CHAPTER 5. RHEOLOGY OF MATRIX, AND FILLED CONDUCTING COMPOSITE MATERIALS

5-1 Introduction to Chapter

The concept behind this thesis was that conducting fillers may be added to a thermoplastic polymer before extrusion to create fibres; these fibres would then be incorporated in to a matrix composite to enhance the surface conductivity. An essential process is therefore to be able to extrude the matrix and its filled counter part. In this chapter, the rheology of the PES polymer system is examined in some detail as a precursor to attempting to produce fibres. It is important to carry out rheological measurements on polymer systems in order to determine the best processing conditions which will be utilised in an industrial environment. Specifically, optimum conditions for the spinning of good quality fibres will be investigated.

5-2 Materials

The commercial PES-based co-polymer and Radel A-100 were the main polymers utilised throughout these studies. A discussion of the synthesis and structures of these materials can be found in the materials section in Chapter 4. In addition 10 % nanographite / PES-based co-polymer blends were also used. The discussion relating to the nanographite can be found in the materials section in Chapter 2.

5-3 Results

Before any rheological studies were carried out, a TGA (in an air environment) was performed on both the PES-based co-polymer and Radel A-100 in order to determine if any degradation is apparent at the high temperatures (up to 280°C) utilised in these studies. From Figure 5-1 it is seen that both traces are similar, with rapid mass loss occurring in the region of 520-610°C, and also at 650-710°C; this is indicative of a shift in the dominant degradation mechanism at this temperature. As there is no apparent mass loss until these high temperatures, it is assumed that rheologal studies can be carried out certainly until 300°C with no apparent issues with polymer degradation.

The temperatures utilised throughout this chapter are 240-280°C. This temperature range was chosen as it is 40-80°C above the T_g of ~197°C, see Figure 5-2 for Radel A-100 DSC trace and Figure 5-3 for PES-based co-polymer DSC trace. Therefore, at the chosen experimental temperature ranges the polymers should be well above T_g and should therefore be fully flowing.

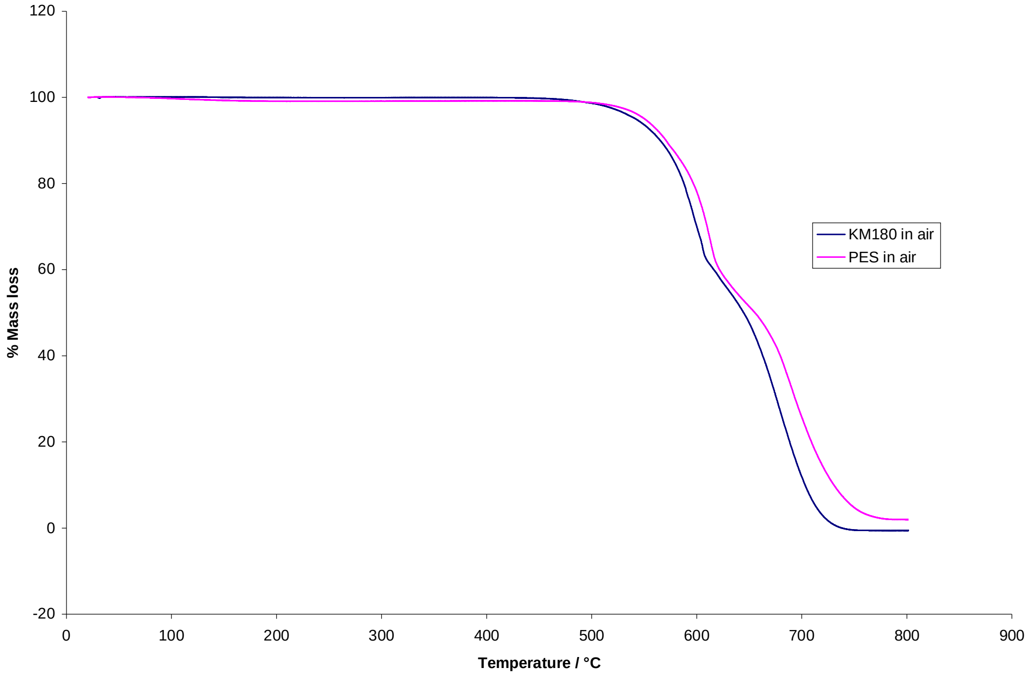

Figure 5-1– TGA of PES materials in air

5-3-1 Strain / Stress Sweeps

The domain of the linear viscoelastic region was established by an oscillatory strain sweep experiment. In this experiment, the strain amplitude of the shear flow was increased from 0.001 rad through to 0.5 rad, with the frequency being kept constant, at a value of 5 rad s^{-1}.

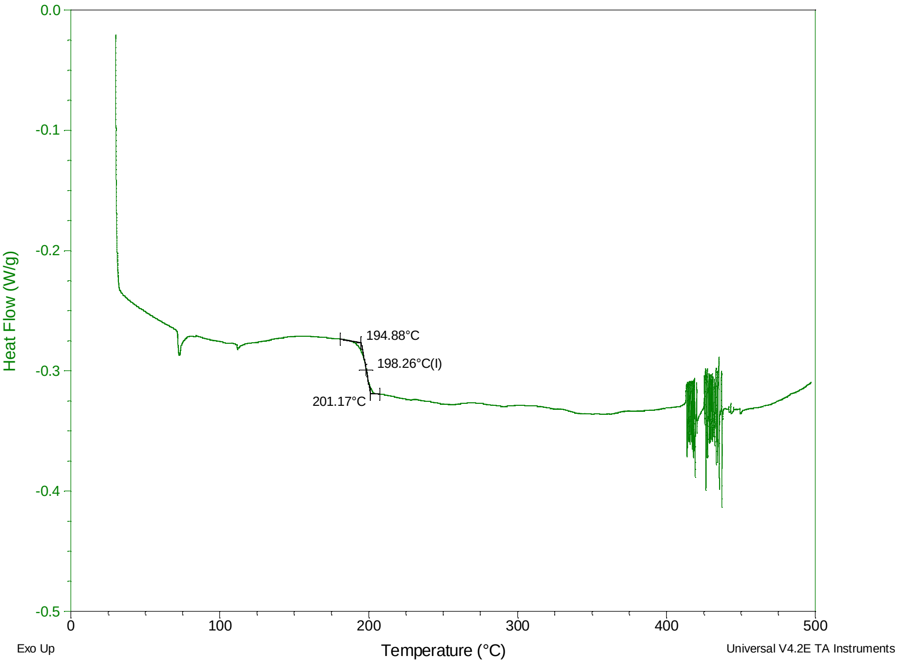

Figure 5-2 – DSC trace for Radel A-100

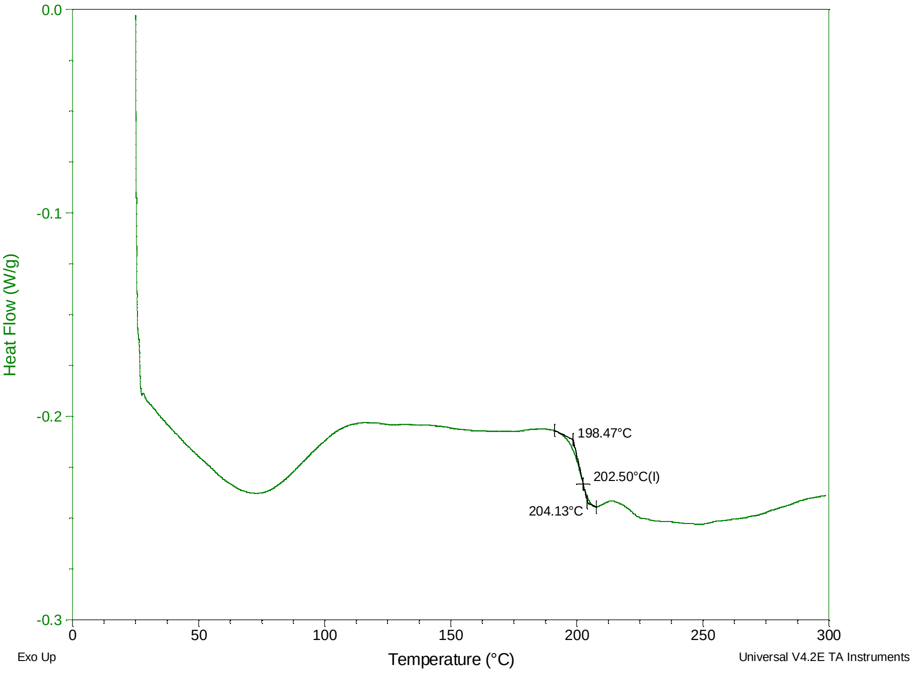

Figure 5-3 - DSC trace for PES-based co-polymer

Strain sweep experiments were carried out at both 240 and 280°C. Resultant PES-based co-polymer strain sweep graphs can be seen for both temperatures in Figure 5-4 and Figure 5-5.

