

Recyclability of Flame Retarded Polycarbonate: Comparison of Non-halogenated to Halogenated Flame Retardants

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Abstract

Plastic waste from Electrical and Electronic Equipment (WEEE) is an increasing problem. Plastics, such as, HIPS, ABS and polycarbonate (PC) must often be disposed of as hazardous waste because of contact with heavy metals in WEEE. Consequently, it is desirable to separate and recycle these plastics. The main focus of this presentation will be on polycarbonate. One of the concerns here is keeping or enhancing the flame retardant properties of PC so that the material can be reused in equipment housings. Using data on potassium diphenylsulfone sulfonate (KSS) as a flame retardant, it is shown that the flame retardancy of recycled PC can be enhanced. One major advantage of using KSS is that it is non-halogenated, playing an important role as the government eliminates the use of halogenated flame retardants because of potential unhealthy environmental effects. In this study, a PC containing KSS and one containing a halogenated FR are put through a recycling process -- drying, extrusion, pelletizing, drying, injection molding, and granulating. This process is repeated up to eight times. Mechanical results were assessed by Izod impact and tensile tests. Thermogravimetric analysis and capillary rheometry were also performed. Results show that the non-halogenated flame retardant polycarbonate holds up just as well as the halogenated flame retardant polycarbonate. It is concluded that potassium diphenylsulfone sulfonate is likely to be an excellent non-halogenated flame retardant for recycled polycarbonate.

1. Introduction

In the ever growing world of plastics, it is time that recycling plays just as significant of a role as did the evolution of polymers decades ago. Primarily focusing on waste from electrical and electronic equipment (WEEE), much is to be learned about recycling a plastic material back to original properties. Plastics contained in WEEE include polycarbonate (PC), acrylonitrile butadiene styrene, high impact poly styrene, and blends of these, such as, PC/ABS. Properties that may be degraded while recycling include mechanical, flammable, thermal, rheological, molecular, optical etc. Bringing these properties back up to par may include the addition of different additives. Many additives exist for all types of polymers and one that works for one polymer might not work for all. This study will focus primarily on Bisphenol A Polycarbonate.

Polycarbonate (PC) engineering resins are amorphous, clear polymers that exhibit superior dimensional stability, good electrical properties, good thermal stability, and outstanding impact strength¹. To make the polymer resistant to flames, flame retardants are added. The flame retardant involves disruption of the burning process so that it is terminated within an acceptable period of time, preferably before ignition actually occurs². These flame retardants are most commonly in the form of organic halogen compounds, such as brominated aromatic compounds^{3,4}. There is a serious problem with such halogen compounds, however: during burning, the compounds generate toxic substances that can injure people and contaminate the environment⁵.

In response to this problem, we have looked at a non-halogenated flame retardant, potassium diphenylsulfone sulfonate, and studied its effect on polycarbonate in a recycling process. These results were compared with that of a halogenated (brominated) flame retarded polycarbonate during the same recycling process.

2. Experimental

2.1. Materials

Two forms a polycarbonate were provided by Bayer Material Science; Makrolon 2608 and 6555. Makrolon 2608 (PC No FR) is a non-flame retarded, medium viscosity grade of polycarbonate. Makrolon 6555 (PC Br FR) is a brominated flame retarded, medium viscosity grade of polycarbonate. To flame retard the Makrolon 2608, potassium diphenylsulfone sulfonate, KSS FR[®] was provided by Flame Retardant Associates and produced by Sloss Industries.

2.2. Processing the Material

A recycling process (see Figure 1) consisting of an oven, extruder, pelletizer, oven, injection molder, and granulator, was used to process the material. The material was first dried in an oven at 110°C for five hours. The material was then processed through a Brabender counter rotating twin screw extruder at 45 rpms with a temperature profile of 280, 285, 290, and 285°C, from hopper to die, and sent through a water bath and then to a pelletizer. The material was then dried again at 110°C for five hours. All material was then sent through an injection molder where test samples were made. Roughly fifteen samples were kept for testing and the remaining was sent through a granulator. This process was then repeated for eight times. Samples are labeled as V for Virgin and A, B, C, etc. for 1, 2, and 3 recycles.

KSS FR was added to the very first extrusion of PC No FR. It was first dried at 110°C for 4 hours. KSS FR is a white powder and mixing it with the polymer pellets was done by weighing out 2.0g of KSS FR and adding it to 998g of PC No FR, mixing the two together in a ziplock bag and then sending it to the extruder for melt blending. This was done roughly 10 times to acquire the correct amount of starting material. This

material is labeled as PC KSS FR. 0.2 Weight percent of KSS FR is the required amount of to flame retard a 3.2mm thick sample to UL94 v-0.

PC Br FR was processed as given.

