people caught in the blaze. They do this by slowing the burning process, lowering the amount of heat released, and lowering the amount of smoke that is emitted during combustion (Kandola *et al.*, 2013). Not all flame retardant additives are alike. Flame retardant additives can be separated into two different classes: Halogenated, and non-halogenated. Halogenated flame retardants include additives most commonly in the form of organic halogen compounds, such as brominated aromatic compounds, chlorine and fluorine. The second kind, non-halogenated, contain one of many different additives including phosphorous, sulfur and silicon-based chemicals (Beyler and Hirschler, 2002). A lot of effort is being made towards the use non-halogenated additives since they are more environmental friendly and less toxic. Halogenated additives are known to release

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toxic gases on combustion which can have disastrous consequences, especially in the case of an aircraft or an housing complex (Lu and Hamerton, 2002).

As the temperature of a polymer melt is increased, its viscosity decreases both through an increase in the mobility of the polymer molecules and through the thermal degradation of the polymer which can result in scission of the polymer backbone and the reduction of the polymer molecular weight (Kandola *et al.*, 2013). The addition of flame retardant additives can influence the shear and extensional viscosity of the pyrolysing melt, and hence, modify its dripping behavior (Kandola *et al.*, 2013; Kandola *et al.*, 2014; Zhang *et al.*, 2008). Our recent work has shown that measurements of the transient extensional viscosity of neat polycarbonate (PC) as a function of temperature can be an excellent tool for understanding and predicting the dripping dynamics of polymers exposed to high temperature flames (Sur *et al.*, 2019). In the Capillary breakup extensional rheometry measurements presented in Sur *et al.* (Sur *et al.*, 2019), a plug of PC was first heated to temperature and then stretched between two end plates to form a fluid filament. The decay of the filament diameter with time was monitored and used to make measurements of the fluids extensional viscosity and relaxation time as a function of time over a range of temperatures ($T = 260^{\circ}\text{C}$ to 360°C) in both an oxygen-rich and inert environment. Using the high-temperature extensional rheometer the evolution of extensional viscosity over time at temperature ($T = 260^{\circ}\text{C}$ to 360°C) was investigated for the linear, branched and hyper-branched PC in the presence of nitrogen and oxygen. For the linear and branched PC, increasing temperature initially led to a drop in the extensional viscosity due to time-temperature superposition effects. With increasing temperature, evidence of changes to the molecular structure or chain scission was observed. As the temperature was increased still further, a transition temperature was found beyond which a divergence in transient extensional viscosity was observed with time due to the onset of significant crosslinking. This divergence in the transient extensional viscosity was accompanied by a solidification of the fluid filament and a complete suppressing of dripping. The transition temperature for the hyper-branched, branched and linear PC was found to be $T_i = 320^{\circ}\text{C}$, $T_i = 330^{\circ}\text{C}$, and $T_i = 350^{\circ}\text{C}$ respectively. Whereas, in the presence of nitrogen no divergence in transient extensional viscosity was observed for the linear and branched PC. The hyper-branched PC showed more dramatic effects under nitrogen as the oxygen was found to quench the crosslinking resulting from the polymers hydroxyl benzoyl nitrile (HBN) end terminated group. Thus, based on the evolution of the apparent transient extensional viscosity along with results from shear rheology experiments it was concluded that hyper-branched PC had the best anti-dripping properties followed by the

branched and linear PC. This previous study also suggests that alternative additives that can promote crosslinking like the HBN could be highly affective flame retardant additives.

In the past, various techniques have been used to characterize the flammability of polymers. These techniques include- limiting oxygen index (LOI), cone calorimetry, flame spread test and UL94 test (Kandola *et al.*, 2013). The vertical flame test UL 94V (Wang and Zhang, 2013) is a small-scale laboratory test used to classify the flammability of polymers under controlled conditions for polymers where melt dripping is observed. It is a simple test of vertical combustion that classifies materials as V-0, V-1 or V-2. Achieving a V0 classification is the important goal for a polymer to be labeled as the flame retardant. It is known that dripping during a fire test is a complex interaction of physical and chemical processes which can include softening due to increasing sample temperature and viscosity changes (positive or negative) due to chemical decomposition (Kandola *et al.*, 2013). In order to better understand the process of drop formation that can feed a flame and affect a material's flame resistance rating one must fully consider the extensional flow dominated dynamics of dripping and the formation of drops

In this paper, we will investigate the melt dripping characteristics of polycarbonates mixed with a number of different flame retardant additives. In most cases, the addition of flame retardant known to cause thermally induced molecular changes to the polymers chains. These changes, typically lead to an increase in the viscosity of the polymer melt, because the flame resistant additives are often designed to function as plasticizers or as reinforcing fillers (Matzen *et al.*, 2015). The efficiency of these flame retardant additives has been shown to depend on the viscosity of the modified polymers (Matzen *et al.*, 2015; Zhang *et al.*, 2008) and, as we will show here, more precisely on the transient extensional viscosity of the modified polymer melt. There are many questions that needs to be considered while preparing a flame resistant polymer including: what flame retardant additive or combinations of flame retardant additives to choose, how much needs to be added, and what are the material properties like extensional viscosity that indicate when a polymer is flame resistant enough. Through a detailed set of transient extensional viscosity measurements at multiple temperature and across many different material compositions we will begin to answer these questions.

2. Experimental Setup

2.1. Materials

Linear polycarbonate (LEXAN-130) of molecular weight, $M_w = 36$ kg/mol with a polydispersity index of $\text{PDI} = 1.74$ mixed with various flame retardant (FR) were investigated.

Table 1. Thermal properties of the combination of flame retardant additives polycarbonate along with its UL-94 vertical burn test rating for a flame bar thickness of 1.2 mm.

| Sample | Percent flame retardant additive (wt.%) | UL-94 Rating | T_g (°C) | $T_{5\%}$ (°C) | T_{max} (°C) | Residue after TGA (wt.%) |
|--|--|--------------|------------|----------------|----------------|--------------------------|
| Linear PC | - | V2 | 146 | 502 | 512 | 22% |
| Rimar salt and linear PC (PC/Rimar) | 0.08 wt.% Rimar | V0 | 151 | 488 | 518 | 19% |
| KSS and linear PC (PC/KSS) | 0.3 wt.% KSS | V2 | 151 | 506 | 515 | 20% |
| TSAN and linear PC (PC/TSAN) | 0.5 wt.% TSAN | V0 | 155 | 514 | 537 | 22% |
| KSS, TSAN and linear (PC) (PC/KSS/TSAN) | 0.3 wt.% KSS and 0.3 wt.% TSAN | V0 | 154 | 483 | 517 | 20% |
| Rimar, TSAN, THPE and linear PC (PC/Rimar/TSAN/THPE) | 0.08 wt.% Rimar, 0.1 wt.% TSAN and 0.2 mol% THPE | V0 | 150 | 510 | 512 | 20% |

The various flame retardant additives studied included potassium perfluorobutane sulfonate (Rimar), potassium diphenyl sulfone-3-Sulfonate (KSS), polytetrafluoroethylene encapsulated with styrene acrylonitrile resin (TSAN) and 1.1.tris hydroxy phenyl ethane (THPE) were supplied by SABIC innovative plastics. Before being tested in the shear and the extensional rheometers, the polymer pellets were first molded to fit the various plate geometries needed in a hot press under vacuum at $T = 250^\circ\text{C}$. The various composition of the flame retardant additives mixed with the linear PC are listed in Table 1 alongside their UL-94 rating.