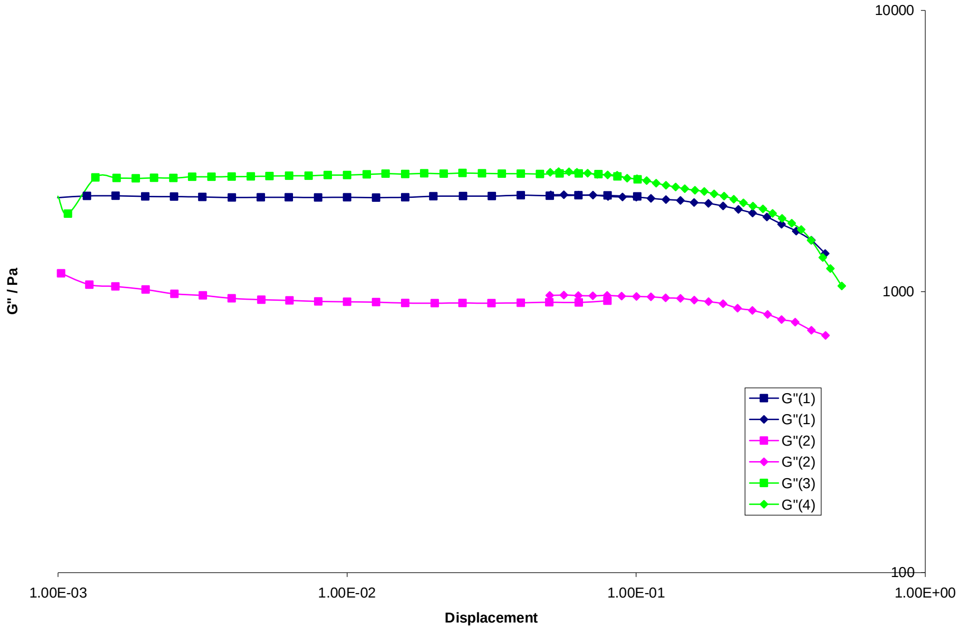

Figure 5-4 – G" graphs of PES-based co-polymer at 280°C

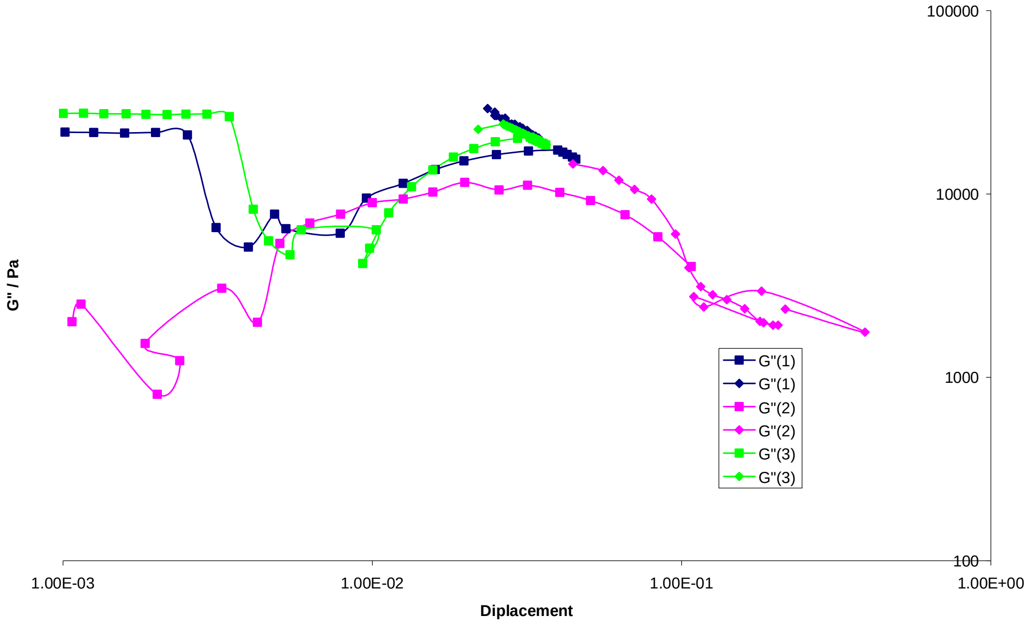

Figure 5-5 - G" graphs of PES-based co-polymer at 240°C

The strain graph at 280°C can be seen in Figure 5-4. From this trace it is seen that two of the curves are fairly reproducible, while the other curve shows a much lower G”, and therefore viscosity. This implies that this particular sample has a lower molar mass than the other samples. The GPC trace for the PES-based co-polymer can be seen in Figure 5-11. From this graph the polymer is seen to have a weight average molecular weight distribution of ~18,500; it is therefore possible that in sampling very small masses – with a 250 µm gap, the sample size required is 0.1 g – any variation in the molecular weight would be apparent in the resultant rheological traces. At the lower temperature of 240°C it is seen that there is not a clear relationship between G” and displacement.

It was observed that, in the case of the Radel A-100 polymer material, it was not possible to measure the lower strain levels, as the stresses involved were at the limit of the instrument, which is 31,830 Pa. It was therefore decided to carry out a stress sweep on both samples. The same frequency of 5 rad s^{-1} was maintained. An oscillating stress of 1-1,000 Pa was applied in the case of PES-based co-polymer and a stress of 30-30,000 Pa was applied in the case of the Radel A-100 material .

Considering the stress sweeps of Radel A-100 at 280°C, see Figure 5-6, it can be seen that both G” and G’ are essentially constant, indicating that the material is in the linear viscoelastic region under these conditions. When one considers the stress sweeps of Radel A-100 at 240°C, see Figure 5-7, it can be seen that there is again not a clear relationship between the stress, G’ and G”. It may be that the apparent oscillation is not real. In certain situations the viscosity of a material may be sufficiently large that the amplitude measured is so small, introducing the generation of large errors which render the data produced invalid. It is also possible that at the stress levels utilised, the measurement of the oscillations are a consequence of the instrument and hence an artefact rather than a material quality. Inspection of the primary data involved in generating Figure 5-6 and Figure 5-7 indicate that the only values above a stress of 15,000 Pa are considered to be valid. Upon re-examination of Figure 5-7 it is seen that at increasing stresses, G” and hence G’ decrease.