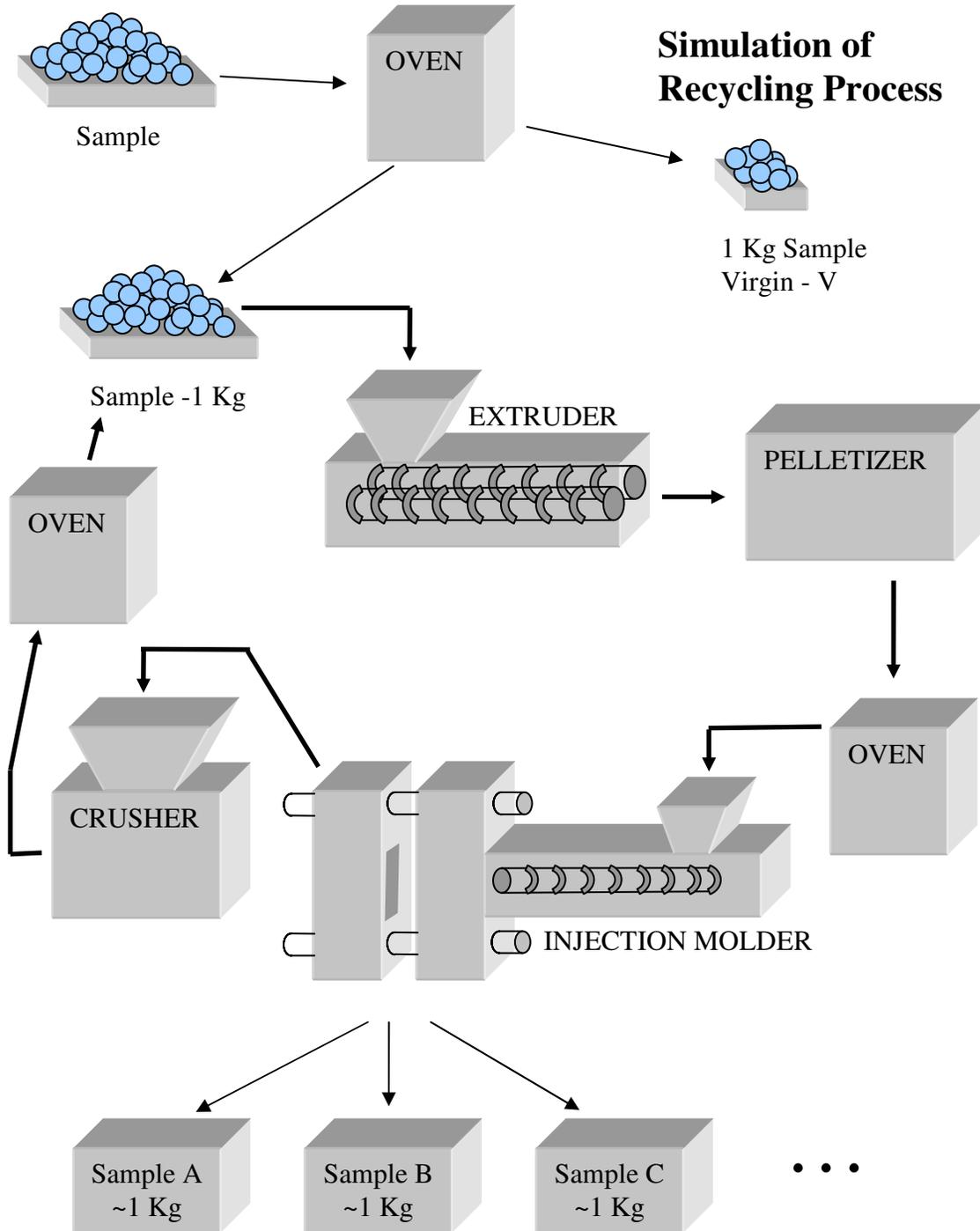


Figure 1 Schematic of Recycling Process

2.3. Experiments and Testing

Flammability, Mechanical, Thermal, Rheological, and Optical properties were assessed after each recycle.

2.3.1. Flammability Tests

Limiting Oxygen Index (ASTM D2863) and UL94 type test were performed on standard sample sizes of dimensions 125mm x 12.7mm x 3.2mm.

2.3.2. Mechanical Tests

IZOD impact test (ASTM D256, Test Method A) was carried out on standard sample of 64mm x 12.7 x 3.2 mm with a notch of 2.5mm. Partial and complete breaks were observed and both reported. Tension tests (ASTM D638) were performed with an INSTRON 5677 with Video Extensometer. Standard dog bone shaped test specimens were pulled at a rate of 1mm/min to obtain Young's Modulus and then ramped up to 5mm/min to obtain the yield stress, percent strain at yield stress, ultimate stress, and elongation at break.

2.3.3. Thermal Analysis

Thermogravimetric Analysis was carried out by a TGA Q500 from TA Instruments at a heating rate 10°C/min under nitrogen and air.

2.3.4. Rheological Analysis

A capillary rheometer, RH2000 from Bohlin Instruments, was used to find the materials viscosity.

2.3.5. Optical Analysis

One of polycarbonates well known properties is transparency. A simple picture was taken to show the transparency of the polymer.

3. Results and Discussion

3.1. Flammability Tests

For virgin PC No FR, UL94 is v-2 and LOI is 28%. Upon adding the 0.2wt% of KSS FR, UL94 goes to v-0 and LOI goes to 37%. For virgin PC Br FR, UL94 is v-0 and LOI is 37%. Throughout the recycling process, LOI and UL94 stay typically the same: LOI of 37-39 and UL94 v-0 for the PC Br FR and LOI of 36-37 and UL94 v-0 for the PC KSS FR. This shows that flame retardancy is being held throughout the recycling process. Figure 2 shows the graphical representation of the two results plotted against number of recycles.

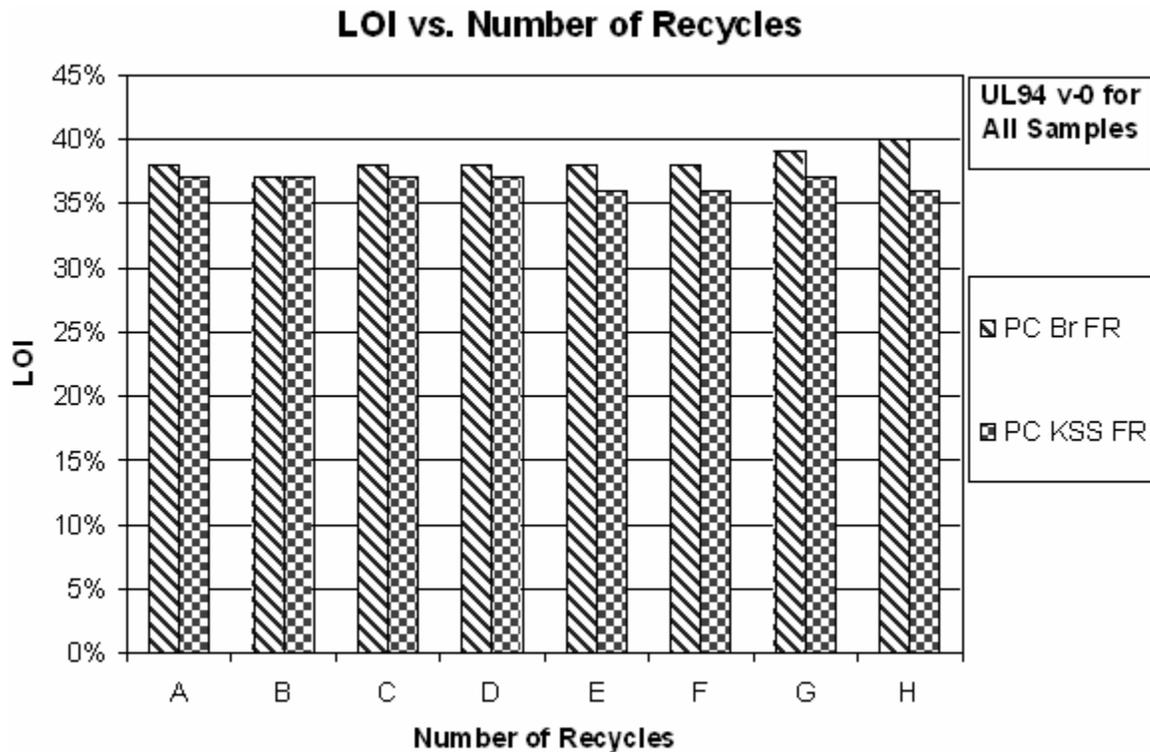


Figure 2 LOI and UL94 vs Number of Recycles for PC Br FR and PC KSS FR

3.1.1. Mechanical Tests

IZOD Impact Strength showed the most deviation among any test. In general, virgin material would start out with all partial breaks, 'A' material would typically have mostly partial breaks. 'B' would show less partial breaks, and so on. If the break was not partial it was complete. Partial breaks show much higher impact strength than complete breaks. Figure 3 shows graphically the decrease and transition from partial to complete breaks throughout the recycling process. It is worthy to note that for the PC KSS FR more partial breaks were observed throughout the recycling process than the PC Br FR.

