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Peroxide-Crosslinked Flexible Tubing Decrosslinked by Ultrasonically Aided Extrusion: Rheology, Structure and Performance

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Abstract

The ultrasonically aided decrosslinking of peroxide-crosslinked flexible LDPE tubing (PEX-A) in a TSE at different processing temperatures, flow rates and ultrasonic amplitudes was carried out. The structure, tensile, thermal and dynamic properties of decrosslinked PEX-A were studied. It was found that tensile and thermal properties of decrosslinked PEX-A were insignificantly affected by the flow rate but strongly affected by ultrasonic amplitude. The higher processing temperature resulted in lower crystallinity values and higher crosslink density. An increase of ultrasonic amplitude led to a decrease of crosslink density and gel fraction in decrosslinked PEX-A. These findings were supported by SEM observations. Cole-Cole plots revealed that at the highest ultrasonic amplitude of 13 μm the decrosslinked PEX-A becomes more decrosslinked with its molecular structure becoming closer to that of the virgin LDPE regardless of processing temperature. The extracted PEX-A sol showed higher resemblance to virgin LDPE which could be due to some chains that were never crosslinked in the first place. However, the storage modulus and complex viscosity values of the sol were lower than those of the original LDPE. The temperature dependence of the storage modulus, loss modulus, and tan δ of crosslinked and decrosslinked PEX-A was also measured. The storage and loss moduli at 25°C showed an increasing trend with the ultrasonic amplitude. The minimum and maximum values of tan δ and the corresponding temperatures also increased with an increase in the ultrasonic amplitude. The virgin LDPE and the ultrasonically decrosslinked PEX-A processed at 200°C, at amplitude of 13 μm and flow rate of 2 lb/hr were, respectively, shown modulus of 311 MPa and 156 MPa, yield stress of 7.1 MPa and 8.6 MPa, stress at break of 14.5 MPa and 11.6 MPa, yield strain of 0.13 and 0.24, strain at break of 3.9 and 3.9.

Keywords: Amplitude; Crosslinked Polymers; Consumer Plastics; Polypropylene; Viscosity

Introduction

Among various polymer wastes, management of crosslinked plastics is a major environmental problem requiring a solution. Recycling of crosslinked polymers and flexible tubings is a great challenge due to the presence of a three-dimensional network. The decrosslinking of consumer plastics and rubber, such as crosslinked polypropylene (XPP), polyethylene (XPE) and rubber products is of great importance for maintaining clean environment through recycling. The ability to efficiently decrosslink these plastics and rubbers allow for greater recycling capabilities and cost savings in blended materials. The effective decrosslinking of the XPE is dependent on developing a technology which may preferentially break the crosslinks without a severe degradation of the main chains. If the crosslink bonds are different than the main chain bonds in their chemistry, a preferential breakage of the crosslink network is possible. However, if these bonds are basically identical with each other, preferential breakage of the crosslink network will be very difficult. Presently, XPE can be categorized based on their crosslink chemistry into three kinds: peroxide-crosslinked, irradiation-crosslinked and silane-crosslinked PE. The crosslink bonds in the first two methods are basically identical with the main chain bonds because they are all single C-C bonds. The crosslink bonds in the silane-crosslinked PE are the Si-O bonds which are different than the single C-C bonds in the main chain. The majority of studies on the decrosslinking of XPE were focused on using supercritical fluid including methanol, ethanol and water [1-8]. Such a method seems to be very effective on silane-crosslinked low-density PE (XLDPE) by using supercritical methanol with gel fraction being reduced practically to 0% without degradation of main chains [2,4,5]. The successful preferential decrosslinking of XLDPE is due to the presence of silicon-oxygen bonds that can be decomposed via methanolysis reaction. Attempts on decrosslinking of peroxide- and irradiation-crosslinked XPE are also done by mechanochemical milling [9,10]

and by modular intermeshing co-rotating twin-screw extrusion [11] with substantial decrease in gel fraction. In addition, recycling of power transmission cable insulated with XPE and its separation by the thermo-chemical, thermo-mechanical, microwave-mechanical means have been attempted [12].

Also, the ultrasonic decrosslinking of peroxide-crosslinked XHDPE was investigated by using two setups of ultrasonic devices [13]. The first setup was a static ultrasonic device with a sample placed between the ultrasonic cylindrical horn and the metal plate with the adjustable gap between the horn and plate. A controlled pressure was applied on the circular sample by pressing the horn against the sample. Another set was an ultrasonic single-screw extruder with the ultrasonic horn placed at the die exit. Studies using both devices indicated a significant reduction of the gel fraction and crosslink density of the XHDPE with an increase of the pressure, ultrasonic treatment time and amplitude and a decrease of the gap. A universal curve of the normalized gel fraction against the normalized crosslink density of the decrosslinked XHDPE with some scattering was observed regardless of the processing equipment and processing conditions. It was concluded that the mechanism of the ultrasonically induced decrosslinking in both static and continuous device are the same. However, performance characteristics of decrosslinked XHDPE was poor, due to generation of a low molecular fraction via thermal degradation caused by a significant temperature rise during ultrasonic treatment due to lack of cooling. In subsequent studies [14-18], better techniques were developed using single- and twin-screw extruders with ultrasonic horns being under controlled cooling and placed in the extruder barrel. In these cases, decrosslinked XHDPE and XLDPE showed good performance properties.

The present study is aimed to carry out ultrasonic decrosslinking of flexible tubing of XLDPE using an ultrasonic twin-screw extruder (TSE). In contrast to our earlier study [16], which utilized the film grade LDPE, the present study is devoted to ultrasonic decrosslinking XLDPE powder generated from industrial flexible tubes. The ultrasonic extrusion was carried out at different processing temperatures, flow rates and ultrasonic amplitudes. The effect of processing conditions on the tensile, thermal and dynamic properties of decrosslinked XLDPE is elucidated.

Experimental

Materials

The low-density polyethylene (LDPE) sample (PE-A) and peroxide-crosslinked PEX-A were kindly provided by Borealis. This polymer is utilized for flexible pipe production. The virgin PE-A had a density of 922 kg/m^3 and a melt flow index of 2.0 g/10min. A small amount of carbon black was incorporated in PEX-A. PEX-A was decrosslinked in the ultrasonic TSE at 200°C and 250°C at ultrasonic amplitudes of 0 μm, 7.5 μm, and 13 μm, and flow rates of 1 lb/hr and 2 lb/hr. The twelve samples of decrosslinked extrudates PEX-A from the ultrasonic TSE were collected for further analysis. Also, for comparative purposes, non-extruded PE-A and PEX-A were used.

Processing

Table 1: Temperature profile during extrusion of PEX-A in ultrasonic TSE at various flow rates, ultrasonic amplitudes, and processing temperatures.

Material	Flowrate (lb/hr)	Ultrasonic Amplitude (μm)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)	Zone 5 (°C)	Zone 6 (°C)	Die (°C)
PEX-A	1	0	179.7 ± 0.5	199.7 ± 0.5	206.0 ± 0.0	200.0 ± 0.0	200.0 ± 0.0	199.7 ± 0.5
		7.5	179.3 ± 0.5	199.3 ± 0.5	218.0 ± 0.0	200.0 ± 0.0	200.0 ± 0.0	199.7 ± 0.5
		13	179.3 ± 0.5	212.3 ± 0.9	240.3 ± 0.9	200.0 ± 0.0	199.3 ± 0.5	200.0 ± 0.0
	2	0	179.7 ± 0.5	199.3 ± 0.0	211.0 ± 0.0	199.3 ± 0.5	205.0 ± 0.0	199.7 ± 0.5
		7.5	179.3 ± 0.5	200.0 ± 0.0	220.3 ± 0.5	200.0 ± 0.0	206.7 ± 0.5	199.7 ± 0.5
		13	179.3 ± 0.5	206.3 ± 0.9	248.3 ± 0.9	209.3 ± 1.7	207.7 ± 1.2	199.7 ± 0.5
	1	0	179.7 ± 0.5	249.3 ± 0.5	249.7 ± 0.5	249.7 ± 0.5	249.7 ± 0.5	250.0 ± 0.0
		7.5	179.3 ± 0.5	249.3 ± 0.5	249.7 ± 0.5	249.7 ± 0.5	249.7 ± 0.5	249.7 ± 0.5
		13	179.7 ± 0.5	249.3 ± 0.5	251.7 ± 0.5	250.0 ± 0.0	250.0 ± 0.0	249.3 ± 0.5
	2	0	178.5 ± 1.5	249.5 ± 0.5	250.5 ± 0.5	249.5 ± 0.5	250.0 ± 0.0	249.0 ± 0.0
		7.5	179.3 ± 0.5	249.7 ± 0.5	250.3 ± 0.5	249.7 ± 0.5	249.3 ± 0.5	249.7 ± 0.5
		13	179.3 ± 0.5	249.3 ± 0.5	267.0 ± 0.0	249.7 ± 0.5	249.3 ± 0.5	249.0 ± 0.8

The ultrasonic decrosslinking was carried out on PEX-A in an ultrasonically aided TSE, schematically depicted in Figure 1a. Screw configuration is shown on Figure 1b. Various processing temperatures, flow rates and ultrasonic amplitudes were used. Specifically, processing temperatures of 200°C and 250°C, flow rates of 1 lb/hr and 2 lb/hr, and ultrasonic amplitudes of 0 μm (without treatment), 7.5 μm and 13 μm were used. Table 1 shows the temperature profile in the ultrasonic TSE during steady state

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decrosslinking extrusion process. Temperature at the feed zone (Zone 2) was held at 180°C, and the melt zone (Zone 3) and die zone were held at 200°C and 250°C, respectively. Zone 4 and 5 are before and after the ultrasonic zone, respectively. All values reported here are the average of 3 sets of data that was recorded while the extrudate was being collected. The errors are the standard deviation of the entire data set.

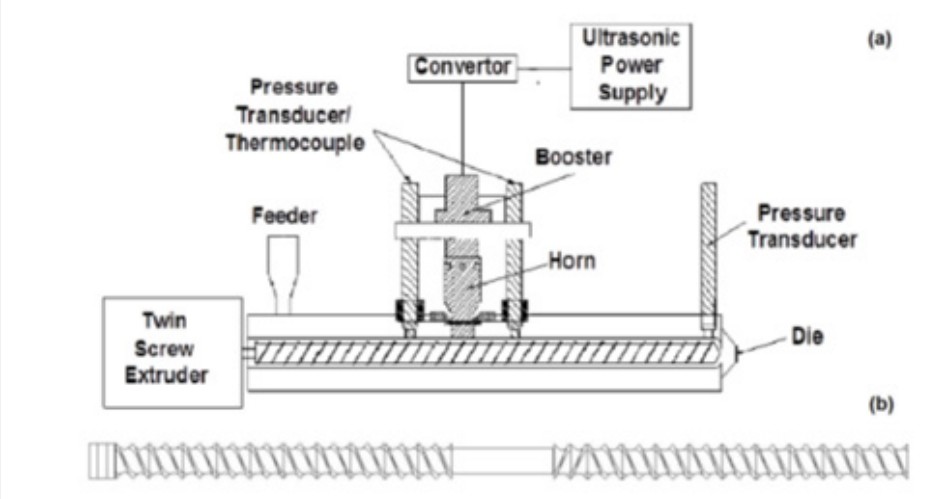

Figure 1: (a) Ultrasonic TSE and (b) Decrosslinking Screws.

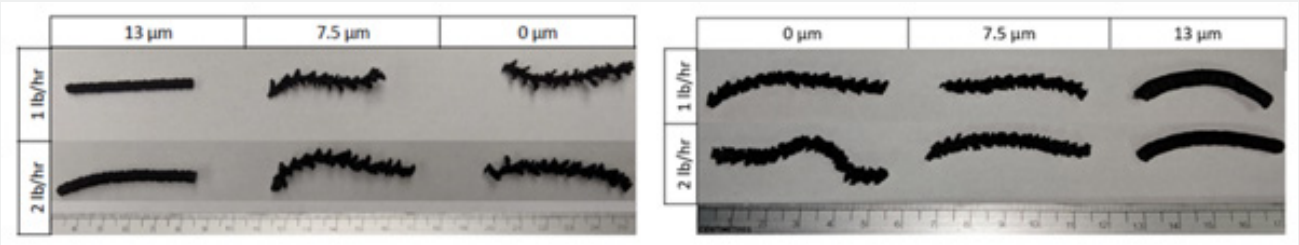

Figure 2: Photographs of extrudates from ultrasonic TSE operating at various ultrasonic amplitudes and flow rates at a processing temperature of 200°C (left) and 250°C (right).

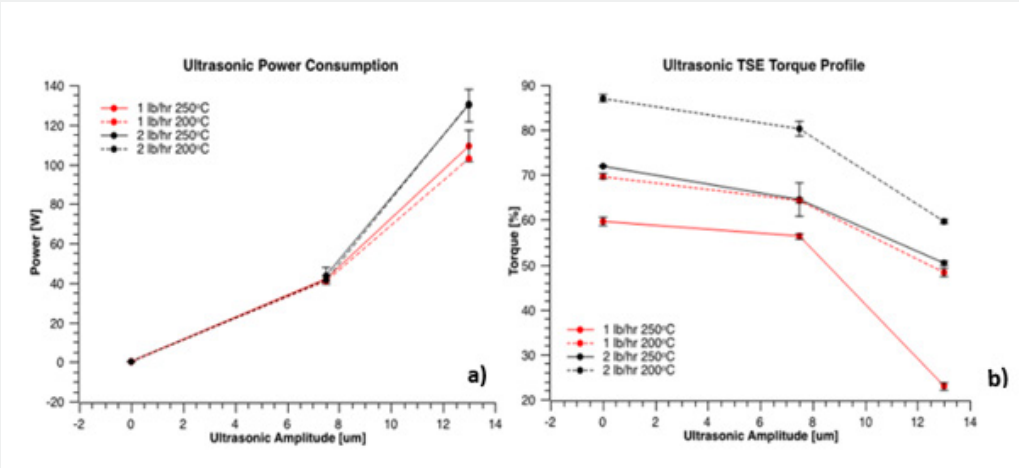

Figure 3: Ultrasonic power consumption (a) and extruder torque (b) as a function of ultrasonic amplitude during extrusion of PEX-A at processing temperature of 200°C and 250°C and flow rates of 1 lb/hr and 2 lb/hr..

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Test specimen in sheet forms were prepared by compression molding in a mold of dimensions 13 cm x 25 cm x 0.2 cm. Once the mold reached 200°C, 100 g of the pelletized LDPE or PEX was evenly spread in the mold. The mold was then transferred back to the compression molding machine, where the material was left to melt for 5 minutes. During this time, the pressure was slowly increased from 0 to 7,000 psi (48.3 MPa). The closed mold was held under pressure at a temperature of 200°C for 20 minutes. The mold was transferred to another compression molding machine to be quenched by being kept at room temperature for 45 minutes under a pressure of 2,000 psi. Then the molded sheet was removed from the mold. Samples for tensile testing, DSC, Soxhlet extraction, SEM, DMA and rheological testing were made from the sheet.

Testing Methods

Tensile testing was carried out by using an Instron Tensile Tester (Model 5567) with a 1 kN loadcell. The crosshead speed was 25 mm/min. Dumbell specimens were cut from the compression molded sheet via a cutting die with a width of 4.84 mm and gauge length of 16 mm. The distance between the Instron grips was 16 mm. This value is used as the initial length to calculate strain. The stress-strain curves were measured to determine a modulus at 1% strain, yield stress, yield strain, strain and stress at break. A minimum of 5 specimens were tested and the average values were reported with their respective standard deviation. Test results were excluded if there were visible nonuniformities in the 16 mm test region.