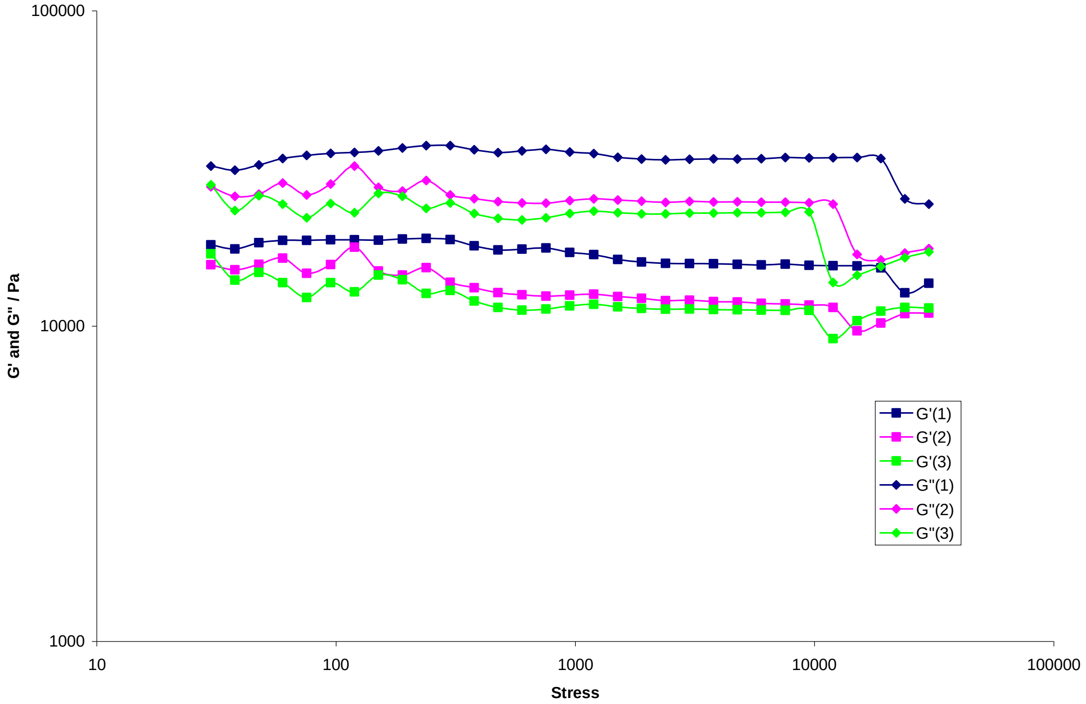

Figure 5-6- Stress sweep of Radel A-100 at 280°C

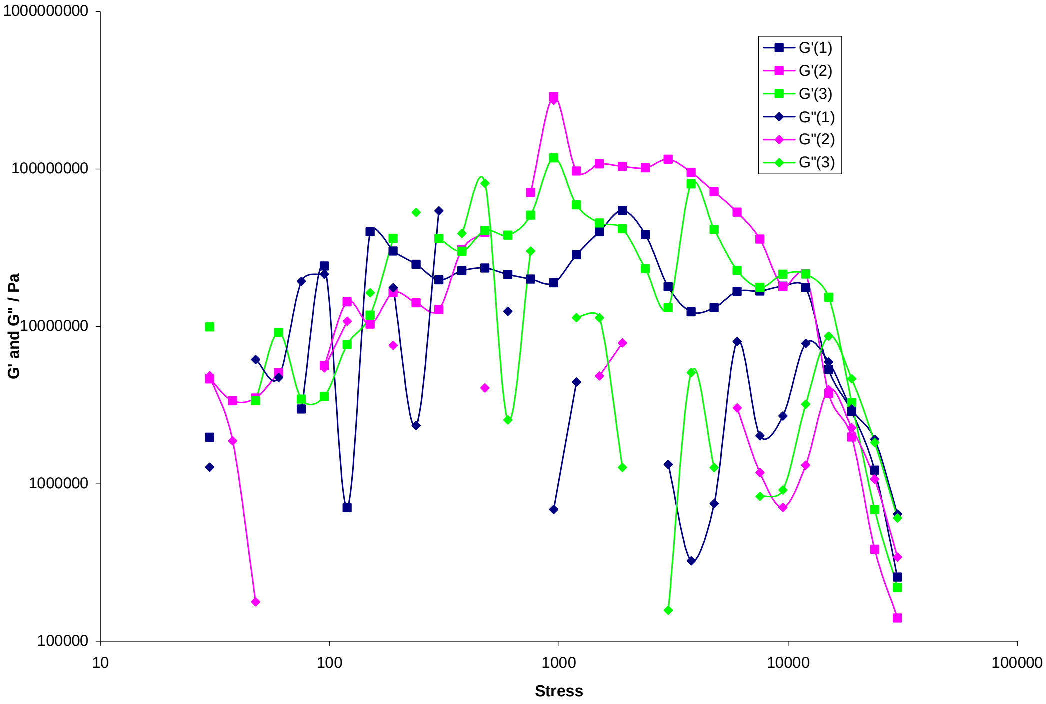

Figure 5-7 – Stress sweep of Radel A-100 at 240°C

It can be seen from the Radel A-100 stress sweep graphs that there is a problem regarding the validity of the experimental data. Because of the high level of the viscosities at the lower stresses, the displacements are very small, typically 3 x 10^{-7} rad, leading to large errors in the data. It is only at the higher values of temperature and stress that more reasonable displacements are found. The strange reduction in G’ and G” followed by an increase is not physically meaningful and hence questions the validity of the data.

The erratic behaviour shown here may be associated with stick slip behaviour. This phenomenon is associated with the yielding of a material at the plates leading to erratic shear stress fields being created. This can also be reflected in edge effects i.e if the sample does not fill the gap completely there is the possibility of surface tension varying with the stress field. Figure 5-8 indicates how the effects of evaporation and, or, shrinkage may affect the way in which the fluid will fill the gap and influence the rheological measurements.

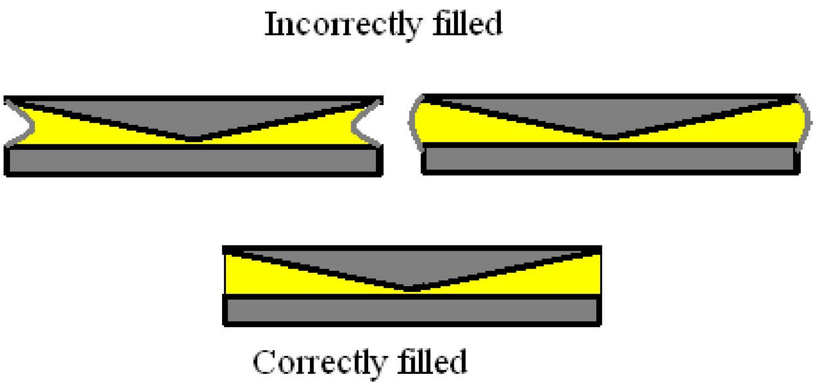

Figure 5-8 – Correctly and incorrectly filled gap situations

The stress sweeps associated with the PES-based co-polymer can be seen in Figure 5-9 and Figure 5-10. It can be seen that at 240°C, both G” and G’ decrease at increasing stresses, whereas at 280°C they are essentially constant – again showing the viscoelastic nature of the material under these conditions. PES-based co-polymer is exhibiting characteristics of a typical viscoelastic material, but one which is not necessarily entangled.

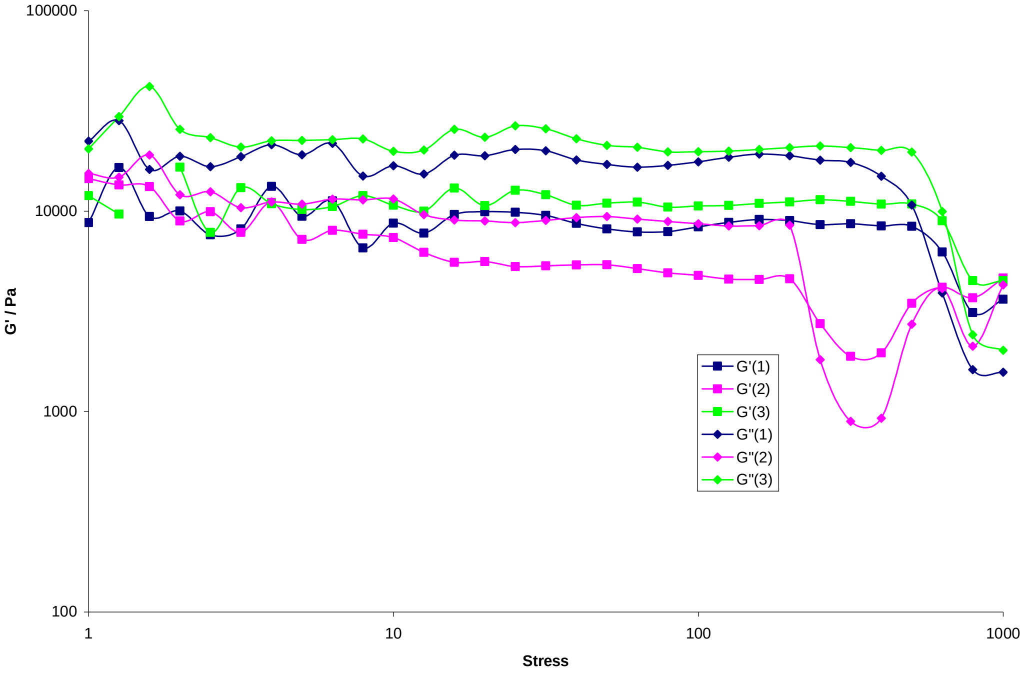

Figure 5-9 - Stress sweep of PES-based co-polymer at 240°C

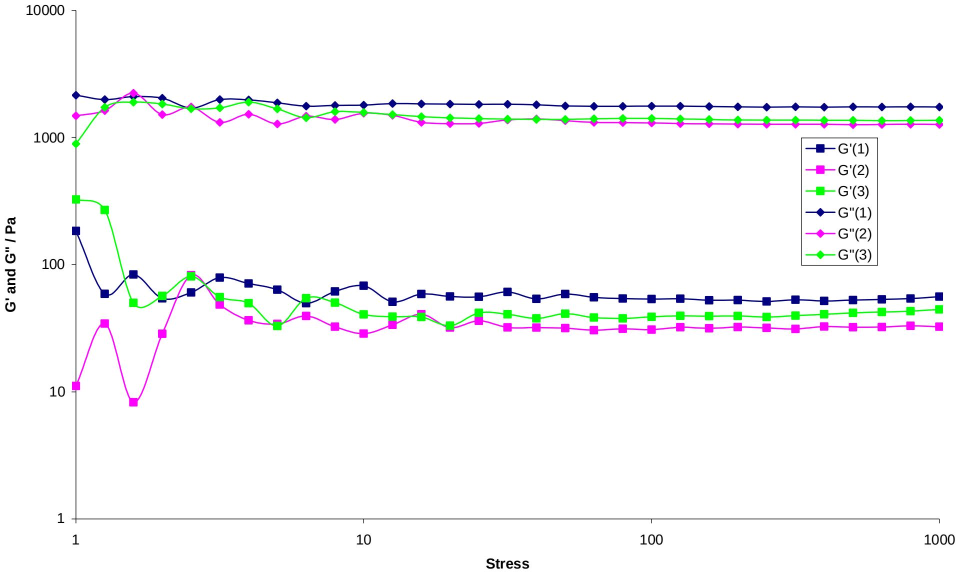

Figure 5-10- Stress sweep of PES-based co-polymer at 280°C

In order to directly compare the materials and observe the degree of temperature dependence on the rheological values obtained, comparisons of the dynamic viscosity, G” and G’ were observed for the same experimental conditions for the two temperatures. In the case of the Radel A-100 the stress applied was a constant 10,000 Pa and in the case of the PES-based co-polymer the stress applied was 100 Pa. The resultant table can be seen in Table 5-1. It can be seen from this table that, in all cases, G”, G’ and η* values decrease with increasing temperature, as would be expected. It can also be seen from this table that the viscosities of the two materials are very different. For example, in the case of Radel A-100 the viscosity goes from 3,573,000-4,288,000 Pa s at 240°C, and from 5,115-7,501 Pa s at 280°C. The PES-based co-polymer has a viscosity of 1,976-4,490 Pa.s at 240°C moving to 260-353 Pa s at 280°C.