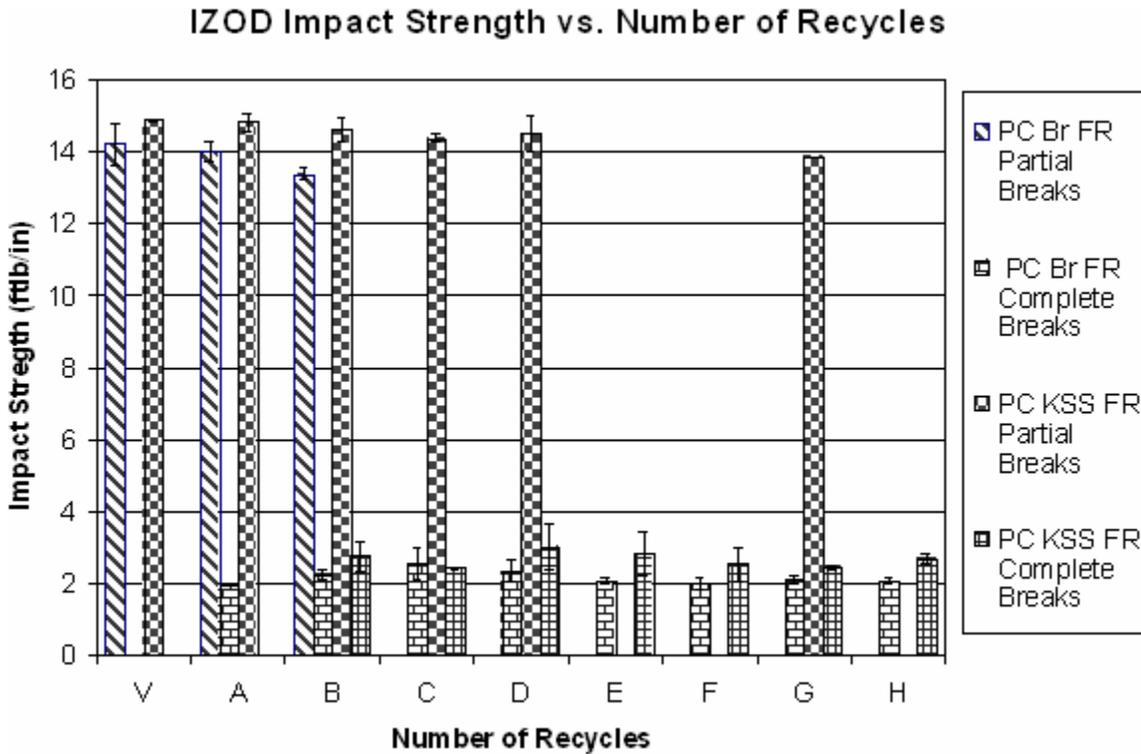


Figure 3 IZOD Impact Strength vs. Number of Recycles for PC Br FR and PC KSS FR

Young's Modulus, Yield Stress, and Strain at Yield stayed relatively consistent throughout the entire recycling process. Figure 4, Figure 5, and Figure 6 show graphically Young's modulus, yield stress, and strain at yield for both PC Br FR and PC KSS FR, respectively.