Differential scanning calorimetry (DSC) tests utilized a TA Instruments DSC (Model Q2000). 5-10 mg samples were cut from the compression molded sheet and sealed in an aluminum hermetic pan. Samples were characterized using the following procedure: heating from 40°C to 200°C at 10°C/min, holding at 200°C for 10 minutes, cooling from 200°C to 40°C at 10°C/min, holding at 40°C for 10 minutes followed by heating from 40°C to 200°C at 10°C/min. The melting point and enthalpy of melting were calculated from the second heating cycle. For crystallinity calculations the melting enthalpy of 282 J/g for a pure polyethylene crystal was used. The average values were reported with their respective standard deviation. Tests were repeated at least 2 times.

Soxhlet extraction tests followed ASTM D 2765, test method C. A rectangle of about 0.5 g was cut from the compression molded sheet and precisely weighed and placed in 100 mL of xylene. The xylene was held at 110°C in an oil bath. The sample was left to swell in xylene for 24 hours. Then, it was removed by pouring the xylenes and sample onto a 60 mesh wire cloth. The weights of swollen sample before drying and after drying were measured. The swollen sample was quickly removed and its surface wiped and transferred to a sealed weighing container after its removal from the xylene. The quick transfer (~10 s) into a sealed container ensured minimal solvent loss to the atmosphere before weight measurements. The gel was dried for 24 hours in a vacuum oven at 100°C. A density of 0.922 g/cm3 and an interaction parameter, χ, of 0.28 was used for crosslink density calculations. This test allowed gel fraction and crosslink density to be calculated. Tests were repeated at least 3 times. The xylene was captured after filtering the gel. This material was then dried for 24 hours in a vacuum oven at 100°C to obtain sol. To ensure no xylenes were present in the sol, the dried sample was weighed and re-heated in the oven to ensure no weight change. The sol was compression molded at 200°C and 7,000 psi (48.3 MPa) for 15 minutes.

Thermal Gravimetric Analysis (TGA) tests utilized a TA Instruments TGA Q50. Samples were characterized using the following procedure under an air atmosphere: ramp 20°C/min from 30°C to 700°C. Tests were done at least 2 times. This test allowed us to obtain thermal degradation temperatures from %wt loss curves as a function of temperature.

A stress-controlled Discovery Hybrid Rheometer (DHR–II) was used for measuring the rheological properties of the materials with a 25 mm stainless steel parallel plate. The compression molded sheets were cut into 25 mm discs with a die. The tests were performed to investigate the frequency dependence of storage and loss moduli, tan δ, and complex dynamic viscosity in the frequency range of 0.01 to 100 rad/s. For 200°C processing temperature, the linear viscoelastic region was determined by performing a stress amplitude sweep in the stress range of 0.01 to 1000 Pa at 160°C. A constant stress of 100 Pa was used. The samples decrosslinked at 250°C were tested with a new method to improve reproducibility, in which the temperature during sample loading was kept at 110°C and the axial force was 1 N. After a few minutes, the temperature was set to 160°C. As the temperature increased, the axial force too was increased to 20 N in a step wise manner. A constant stress of 100 Pa was used. Tests on sol samples using the final axial force of 10 N and a constant stress of 10 Pa. All tests were repeated twice, and the average values were reported.

SEM imaging utilized a JEOL-7401 with an accelerating voltage of 1kV. Samples were cut from the compression molded sheets and cracked after being cooled with liquid nitrogen. Samples were first etched in a 1:1 volume solution of phosphoric acid and sulfuric acid with 1 wt% of potassium permanganate. All samples were submerged in the etching solution for one hour. The samples were then rinsed for one minute in a 7:2 volume solution of distilled water and sulfuric acid. Next, the samples were rinsed for one minute in H_2O_2. Then the samples were rinsed with distilled water for two minutes. Finally, the samples were rinsed with methanol for one minute. Before imaging, the etched samples were sputter coated with a Quorum Technologies K575X for 60 seconds at 190 mA.

Dynamic mechanical measurements were performed using a Dynamic Mechanical Analyzer (DMA) TA Q800. The compression molded sheets were cut into a rectangular specimen with dimensions 33 mm x 6.4 mm. The length between the clamps was kept near 4.5 mm. The samples were tested in a tension mode from 25°C to 175°C at a heating rate of 3°C/min, 0.1% strain and 1Hz frequency. The values of storage and loss moduli and tan δ

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at 25°C were recorded and compared for samples obtained at different ultrasonic amplitudes. The minimum and maximum values of loss tangent (tan δ) and the corresponding temperatures were recorded. These temperatures were indicators of the melting point and softening point of the sample, respectively. The tests were repeated twice and the average values were reported.

Results and Discussion

Process characteristics

Figure 2 shows the extent of melt fracture present in the extruded samples obtained at ultrasonic amplitudes of 0 μm (no ultrasound imposed), 7.5 μm and 13 μm and flow rates of 1 lb/hr and 2 lb/hr. It is seen from Figure 2, that the extrudates obtained at 200°C (left figure) that was treated at an ultrasound amplitude of 13 μm are noticeably smother at both feed rates. These extrudates were easily pelletized during extrusion. In contrast, the extrudates obtained without ultrasonic treatment and with ultrasonic treatment at an ultrasonic amplitude of 7.5 μm experienced very high degrees of melt fracture. These extrudates were too brittle to be pelletized on-line during extrusion. So they were pelletized in a separate stage after extrusion. In order to find the effects of processing temperature, the ultrasonic TSE was also operated at 250°C with extend of melt fracture shown in Figure 2 (right figure). All extrudates appeared to be stronger than those obtained at 200°C. Unlike the prior tests at 200°C, the extrudates at the increased processing temperature were all able to be directly pelletized on-line without breakage. The extrudate of 13 μm 250°C is seen to have even more smooth surface, than the extrudate of 13 μm 200°C.

Figure 3 shows the ultrasonic power consumption (a) and extrusion torque (b) as a function of ultrasonic amplitude at processing temperatures of 200°C and 250°C. The ultrasonic power consumption increases with the increase of ultrasonic amplitude due to a reduction of viscosity of decrosslinked material but does not significantly change with processing temperature due to a little effect of the temperature on the loss modulus of material at high ultrasonic frequency (40 kHz). The torque value decreases significantly with the increase of ultrasonic amplitude and processing temperature due a reduction of viscosity of decrosslinked material.

The die pressure as a function of ultrasonic amplitude is shown Figure 4 at different flow rates for a processing temperature of 200°C. The pressure difference between a flow rate of 1 and 2 lb/hr is nearly a constant 0.8 MPa regardless of ultrasonic amplitude. There is a negligible difference between the die pressure without ultrasonic treatment and with ultrasonic treatment of 7.5 μm. This is due to the fact that there is no significant diffrences in complex dynamic viscosity of these samples, as shown later in the study. However, at 13 μm, there is a drop in die pressure by 1.2 MPa at both flow rates, since a significant decrease in complex dynamic viscosity occurred at this amplitude, as reported below. These observations on die pressure variation with ultrasonic amplitude are similar for those shown for crosslinked film grade LDPE studied earlier [16]. However, due to a lower crosslinked density and gel fraction of present LDPE, as reported below, in comparison with the LDPE film grade [16], the die pressure value were lower in the present case.

Stress-strain behavior

Figure 5 shows the stress-strain behavior of samples obtained at different ultrasonic amplitudes at a flow rate of 1 lb/hr (left) and 2 lb/hr (right) when processed at 200°C. It is seen that PEX-A decrosslinked by the ultrasonic TSE provides a significant improvement in its mechanical performance. From the stress-strain curves obtained at processing temperatures of 200°C and 250°C, the modulus at 1% strain, yield stress, yield strain, strain at break, and stress at break were determined. These values are reported in Figure 6 and Figure 7 as a function of the ultrasonic amplitude. As seen from Figure 7, the enhancement of ultimate properties also occurs at a processing temperature of 250°C.

However, at this elevated processing temperature ultimate properties are found to be lower than at 200°C. At 1 lb/hr, the increased processing temperature results in a decrease of modulus, stress at break, and strain at break, but an increase in stress at break. The ultrasonically decrosslinked PEX-A sample obtained at 200°C and 250°C with an amplitude of 13 μm and a flow rate of 1 lb/hr has, respectively, a modulus of 147 MPa and 110 MPa, yield stress of 8.6 MPa and 10.7 MPa, stress at break 11.5 MPa and 9.4 MPa, and strain at break of 4.2 and 0.46. At 2 lb/hr, the increased processing temperature results in a decrease in modulus, yield stress, strain at break, and no significant change in stress at break. The ultrasonically decrosslinked sample of PEX-A processed at 200°C and 250°C with an amplitude of 13 μm and a flow rate of 2 lb/hr shows, respectively, a modulus of 156 MPa and 89 MPa, yield stress of 8.6 MPa and 7.3 MPa, stress at break of 11.6 MPa and 11.7 MPa, and strain at break of 3.9 and 1.88. Unlike the samples processed at 200°C, at processing temperature of 250°C flow rate affects the stress-strain behavior of the ultrasonically decrosslinked PEX-A, namely a flow rate of 1 lb/hr outperforms a flow rate of 2 lb/hr. Similar to the samples processed at 200°C, at a processing temperature of 250°C the general trend suggests that an increase in ultrasonic amplitude leads to an increase in tensile properties. Comparing the stress-strain behavior of crosslinked and decrosslinked LDPE for manufacturing flexible tubing of the present study with those of film grade LDPE, studied in [16], show that the LDPE of the current study exhibits significantly less yielding and strain hardening behavior than the film grade LDPE. To ensure that the compression molding temperature of 200°C is adequate for preparing test specimen sheets, PEX-A decrosslinked at an ultrasonic amplitude of 13 μm obtained at flow rates of 1 lb/hr and 2 lb/hr were also molded at 220°C and their tensile properties were measured. Comparison of mechanical properties of obtained samples at molding temperatures of 200°C and 220°C is given in Table 2. As seen from Table 2, an increase in modulus at 1% strain, a decrease in yield stress and yield strain with some minor changes in the stress at break and strain at break takes place, indicating that the molding temperature of 200°C used in the present study is adequate.

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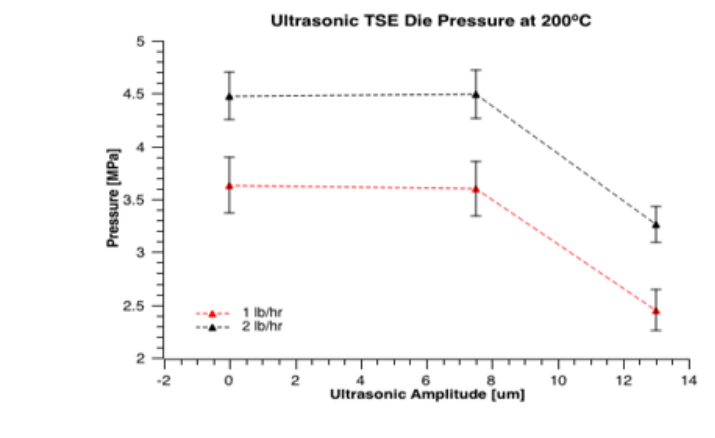

Figure 4: Dependence of die pressure in ultrasonic TSE as a functon of ultrasonic amplitude for PEX-A extruded at 200 °C at flow rates 1 and 2 lb/hr.

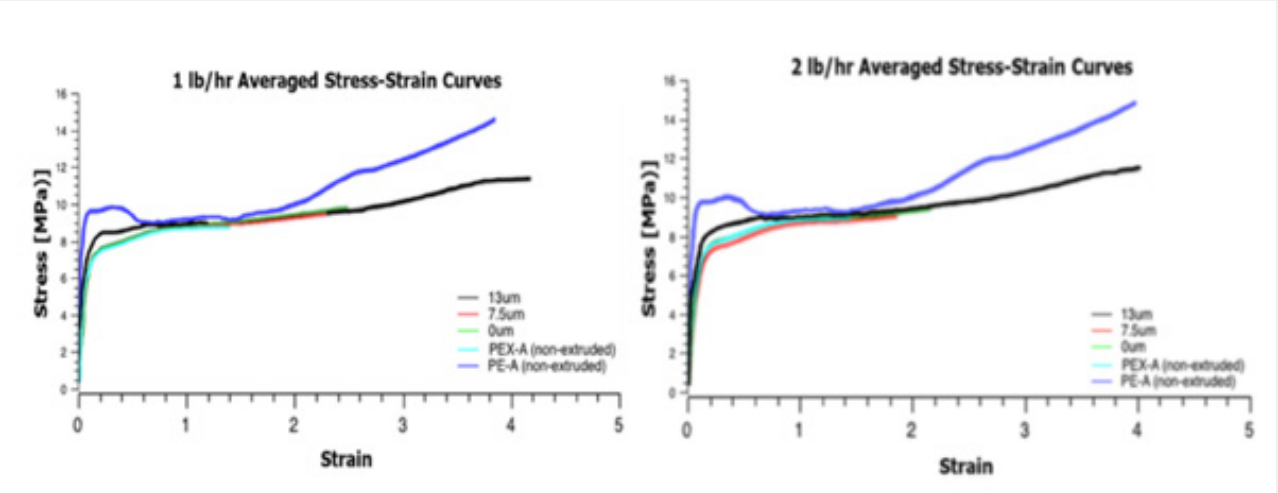

Figure 5: Stress-strain curves of PEX-A extruded in ultrasonic TSE at 200°C, 1 lb/hr (left) and 2 lb/hr (right), and various ultrasonic amplitudes. Curves for non-extruded PEX-A, non-extruded PE-A are also shown.

Table 2: Comparison of tensile properties of compression moldings of PEX-A decrosslinked in ultrasonic TSE at 200°C with an ultrasonic amplitude of 13 μm and flow rates of 1 lb/hr and 2 lb/hr and prepared at molding temperatures of 200°C and 220°C.