2.2. Thermal analysis

Thermal properties of the PC/FR additives samples were measured using a differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Differential scanning calorimetry were performed using a Q100 (TA Instruments) at a heating rate of $10^\circ\text{C}/\text{min}$ in the presence of nitrogen. The glass transition temperature, T_g , was found to be $T_g = 146^\circ\text{C}$ for the linear PC. As seen in Table 1, a variation in T_g by 5- 10°C was observed because of the variation in the molecular weight of the different blends. Thermogravimetric measurements were performed using a Q-5000 (TA Instruments) under nitrogen at a heating rate of $T = 20^\circ\text{C}/\text{min}$. All the samples decomposed in a single decomposition step. The onset of decomposition temperature, $T_{5\%}$, set to be when the mass loss equaled 5 wt.%, was found to be $T_{5\%} = 502^\circ\text{C}$ for the linear PC. Along with the temperature for onset of degradation the temperature of maximum rate of degradation, T_{max} , is also presented in the Table 1. On its own, addition of Rimar showed the earliest onset of decomposition while TSAN appeared to have a retardation effect on the onset of decomposition. The onset decomposition temperature and the maximum weight loss temperature varied by as much as $\pm 20^\circ\text{C}$ with the different flame retardant additives. All the TGA data is presented in Table 1. The maximum weight change was observed for the linear PC and PC/KSS which was found

to be 80 and 81 wt.% respectively. The residue for all the samples at the end of the experiment varied between 20 to 25 wt.%.

2.3. Capillary breakup extensional rheology

A schematic diagram of the capillary breakup extensional rheometer (CaBER) with its main components is shown in Fig. 1. The design of the CaBER was based on previous design found in the literature (McKinley and Sridhar, 2002). Here we have customized it for high temperature measurements by building an oven around it that can reach up to 400°C using three 250W resistance heaters (Omega-WS series). The oven temperature is controlled using a PID temperature controller (Omega-CN-2110) with a temperature accuracy of $\pm 2^\circ\text{C}$. The oven is made of an inner and outer box fabricated from steel plates with insulation between the two boxes to reduce heat transfer out of the oven. The thickness of insulator was designed to maintain an inside temperature of $T = 400^\circ\text{C}$ and without exceeding an outside oven surface temperature of 35°C . A thickness of 6.25 cm of a silica-based insulator (Microsil, Zircar) with a thermal conductivity of $k = 0.024 \text{ W/mK}$ was used to maintain the outside temperature below 35°C . Rectangular openings were cut into the sides of both the inner and outer box and covered with a Pyrex glass to allow optical access for the camera to allow for visualization of the filament diameter so that it could be measured optically as a function of time. The diameter measurements had a resolution of $6.3 \mu\text{m}/\text{pixel}$ based on the maximum magnification of the lens and the pixelation of the camera sensor. Provisions were made for supplying nitrogen and air into the oven so that measurements could be made in an inert or an oxygen rich environment. The top plate was connected to a linear motor (LinMot-C1250) using a glass mica rod to reduce heat flow out of the oven and minimize the risk of heat damages to the motor. The motor was capable of stretching the fluid at speeds up to 200 mm/s . An edge detection software (Edgehog) was used to capture the diameter decay with time with subpixel resolution.

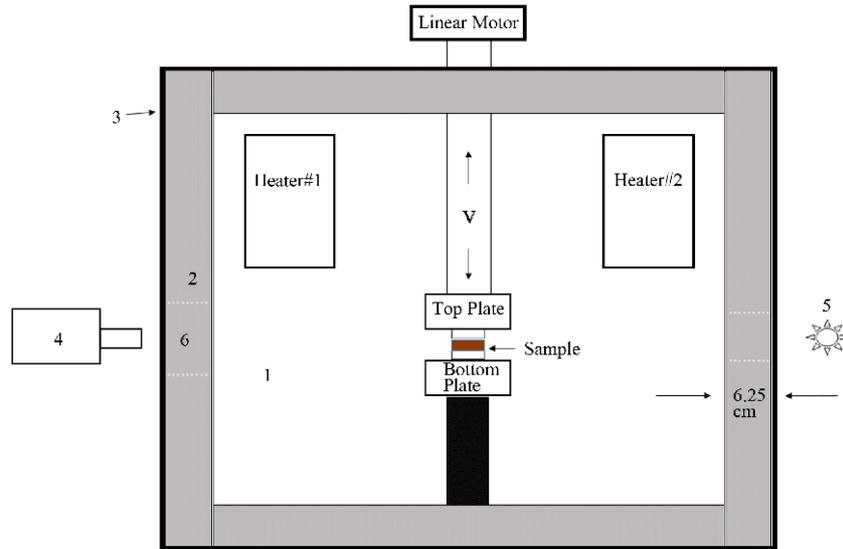


Fig. 1. Front view of the high temperature extensional rheometer. The figure includes: (1) Inner box with the heaters, top plate and the bottom plate, (2) heat shield (silica based insulation) of thickness 6.25 cm on all sides, (3) outer box with the motor mounted on top, (4) camera for visualizing the stretch, (5) light source, and (6) windows for filament observation.

In order to calculate the transient extensional viscosity, the diameter decay was fit with a spline and then differentiated.

Capillary breakup extensional rheometry measurements have become an increasingly common technique for determining the extensional rheology of viscoelastic fluids (Anna and McKinley, 2001; Bazilevsky *et al.*, 1990; Clasen *et al.*, 2006; Entov and Hinch, 1997; Kojic *et al.*, 2006; McKinley and Tripathi, 2000; Plog *et al.*, 2005; Rodd *et al.*, 2005; Stelter *et al.*, 2000; Yesilata *et al.*, 2006). In the CaBER experiments presented here, a cylindrical sample melt cast using a hot press under vacuum was placed between two cylindrical plates at room. The oven was then turned on and heated to the desired experimental temperature with a ramp of 5°C/min. Once the oven reached the desired temperature the sample was then stretched with the top plate moving at a velocity of 0.01 m/s² until a gap of $3L_0 = 6.75$ mm was reached. Here $L_0 = 2.25$ mm is the initial starting gap between the plates and $R_0 = 2.25$ mm is the initial radius of the sample melt. The stretch was then stopped and the capillary thinning of the liquid bridge that was formed between the two endplates subsequently produced a uniaxial extensional flow from which the extensional viscosity and relaxation time of the test fluid could be measured.

The breakup of the fluid filament is driven by capillary stresses and resisted by a combination of inertial, viscous and elastic stresses developed within the flow. The specific balance of forces that dictate the breakup regime of the fluid depend on the properties of the fluid. As the fluids we will investigate here are all quite viscous, inertial effects can in all cases be safely neglected as the Ohne-

sorge number is in all cases $Oh \gg 1$. In the viscous-capillary regime, capillary decay is opposed by viscous stresses. In this regime, the extensional viscosity of the fluid can be determined by measuring the change in the filament diameter as a function of time. Papageorgiou (Papageorgiou, 1995) showed that for a Newtonian fluid with a constant shear viscosity, η , the radius of the fluid filament will decay linearly with time such that,

$$R_{mid}(t) = 0.07095(t_b - t)\sigma/\eta. \quad (1)$$

Here σ is the surface tension, η is the shear viscosity and t_b is the time at breakup. In the Newtonian limit the extensional viscosity is equal to $\eta_E = 3\eta$ and can be calculated from the decay of the radius with time. In order to calculate the apparent transient extensional viscosity of a fluid undergoing a visco-capillary decay, like those observed here, the diameter measurements as a function of time were first fit with a spline to smooth the data and then differentiated before substituting into the following equation (Rosello *et al.*, 2019; Sur and Rothstein, 2018; Sur *et al.*, 2019).

$$\eta_E^+ = -\frac{0.231\sigma}{dR_{mid}/dt}. \quad (2)$$

The value of the surface tension was taken from the literature to be $\sigma = 34.2$ mN/m.