The difference in the materials viscosities is reflected in the different molecular weight distributions of the materials; see Table 5-2 which displays GPC results (graphs can be seen in Figure 5-11, Figure 5-12 and Figure 5-13). It can be seen from the table that the PES-based co-polymer has a weight average molecular weight of 18,500 and Radel A-100 has a weight average molecular weight of 47,000. As such one would expect a higher viscosity in the case of the Radel A-100 polymer i.e. the higher molecular mass fraction in Radel-A100 is probably responsible for the higher viscosity.

It is also seen from Table 5-2 that the molecular weight of the PES-based co-polymer increases after shearing – going from ~18,200 to ~22,000. This may be due to additional polymerisation, or, more probably, reacting end groups.

The dominant rheological properties of the polymers can also be seen by looking at Table 5-1. For the PES-based co-polymer the viscous modulus is larger than the elastic modulus in all occasions, indicating pronounced viscous but not necessarily viscoelastic properties of this material. The converse is true when one considers the Radel A-100 polymer at 240°C – in this case the elastic modulus is higher, indicating pronounced viscoelastic (gel) properties of this material under these experimental conditions. At 280°C the dominant rheological property switches to the viscous modulus. The observed change in behaviour is usually associated with a change in the molar mass of the polymer system, but can be further complicated by the effect of interaction between chains through the terminal groups. The principal difference between the PES-based co-polymer and Radel A-100 is that the former has terminal amine groups which have the potential to interact together, whereas the latter has terminal chlorine groups which should not show significant interaction. The IR spectra of the two polymers can be seen in Figure 5-14. From this figure it can be seen that there is no significant difference between the samples, and the presence of the different end groups cannot be easily seen. We therefore cannot be entirely certain as to the exact structures of the polymers utilised.

5-3-2 Sampling

It is noted at this point that samples used in the rheological measurements are very small. The gap utilised for most of this chapter is 250 µm, which requires sample sizes of the order of approximately 0.1 g; although it must be emphasised that other experimental techniques require small sample sizes also, with GPC utilising 60 mg of polymer. Therefore non representative sampling cannot be fully responsible for the poor reproducibility of the rheological experimental results.

Radel A-100 would be expected to show entanglement behaviour whereas the PES-based co-polymer would not. Both polymers have similar values of M_w/M_n but the higher value in Radel A-100 would imply that there is probably a higher molar mass tail in this polymer than in the PES-based co-polymer. It is therefore concluded that the viscoelasticity of Radel A-100 is due to entanglement behaviour, and the effects of the PES-based co-polymer are a consequence of end group interactions.

In addition, there is the potential of microphase separation occurring within the sample, meaning that with the small sample sizes used it may not be possible to obtain the same molecular weight distribution of polymer molecules every time. All of these effects could be contributing to the problems found in reproducing experimental results.

Table 5-1 – η^*, G' and G" values of both PES materials at the stress levels stated

	Radel A-100 (Stress 10,000 Pa)		PES-based co-polymer (Stress 100 Pa)	
	240°C	**280°C**	**240°C**	**280°C**
η^* / Pa s	3,635,000	7,501	3,893	352
	3,573,000	5,443	1,976	260
	4,288,000	5,115	4,490	282
G' / Pa	18,000,000	15,600	8,345	54
	17,900,000	11,660	4,780	31
	21,500,000	11,222	10,610	39
G" / Pa	2,701,000	34,160	17,610	1763
	709,412	24,630	8,662	1302
	914,260	23,020	19,810	1412

Table 5-2 –GPC molecular weights

Sample Description	**Mw**	**Mn**	**Mw/Mn**
PES-based co-polymer	18,510	8,170	2.3
	18,540	8,200	2.3
Radel A-100	47,310	15,470	3.1
	47,130	15,520	3.0
PES-based co-polymer (after shearing)	22,020	7,170	3.1
	21,990	6,300	3.5