Material	Flowrate (lb/hr)	Ultrasonic Amplitude (μm)	Molding Temperature (°C)	Modulus at 1% (MPa)	Yield Strain	Yield Stress (MPa)	Strain at Break	Stress at Break (MPa)
PEX-A	1	13	200	147 ± 8	0.20 ± 0.02	8.6 ± 0.1	4.2 ± 0.3	11.5 ± 0.2
			220	173 ± 4	0.12 ± 0.01	7.7 ± 0.3	4.1 ± 0.3	11.5 ± 0.5
PEX-A	2	13	200	156 ± 2	0.24 ± 0.02	8.6 ± 0.1	3.8 ± 0.3	11.6 ± 0.3
			220	168 ± 10	0.13 ± 0.02	7.4 ± 0.4	3.8 ± 0.3	11.1 ± 0.5

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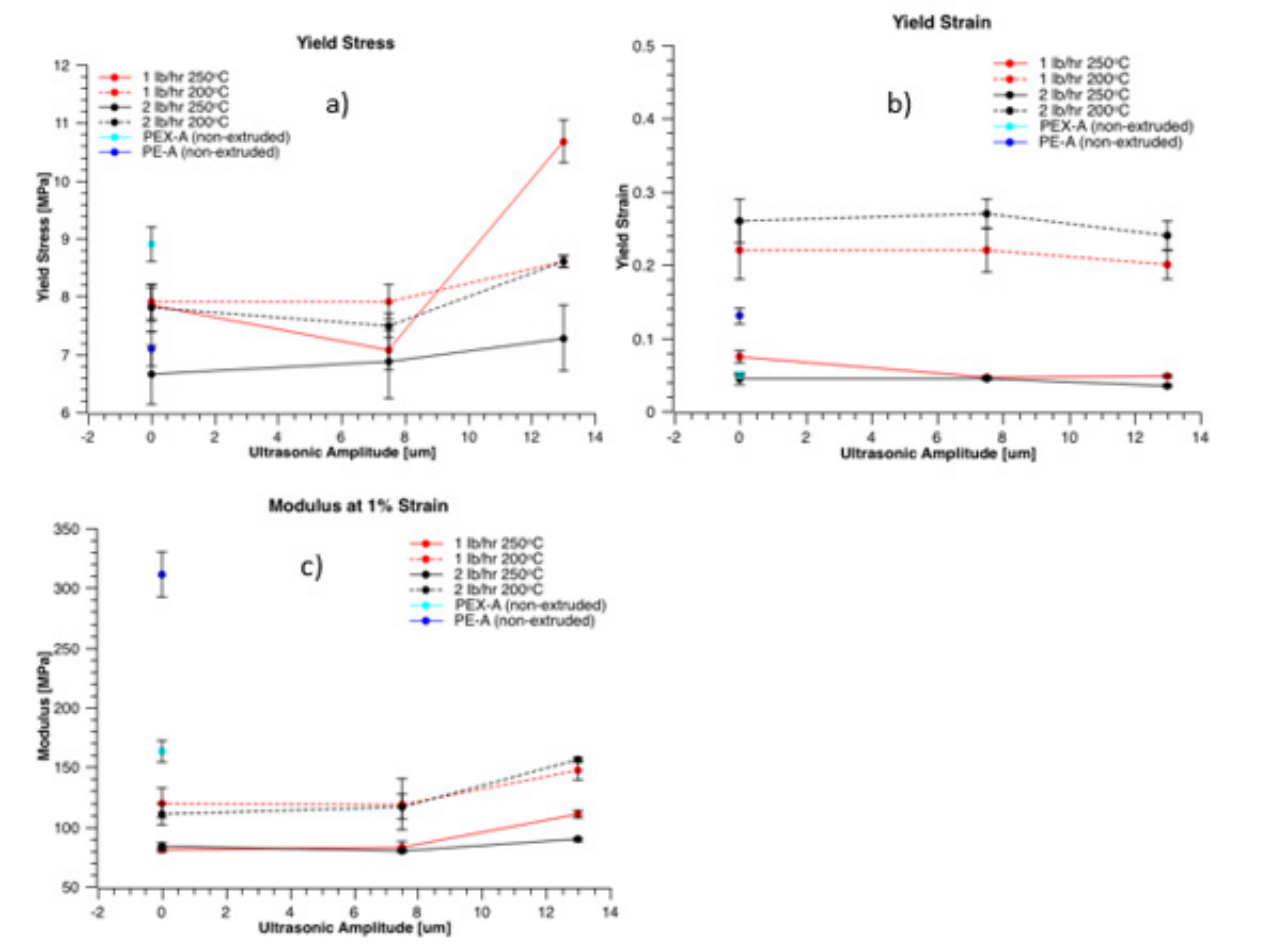

Figure 6: Yield stress (a), yield strain (b), and modulus at 1% strain (c), of extruded PEX-A in TSE as a function of ultrasonic amplitude at various processing temperatures and flow rates. Properties of non-extruded PEX-A, and non-extruded PE-A are also shown.

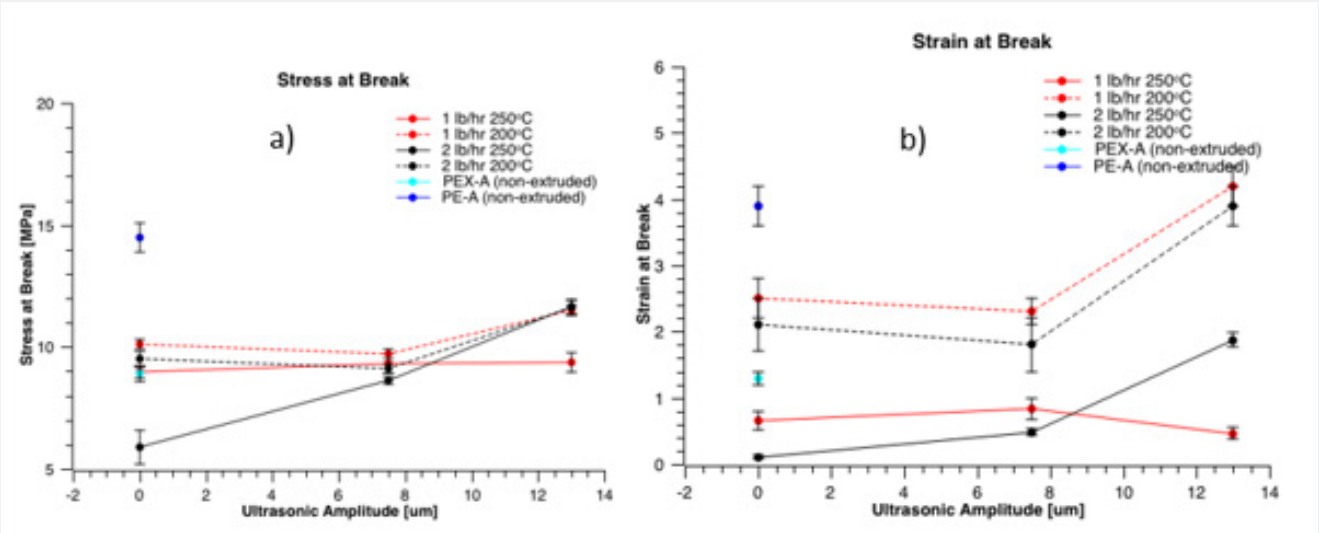

Figure 7: Stress at break (a) and strain at break (b) of extruded PEX-A in TSE as a function of ultrasonic amplitude at various processing temperatures and flow rates. Properties of non-extruded PEX-A, and non-extruded PE-A are also shown.

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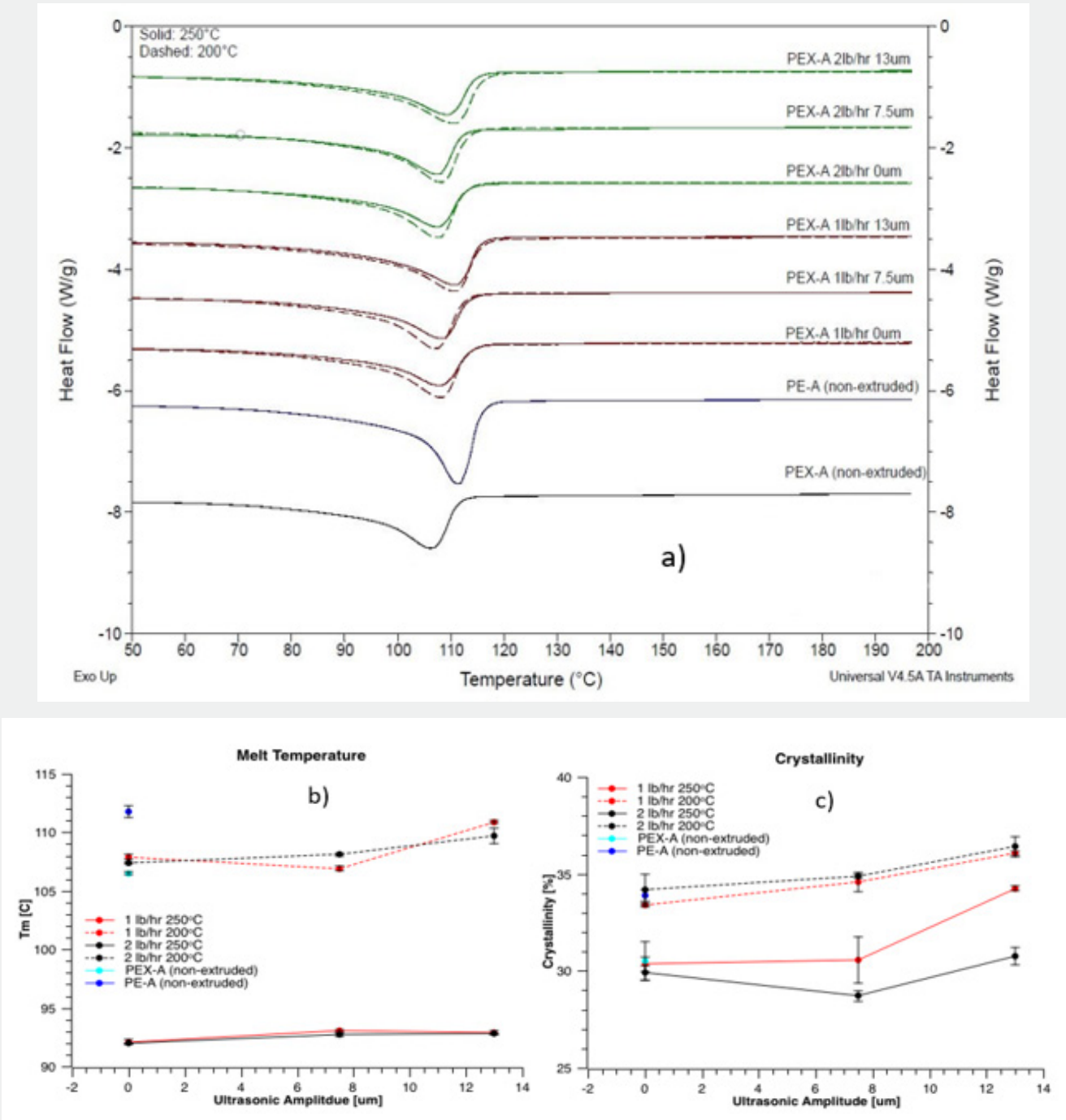

Figure 8: DSC heat flow curves for PEX-A extruded at 200°C (dashed lines) and 250°C (solid lines) at different ultrasonic amplitudes (a), melting point (b) and crystallinity (c) of extruded PEX-A as a function of ultrasonic amplitude at various flow rates. Results for non-extruded PEX-A and non-extruded PE-A are also shown.

Crystallinity and melting behavior

Figure 8 shows the DSC heat flow curves (a), melting point (b) and crystallinity (c) of various decrosslinked PEX-A samples, non-extruded PEX-A and non-extruded PE-A. The measured values are given in Table 3. At a processing temperature of 250°C and flow rate. of 2 lb/hr (solid green lines in Figure 8 a,b, the melting point increased with imposition of ultrasound. Specifically, Tm of the untreated sample is 107.1°C, while Tm of the sample treated at the ultrasonic amplitude of 13 μm is 109.4°C. Similarly, crystallinity value increased from 29.9% to 30.8%. At a processing temperature of 250°C and a flow rate of 1 lb/hr (solid red lines), similar melting points were seen. Specifically, Tm of the untreated sample is 108.0°C, while Tm of the sample

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treated at the ultrasonic amplitude of 13 μm is 110.7°C. Similarly, crystallinity value increased from 30.3 to 34.3%, being higher then crystallinity of non-extruded PEX-A. Clearly, the increased processing temperature decreased the crystallinity and had little effect on melting temperature. The highest crystallinity of 39.9% is seen for PE-A. The observation of behaviors of melting temperature and crystallinity of crosslinked tube-grade LDPE of the present study are similar to film-grade LDPE studied earlier [16].

Table 3: Melting point, crystallinity, gel fraction, and crosslink density of extruded PEX-A in TSE at various processing temperatures, flow rates, and ultrasonic amplitudes. Results for non-extruded PEX-A and non-extruded PE-A are also shown.

Material	Processing Temperature (°C)	Flowrate (lb/hr)	Ultrasonic Amplitude (μm)	Tm (°C)	Crystallinity (%)	Gel fraction	X-link Density (kmole/m^3)
PEX-A	200	1	0	107.9 ± 0.2	33.4 ± 0.1	0.50 ± 0.02	0.0102 ± 0.001
			7.5	106.9 ± 0.2	34.6 ± 0.5	0.43 ± 0.04	0.0080 ± 0.001
			13	110.9 ± 0.1	36.1 ± 0.1	0.30 ± 0.08	0.0046 ± 0.001
		2	0	107.4 ± 0.1	34.2 ± 0.8	0.53 ± 0.02	0.0110 ± 0.001
			7.5	108.1 ± 0.1	34.9 ± 0.1	0.54 ± 0.03	0.0132 ± 0.002
			13	109.7 ± 0.7	36.4 ± 0.5	0.36 ± 0.01	0.0069 ± 0.001
	250	1	0	108.0 ± 0.1	30.3 ± 0.4	0.56 ± 0.05	0.0134 ± 0.002
			7.5	108.1 ± 0.1	30.6 ± 1.2	0.57 ± 0.04	0.0143 ± 0.001
			13	110.7 ± 0.1	34.3 ± 0.1	0.13 ± 0.03	0.0065 ± 0.001
		2	0	107.1 ± 0.1	29.9 ± 0.4	0.58 ± 0.01	0.0173 ± 0.001
			7.5	108.1 ± 0.6	28.7 ± 0.3	0.58 ± 0.01	0.0159 ± 0.001
			13	109.4 ± 0.1	30.8 ± 0.4	0.38 ± 0.02	0.0072 ± 0.001
PE-A (non-extruded)	n/a	n/a	0	111.8 ± 0.5	39.9 ± 0.3	0.00 ± 0.00	0.0000 ± 0.000
PEX-A (non-extruded)			0	106.5 ± 0.1	30.5 ± 1.0	0.59 ± 0.01	0.0250 ± 0.001

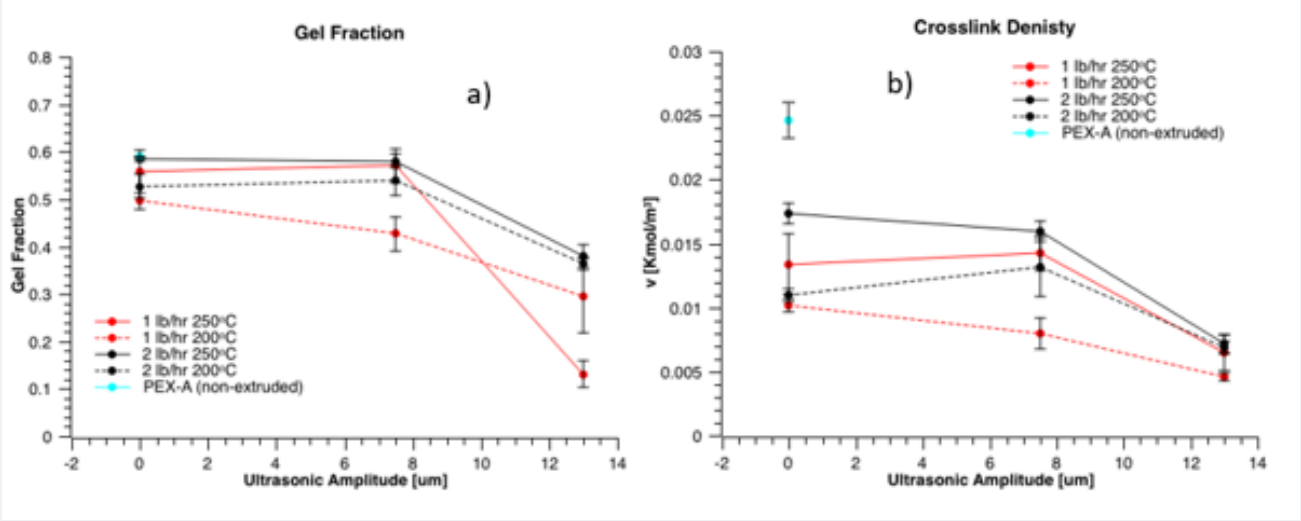

Figure 9: Gel fraction (a) and crosslink density (b) of PEX-A extruded in ultrasonic TSE as a function of ultrasonic amplitude at various processing temperatrues and flow rates. Results for non-extruded PEX-A and non-extruded PE-A are also shown.