3. Results and Discussions

3.1. Shear rheology

The shear rheology of the linear PC with different flame retardant additives was studied as a function of tempera-

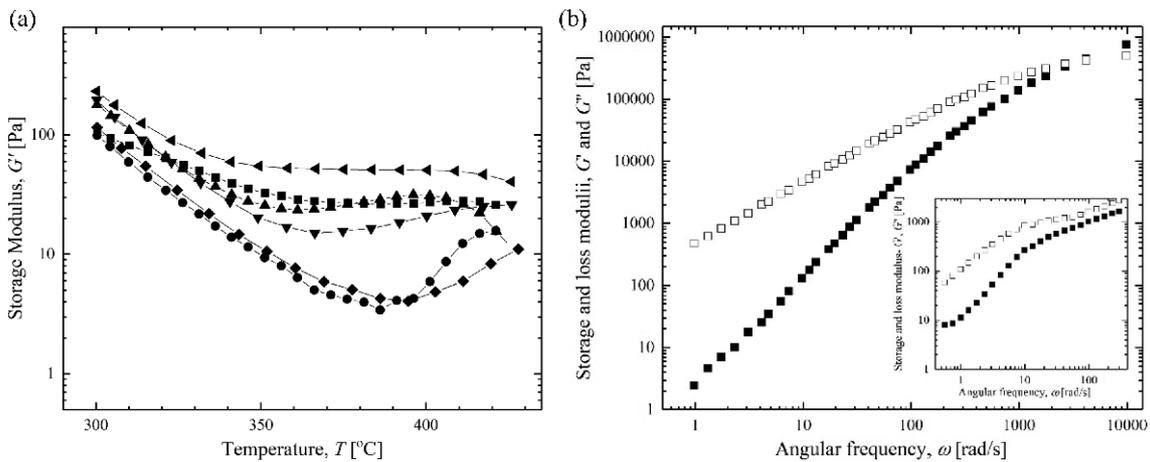


Fig. 2. Plot of the (a) Storage modulus, G' , as a function of temperature, T , at an angular frequency of $\omega = 10$ rad/s for the PC/0.08% Rimar salt (\blacktriangledown), PC/0.08 wt.% Rimar/0.1 wt.% T-SAN/0.2 mol% THPE (\blacksquare), PC/0.3 wt.% KSS (\bullet), PC/0.5 wt.% T-SAN (\blacktriangleleft), PC/0.3 wt.% KSS/0.3 wt.% T-SAN (\blacktriangle) and linear PC (\blacklozenge) in the presence of nitrogen (b) Storage, G' (\blacksquare), and loss modulus, G'' (\square), of the linear PC as a function of angular frequency, ω , shifted to a reference temperature of $T_{ref} = 300^\circ\text{C}$. The inset in Fig. 2b shows the plot of G' (\blacksquare) and G'' (\square) as a function of angular frequency at $T = 380^\circ\text{C}$ for the linear PC.

ture using an ARES-G2 rheometer (TA instrument) with temperatures varying from $T = 300^\circ\text{C}$ to 430°C at a frequency of $\omega = 10$ rad/s in the presence of nitrogen. Before starting the analysis of the temperature sweep it is important to note that the frequency was selected such that the material response was in the terminal regime. This was important in order to interpret the deviations in the expected storage modulus variation due to temperature changes close to changes resulting from crosslinking as the temperature was increased. In the terminal regime if the angular frequency is held fixed, the storage modulus should decrease with increasing temperature due to the principles of time temperature superposition because the effective frequency decreases with increasing temperature. As a result in the terminal regime the elastic modulus is expected to scale like $G' \sim a_t^2 \omega^2$ where a_t is the shift factor. Thus any deviation in the storage modulus away from this decay with increasing temperature would indicate a change in the material resulting from temperature induced changes to polymer like crosslinking or scission. To ensure that the selected frequency of $\omega = 10$ rad/s was in the terminal regime, a series of frequency sweeps were performed for the linear PC at non-degrading temperatures from $T = 220^\circ\text{C}$ to 280°C and all the data were shifted using TTS to a reference temperature of $T = 300^\circ\text{C}$. As observed from the Fig. 2b, it is clear that the response of the linear PC was in the terminal regime and thus the data in Fig. 2b can be treated quantitatively to determine the onset temperature of polymer degradation. The storage modulus of linear PC and PC/KSS in Fig. 2a were found to decrease with expected slope as the temperature was increased from $T = 300^\circ\text{C}$ to 380°C . Beyond $T = 380^\circ\text{C}$, the storage modulus was found to increase. This deviation from the time temperature superposition response was

likely due to the buildup of molecular structure due to either crosslinking or charring. The deviation from TTS was found to occur at a lower temperature of $T = 340^\circ\text{C}$ for the PC/TSAN. Similar trends were observed for PC/0.08 wt.% Rimar, PC/0.08 wt.% Rimar/0.1 wt.% TSAN/0.2 mol% THPE and PC/0.3 wt.% KSS/0.3 wt.% TSAN where the deviation from TTS was observed at temperatures $T = 360^\circ\text{C}$, $T = 340^\circ\text{C}$ and $T = 350^\circ\text{C}$ respectively. It is important to note here that, though the storage modulus was found to be sensitive to the onset of crosslinking in the material, no direct information about the effect of these changes on the dripping of the polymer could be garnered from this data.

Past studies have shown that presence of oxygen degrades the PC and leads to changes in the molecular backbone structure (Jang and Wilkie, 2005; Lee, 1964; Zhou *et al.*, 2007) leading to crosslinking and charring. Thus, it is difficult to differentiate the effect of the flame retardant additives degradation mechanism from the neat PC in an oxygen-rich environment. The environment of the decomposing sample will therefore affect the degradation pathway so it is important to make it as close to combustion conditions as possible. It has been shown that in the case of combustion, the effect of oxygen during combustion may be quite minimal because oxygen has been shown not to be present in the degrading polymer (Jang and Wilkie, 2005). This is likely the result of the oxygen in the environment being depleted by the burning flames. As a result most temperature sweep measurements are performed in the presence of nitrogen as we have presented here in the case of shear rheology. However, for completeness we will study the extensional rheology of these PC in both air and nitrogen to observe the competing or additive effects of oxidation during stretching and dripping of these poly-

mers with and without flame additives.

3.2. High temperature extensional rheology

3.2.1. Linear polycarbonate

In Fig. 3, the apparent transient extensional viscosity, η_E^+ , is plotted as a function of the Hencky strain, ε , for the linear PC at temperatures ranging from $T=320^\circ\text{C}$ to $T=360^\circ\text{C}$ in air and in nitrogen. All experiments were performed three times in the presence of either air or nitrogen for the entirety of the heating cycle and the stretch. For those temperature at which a steady-state extensional viscosity values were achieved, a maximum variation of 20% was observed between each data set of experiments, while for those temperatures where a divergence in the apparent transient extensional viscosity was observed, a variation in the Hencky strain is mentioned which was within a range of $\varepsilon_{err} = \pm 0.5$. In all the figures that follow, the average values over several runs have been presented for all the cases. New samples were used for each measurements at each temperatures. From the shear rheology in Fig. 2, it is clear that all the samples appear to be chemically stable at temperatures below $T=340^\circ\text{C}$. Thus, an initial temperature of $T=320^\circ\text{C}$ was chosen as a baseline against which the higher temperature measurements were compared to understand the physical and chemical changes occurring to the polymer melts as were exposed to the heat. Using the shift factors from time temperature superposition (TTS), all the extensional viscosities in Fig. 3 through Fig. 10 have been shifted to a reference temperature of $T=320^\circ\text{C}$ using the relation $\eta_E^+(T) = a_T \eta_E^+(T_{ref})$, where a_T is the shift factor, T_{ref} is the reference temperature and T is the temperature from which the extensional viscosities are shifted.