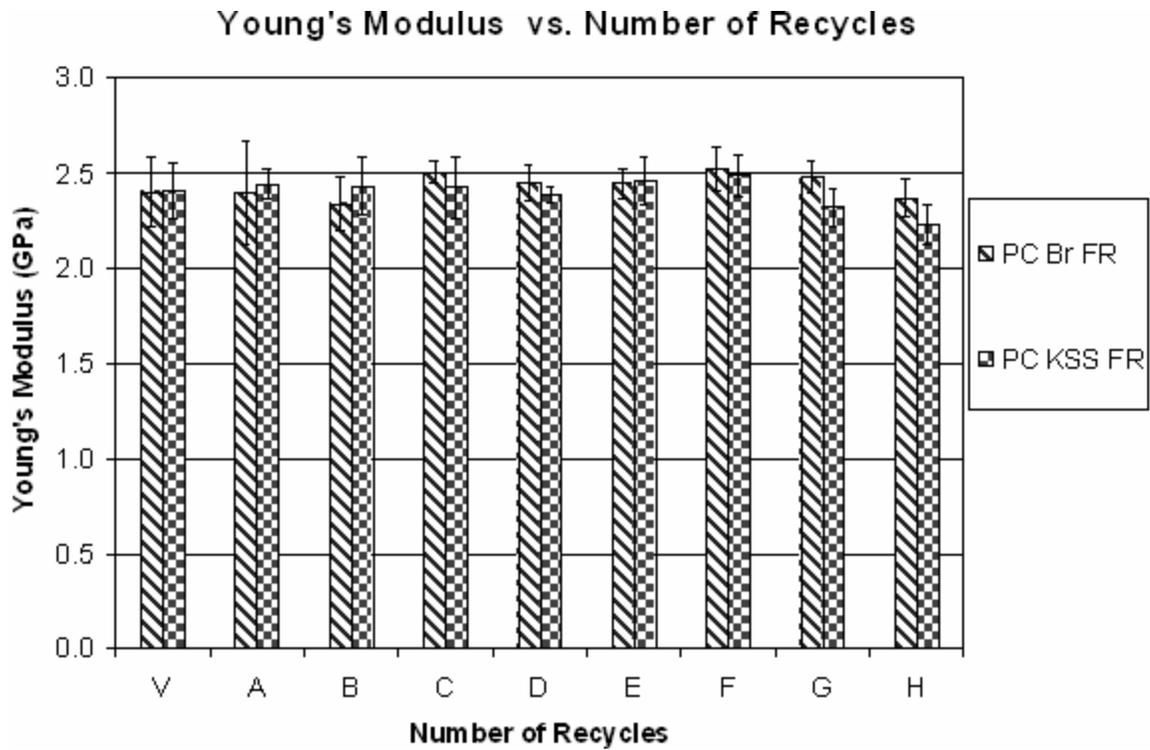


Figure 4 Young's Modulus vs Recycles for PC Br FR and PC KSS FR

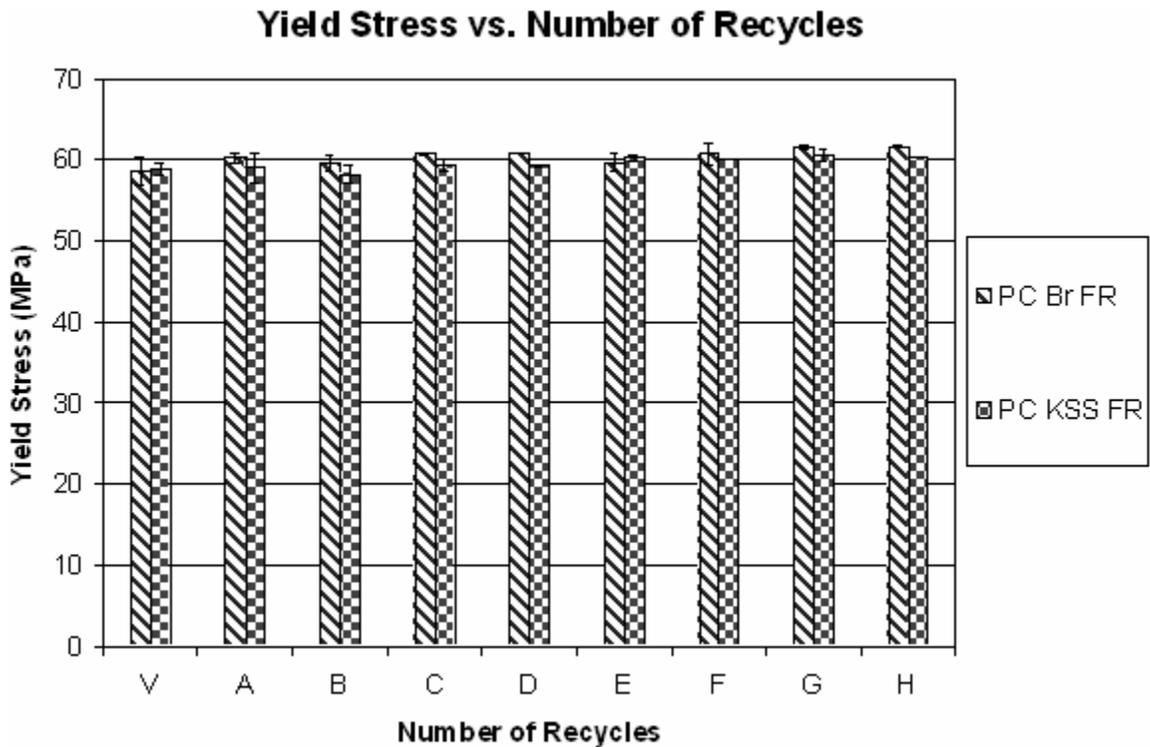


Figure 5 Tensile Stress at Yield vs. Number of Recycles for PC Br FR and PC KSS FR

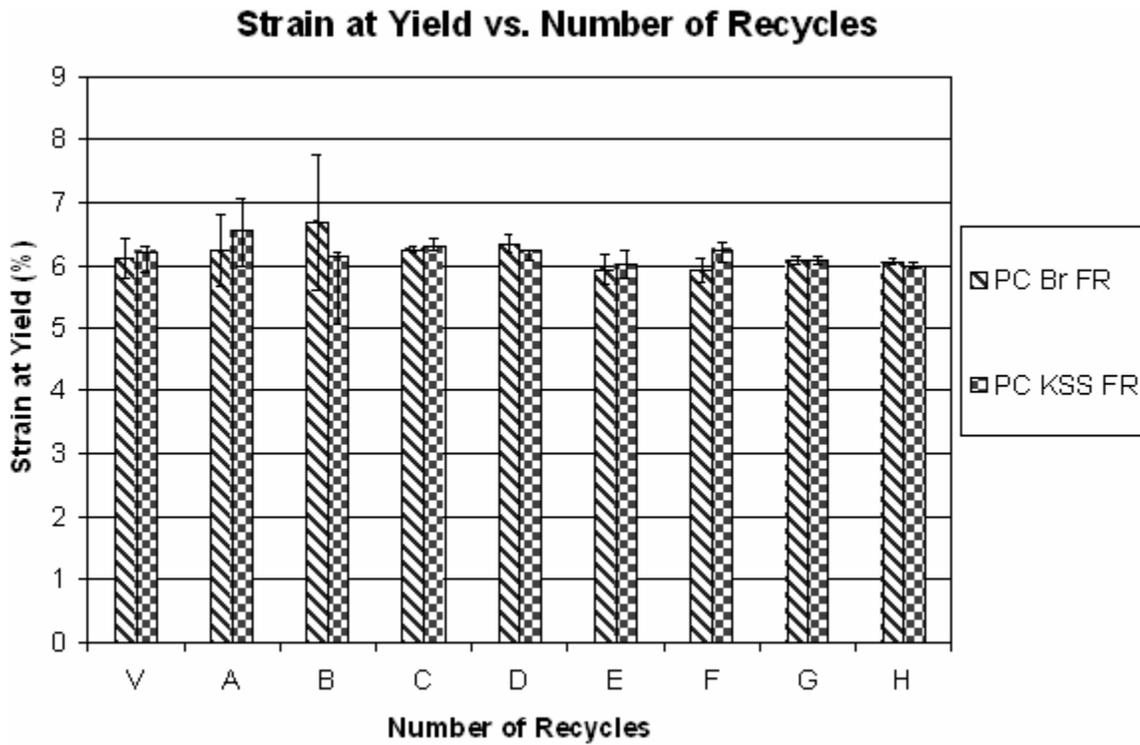


Figure 6 Strain at Yield vs. Number of Recycles for PC Br FR and PC KSS FR

Ultimate stress and elongation slightly went down during the first few recycles but stayed relatively constant throughout for both the PC Br FR and PC KSS FR. Figure 7 and Figure 8 show graphically the ultimate stress and elongation for the two materials, respectively.