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Gel fraction and crosslink density

Figure 9 shows the effect of ultrasonic treatment of PEX-A on its gel fraction and crosslink density. At a processing temperature of 200°C and both flow rates a significant decrease in gel fraction and crosslink density occurs with an increase of the ultrasonic amplitude. This decrease of gel fraction and crosslink density is also observed at higher processing temperature (250°C), but to less extent. Increasing the processing temperature resulted in higher gel fraction and crosslink density when compared to a processing temperature of 200°C. However, at 13 μm and processing temperature of 200°C and 250°C crosslink density values begin to converge. In particular, Figure 9 (b) shows that at 250°C and 1 lb/hr, crosslink density decreased from 0.0134 kmol/m3 for the sample obtained at 0 μm to 0.0065 kmol/m3 for the sample obtained at 13 μm. At 200°C and 1 lb/hr, crosslink density decreased from 0.0102 kmol/m3 at 0 μm to 0.0046 kmol/m3 at 13 μm.

At 250°C and 2 lb/hr, crosslink density decreased from 0.0173 kmol/m3 at 0 μm to 0.0072 kmol/m3 at 13 μm. At 200°C and 2 lb/hr, crosslink density decreased from 0.0110 kmol/m3 at 0 μm to 0.0069 kmol/m3 at 13 μm. This indicates that the ultrasonic treatment in TSE indeed leads to significant decrosslinking of PEX-A. A similar trend is also seen for the gel fraction in Figure 9 (a), showing the reduction of gel fraction as the ultrasonic amplitude increases. Again, this observation further supports the decrosslinking capabilities of the ultrasonic TSE. It should be noted that the tube-grade LDPE of the present study is crosslinked less (crosslink density is 0.025 kmol/m3 and gel fraction is 0.59) than the film-grade LDPE studied earlier (0.084 kmol/m3 and gel fraction of 0.93) [16]. Accordingly, decrosslinked PEX-A exhibits a lower crosslink density and gel fraction in comparison with those of earlier study.

Thermogravimetric analysis

To investigate the decrease in tensile properties of decrosslinked PEX-A processed at 250°C, samples were subjected to TGA testing. Results of their thermal degradation are shown in Table 4 and Figure 10 as a function of the weight loss (a) and the rate of the weight loss (b) versus temperature. The ultrasonically treated PEX-A experiences fairly similar weight loss, whereas the non-extruded PEX-A and PE-A start to decompose strongly at a lower temperature Figure 10. As shown in Table 1, the highest temperature that the melt reached in the ultrasonic TSE were 267°C and 248°C at 2 lb/hr and at an ultrasonic amplitude of 13 μm for processing temperature of 250°C and 200°C, respectively. At 1 lb/hr and 13 μm the melt temperatures were 252°C and 240°C, respectively. The onset of thermal degradation appears to occur around 270°C for all materials tested as seen from the rate of the weight loss curves in Figure 10 (b). This could help explain why at a flow rate of 1 lb/hr tensile properties sometimes outperform those at a flow rate of 2 lb/hr. Also, as seen from Figure 10 (b), the maximum rate of the weight loss has two peaks. The first and second peak occur at a temperature of about 450°C and 500°C. It is also evident that the decrosslinked PEX-A obtained at a processing temperature of 200°C exhibits a higher value of the thermal degradation rate than that obtained at a processing temperature of 250°C. Evidently, at the higher processing temperature some degradation has already taken place during extrusion decreasing the rate of its thermal degradation.

Table 4: Thermal degradation of PEX-A extruded at 13 μm at various processing temperature and flow rate. Results for non-extruded PEX-A and non-extruded PE-A are also shown.

Material	Processing Temperature (°C)	Flowrate (lb/hr)	Ultrasonic Amplitude (μm)	95 wt% (°C)	90 wt% (°C)	85 wt% (°C)	80 wt% (°C)
PEX-A	200	1	13	390 ± 9	439 ± 1	446 ± 1	450 ± 1
		2		405 ± 18	438 ± 2	447 ± 2	451 ± 3
	250	1		405 ± 4	439 ± 3	444 ± 3	447 ± 3
		2		382 ± 1	431 ± 1	440 ± 1	446 ± 0
PE-A (non-extruded)	n/a	n/a	0	389 ± 17	406 ± 18	413 ± 20	418 ± 22
PEX-A (non-extruded)				301 ± 0	324 ± 1	344 ± 0	363 ± 1

Rheological behavior

Dynamic properties of the control sample, virgin PE-A (LDPE), were measured. Accordingly, Figure 11 shows the frequency dependence of the storage modulus (a), loss modulus (b), loss tangent (c), and complex viscosity (d) at 160°C. The storage and loss moduli increase, and the loss tangent and complex viscosity values decrease with an increase in angular frequency. These dependencies show that within the frequency range utilized in rheological tests, the virgin PE-A is in the terminal zone of its dynamic behavior. It is also seen from Figure 11 d that the virgin LDPE exhibits a Newtonian behavior at low angular frequencies, followed by strong non-Newtonian behavior at high frequencies caused by high molecular weight and long chain branching of the polymer.

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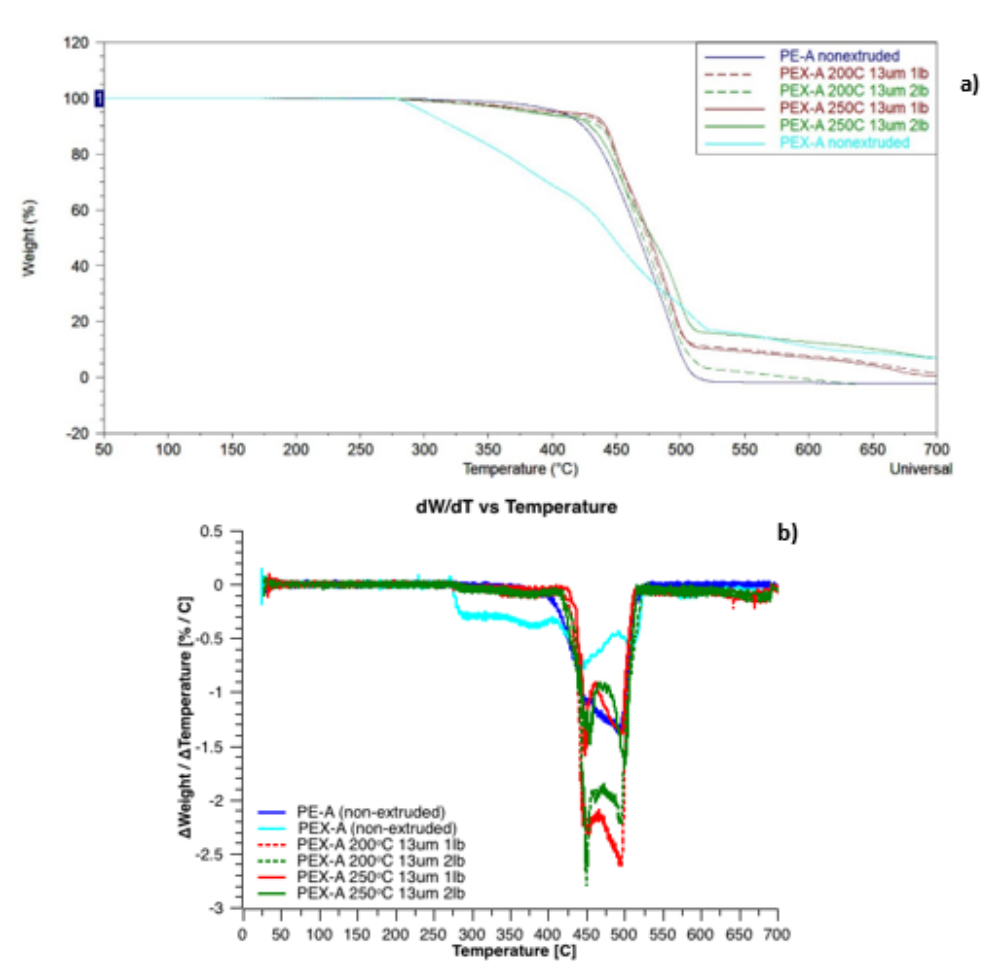

Figure 10: Weight loss (a) and rate of weight loss (b) vs. temperature of PEX-A extruded in ultrasonic TSE at 13 µm, 200°C and 250°C, and 1 lb/hr and 2 lb/hr. Results for non-extruded PEX-A and PE-A are also included.

The frequency dependences of the storage modulus (Figure 12), loss modulus (Figure 13), loss tangent (Figure 14), and complex viscosity (Figure 15) of PEX-A decrosslinked at 200°C at flow rates of 1 lb/hr and 2 lb/hr with ultrasonic treatment at amplitudes of 0 µm, 7.5 µm and 13 µm was measured at 160°C. As seen from Figures 12 and 13, the storage and loss moduli increase with frequency for the decrosslinked PEX-A. Also, the storage and loss moduli of the decrosslinked PEX-A decrease with an increase in the ultrasonic amplitude. This observation is attributed to a rupture of the crosslink network with ultrasonic treatment, as indicated earlier in Table 3 and Figure 9. The slope of the storage and loss moduli vs. frequency also increases with an increase in the ultrasonic amplitude suggesting the increased extent of decrosslinking at higher ultrasonic amplitudes. At lower frequencies the slope is lower suggesting a solid-like behavior of the materials in this frequency range due the presence of a gel. An increase in the flow rate leads to a slight increase in the storage and loss moduli values for ultrasonic amplitudes of 0 µm and 7.5 µm. This increase is also reflected in the higher value of the crosslink density and gel fraction at higher flow rate, as depicted in Figure 9 and Table 3.

As seen from Figure 14, the loss tangent values do not have a very strong dependence on angular frequency. The loss tangent values at both flow rates increase with an increase in the ultrasonic amplitude. This trend in the loss tangent values also suggests that the extent of decosslinking increases with an increase in the ultrasonic amplitude. From Figure 14 it is also observed that the slope of the tan δ vs. angular frequency is lower at lower frequencies and higher at higher frequencies. This low value of the slope is indicative of the gel-like crosslinked component present in the sample being tested. The effect of flow rate on loss tangent values can be studied by comparing Figure 14 (a) and 14 (b). The loss tangent values decrease with an increase in flow rate which confirms that the extent of decrosslinking decreases with an increase in the flow rate. This observation is also supported by the crosslink density and gel fraction values in Figure 9 and Table 3.

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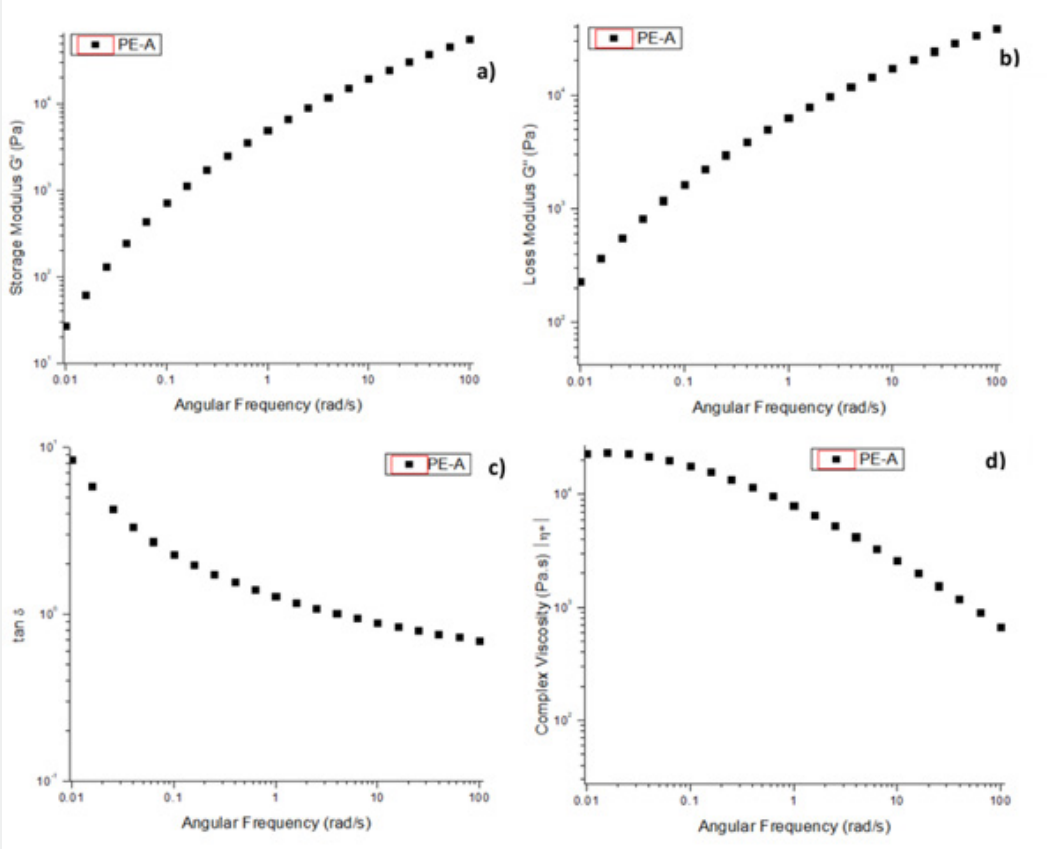

Figure 11: Storage modulus (a), loss modulus (b), tan δ (c), and complex viscosity (d) as a function of angular frequency at 160°C in linear region for virgin PE-A (LDPE).

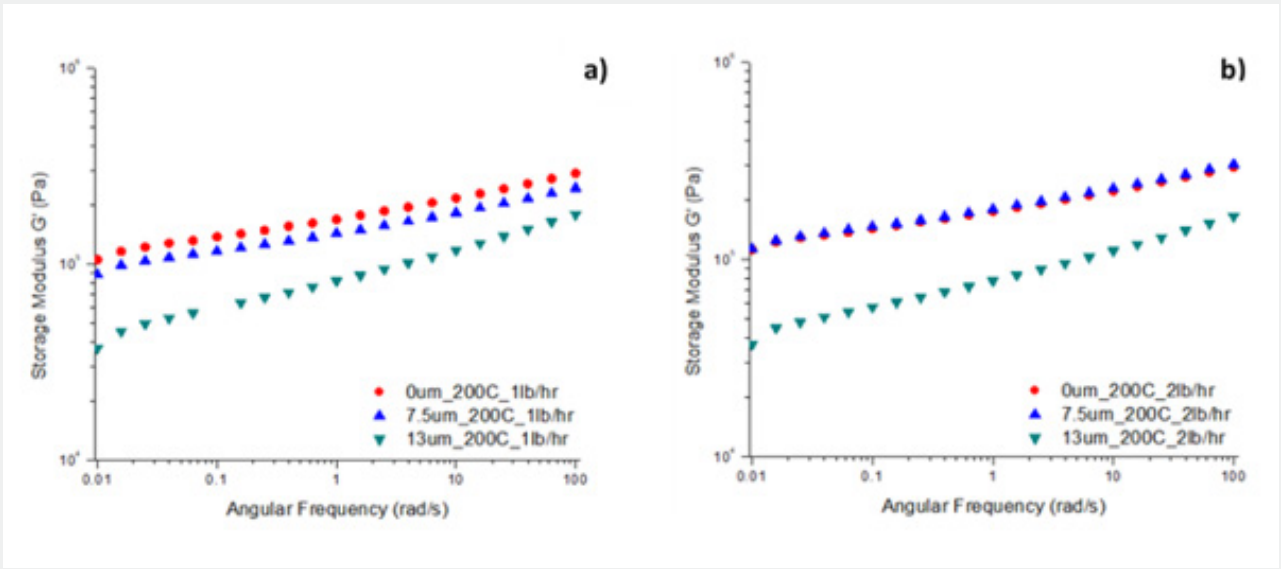

Figure 12: Storage modulus G' vs. angular frequency for decrosslinked PEX-A obtained at flow rates of 1 lb/hr (a)and 2 lb/hr (b) and temperature of 250°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm.