Plotted in this way, any deviation of the apparent transient extensional viscosity curve from the reference curve

signifies a change in molecular structure due to crosslinking or chain scission. As can be observed from Fig. 3a, for an initial temperature increase from $T=320^\circ\text{C}$ to 340°C , the transient extensional viscosities were found to match the prediction of the TTS and thus collapse into a single curve. As the temperature was further increased to $T=350^\circ\text{C}$, the transient extensional viscosity of the neat linear PC was found to increase significantly and diverge due to significant crosslinking. Whereas, in the presence of nitrogen, the transient extensional viscosities were found to match the prediction of the TTS up to $T=340^\circ\text{C}$. Beyond $T=360^\circ\text{C}$, a reduction in the steady-state value of the extensional viscosity from the reference extensional viscosity by a factor of three was observed. This observation suggests chain scission occurring under nitrogen at these high temperatures. Note that these observation of loss of the steady-state extensional viscosity at $T=360^\circ\text{C}$ for the linear PC under nitrogen is not consistent with the shear rheology measurements which showed a deviations from TTS which always showed a growth in the viscosity and elasticity of the sample suggesting cross-linking under nitrogen and not chain scission. The origin of these differences is not clear, but if it is a direct result of the flow type, shear or extension, then it is imperative that the flow type more closely resulted to dynamics of dripping should be used to study the response of the fluid at temperature. The transient extensional viscosity was eventually found to diverge at $T=380^\circ\text{C}$ in the presence of nitrogen as it did under oxygen due to crosslinking. At that moment, the filament stopped draining and fully solidified resulting in a measured extensional viscosity that became infinite. From the literature, it has been shown, that the thermal degradation of polycarbonate in nitrogen occurs through one fast major degradation step followed by two minor slow degradations steps. While, under air, an additional minor slow degradation step has been observed (Li and

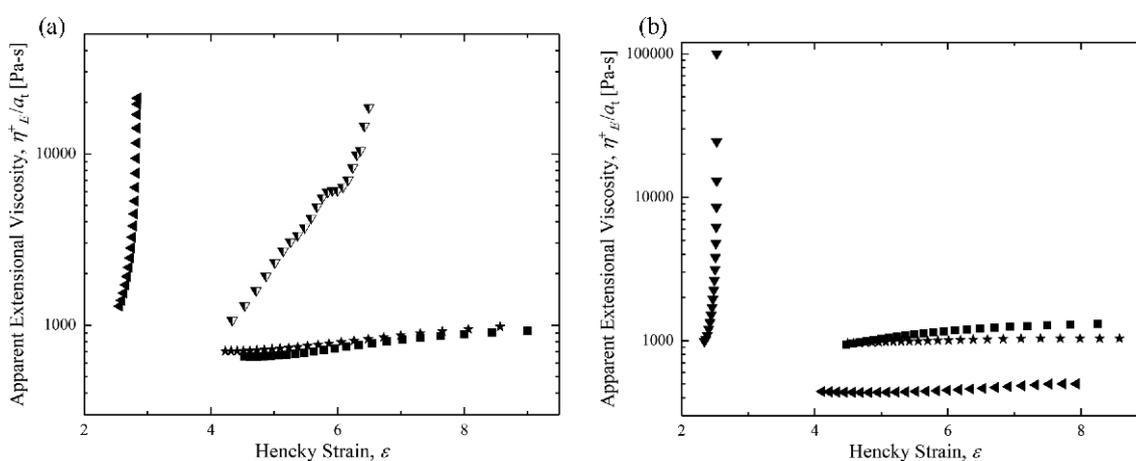


Fig. 3. Capillary breakup extensional rheology measurement of apparent transient extensional viscosity, η_E^+ , as a function of Hencky strain, ε , for the linear polycarbonate in (a) air and in (b) nitrogen at temperatures of $T=320^\circ\text{C}$ (■), $T=340^\circ\text{C}$ (★), $T=350^\circ\text{C}$ (▼), $T=360^\circ\text{C}$ (◄) and $T=380^\circ\text{C}$ (▽). All extensional viscosities have been shifted to a reference temperature of $T=320^\circ\text{C}$.

Huang, 1999). The decomposition of PC is initiated by chain scission of the polymer at the weak O-CO₂ group. This chain scission results in the reduced molecular weight of the PC and a reduction in the extensional viscosity. No degradation is generally seen until a temperature of $T = 340^\circ\text{C}$. Crosslinking has been shown to take place at higher temperatures and it is a process that generally occurs after some stripping of the substituents and involves the creation of bonds between two adjacent polymer chains (Beyler and Hirschler, 2002). This process is very important in the formation of chars, since it generates a structure with a higher molecular weight that is less easily volatilized. As seen in our experiments, cross-linking also dramatically increases the extensional viscosity of the polymer melts thus resisting dripping. The net result is a decreased likelihood in dripping when exposed to flames (Sur *et al.*, 2019). From the UL-94 tests performed in the SABIC labs, the linear PC had a poor V-2 rating over 1.2 mm thickness which means that further improvements are needed to achieve the desired V-0 rating and achieve the necessary flame resistance.

3.2.2. Polycarbonate with 0.08 wt.% Rimar salt

In Fig. 4, the apparent transient extensional viscosity is plotted as a function of the Hencky strain for the PC with 0.08 wt.% Rimar salt for temperatures ranging from $T = 320^\circ\text{C}$ to $T = 360^\circ\text{C}$ in air and in nitrogen. All data has been shifted to a reference temperature of $T = 320^\circ\text{C}$ using TTS. Rimar salt have been shown to be an effective flame retardant additive as it reduces the dripping likelihood of a polycarbonate even when added in the small amount tested here (Huang *et al.*, 2006; Levchik and Weil, 2005). In the presence of air, during the initial temperature rise from $T = 320^\circ\text{C}$ to $T = 330^\circ\text{C}$, PC/Rimar was found to be stable. The transient extensional viscosity was found to

diverge at a temperature of $T = 340^\circ\text{C}$ and beyond. When compared to the linear PC in the presence of nitrogen, a steady-state extensional viscosity of $\eta_E^+ = 5000$ Pa.s was observed for the PC/Rimar which was higher by a factor of three. This is consistent with the higher storage and loss modulus observed for the PC/Rimar system presented in Fig. 2a. Thus, the addition of Rimar salt made the PC melt both more elastic and more viscous in addition resulting in a 5°C increase in the glass transition temperature. Interestingly with the addition of Rimar salt the transient extensional viscosity was found to diverge at temperature $T = 340^\circ\text{C}$ both in the presence of air and nitrogen. Compare to the neat linear PC, which did not diverge until $T = 360^\circ\text{C}$. In fact, the steady-state extensional viscosity initially decreased with increasing temperature for the neat linear PC. The decrease in the divergence temperature under nitrogen is a desirable characteristic of a flame retardant additive because of the earlier onset temperature of crosslinking as was observed in the shear rheology data in Fig. 2a. However, the magnitude in the observed change in the elastic modulus was only a few percent at $T = 340^\circ\text{C}$ and could easily be overlooked. The divergence in the transient extensional viscosity data cannot be easily overlooked and it clearly signals a transition from dripping to not dripping of the polymer melt when exposed to heat. This information about the dripping nature of the polymer cannot be easily inferred from the shear rheology data making extensional viscosity measurements an even more powerful tool for understanding flame retardation. The high rate of crosslinking of the PC/Rimar salt has been shown by Huang *et al.* (2006). In their study, the PC/Rimar was found to have crosslinking rate twice as fast as the neat linear PC. Rimar salt has been shown to be a very efficient flame retardant additive and is particularly effective when added to PC where it has been found to achieve