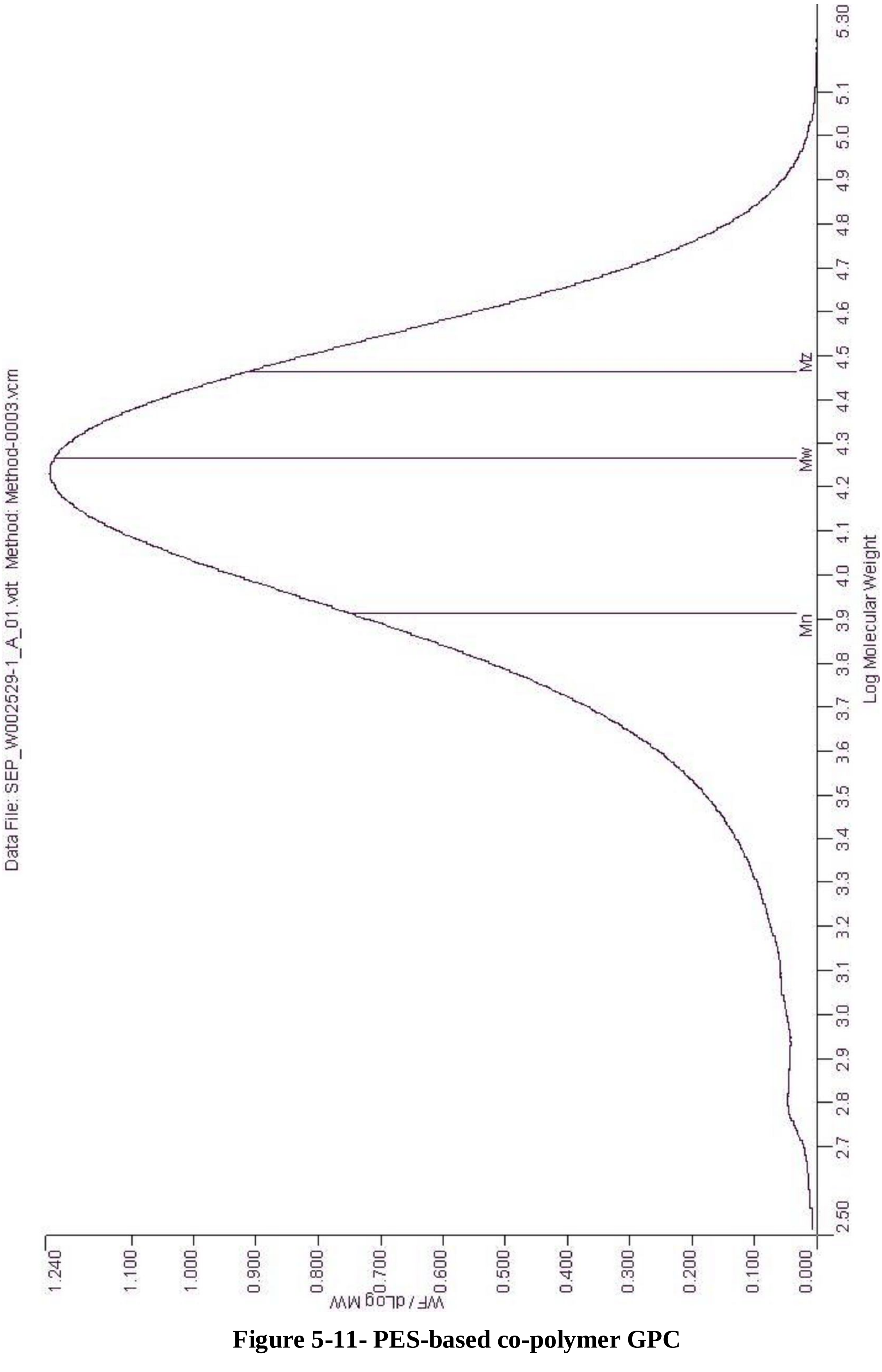

Figure 5-11- PES-based co-polymer GPC

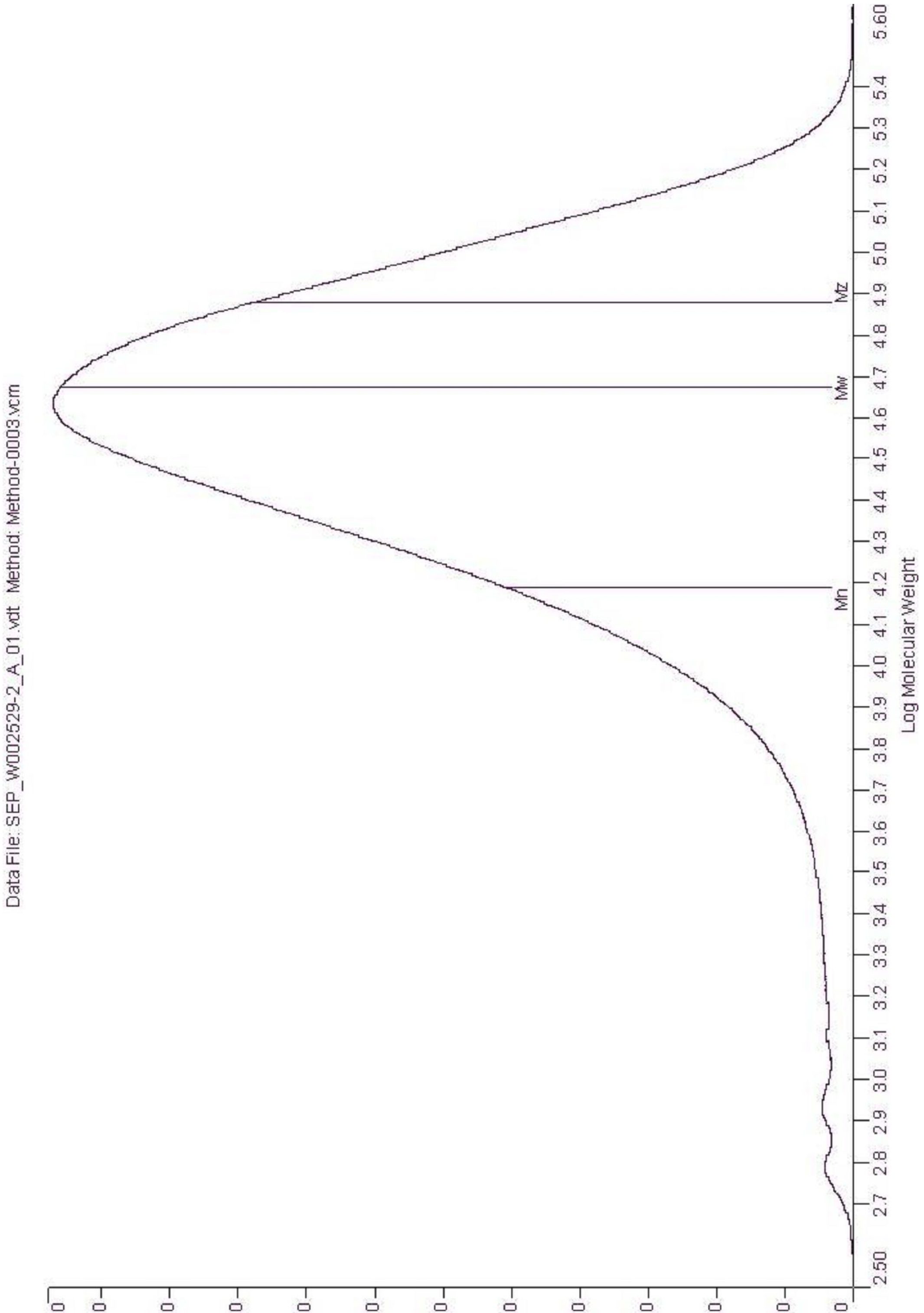

Figure 5-12 – Radel A-100 GPC

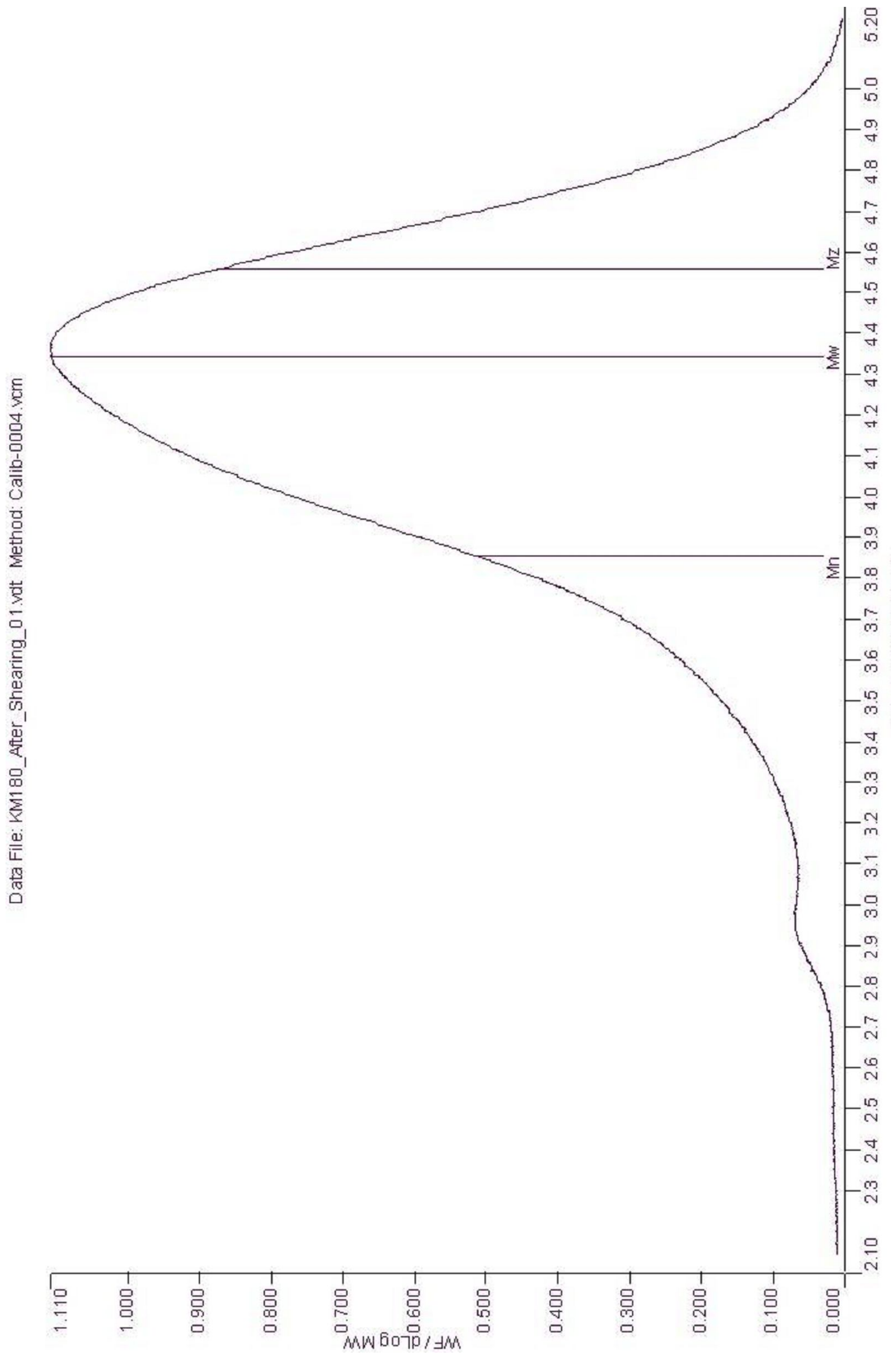

Figure 5-13 – PES-based co-polymer after shearing GPC

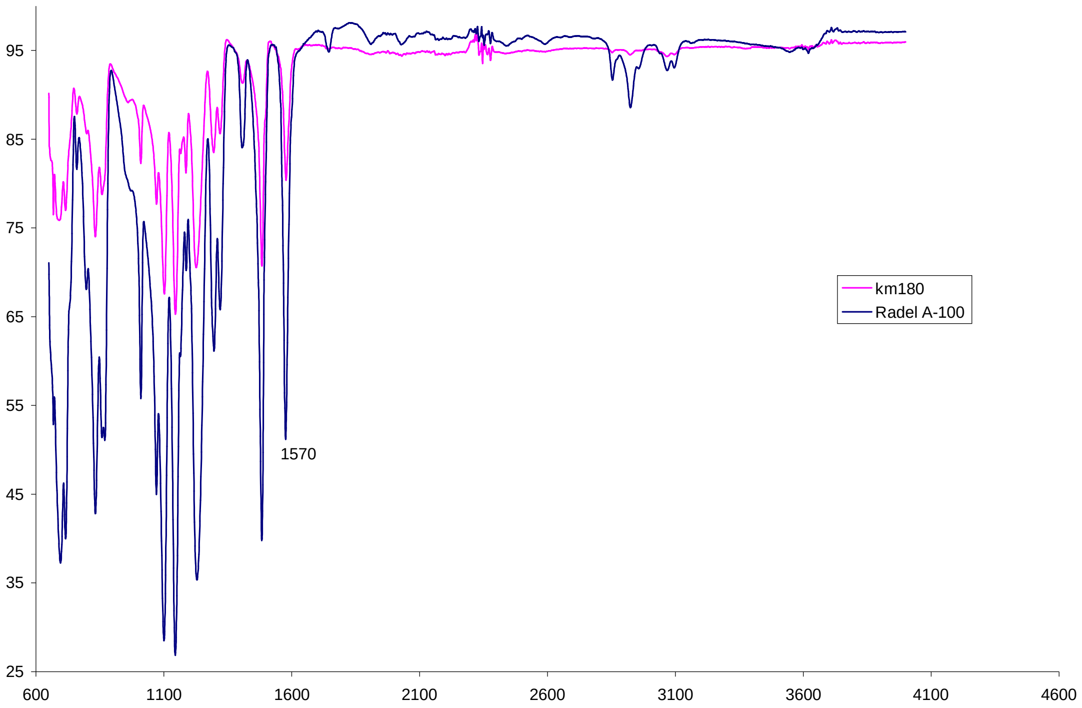

Figure 5-14 – IR spectra of PES-based co-polymer and Radel A-100

5-3-3 Frequency Sweeps

Once the linear viscoelastic region had been determined, it is useful to explore the level of viscoelastic behaviour over various timescales, to further characterize the nature of the samples. The method utilised for this purpose is, generally, a frequency sweep.

Frequency sweeps were carried out on the PES-based co-polymer and the Radel A-100 materials between frequencies of 0.1 -100 rad s^{-1}. Five frequency sweeps were carried out on the same sample for a specific temperature. Again temperatures between 240-280°C were employed. In the case of the PES-based co-polymer, frequency sweeps were carried out from the lowest value through to the highest, see Figure 5-15, Figure 5-16, Figure 5-17, Figure 5-18 and Figure 5-19. Additional graphs (at temperatures of 270 and 280°C) are included to show the frequency behaviour from the highest through to the lowest frequencies (referred to as reverse frequency graphs), for purposes of comparison, see Figure 5-20 and Figure 5-21. In the case of the Radel A-100 the sweeps were carried out from the highest frequency to the lowest frequency. In principle the frequency sweeps should give the same results whether you chose to carry out the experiments from low to high frequency or high to low frequency, if there are no non-linear effects, such as shear thickening. However as it can take a considerable time to reach the lower frequencies there can be a tendency to carry out the experiments from the high to the low frequencies.

Resultant graphs can be seen in Figure 5-22**,** Figure 5-23, Figure 5-24, Figure 5-25 and Figure 5-26. From the graphs concerning PES-based co-polymer it can be seen that the runs for the lowest temperature of 240°C all lie on top of each other, indicating that the material is behaving in exactly the same way after multiple sweeps. As the temperature is increased it can be seen that there is a tendency for the G” to increase with successive runs. In all cases it can be seen that the G” value builds up as the run progresses, and then falls to a lower value as the next run starts. This implies that there are now shear stress sensitive processes in the material.