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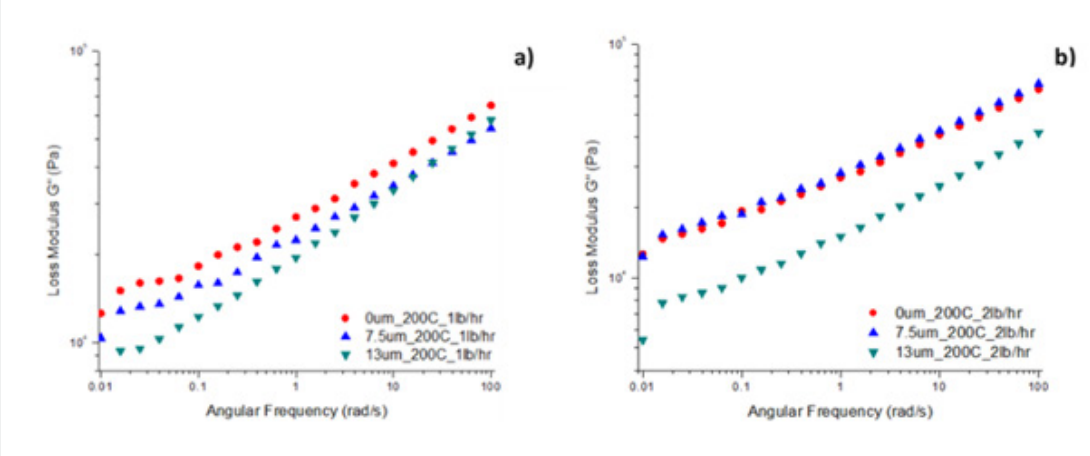

Figure 13: Loss modulus G" vs. angular frequency for decrosslinked PEX-A obtained at flow rates of 1 lb/hr (a) and 2 lb/hr (b) and temperature of 200°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm

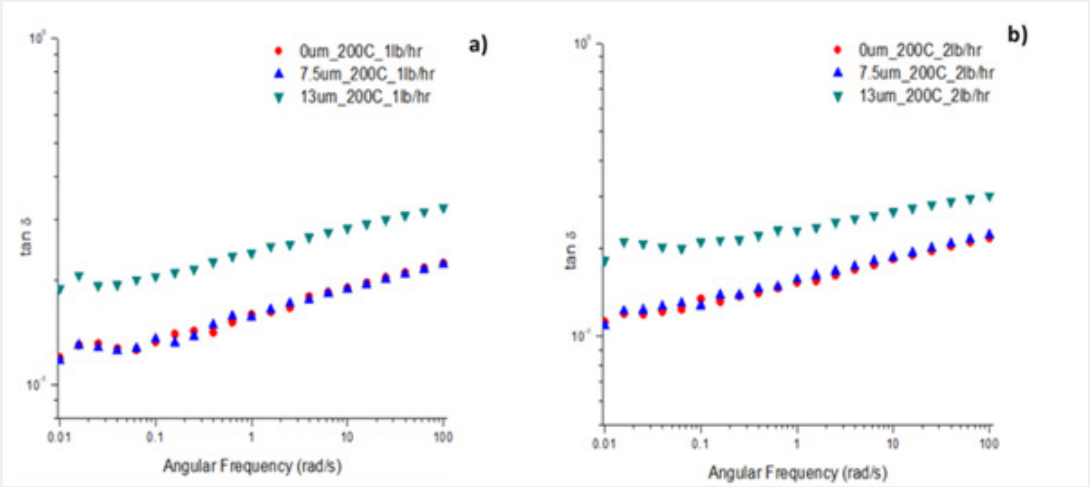

Figure 14: Loss tangent vs. angular frequency in linear region for decrosslinked PEX-A obtained at flow rates of 1 lb/hr (a) and 2 lb/hr (b) at temperature 200°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm.

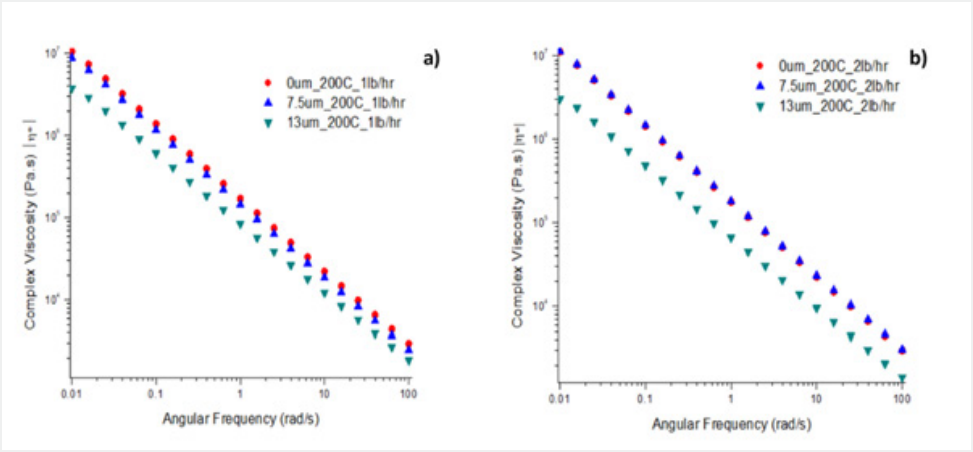

Figure 15: Complex viscosity vs. angular frequency in linear region for decrosslinked PEX-A obtained at flow rates of 1 lb/hr (a) and 2 lb/hr (b) and temperature 200°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm.

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As seen from Figure 15, the complex dynamic viscosity reduces almost linearly with an increase in angular frequency, indicating a power-law behavior of the decrosslinked PEX-A. An increase in the ultrasonic amplitudes results in a decrease in the complex viscosity values over the entire frequency range. This proves that decrosslinking indeed took place due to the ultrasonic treatment and the effect amplified with an increase in the amplitude. The effect of ultrasonic treatment on the complex viscosity is lower in case of ultrasonic amplitude of 0 μm and 7.5 μm but becomes substantial at an ultrasonic amplitude of 13 μm. The lower complex viscosity values in case of lower flow rates can be due to the higher degree of decrosslinking, which is also supported by lower value of measured crosslink density and gel fraction. obtained at an amplitude of 13 μm. In turn, the latter results move closer to those of the virgin PE-A indicating that with an increase of ultrasonic amplitude decrosslinked PEX-A becomes more decrosslinked and its molecular structure becomes more closer of that of the virgin PE-A.

The frequency dependenies of the storage modulus (Figure 17), loss modulus (Figure 18), loss tangent (Figure 19), and complex viscosity (Figure 20) of the crosslinked PEX-A and decrosslinked PEX-A obtained at a processing temperature of 250°C and flow rates of 1 lb/hr (a) and 2 lb/hr (b) with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm were measured at 160°C. Figure 17 and Figure 18 show that the storage and loss moduli increase with frequency for the crosslinked PEX-A and decrosslinked PEX-A. The storage and loss moduli of the decrosslinked PEX-A decreases with an increase in the ultrasonic amplitude. This behavior suggests that the ultrasonic treatment leads to the rupture of the crosslink network, as indicated earlier by measurements of gel fraction and crosslink density depicted in Figure 9 and Table 3. The values of storage and loss moduli are seen to be lower for 1 lb/hr than those for 2 lb/hr. This observation is consitent with lower crosslink density values for samples extruded at the lower flow rate. Also, it can be seen from Figure 17 and Figure 18 that the slope of the storage and loss moduli vs. angular frequency increases with an increase in the ultrasonic amplitude. This is also indicative of the increased extent of decrosslinking with an increase in ultrasonic amplitude. From Figures 17 and 18, it can also be observed that the slope of the graph is lower at lower frequencies, which can be attributed to the presence of a gel in the sample. The slope of the graphs for samples decrosslinked at 13 μm is significantly higher than that for 0 μm, and 7.5 μm for both flow rates which confirms the highest extent of decrosslinking in former samples. This conclusion is also supported by the low values of crosslink density as shown in Table 3.

As seen from Figure 19, the loss tangent values have a very strong dependence on the angular frequency for samples decrosslinked at 13 μm at both the flow rates. However, this dependence is weak for ultrasonic amplitudes of 0 μm and 7.5 um. This confirms that among various ultrasonic amplitudes the extent of decrosslinking is highest at an ultrasonic amplitude 13 μm. At flow rates of 1 lb/hr and 2 lb/hr the loss tangent values increase with an increase in ultrasonic amplitude. This trend is due to a decrease in the crosslink density with increasing ultrasonic amplitudes. From Figure 14 it is also observed that the slope of the tan δ vs. angular frequency is lower at lower frequencies and higher at higher frequencies. This small value of the slope is indicative of the gel-like crosslinked component contained in the sample being tested. The loss tangent values also decrease with an increase in flow rate which confirms that the extent of decrosslinking decreases with an increase in the flow rate.

Figure 20 shows the complex viscosity vs. angular frequency for crosslinked PEX-A and decrosslinked PEX-A obtained at flow rates 1 lb/hr (a) and 2 lb/hr (b) at a processing temperature of 250°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm. It is seen from Figure 15, the complex dynamic viscosity reduces almost linearly with an increase in angular frequency, indicating a power-law behavior of the crosslinked PEX-A and decrosslinked PEX-A. The complex viscosity values decreased with an increase in the ultrasonic amplitude indicating a higher effect of decrosslinking at higher ultrasonic amplitudes. The complex viscosity values are lower at lower flow rates which prove that the effect of decrosslinking was higher at the lower flow rate than that at the higher flow rate. This trend is consistent with the crosslink density values in Table 3, as well as the trend observed in storage modulus values. Comparison of dynamic properties of the crosslinked PEX-A and decrosslinked PEX-A samples with those of the virgin PE-A clearly indicates the absence of terminal region in crosslinked and decrosslinked samples.

Figure 21 shows the storage modulus as a function of the loss modulus (Cole-Cole plots) for all the decrosslinked PEX-A along with that of crosslinked PEX-A and virgin PE-A. It is seen that results for PEX-A decrosslinked at amplitudes of 0 μm and 7.5 μm at both the flow rates lie well above the results obtained at an amplitude of 13 μm. The results for PEX-A decrosslinked at 13 μm at flow rates of 1 lb/hr and 2 lb/hr move closer to those of the virgin PE-A indicating a molecular structure of these samples is being closer to that of the virgin PE-A due to higher extent of decrosslinking. However, the presence of a gel in these samples is the main reason for the deviation of their Cole-Cole plot from that of the virgin PE-A.

The frequency dependence of the storage modulus (a), loss modulus (b), loss tangent (tan δ) (c), and complex viscosity (d) of sol fraction extracted from the crosslinked PEX-A and decrosslinked samples extruded at 200°C and 250°C at flow rates 1 lb/hr and 2 lb/hr at ultrasonic amplitude of 13 μm is presented in Figure 22. The storage moduli values increase with an increase in the angular frequency, as seen in Figure 22 (a). The values of the storage moduli of the sol samples are significantly lower than those of the decrosslinked samples due to the absence of a gel that was present in these samples. However, these values at low frequencies are still drastically higher than those for virgin PE-A which is possibly due to the presence of the fraction of high molecular weight branched structure generated by decrosslinking. The slope of the storage moduli vs. angular frequencies is lower at lower values of frequencies.

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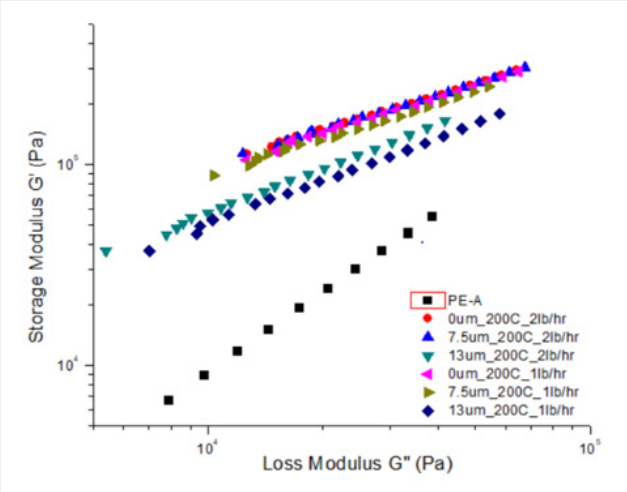

Figure 16: Storage modulus as a function of the loss modulus (Cole-Cole plots) for PE-A, decrosslinked PEX-A obtained at flow rates 1 lb/hr (a) and 2 lb/hr (b) and temperature 200°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm. Cole-Cole plot for the virgin PE-A is also given.

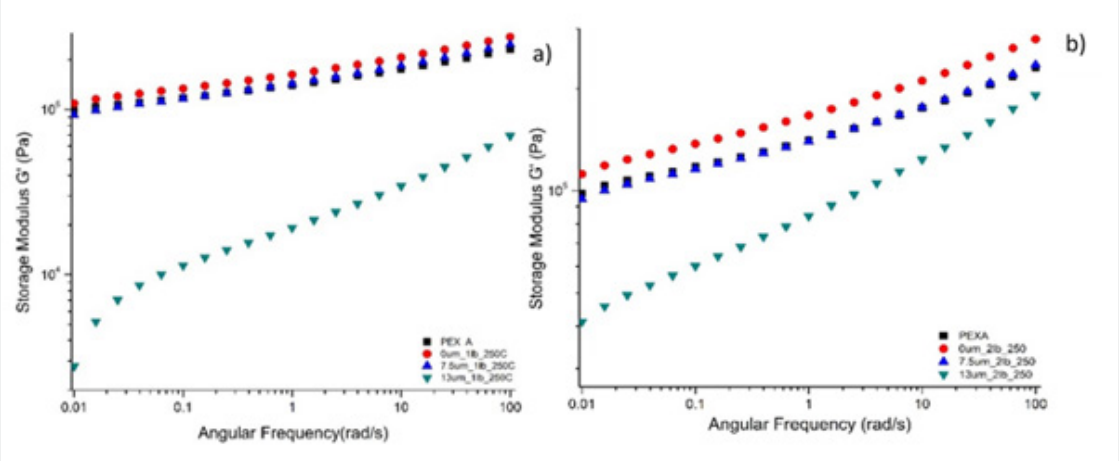

Figure 17: Storage modulus G' vs. angular frequency for crosslinked PEX-A and decrosslinked PEX-A obtained at processing temperature of 250°C for flow rates of 1 lb/hr (a) and 2 lb/hr (b) and with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm.