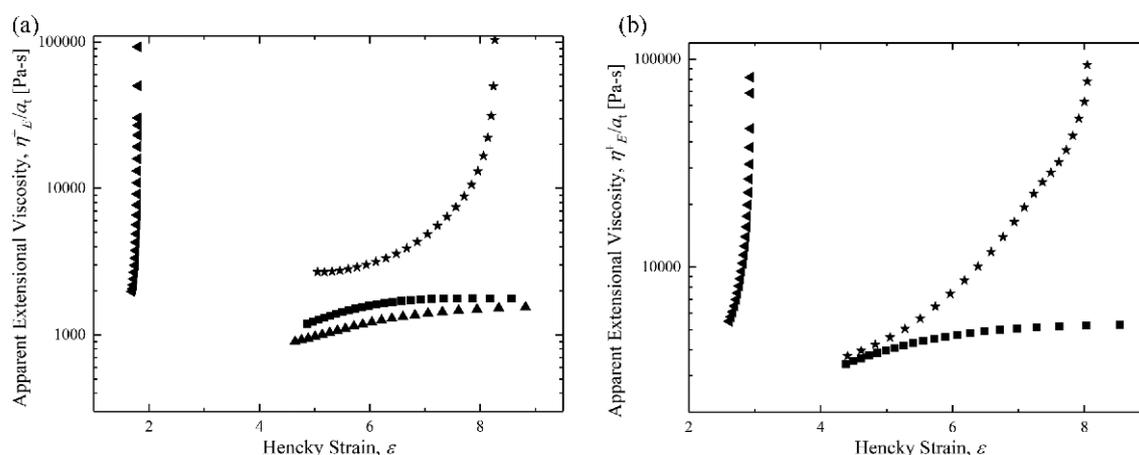


Fig. 4. Capillary breakup extensional rheology measurement of apparent transient extensional viscosity, η_E^+ , as a function of Hencky strain, ϵ , for the linear polycarbonate with 0.08 wt.% Rimar salt (PC/Rimar) in (a) air and in (b) nitrogen at temperatures of $T = 320^\circ\text{C}$ (■), $T = 330^\circ\text{C}$ (▲), $T = 340^\circ\text{C}$ (★) and $T = 360^\circ\text{C}$ (◄). All extensional viscosities have been shifted to a reference temperature of $T = 320^\circ\text{C}$.

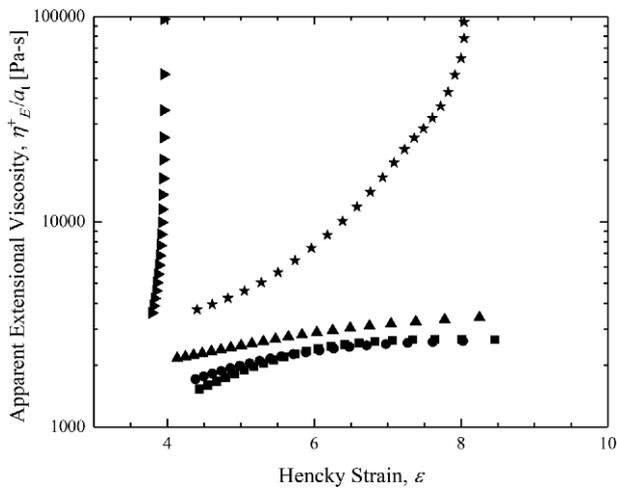


Fig. 5. Capillary breakup extensional rheology measurement of apparent transient extensional viscosity, η_E^+ , as a function of Hencky strain, ϵ , for the linear polycarbonate with different wt.% of Rimar salt (■) 0.02 wt.%, (●) 0.04 wt.%, (▲) 0.06 wt.%, (★) 0.08 wt.% and (▼) 0.1 wt.% at temperature of $T=320^\circ\text{C}$ in nitrogen.

a V0 rating with as low as 0.05-0.1 wt.% Rimar addition (Levchik and Weil, 2005). Here we stretched a sample with 0.08 wt.% Rimar salt. It has been speculated that aromatic sulfonates promote isomerization of polycarbonate which leads to higher concentrations of CO_2 and dilution of combustion products as well as faster crosslinking and char formation. Additionally, the aromatic sulfonates has been shown to accelerate Fries-type rearrangement which also results in faster decomposition and crosslinking (Levchik and Weil, 2005). From the UL-94 tests performed in the SABIC labs, the PC/Rimar had a V-0 rating.

In Fig. 5, the apparent transient extensional viscosity is plotted as a function of the Hencky strain, ϵ for the different

wt.% of Rimar salt at a temperature of $T=340^\circ\text{C}$ in the presence of nitrogen. A systematic study of the effect of variation in the concentration of the salt on the evolution of transient extensional viscosity was performed. The tests were performed at a fixed temperature of $T=340^\circ\text{C}$ to find the divergence in the transient extensional viscosity as a function of concentration of the salt. As observed in Fig. 5, at concentrations of 0.02 wt.% and 0.04 wt.% the steady-state value of the extensional viscosity was found to be similar to each other at roughly $\eta_E^+ = 2500$ Pa.s. As the concentration was increased to 0.06 wt.%, there was a slight increase in the steady-state extensional viscosity but nothing significant and the filament was found to breakup. On further increasing the concentration to 0.08 wt.% and 0.1 wt.% a clear divergence in the transient extensional viscosity was observed. Through this study it can also be observed that the high temperature capillary breakup extensional measurements were highly sensitive to variation in concentration of the salts and thus could be used to optimize the concentration of flame retardant additives.

3.2.3. Polycarbonate with 0.3 wt.% KSS salt

In Fig. 6, the apparent transient extensional viscosity is plotted as a function of the Hencky strain for the PC with 0.3 wt.% KSS salt for temperatures ranging from $T=320^\circ\text{C}$ to $T=380^\circ\text{C}$ in air and in nitrogen shifted to a reference temperature of $T=320^\circ\text{C}$ using TTS. For an initial temperature rise from $T=320^\circ\text{C}$ to 340°C in air the effects of thermal degradation are observed as the shifted steady-state extensional viscosity was found to decrease by a factor of three from the reference extensional viscosity value at $T=320^\circ\text{C}$. No degradation was observed for the linear PC in air over a similar temperature range. As the temperature was further increased the transient extensional viscosity was found to diverge at a temperature of $T=360^\circ\text{C}$