When one considers the results for the Radel A-100 polymer it can be seen that at the lowest temperature of 240°C there is a tendency for the G” to increase with successive runs, with the value building up to a maximum as the run progresses and then falling as the next run starts. For the higher temperatures it can be seen that, at the lower frequencies, the graphs practically lie on top of each other, as the frequencies increase the behaviour deviates significantly from the curves seen thus far.

In addition a frequency sweep of the 10 % nanographite was also carried out, and can be seen in Figure 5-27. It is seen here that the G” values are much higher than was obtained for the PES-based co-polymer – indeed the smallest difference is found for the material at 240°C. The PES-based co-polymer shows a value of 2,685 Pa, whereas with the inclusion of nanographite the value moves to 27,610 Pa, which is more than ten times higher. It is obvious that the nanographite is increasing the viscosity to a large extent. It may be that the nanographite is interacting with the polymer to form a large structure, which creates increased friction and therefore increased viscosity.

In order to compare the temperature dependence of the graphs a table showing G" values for successive runs, and increasing temperatures at an angular frequency of 1 rad s^{-1} can be seen in Table 5-3. One would expect that as the temperature is increased G" values should decrease. It can be seen from the table that for the PES-based co-polymer material there are anomalous results at 260°C, where it can be seen that G" values are much higher than would be expected. This indicates that there is more structure present than would necessarily be expected under these conditions. The PES-based co-polymer with its -NH_2 and -OH end groups, has the potential to react to form a pseudo-high molecular weight material through the formation of hydrogen bonds, leading to the build up of a large structure. It is proposed that this is what is occurring at 260°C. At the higher temperatures of 270 and 280°C, the structure could again break down leading to the lower G" values reported. When one considers the Radel A-100 polymer, it is solely chlorine terminated; therefore, in this case, there exists no possibility of the build up of a pseudo structure through end group reactions.

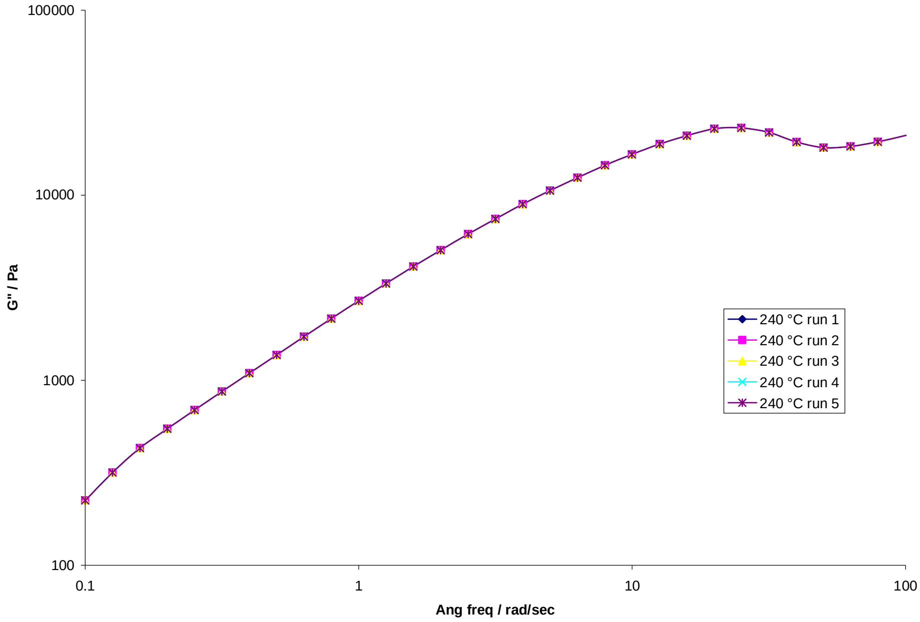

Figure 5-15 – Frequency sweeps of PES-based co-polymer carried out at 240°C on same sample

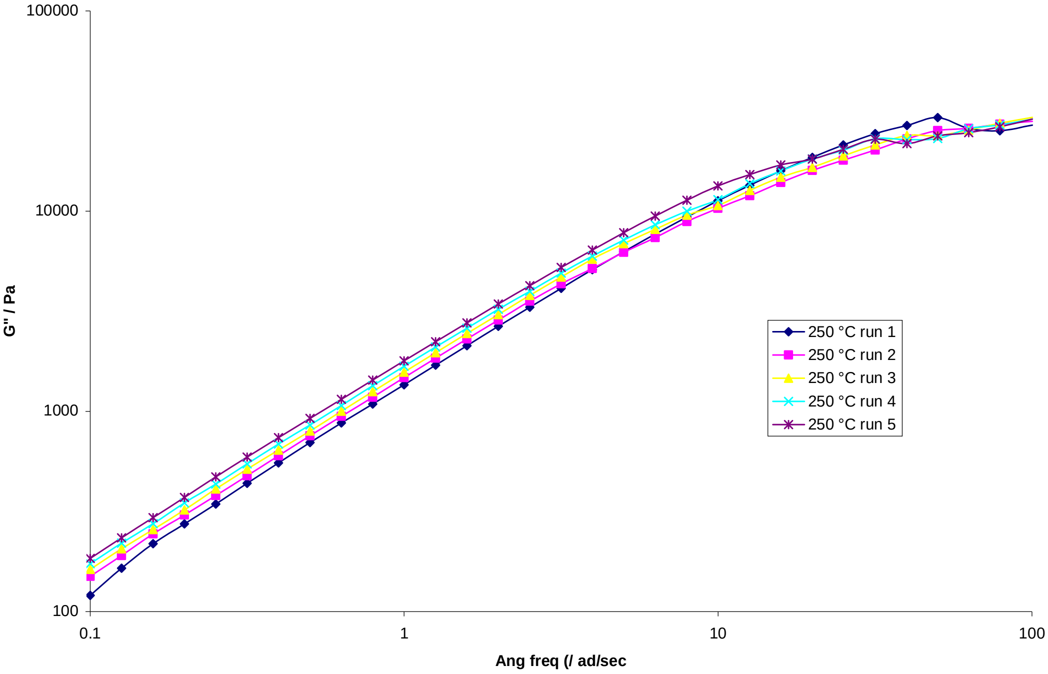

Figure 5-16 – Frequency sweeps of PES-based co-polymer carried out at 250°C on same sample