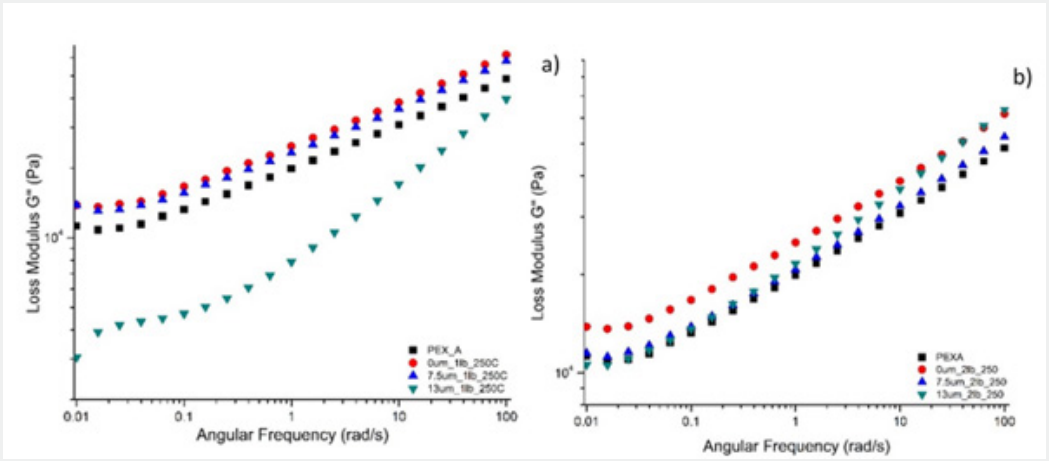

Figure 18: Loss modulus G" vs. angular frequency for crosslinked PEX-A and decrosslinked PEX-A obtained at a processing temperature of 250°C and flow rates of 1 lb/hr (a) and 2 lb/hr (b) and temperature of with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm.

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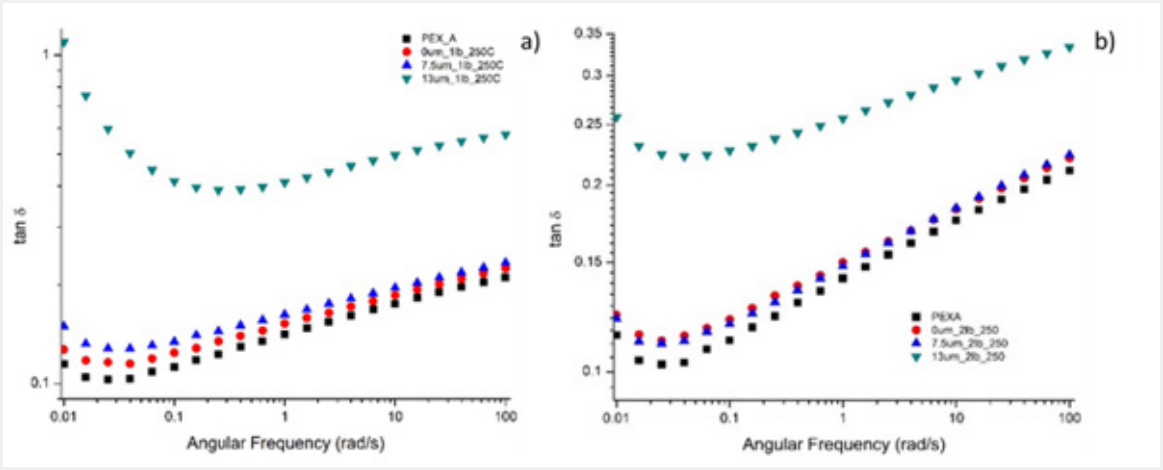

Figure 19: Loss tangent vs. angular frequency for crosslinked PEX-A and decrosslinked PEX-A obtained at flow rates 1 lb/hr (a) and 2 lb/hr (b) at a processing temperature of 250°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm.

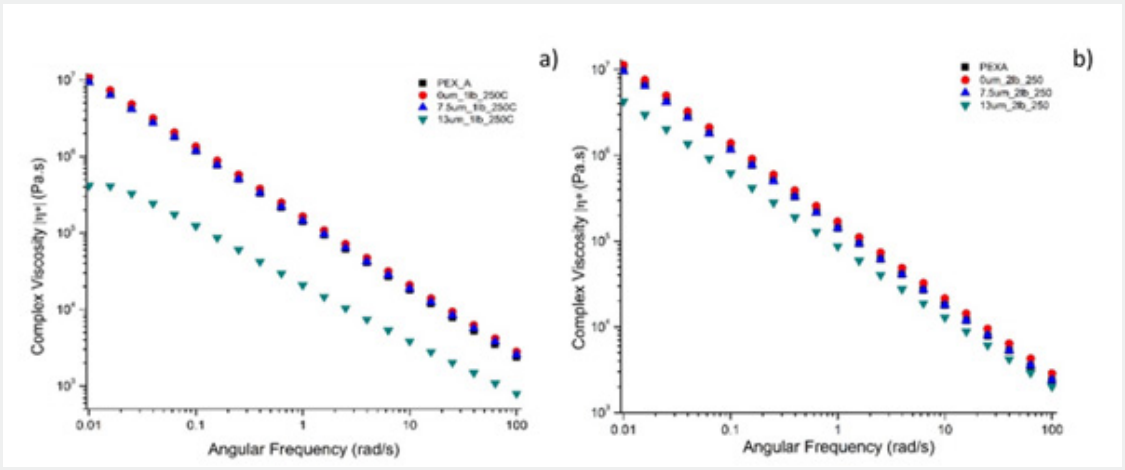

Figure 20: Complex viscosity vs. angular frequency for crosslinked PEX-A and decrosslinked PEX-A obtained at flow rates 1 lb/hr (a) and 2 lb/hr (b) at a processing temperature of 250°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm.

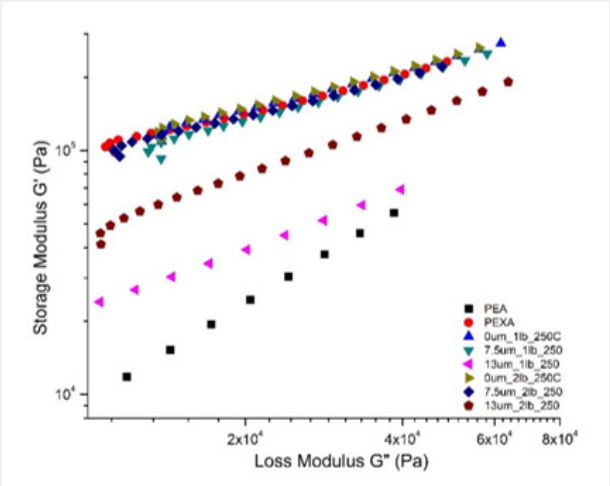

Figure 21: Storage modulus as a function of the loss modulus (Cole-Cole plots) for crosslinked PEX-A and decrosslinked PEX-A obtained at flow rates 1 lb/hr (a) and 2 lb/hr (b) and temperature 250°C with ultrasonic treatment at amplitudes of 0 μm, 7.5 μm and 13 μm. Cole-Cole plot for the virgin PE-A is also given.

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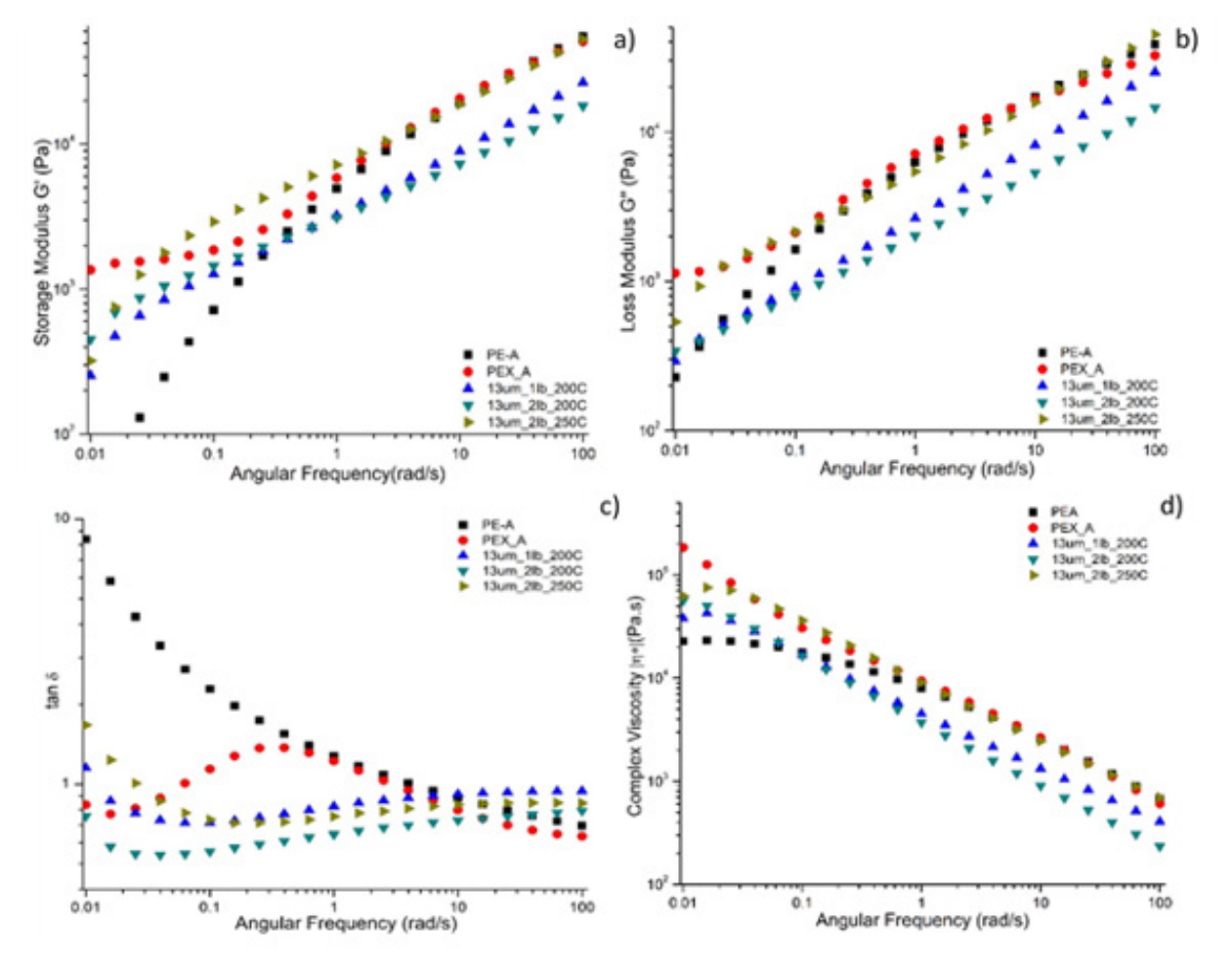

Figures 22: Storage modulus G' (a), loss modulus G" (b), loss tangent (tan δ) (c), and complex viscosity | *| (d) vs. angular frequency for the virgin PE-A and the sol extracted from PEX-A and decrosslinked PEX-A at 200°C and 250°C with an ultrasonic amplitude of 13 μm and flow rates of 1 lb/hr and 2 lb/hr.

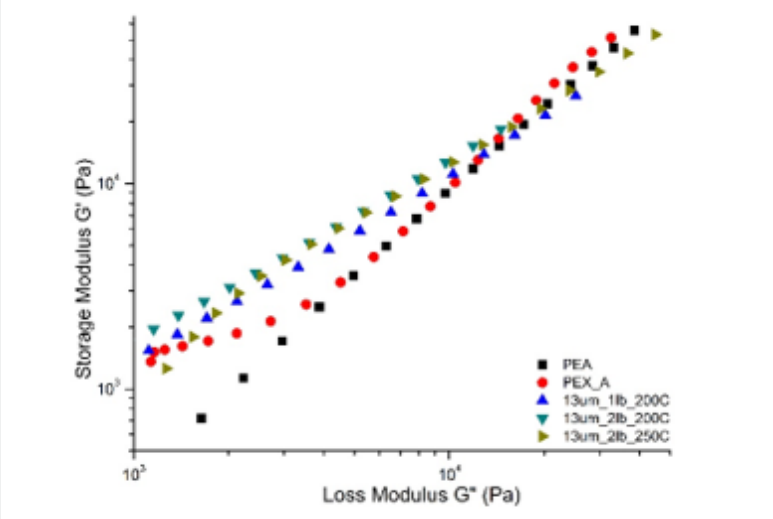

Figure 23: Storage modulus as a function of the loss modulus (Cole-Cole plots) of PE=A and the sol extracted from PEX-A and decrosslinked PEX-A obtained at flow rates 1 lb/hr and 2 lb/hr, temperature of 200°C and 250°C with ultrasonic treatment at amplitudes of 13 μm.

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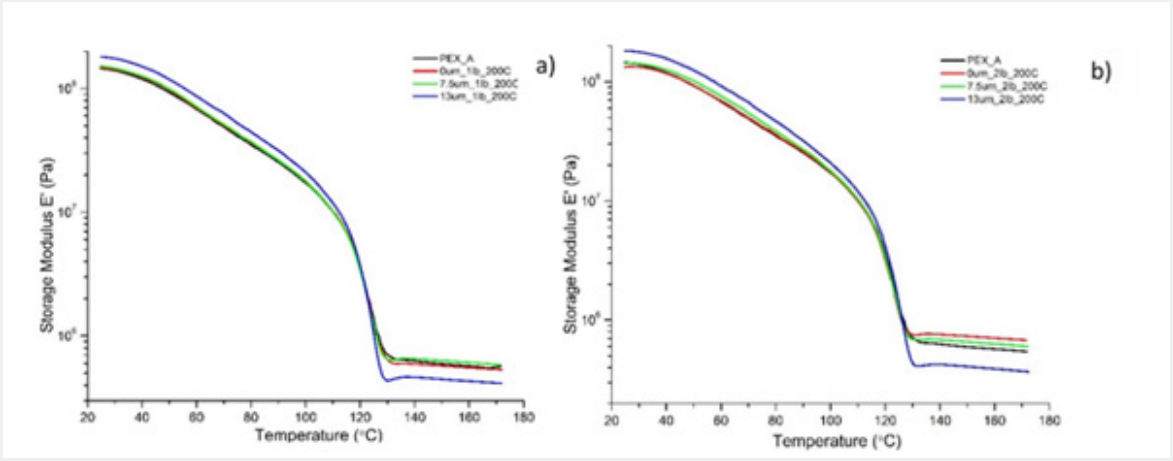

Figure 24: Storage modulus, E', as a function of temperature for PEX-A and decrosslinked PEX-A obtained at a processing temperature of 200°C with ultrasonic treatment of amplitudes 0 μm,7.5 μm, and 13 μm at flow rates of a) 1 lb/hr and b) 2 lb/hr.

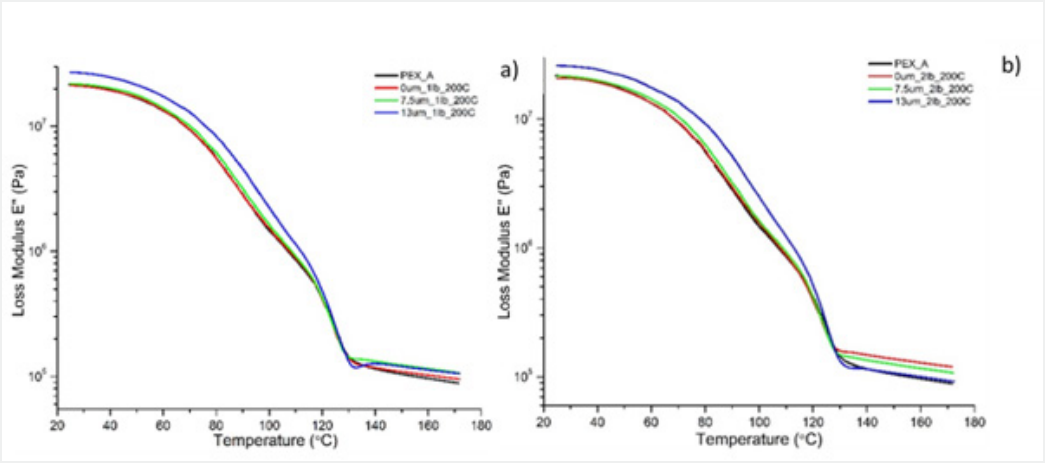

Figure 25: Loss modulus, E", as a function of temperature for PEX-A and decrosslinked PEX-A obtained at a processing temperature of 200°C with ultrasonic treatment of amplitudes 0 μm,7.5 μm, and 13 μm at flow rates of a) 1 lb/hr and b) 2 lb/hr.