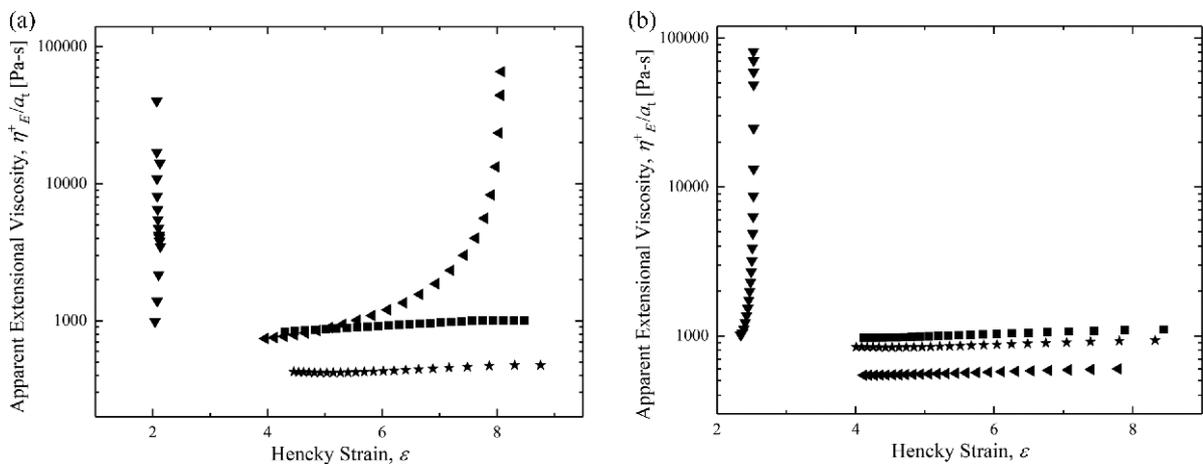


Fig. 6. Capillary breakup extensional rheology measurement of apparent transient extensional viscosity, η_E^+ , as a function of Hencky strain, ϵ , for the linear polycarbonate with 0.3 wt.% KSS salt in (a) air and in (b) nitrogen at temperatures of $T=320^\circ\text{C}$ (■), $T=340^\circ\text{C}$ (★), $T=360^\circ\text{C}$ (◄) and $T=380^\circ\text{C}$ (▼). All extensional viscosities have been shifted to a reference temperature of $T=320^\circ\text{C}$.

and beyond in the presence of air. In the presence of nitrogen, the transient extensional viscosity was found to collapse onto the reference extensional viscosity value until $T = 340^\circ\text{C}$. With further increase to the temperature at $T = 360^\circ\text{C}$, a deviation from the reference extensional viscosity was observed as the transient extensional viscosity was found to decrease by a factor of two due to the direct effect of the thermal degradation. As the temperature was increased to $T = 380^\circ\text{C}$, a clear divergence in the transient extensional viscosity was observed similar to what was seen for the linear PC at that temperature. Due to the lack of extensional viscosity enhancement, this sample was not expected to perform well in the UL-94 tests and it did not. From the UL-94 tests performed in the SABIC labs, the PC/KSS had a V-2 rating. In fact, the transient extensional viscosity in air suggest that the system will perform even worse than the neat PC. Liu *et al.* (2006) have studied the effect of addition of KSS salt to PC through TGA, FTIR and UL94 testing. They showed that a small amount (0.01-0.3 wt.%) of KSS strongly influences the thermal degradation of PC. With an increase in loading of KSS up to 3 wt.% they saw a decrease in the $T_{5\%}$ but they observed that beyond a loading of 0.1 wt.% of KSS there was a decrease in the maximum mass loss rate of PC and lower LOI values which led to poor flame retardancy. So why use KSS at all? It is a flame poison and the off gases will extinguish nearby flames. On its own, it may not prevent dripping, but in combination with another additive that does increase the extensional viscosity of the polymer, the addition of the flame poisoning effects may be quite desirable. Thus mixtures of flame retardant additives with PC have been tested whose results will be presented later in the paper.

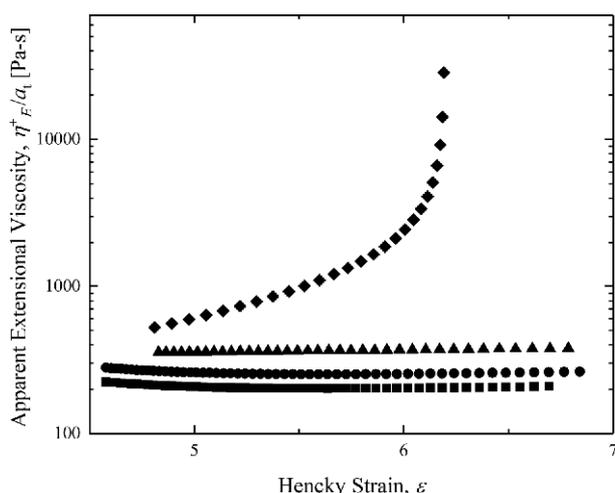


Fig. 7. Capillary breakup extensional rheology measurement of apparent transient extensional viscosity, η_E^+ , as a function of Hencky strain, ϵ , for the linear polycarbonate with different wt.% of KSS salt (■) 0.03 wt.% (●) 0.08 wt.% (▲) 0.3 wt.% and (◆) 0.5 wt.% at temperature of $T = 360^\circ\text{C}$ in nitrogen.

In Fig. 7, the apparent transient extensional viscosity is plotted as a function of the Hencky strain for the different wt.% of KSS salt at a temperature of $T = 360^\circ\text{C}$ in nitrogen. A systematic study of the effect of variation in the concentration of the salt on the evolution of transient extensional viscosity was also performed. The tests were performed at a fixed temperature of $T = 360^\circ\text{C}$ to find the divergence in the transient extensional viscosity as a function of concentration of the salt. As observed in Fig. 7, at concentrations of 0.03 wt.% and 0.08 wt.% the steady-state extensional viscosity was found to be similar to each other and lower by a factor of two as compared to the extensional viscosity at 0.3 wt.% KSS salt. As the concentration was increased to 0.5 wt.% a clear divergence in the transient extensional viscosity was observed which shows that a higher loading of KSS salt was required in order to improve the anti-dripping properties of the PC.

3.2.4. Polycarbonate with 0.5 wt.% T-SAN

In Fig. 8, the apparent transient extensional viscosity is plotted as a function of the Hencky strain for the linear PC with 0.5 wt.% TSAN for temperatures ranging from $T = 320^\circ\text{C}$ to $T = 380^\circ\text{C}$ in air and in nitrogen. All the transient extensional viscosities in Fig. 8 have been shifted to a reference temperature of $T = 320^\circ\text{C}$ using TTS. The evolution of the transient extensional viscosity of the PC/TSAN presents qualitatively similar trends in the presence of air and nitrogen. In each case, a slow increase in the transient extensional viscosity was observed beyond $T = 320^\circ\text{C}$ followed by a divergence of the transient extensional viscosity at temperatures beyond $T \geq 350^\circ\text{C}$. This sample was found to be nearly insensitive to the presence of oxygen. In that way it is similar to PC/Rimar although the divergence temperature for PC/TSAN system was about 10°C higher than that of the PC/Rimar. TSAN is comprised of PTFE dispersed in styrene acrylonitrile (SAN) matrix. PTFE is a completely inert polymer which is not affected by the chemical agents and also thermally stable until $T = 250^\circ\text{C}$ (Odochian *et al.*, 2011; 2013). Odochian *et al.* (2013) have showed through TGA-FTIR analysis that the thermal degradation of PTFE proceeds in two steps. First step involves the elimination of the gases evolved from the decarboxylation of the $-\text{COOH}$ group followed by a zipper depolymerization with the formation of the monomer C_2F_4 . PTFE has proven to be a very effective additive in improving the flame retardant behavior of aryl phosphates in PC/ABS blend (Pawlowski and Scharrel, 2007). From the UL-94 tests performed in the SABIC labs, the PC/0.5% TSAN had a V-0 rating as expected from the transient extensional viscosity data.