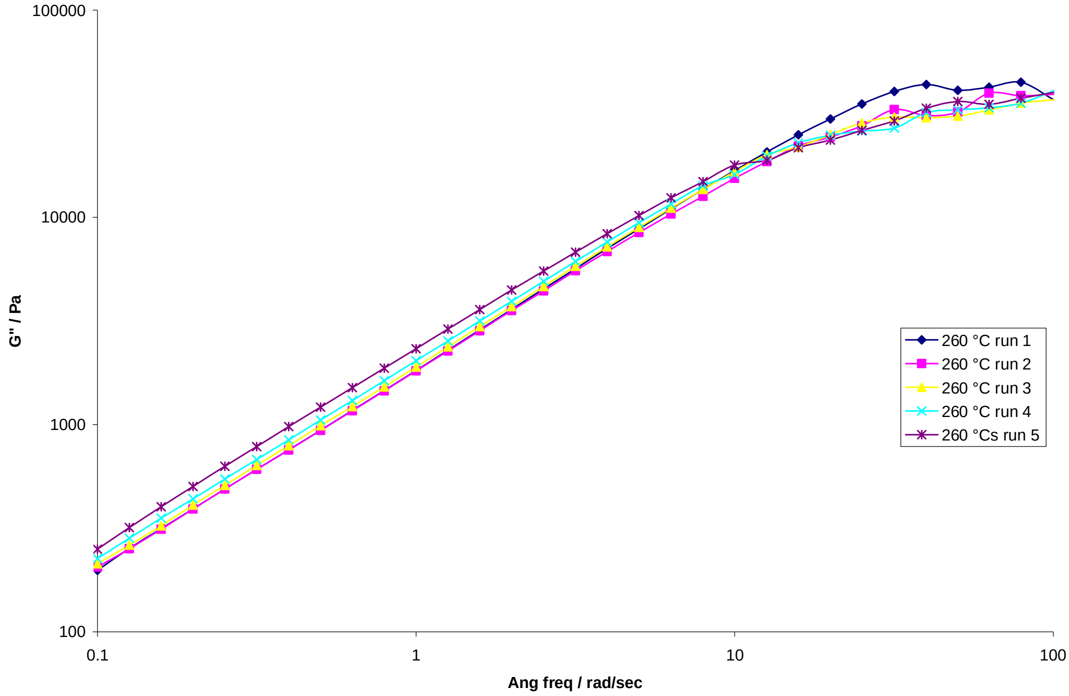

Figure 5-17 – Frequency sweeps of PES-based co-polymer carried out at 260°C on same sample

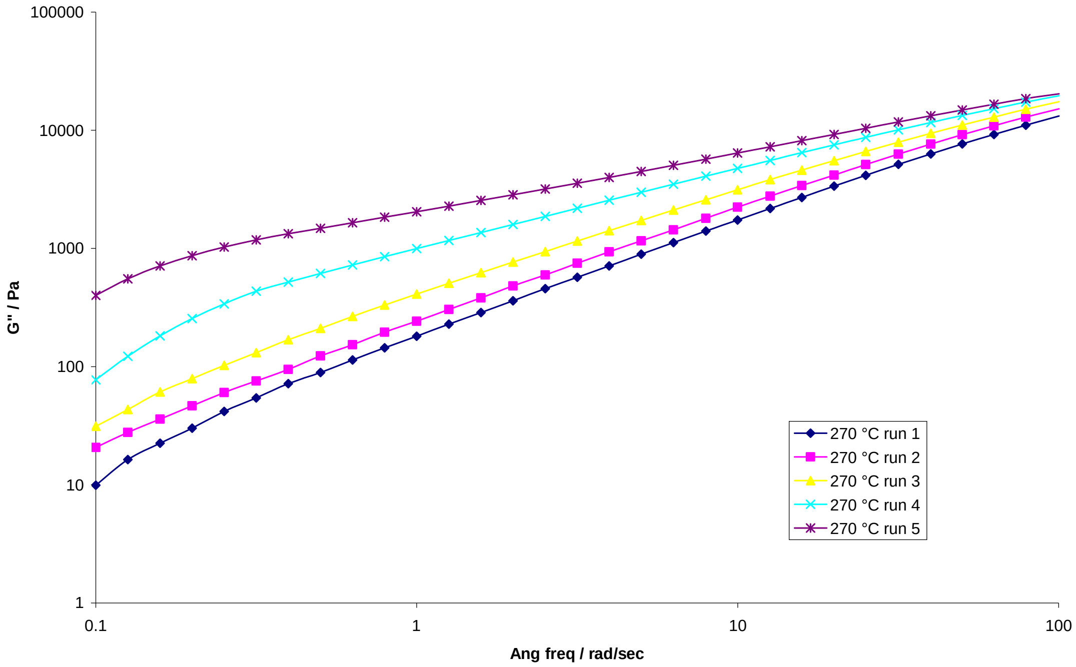

Figure 5-18 – Frequency sweeps of PES-based co-polymer carried out at 270°C on same sample

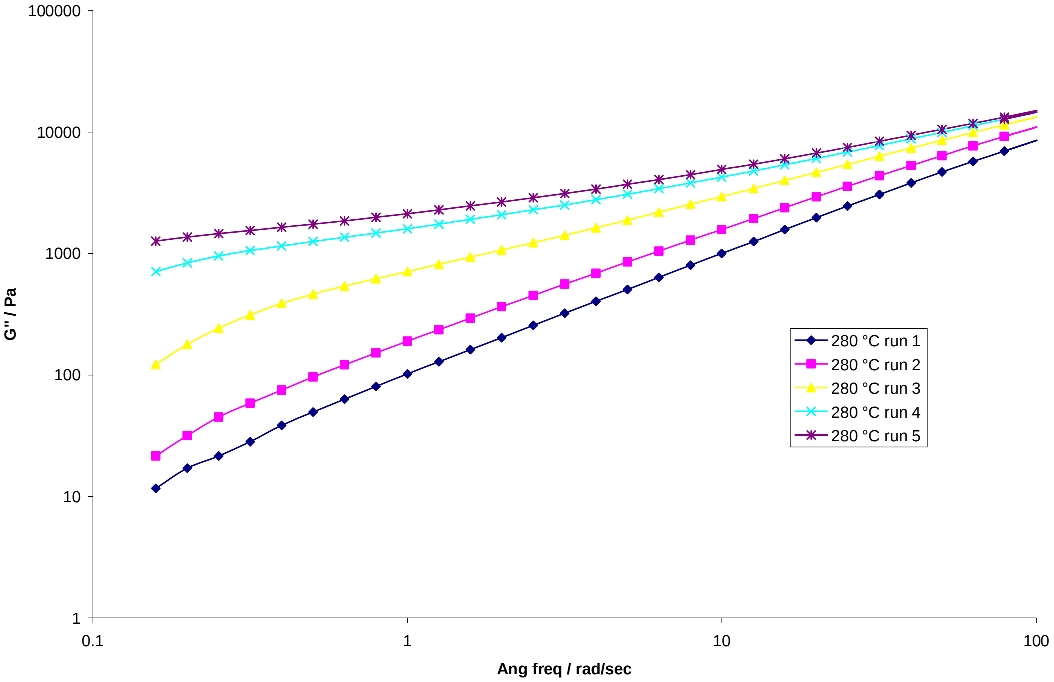

Figure 5-19 – Frequency sweeps of PES-based co-polymer carried out at 280°C on same sample