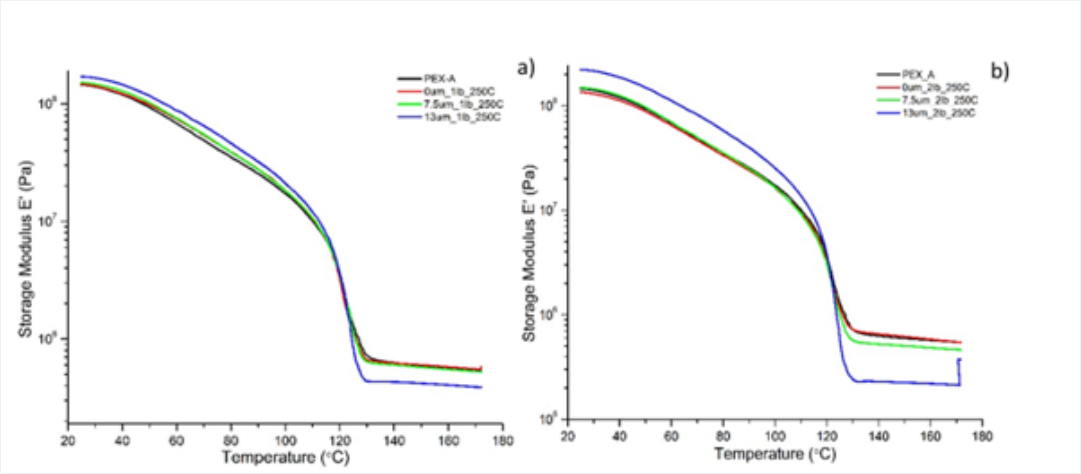

Figure 26: Storage modulus E', as a function of temperature for PEX-A and decrosslinked PEX-A obtained at a processing temperature of 200°C with ultrasonic amplitude of 0 μm,7.5 μm, and 13 μm at flow rates of 1 lb/hr and 2 lb/hr.

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It can also be seen from Figure 22 (a) that the storage modulus curve for PEX-A sol sample has lower slope values at lower frequencies, the cause for this change of slope is not understood. The loss modulus value increases with the angular frequency as shown in Figure 22 (b). It can be observed from Figure 22 (c) that the tan δ of decrosslinked sol samples has a weaker dependence on angular frequency, but the dependence of tan δ of PEX-A sol on angular frequency is comparatively stronger. The complex viscosity (Figure 22 (d)) decreases almost linearly for the PEX-A sol and decrosslinked sol samples suggesting a power-law behavior. Figure 23 shows the storage modulus vs. loss modulus curves for sol samples of PEX-A and decrosslinked PEX-A samples. The Cole-Cole plot for virgin PE-A is also provided. It can be seen from Figure 23 that almost all the samples coincide with PE-A at higher frequencies, with PEX-A sol curve lying closest to the PE-A curve. This near resemblance can be attributed to the chains which were not cured in the first place, thus giving virgin PE-A like behavior.

DMA analysis

Figures 24 and 25 show, respectively, the temperature dependence of the storage modulus, E', and loss modulus, E", for PEX-A and decrosslinked PEX-A extruded at 200°C at ultrasonic amplitudes of 0 μm, 7.5 μm, and 13 μm and flow rates of 1 lb/hr (a) and 2 lb/hr (b), obtained using DMA. As can be seen from this figure, the storage and loss moduli values increase with an increasing ultrasonic amplitude for both the flow rates at low temperatures. At high temperatures (~130°C), the sample is above the melting point and therefore becomes unstable, such that the trend in the data becomes unreliable. On comparison of Figures 24 (a) and 24 (b) it can be seen that the effect of flow rates on E' is insignificant.

Figures 26 and 27 show, respectively, the temperature dependence of the storage modulus, E', and loss modulus, E". for PEX-A and decrosslinked PEX-A extruded at 250°C at ultrasonic amplitudes of 0 μm, 7.5 μm, and 13 μm for flow rates of 1 lb/hr (a) and 2 lb/hr (b). It can be seen that irrespective of the flow rates, the storage and loss moduli values increase with an increase in the ultrasonic amplitude. The crosslinked PEX-A sample has lowest value of the storage modulus compared to the decrosslinked samples. Figure 26 compares the dependence of the storage modulus and loss modulus of decrosslinked samples extruded at 200°C (a), and 250°C (b) as a function of ultrasonic amplitude for both flow rates at 25°C. The figures display an increase in the storage and loss moduli values with increasing ultrasonic amplitudes for both the flow rates at both the processing temperatures. The increase in storage moduli values with increasing ultrasonic amplitude is in coherence with the increasing modulus at 1% strain value with increasing ultrasonic amplitude, as previously shown in Figure 8 (c) and Table 4. Figure 28 also shows that the dependence of storage and loss moduli values on flow rate is insignificant.

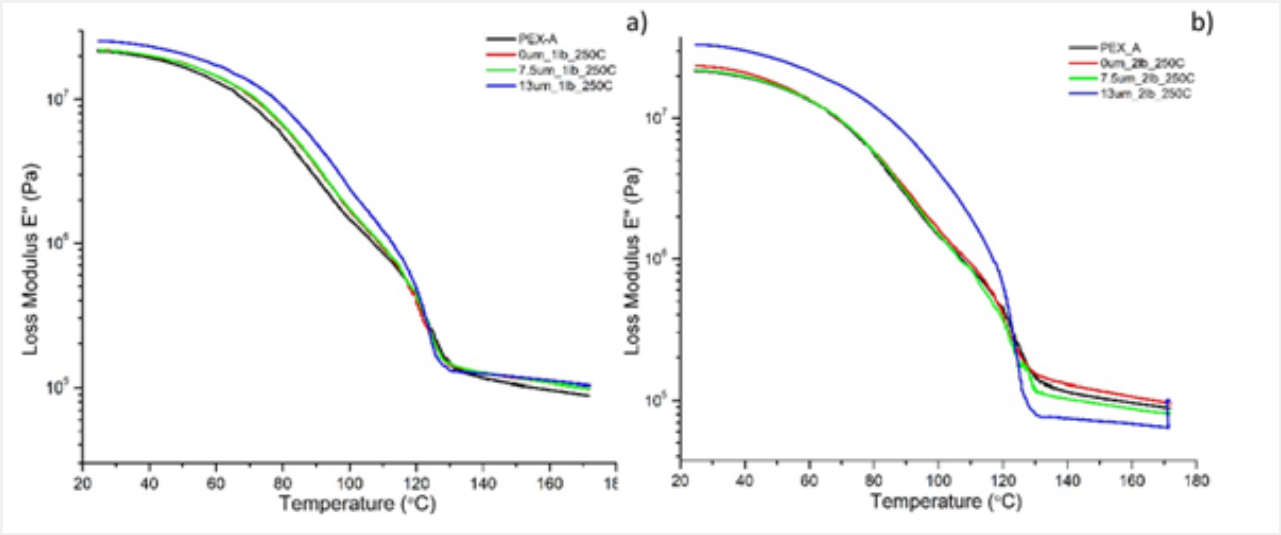

Figure 27: Loss modulus, E" as a function of temperature for PEX-A and decrosslinked PEX-A obtained at a processing temperature of 200°C with ultrasonic amplitude of 0 μm,7.5 μm, and 13 μm at flow rates of 1 lb/hr and 2 lb/hr.

The tan δ values are plotted as a function of temperature (Figure 29) for PEX-A and decrosslinked PEX-A obtained at a processing temperature of 200°C at ultrasonic amplitude 0 μm,7.5 μm and 13 μm for flow rates of 1 lb/hr and 2 lb/hr. Figure 29 shows that the tan δ values do not have a strong dependence on flow rates at the same processing temperature. The temperature corresponding to the maximum of tan δ value can be treated as the softening temperature, whereas the temperature corresponding to the minimum of tan δ value can be considered as the melting point. Similarly, the tan δ values for PEX-A and decrosslinked

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PEX-A extruded at 250°C at ultrasonic amplitudes of 0 μm,7.5 μm and 13 μm, and flow rates of 1 lb/hr (a) and 2 lb/hr (b) are plotted as a function of temperature in Figure 30. The effect of flow rates on tan δ values for PEX-A and decrosslinked PEX-A extruded at 250°C is insignificant. The spiking of the tan δ curves in Figures 29 and 30 at temperatures near 130°C can be attributed to the samples being unstable beyond this temperature, which makes the data beyond this point unreliable.

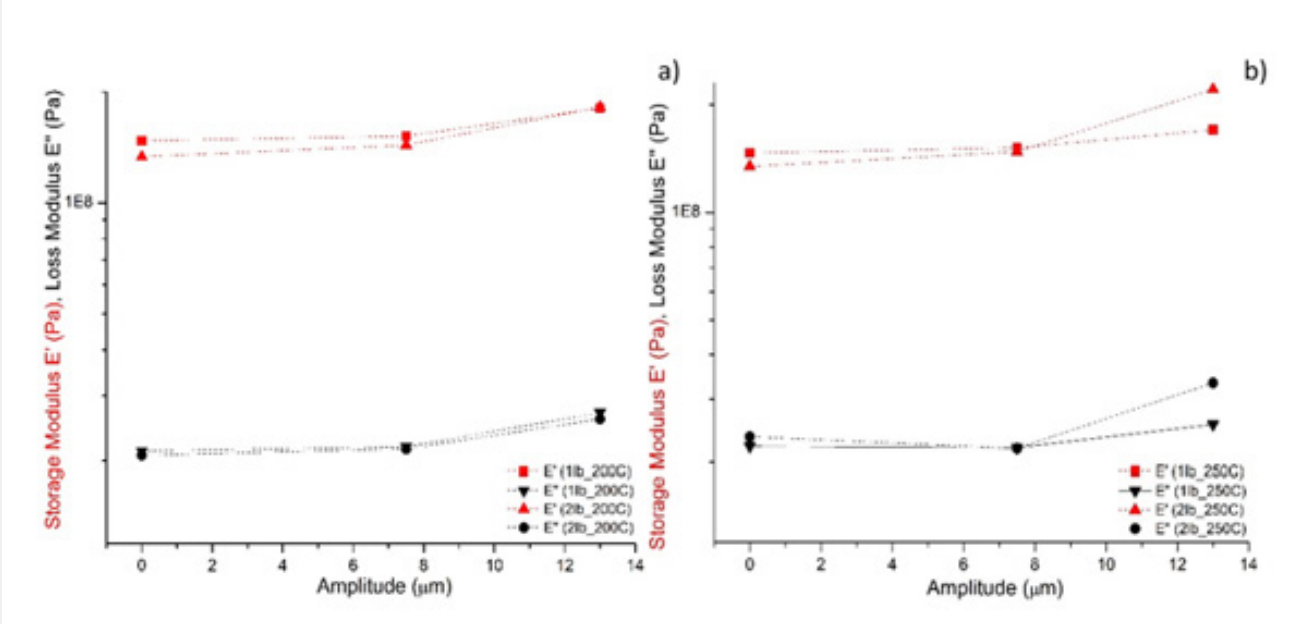

Figure 28: Storage modulus and loss modulus as a function of ultrasonic amplitude for decrosslinked PEX-A extruded at 200°C (a) and 250°C (b) for flow rates of 1 lb/hr and 2 lb/hr.

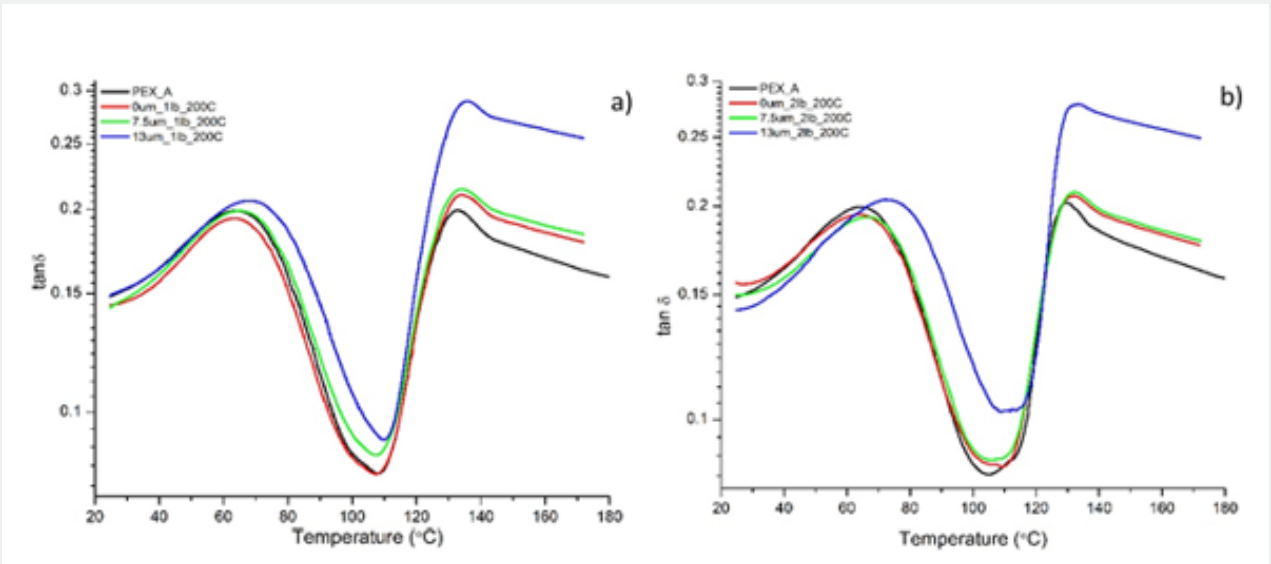

Figure 29: Tan δ as a function of temperature for PEX-A and decrosslinked PEX-A obtained at a processing temperature of 200°C with ultrasonic amplitude of 0 μm,7.5 μm, and 13 μm for flow rates of 1 lb/hr (a) and 2 lb/hr (b).

Figure 31 (a) presents the minimum and maximum values of tan δ of decrosslinked PEX-A for the processing temperatures of 200°C and 250°C and flow rates of 1 lb/hr and 2 lb/hr as a function of the ultrasonic amplitude. It can be seen that this minimum or maximum tan δ value increases with an increase in the ultrasonic amplitude irrespective of the processing temperature or the flow rates. It can also be seen from Figure 31 (b) that the temperatures corresponding to minimum and maximum of tan δ values increase with an increase in the ultrasonic amplitude.