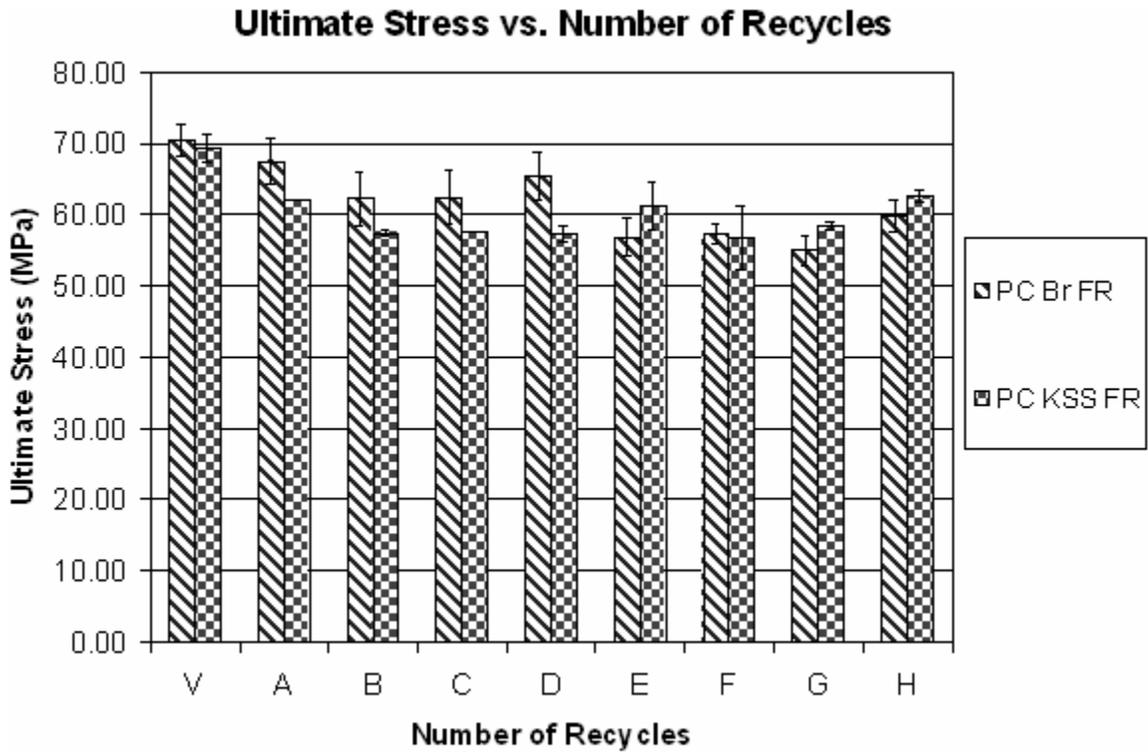


Figure 7 Ultimate Stress vs. Number of Recycles for PC Br FR and PC KSS FR

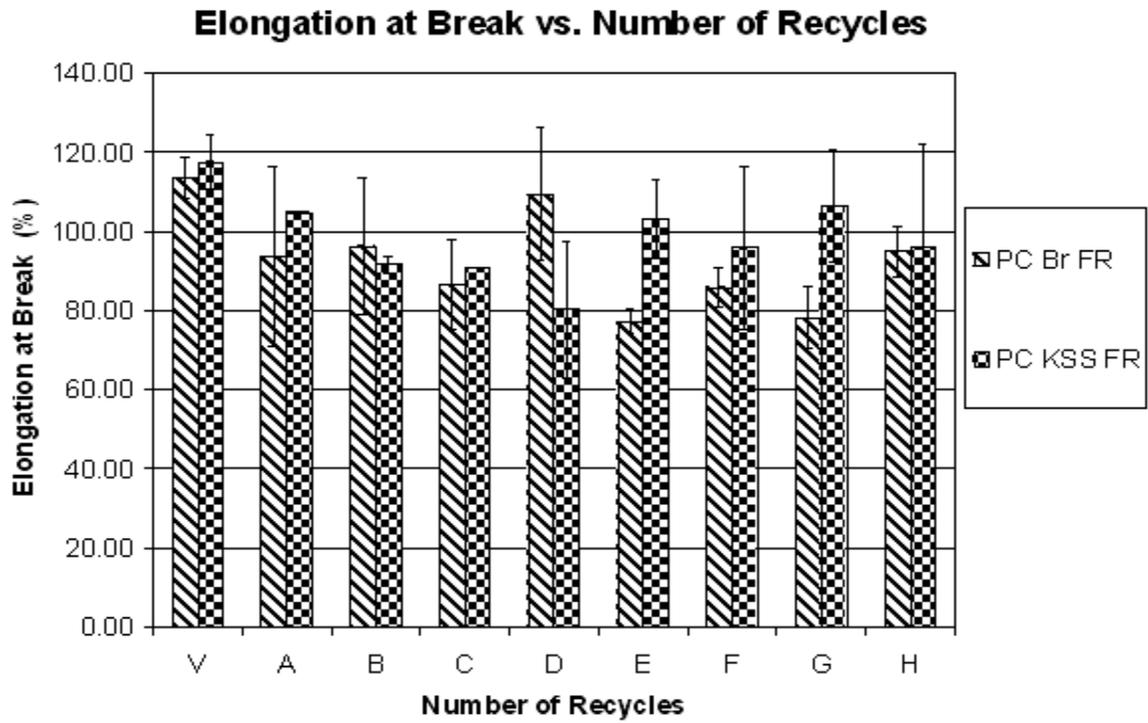


Figure 8 Elongation at Break vs. Number of Recycles for PC Br FR and PC KSS FR

3.1.2. Thermal Analysis

Figure 9 and Figure 10 show TGA curves of PC No FR, PC Br FR, and PC KSS FR in Air and N₂, respectively. For both, the halogenated and non-halogenated polycarbonates the curve shifts to the left, indicating a decrease in thermal stability. TGA curves of PC KSS FR in Air and N₂ (see Figure 11 and Figure 12, respectively) show nearly the same thermal stability as you progress with recycles.