3.2.5. Polycarbonate with 0.3 wt.% KSS and 0.3 wt.% T-SAN

In this section and the following we will present results

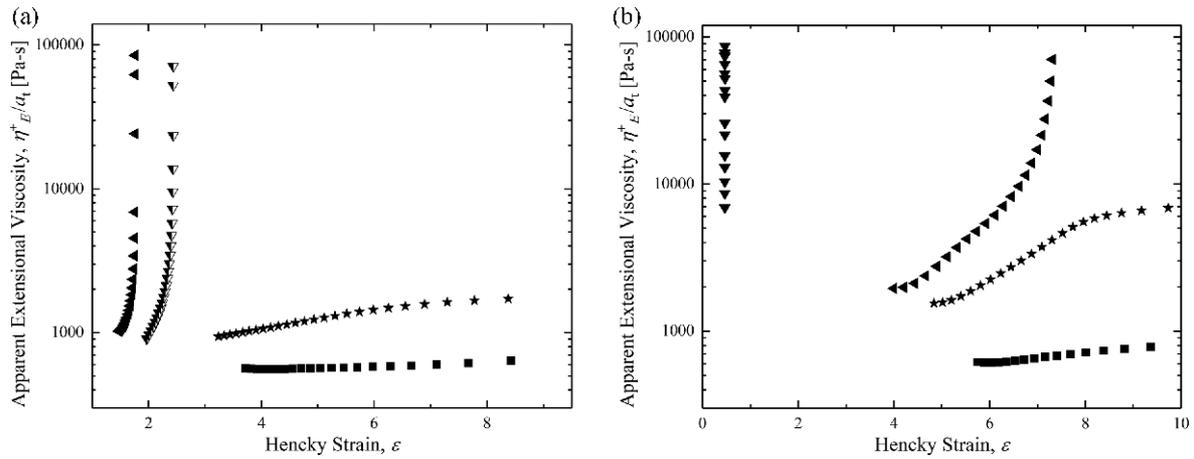


Fig. 8. Capillary breakup extensional rheology measurement of apparent transient extensional viscosity, η_E^+ , as a function of Hencky strain, ϵ , for the linear polycarbonate with 0.5 wt.% TSAN in (a) air and in (b) nitrogen at temperatures of $T=320^\circ\text{C}$ (■), $T=340^\circ\text{C}$ (★), $T=350^\circ\text{C}$ (▼), $T=360^\circ\text{C}$ (◄) and $T=380^\circ\text{C}$ (◃). All extensional viscosities have been shifted to a reference temperature of $T=320^\circ\text{C}$.

for a mixture of various flame retardant additives used in the previous sections. The main idea behind the mixtures was to optimize the concentration of various additives and make the polymer more cost effective. Also since the implementation of environmental directives banning or limiting the use of halogenated compounds, the development of flame retardants has focused on more environmentally friendly alternatives or halogen free additives. In Fig. 9, the apparent transient extensional viscosity is plotted as a function of the Hencky strain for the linear PC mixed with 0.3 wt.% KSS and 0.3 wt.% TSAN salt at temperatures $T=320^\circ\text{C}$ to $T=380^\circ\text{C}$ in air and in nitrogen. This is an interesting mixture because KSS alone acts as a flame poison and was found to have poor dripping properties whereas TSAN is a non-halogen crosslinker which was found to have an earlier onset temperature of

crosslinking. Thus this mixture was blended in order to investigate whether the mixture of T-SAN and KSS would help in improving the dripping properties and thus achieving a better UL-94 rating. As observed in the all the previous cases, a divergence in transient extensional viscosity is observed above a critical temperature. Here, under air and nitrogen the transient extensional viscosity was found to diverge at $T=350^\circ\text{C}$ which was similar to the PC/TSAN sample even though the concentration of TSAN was reduced from 0.5 wt.% to 0.3 wt.%. The addition of TSAN to the KSS salt has clearly allowed the sample achieve a much better anti-dripping properties while maintaining the flame poison properties of the KSS. Like the PC/TSAN case the PC/KSS/TSAN sample was found to insensitive to the presence of oxygen or nitrogen as the increase in the transient extensional viscosity was observed

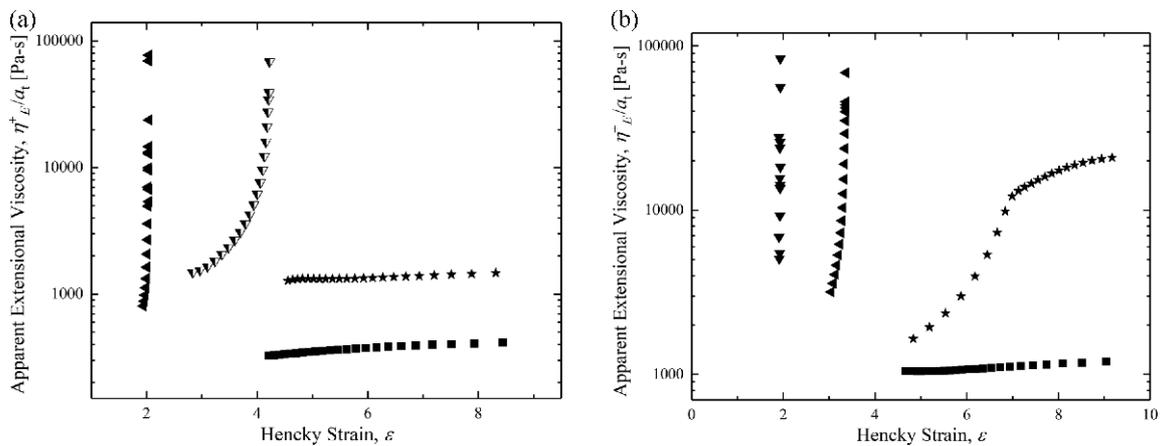


Fig. 9. Capillary breakup extensional rheology measurement of apparent transient extensional viscosity, η_E^+ , as a function of Hencky strain, ϵ , for the polycarbonate with 0.3 wt.% KSS and 0.3 wt.% TSAN salt in (a) air and in (b) nitrogen at temperatures $T=320^\circ\text{C}$ (■), $T=340^\circ\text{C}$ (★), $T=350^\circ\text{C}$ (▼), $T=360^\circ\text{C}$ (◄) and $T=380^\circ\text{C}$ (◃). All extensional viscosities have been shifted to a reference temperature of $T=320^\circ\text{C}$.

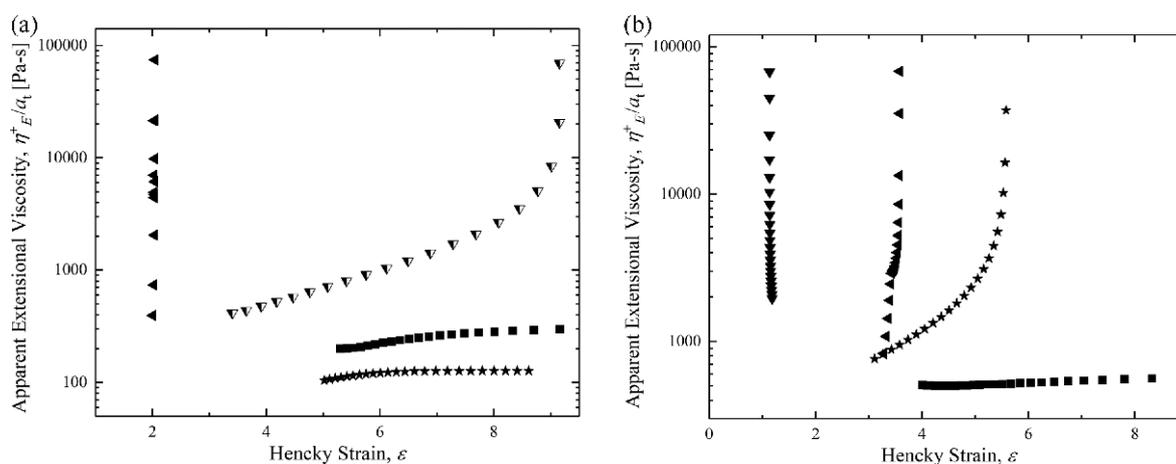


Fig. 10. Capillary breakup extensional rheology measurement of apparent transient extensional viscosity, η_E^+ , as a function of Hencky, ϵ , strain for the polycarbonate with 0.08 wt.% Rimar, 0.1 wt.% T-SAN and 0.2 mol% THPE in (a) air and in (b) nitrogen at temperatures of $T = 320^\circ\text{C}$ (■), $T = 340^\circ\text{C}$ (★), $T = 350^\circ\text{C}$ (▼), $T = 360^\circ\text{C}$ (◀) and $T = 380^\circ\text{C}$ (▼). All extensional viscosities have been shifted to a reference temperature of $T = 320^\circ\text{C}$.

as throughout the temperature range. The presence of KSS appeared to have little effect on the transient extensional viscosity. This mixture was found to be a good flame retardant additive which resulted in a UL94-V0 rating.