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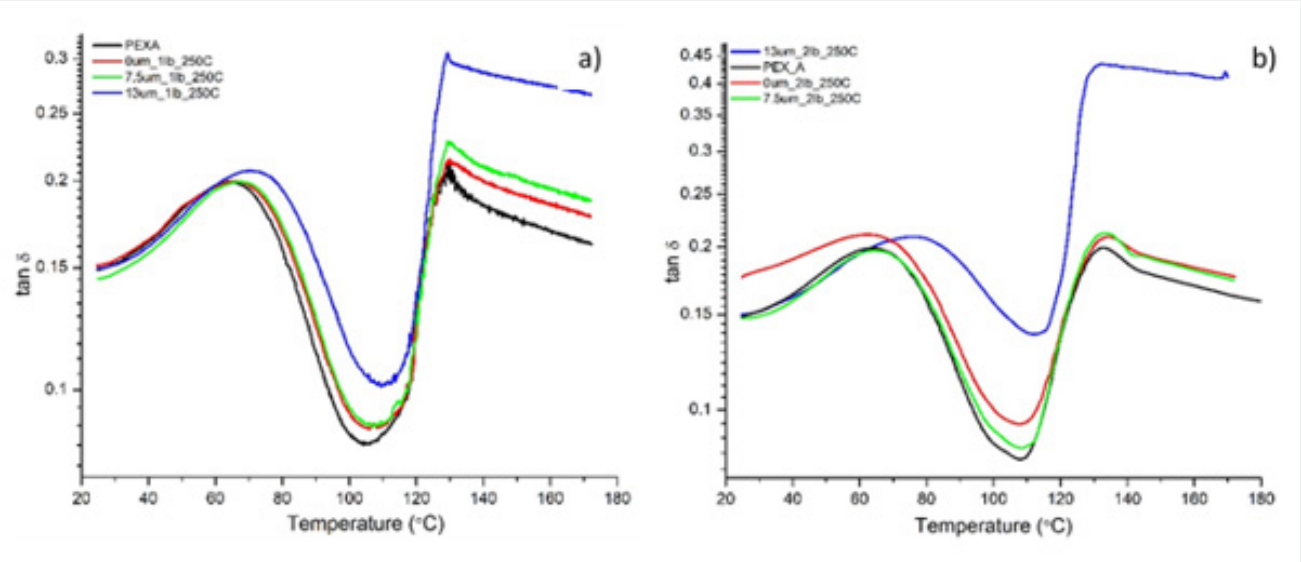

Figure 30: Tan δ as a function of temperature for PEX-A and decrosslinked PEX-A obtained at a processing temperature of 250°C with ultrasonic amplitude of 0 μm,7.5 μm, and 13 μm at flow rates of 1 lb/hr (a) and 2 lb/hr (b).

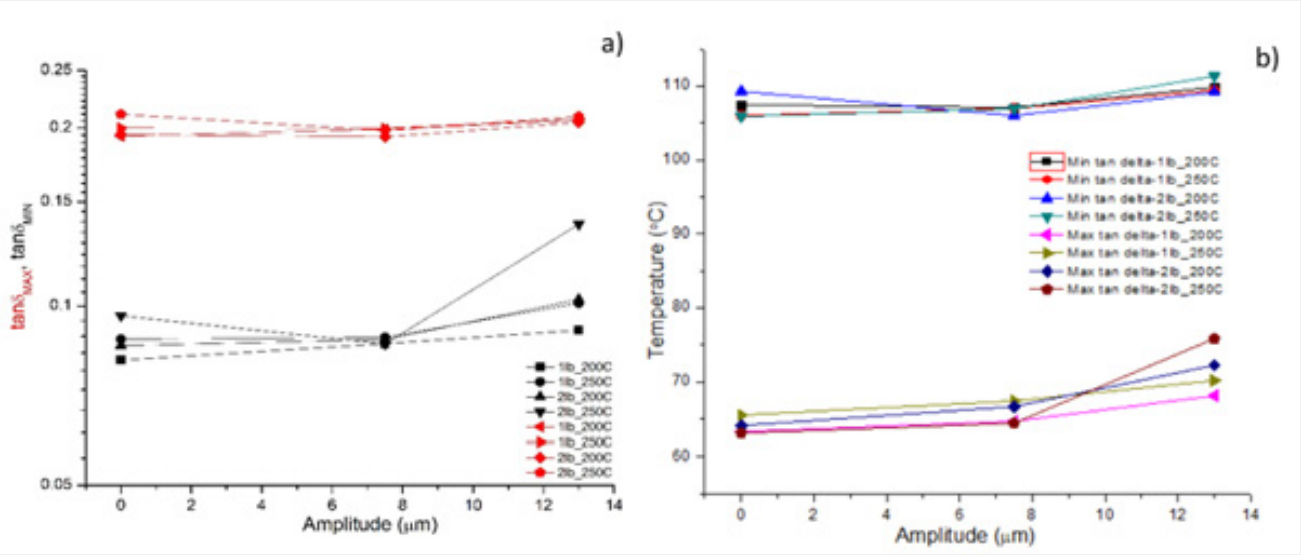

Figure 31: Minimum and maximum tan δ values as a function of ultrasonic amplitude (a) and temperatures corresponding to minimum and maximum tan δ values as a function of ultrasonic amplitude (b) for processing temperatures of 200°C and 250°C and flow rates of 1 lb/hr and 2 lb/hr.

Morphological analysis

SEM images were obtained for PE-A (non-extruded), PEX-A (non-extruded), and PEX-A extruded at 200°C and 250°C with flow rates of 1 and 2 lb/hr and ultrasonic amplitudes of 0, 7.5, and 13 μm (Figure 32). The images shown are for samples that were etched for 60 minutes to expose the gel under the surface. Figure 32 (a) shows PE-A exhibits a smooth surface, indicative of the absence of gel. Figure 32 (b) shows PEX-A (non-extruded) exhibits a large amount of gel. At 0 and 7.5 μm, 200°C, 1 lb/hr flow rate (Figure 32 (c) and e)) shows less gel than 2 lb/hr (Figure 32 (d & f)). However, at 13 μm, 200°C both flow rates (Figure 32 (g and h)) have a similar surface which is closer to that of the virgin PE-A than to PEX-A (non-extruded). Similar observations of morphology were made for samples extruded at processing temperature of 250°C.

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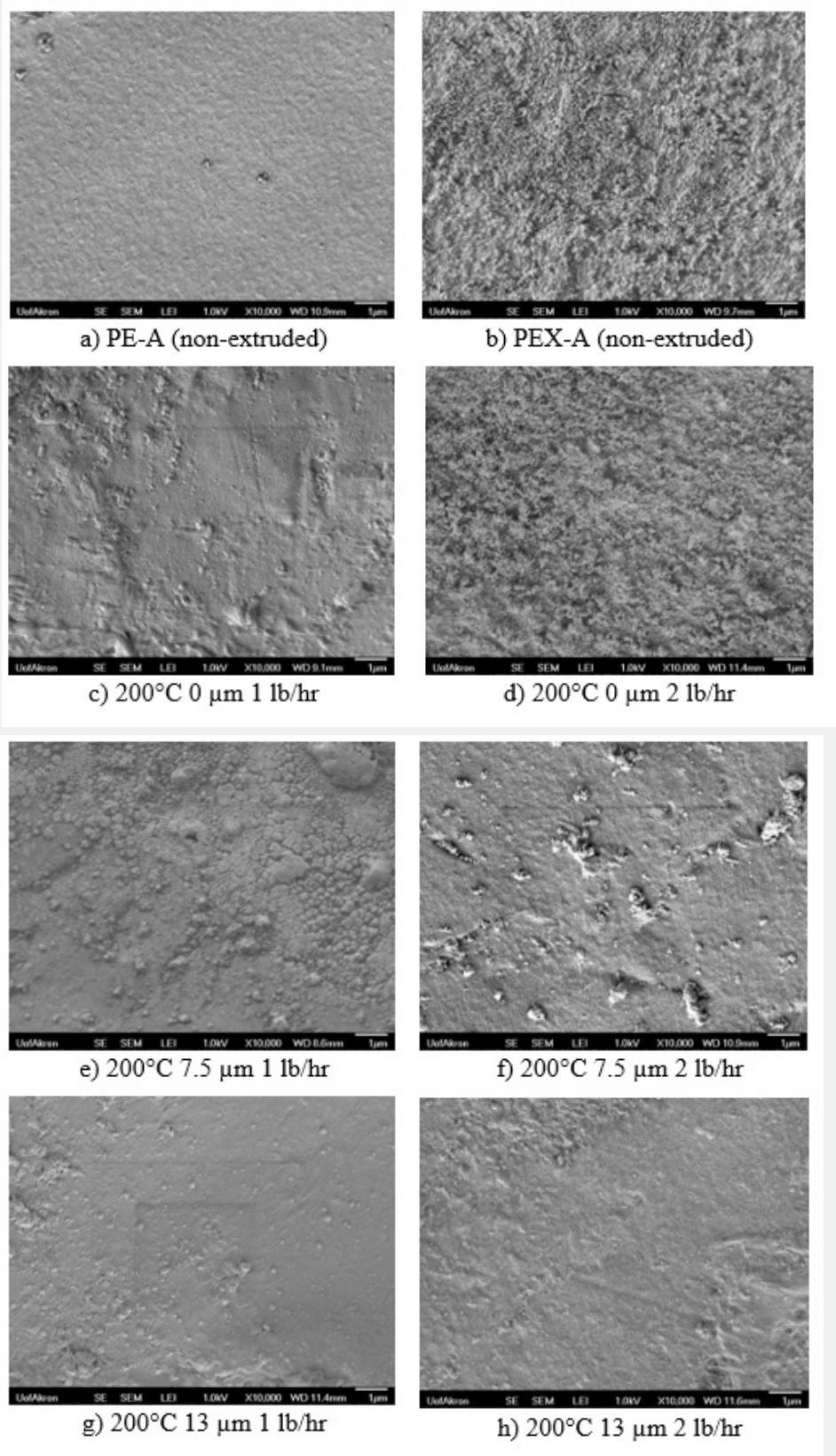

Figure 32: SEM images of PE-A, PEX-A (non-extruded), and PEX-A as a function of ultrasonic amplitude at various flow rates and processing temperatures.

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Conclusion

The ultrasound-aided extrusion of PEX-A in TSE at processing temperatures of 200°C and 250°C, flow rates of 1 lb/hr and 2 lb/hr, and ultrasonic amplitudes of 0 μm, 7.5 μm, and 13 μm was carried out to study the effect of processing temperature, flow rate and ultrasound power on the stress-strain behavior, rheological behavior, structure, morphology and thermal properties of decrosslinked PEX-A. Unlike the samples processed at 200°C, at 250°C the flow rate was found to affect the stress-strain behavior of the ultrasonically decrosslinked PEX-A, namely a flow rate of 1 lb/hr outperforms a flow rate of 2 lb/hr. Similar to the samples processed at 200°C, at 250°C the general trend suggests that an increase in ultrasonic amplitude leads to an increase in tensile properties. Tensile properties tended to decrease when the processing temperature increased from 200°C to 250°C. This decrease was thought to be due to thermal degradation. TGA revealed the onset of thermal degradation near 250°C for 13 μm treated PEX-A extruded at both 200°C and 250°C processing temperatures. This result, in conjunction with the TSE temperature profiles, suggests that PEX-A melt should not exceed 250°C. The thermal properties were slightly affected by the flow rate, but strongly affected by ultrasonic amplitude. The decrosslinked PEX-A extruded at 250°C with a flow rate of 1 lb/hr and 2 lb/hr and an ultrasonic amplitude of 13 μm exhibited, respectively, a modulus of 110 MPa and 89 MPa, yield stress of 10.7 MPa and 7.3 MPa, stress at break of 9.4 MPa and 11.7 MPa and strain at break of 0.46 and 1.88. The modulus, yield strain, and strain at break values were much lower when processed at 250°C.

Melting point was not affected by the increase in processing temperature. However, crystallinity decreased significantly. At 250°C and a flow rate of 1 lb/hr, the melting point, Tm, increased from 108.0°C at 0 μm to 110.7°C at 13 μm. At a flow rate of 2 lb/hr, Tm increased from 107.1°C to 109.4°C. At 250°C, crystallinity increased from 30% to 34% (1 lb/hr) and from 30% to 31% (2 lb/hr). These values are upwards of 6% lower than those measured for PEX-A processed at 200°C. At 250°C and 1 lb/hr, crosslink density decreased from 0.0134 kmol/m3 for the sample obtained at 0 μm to 0.0065 kmol/m3 for the sample obtained at 13 μm. At 200°C and 1 lb/hr, crosslink density decreased from 0.0102 kmol/m3 (0 μm) to 0.0046 kmol/m3 (13 μm). At 250°C and 2 lb/hr, crosslink density decreased from 0.0173 kmol/m3 (0 μm) to 0.0072 kmol/m3 (13 μm). At 200°C and 2 lb/hr, crosslink density decreased from 0.0110 kmol/m3 (0 μm) to 0.0069 kmol/m3 (13 μm). This indicates that the ultrasonic treatment in TSE indeed leads to significant decrosslinking of PEX-A. SEM images futher supports that ultrasonic treatment reduces the gel fraction of PEX-A, which is in agreement with gel fraction measurements.

The dynamic properties of decrosslinked PEX-A obtained at processing temperatures of 200°C and 250°C at different ultrasonic amplitudes and flow rates and non-extruded PE-A were measured. The extent of decrosslinking increases with an increase in the ultrasonic amplitude, which is visible from the reduced values of the storage modulus and complex viscosity. The loss tangent values increase with an increase in the ultrasonic amplitude which proves that the crosslink network was ruptured. The crosslink density reduction is lower for samples extruded at higher flow rates. At 200°C, for 0 μm and 7.5 μm, the storage modulus and complex viscosity values increase with an increase in flow rate, but the loss tangent value decreases. At 250°C, for 0 μm, 7.5 μm, and 13 μm, the storage modulus and complex viscosity values increase with an increase in flow rate, but the loss tangent value decreases. The slope of the dependencies of the storage modulus and loss tangent on angular frequency is lower at lower frequencies which can be attributed to the solid-gel like behavior at lower frequency values. For the non-extruded PE-A, the complex viscosity exhibits a Newtonian behavior at low frequencies followed by non-Newtonian behavior with an increase in frequency. The high molecular weight and long chain branching is responsible for such a behavior of PE-A. Cole-Cole plots revealed that at ultrasonic amplitude of 13 μm the decrosslinked PEX-A becomes more decrosslinked with its molecular structure becoming closer of that of the virgin PE-A. The dynamic properties of the sol fraction of the crosslinked PEX-A and decrosslinked PEX-A samples were also measured. The storage moduli, and complex viscosity values of the sol samples was lower than the original samples which can be attributed to the absence of gel fraction in the sol samples. Cole-Cole plots for the sol samples and PE-A revealed that the samples showed resemblance with PE-A samples at higher frequencies. The resemblance of non-extruded PEX-A sol was however stronger and could possibly be due to the chains that were never crosslinked in the first place.

The temperature dependence of storage modulus, loss modulus, and tan δ for PEX-A and decrosslinked samples extruded at 200°C and 250°C, at ultrasonic amplitudes of 0 μm, 7.5 μm, and 13 μm for flow rates of 1 lb/hr and 2 lb/hr was measured. The effect of flow rates on storage modulus, loss modulus and tan δ was insignificant. The storage and loss moduli increased with an increase in ultrasonic amplitude at 25°C. The increasing trend of storage modulus was consistent with the increasing value of Young's modulus (at 1% strain) obtained from the tensile tests. The minimum and maximum values of tan δ and the corresponding temperatures also increased with an increase in the ultrasonic amplitude. The temperature corresponding to minimum value of tan δ indicates the melting temperature which also increases with ultrasonic amplitude as seen from DSC traces.

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