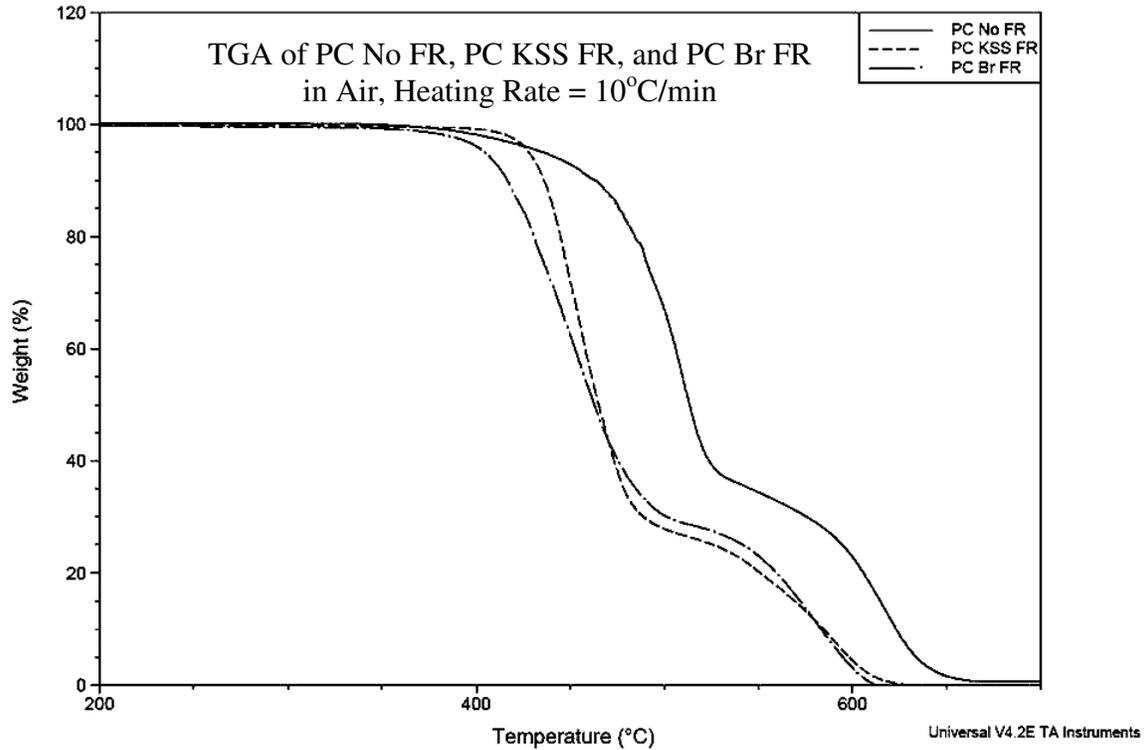


Figure 9 TGA of PC No FR, PC KSS FR, and PC Br FR in Air

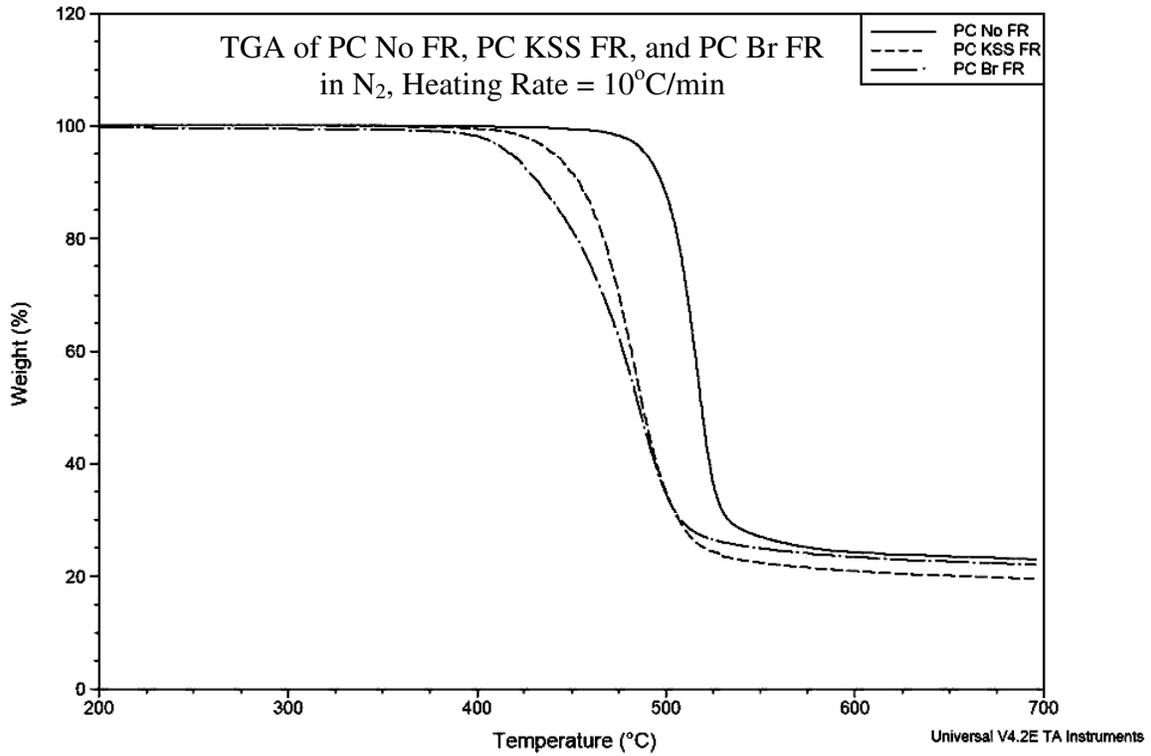


Figure 10 TGA of PC No FR, PC KSS FR, and PC Br FR in N₂

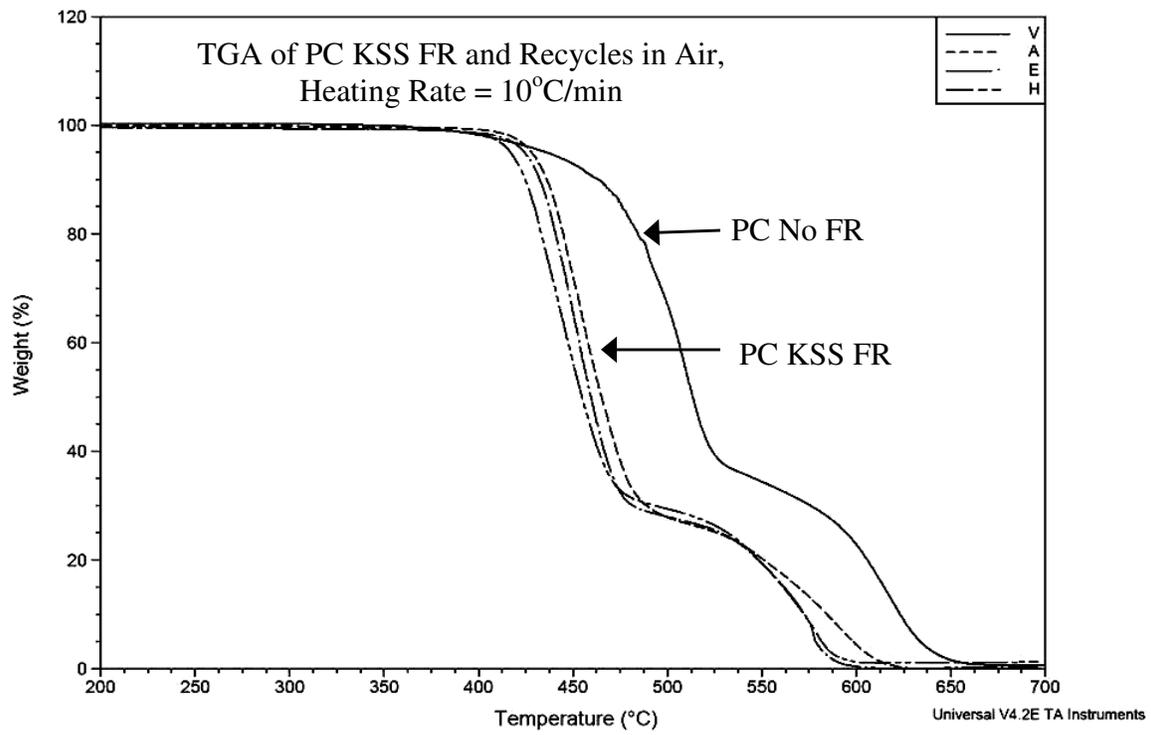


Figure 11 TGA of PC KSS FR and A, E, and H Recycles in Air

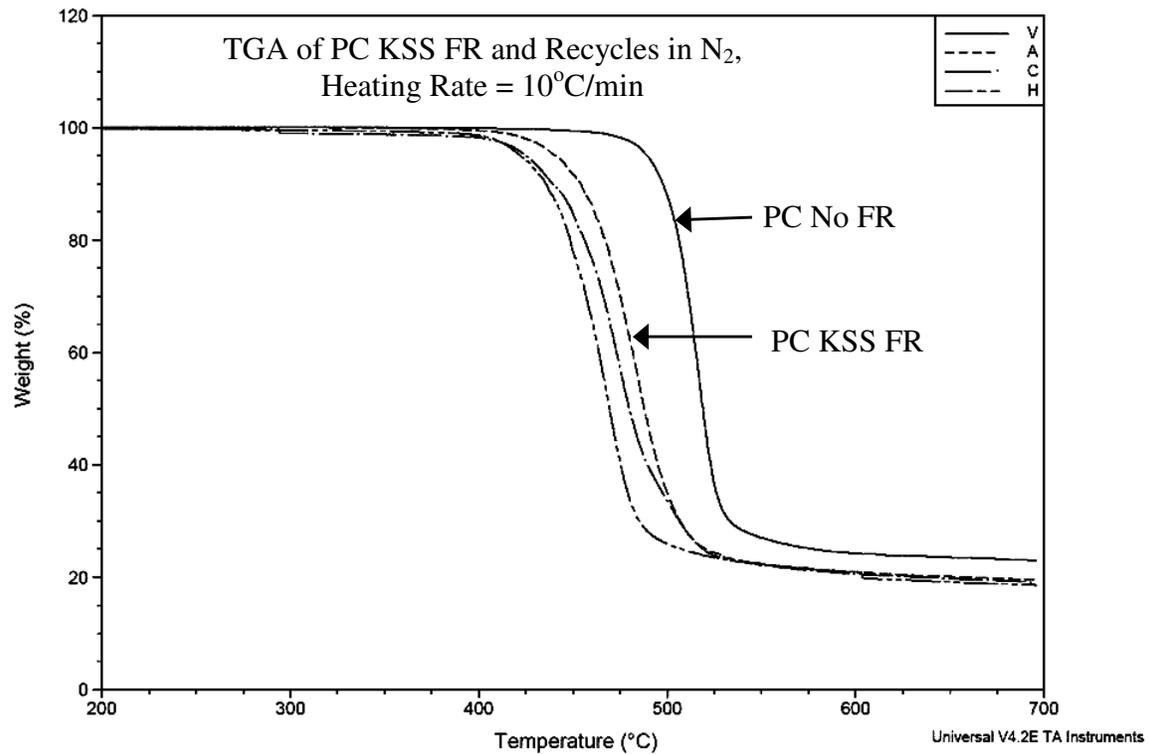


Figure 12 TGA of PC KSS FR and A, C, and H Recycles in N₂

3.1.3. Rheological Analysis

Viscosity versus shear rate data obtained for pure virgin PC No FR was compared to the viscosity data given on Bayer's website. Complete recycling data can be seen graphically in Figure 13 and Figure 14 for PC Br FR and PC KSS FR, respectively. It can be clearly seen with both materials that with each recycle the viscosity curve shifts down slightly. This is most likely due to a decrease in molecular weight. One would expect this with any material that has a thermal and shear history.