3.2.6. Polycarbonate with 0.08 wt.% Rimar salt, 0.1 wt.% TSAN and 0.2 mol% THPE

In Fig. 10, the apparent transient extensional viscosity is plotted as a function of the Hencky strain for the PC with 0.08 wt.% Rimar, 0.1% TSAN and 0.2 mol% THPE at temperatures ranging from $T = 320^\circ\text{C}$ to $T = 360^\circ\text{C}$ in air and in nitrogen shifted to a reference temperature of $T = 320^\circ\text{C}$ using TTS. In this sample both Rimar salt and TSAN was mixed with linear PC along with 0.2 mol% of a branching agent (THPE). Individually, Rimar salt and TSAN additives achieved a rating of UL94-V0 as they were found to induce an onset of crosslinking at a lower temperature and were also found to be insensitive to the presence of oxygen. Thus the idea behind this mixture was to further improve the anti-dripping performance of the PC by mixing two crosslinkers along with a branching agent. The data in Fig. 10 clearly shows that the mixture of Rimar salt and TSAN or perhaps the addition of branching agent negatively affects the performance under air while the transient extensional viscosity under nitrogen appears to follow the best case scenario result of PC/Rimar alone. The three fold reduction in the steady-state extensional viscosity in air has not been observed for any of the other additives or the neat linear PC. Similar reductions have, however, been observed for the branched PC in the presence of air as shown in the studies done by Sur *et al.* (2019). This strongly suggests that the initial drop in the steady-state extensional viscosity under air is the result of the branching agent addition to this mixture. The goal

of creating this mixture was to enhance crosslinking at lower temperatures. However, instead of promoting crosslinking THPE appears to have promoted chain scission or possibly reduced the effectiveness of the Rimar and TSAN in air. On further increasing the temperature beyond $T = 340^\circ\text{C}$ the transient extensional viscosity was found to diverge both in the presence of nitrogen and in air. The rate of crosslinking was found to be faster in the presence of nitrogen as compared to that in air. The transient extensional viscosity was found to diverge at $T = 340^\circ\text{C}$ which was 40°C earlier as compared to the linear PC in the presence of nitrogen. The evolution of the transient extensional viscosity of this mixture under nitrogen was found to be similar to the PC/Rimar. This implies that the path of degradation is being dominated by the Rimar. As a result the UL-94 tests performed in the SABIC labs, the PC/0.08 wt.% Rimar/0.1 wt.% TSAN/0.2 mol% THPE had a V-0 rating as expected from the extensional viscosity data.

4. Conclusion

The variation in the apparent transient extensional viscosity of polycarbonates mixed with flame retardant additives was studied using a newly designed high-temperature capillary breakup extensional rheometer (CaBER). Extensional rheology measurements were performed at temperatures varying from $T = 320^\circ\text{C}$ to 380°C in both an inert and an oxygen-rich environment for all the polycarbonates. The design of the CaBER oven allowed us to make measurements under conditions where polymer degradation was either expected or not. As showed in our previous paper Sur *et al.* (2019), extensional rheology can be used to better understand the dripping behavior of polymers

like polycarbonate when they are exposed to a high temperature heat source like a flame. Thus in our current article using high temperature CaBER experiments we looked at the effectiveness of the various combinations of flame retardant additives mixed with PC based on the evolution of transient extensional viscosity as a function of temperature.

The transient extensional viscosities at various temperatures were shifted to a reference temperature of $T_r = 320^\circ\text{C}$ where the effect of thermal degradation on the samples were negligible. Thus any deviations from the transient extensional viscosity curve at the reference temperature implied the onset of chain scission in some cases or crosslinking in some cases. The divergence temperature for the linear PC was found to be $T = 380^\circ\text{C}$ in the presence of nitrogen. As compared to linear PC, the divergence temperatures in the presence of nitrogen for the PC/Rimar, PC/KSS, PC/TSAN, PC/Rimar/TSAN/THPE and PC/KSS/TSAN were found to be $T = 340^\circ\text{C}$, $T = 380^\circ\text{C}$, $T = 360^\circ\text{C}$, $T = 340^\circ\text{C}$, $T = 360^\circ\text{C}$ respectively. While the presence of Rimar and TSAN considerably improved the flame dripping properties of the PC through significant crosslinking, KSS salt alone had a negative impact on the dripping behavior of the PC as a large drop in apparent transient extensional viscosity was observed on increasing the temperature from $T = 320^\circ\text{C}$ to 360°C and no crosslinking was observed until temperature $T = 380^\circ\text{C}$. An interesting observation was that when KSS was mixed with TSAN, it showed an improvement in the flame retardant properties of the PC, thus demonstrating the sensitivity of our experimental techniques. Rimar salt was found to be an effective anti-drip additives in very small concentration as low as 0.08 wt.%. Similar trends in the deviation of the storage modulus from the temperature sweep measurements were observed although the magnitude of the deviations were not as significant as was observed in the high temperature CaBER measurement. On comparing the UL-94 ratings of the above polymers one can observe that all the samples except linear PC and PC/KSS had a V0 rating. Linear PC and PC/KSS polymers had a V2 rating. Closely looking at the evolution of the apparent transient extensional viscosity between the temperature range of $T = 320^\circ\text{C}$ to $T = 360^\circ\text{C}$ in the presence of nitrogen, either the system was found to be stable or a drop in the transient extensional viscosity was observed for linear PC and PC/KSS system respectively as the temperature was increased whereas an increase or divergence in the transient extensional viscosity was observed for the V0 rated samples. Thus a clear correlation was observed between the ratings of the polymer systems and the evolution of the transient extensional viscosity.

Through our concentration variation study of KSS and Rimar salts we have also shown how high temperature Capillary breakup extensional rheology can be used to

optimize the concentration of flame retardant salts which in turn can help in improving the dripping properties. For example, PC with 0.3 wt.% KSS salt had a V2 ratings whereas as the concentration of KSS salt was increased to 0.5 wt.% as observed from Fig. 7, a clear divergence in the transient extensional viscosity was observed and a transition from a V2 to a V0 rating was achieved. Thus, through these measurements we can create a better design criteria map as addition of more salts increases the cost and also can alters the properties of the polymer. Similarly, for the case of PC with Rimar salt, it was observed that at concentration of 0.08 wt.% and above a V0 rating was achieved whereas below that concentration, a V2 rating was achieved.

Our experiments suggests that through simple visualization of the time diameter decay at different temperatures one can give a quick assessment of the onset temperature of crosslinking which is important in understanding the FR properties of the polymer. We also showed the sensitivity of our experiments to different combinations of FR salts on the dripping properties of the polycarbonate which would enable us to make better formulations which is crucial in improving the dripping properties of the polymers.

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