Viscosity vs. Shear Rate for PC Br FR

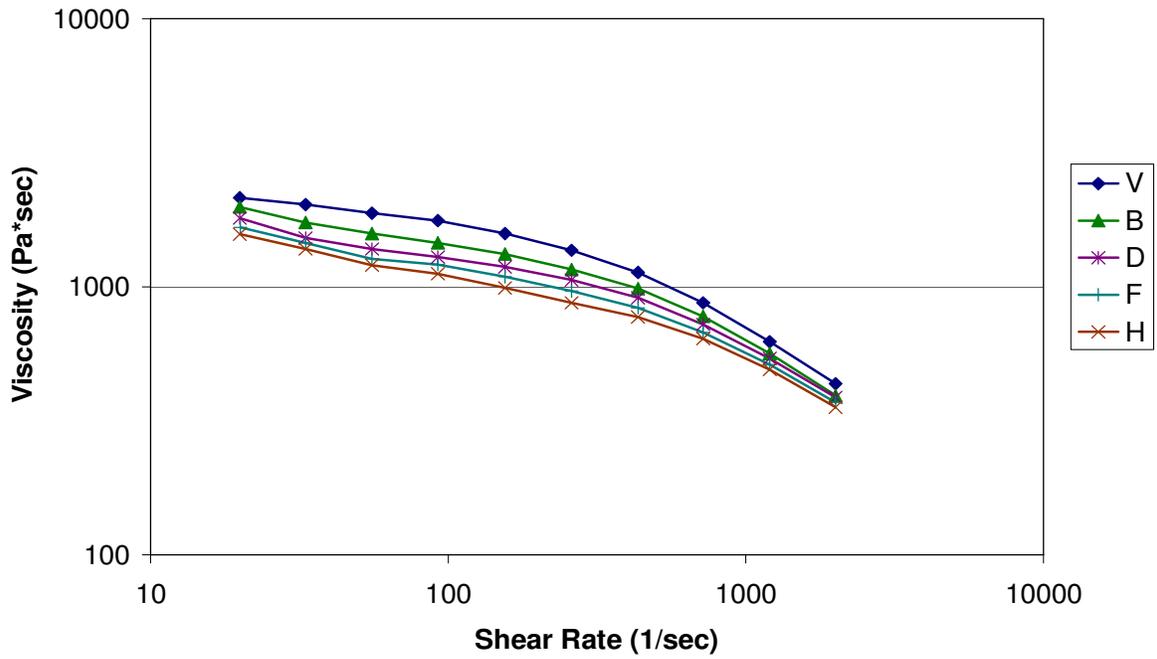


Figure 13 Viscosity vs. Shear Rate of PC Br FR for V, B, D, F, and H Recycles

Viscosity vs. Shear Rate for PC KSS FR

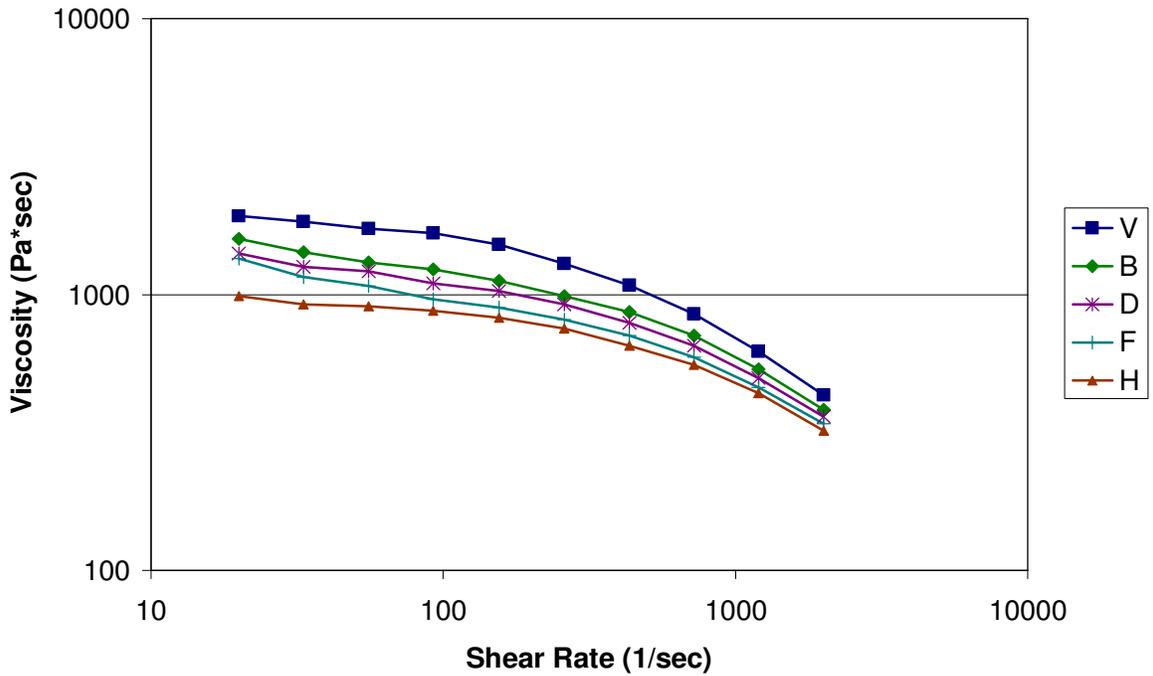


Figure 14 Viscosity vs. Shear Rate of PC KSS FR for V, B, D, F, and H Recycles

3.1.4. Optical Analysis

Pictures of PC Br FR and PC KSS FR are shown in Figure 15 and Figure 16, respectively. From the pictures, one can see that as recycles increase, the color turns more and more brown due to a slight degradation of the polymer. There is not much difference between the two materials, except that PC Br FR virgin material has a slight blue tint, whereas, PC No FR virgin material is clear.

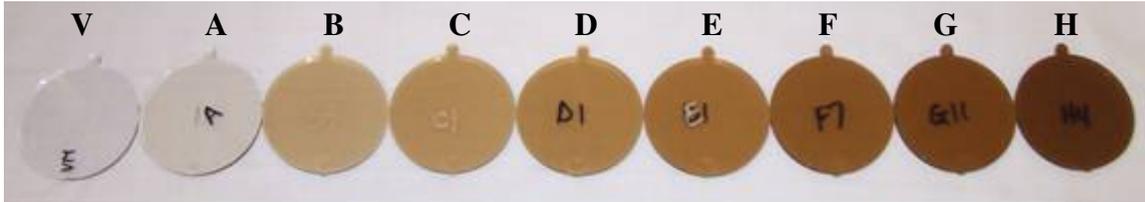


Figure 15 Picture of PC Br FR vs. Number of Recycles

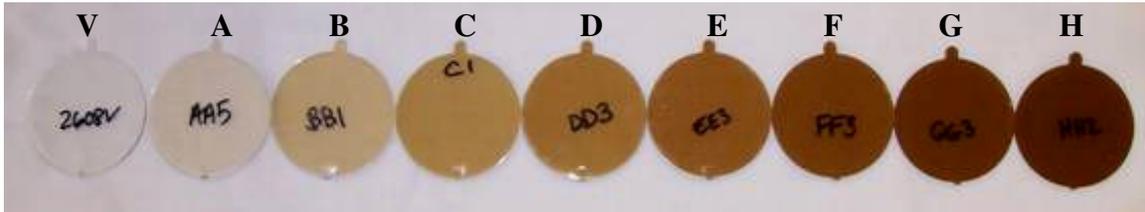


Figure 16 Picture of PC KSS FR vs. Number of Recycles

4. Conclusions

During the recycling of both polycarbonate materials, UL94 v-0 is kept throughout the recycling. The IZOD impact strength and the color of the material suffer the most during recycling. Young's modulus, yield stress, and ultimate stress stay fairly consistent. TGA was kept nearly constant. Viscosity and molecular weight of the PC decreases slightly as shown with the viscosity data. Most importantly, the non-halogenated flame retarded polycarbonate held up just as well as the halogenated flame retarded polycarbonate. Potassium diphenylsulfone sulfonate is potentially a good flame retardant additive for a recycled polycarbonate.

5. Future Work

Gel Permeation Chromatography to measure molecular weight is currently being performed. More recycling experiments are to be performed on a known recycled polycarbonate from a recycling facility. Work will also be performed to show the compatibility of the KSS FR with other known flame retardants. A complete mechanistic study on how the KSS FR is working is also to be performed.

6. Acknowledgements

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7. References

¹ N. R. Lazear, *Polycarbonate: High-Performance Resin*, Advanced Materials & Processes, 147, 2, 43-45, 1995.

² C. J. Hilado, *Flammability Handbook for Plastics*, Fifth Edition, Technomic Publishing Co., INC., Lancaster, Basel, Switzerland, p. 189, 1998.

³ G. Camino and L. Costa, *Performance and Mechanisms of Fire Retardants in Polymer – A Review*, Polymer Degradation & Stability, 20, 271-294, 1998.

⁴ C.F. Cullis, *The Role of Pyrolysis in Polymer Combustion and Flame Retardancy*, J. Analytical & Pyrolysis, 11, 451-463, 1987.

⁵ R. Dumler, et. al., *Thermal Formation of Polybrominated Dibenzodioxins (PBDD) and Dibenzofurans (PBDF) from Bromine Containing Flame Retardants*, Chemosphere, 19, 305-308, 1989.