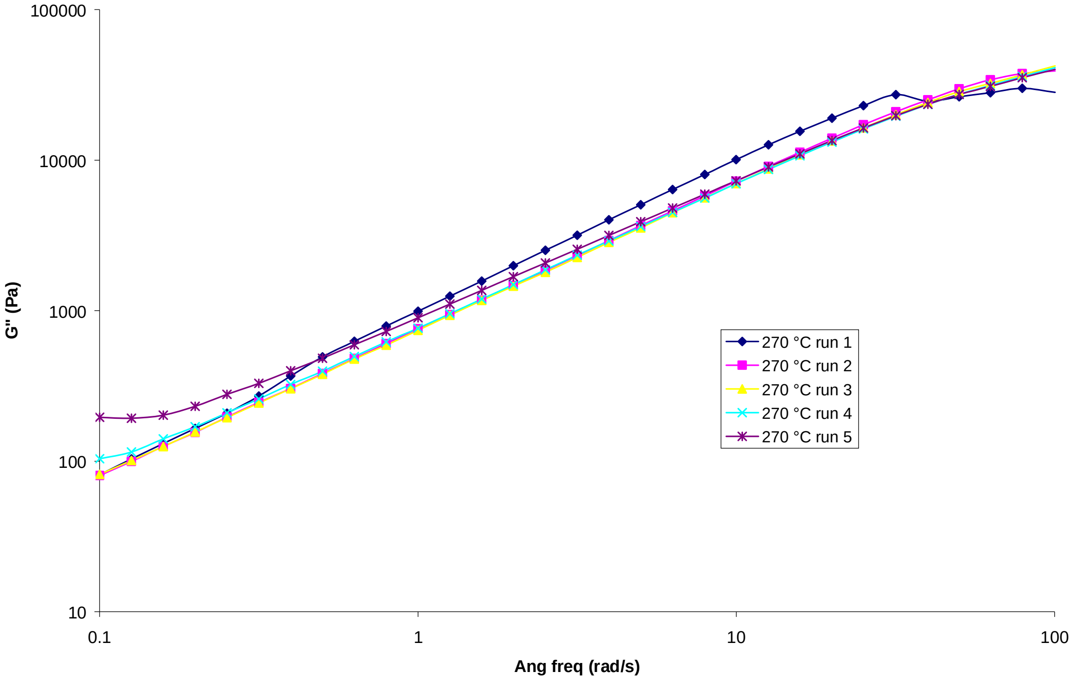

Figure 5-20 – Reverse frequency sweeps of PES-based co-polymer carried out at 270°C on same sample

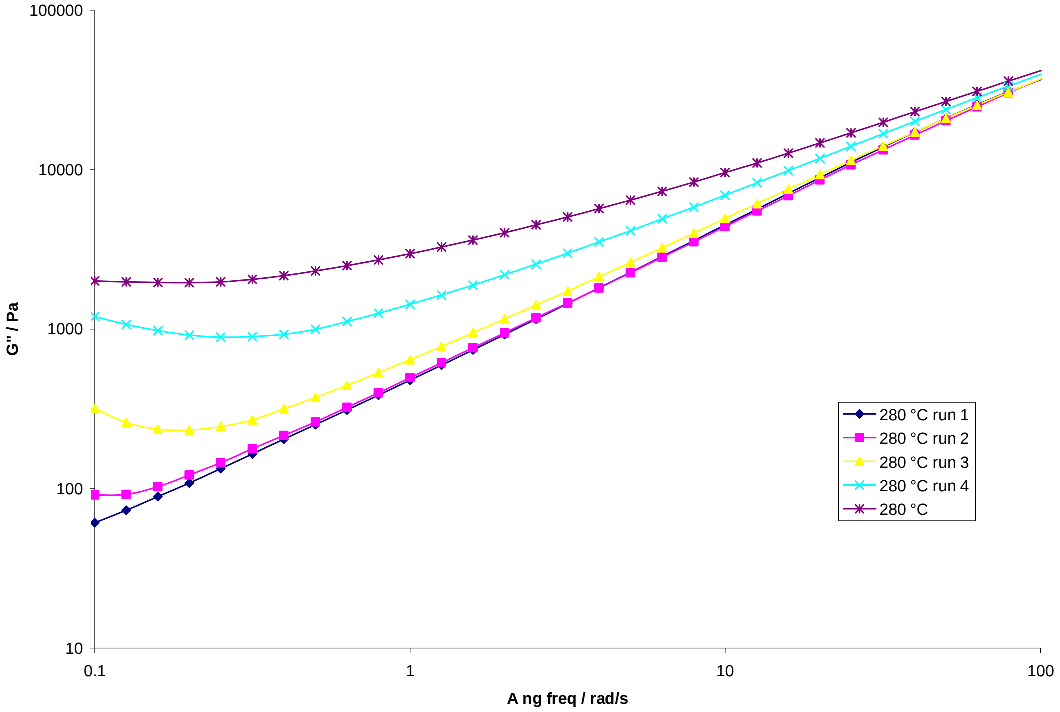

Figure 5-21 – Reverse frequency sweeps of PES-based co-polymer carried out at 280°C on same sample

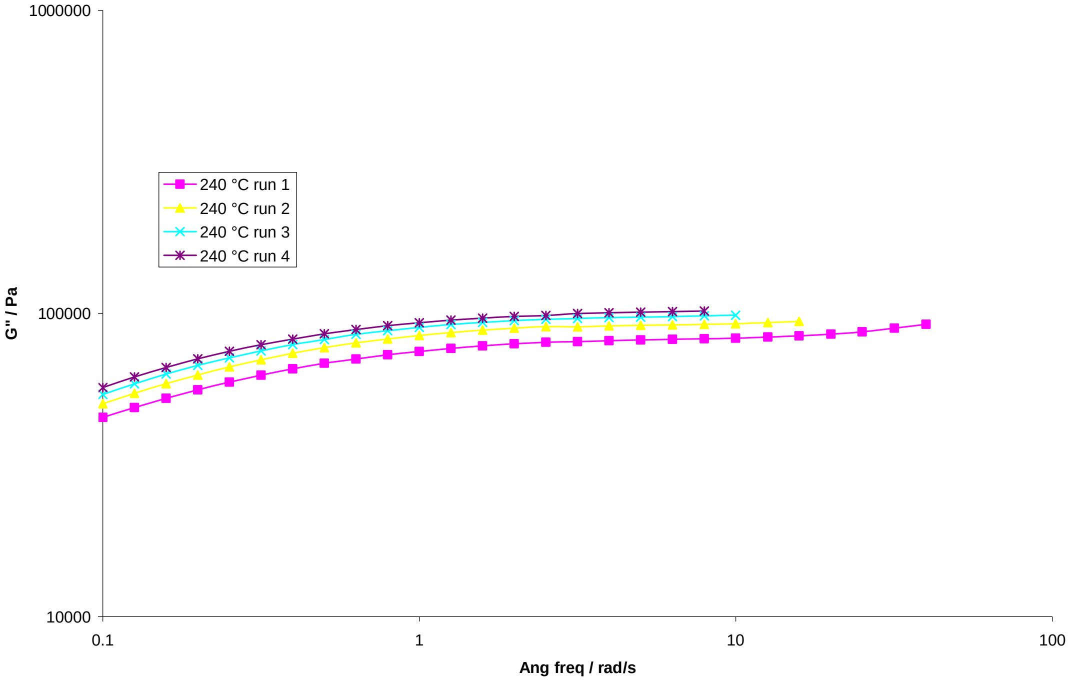

Figure 5-22 – Reverse frequency sweeps of Radel A-100 polymer carried out at 240°C on same sample

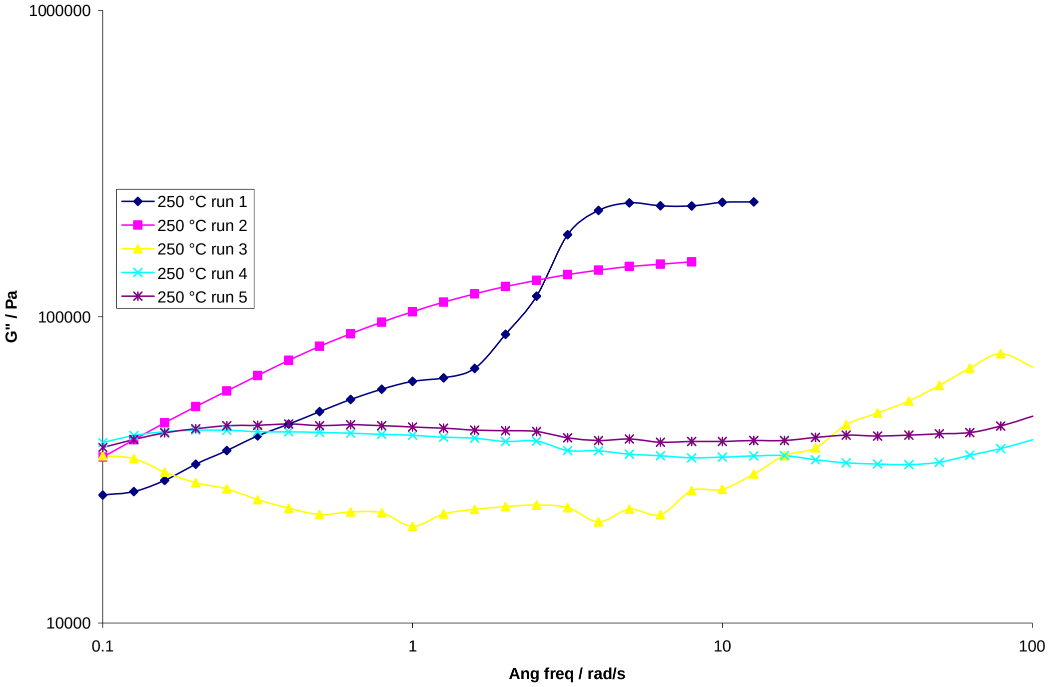

Figure 5-23 – Reverse frequency sweeps of Radel A-100 polymer carried out at 250°C on same sample

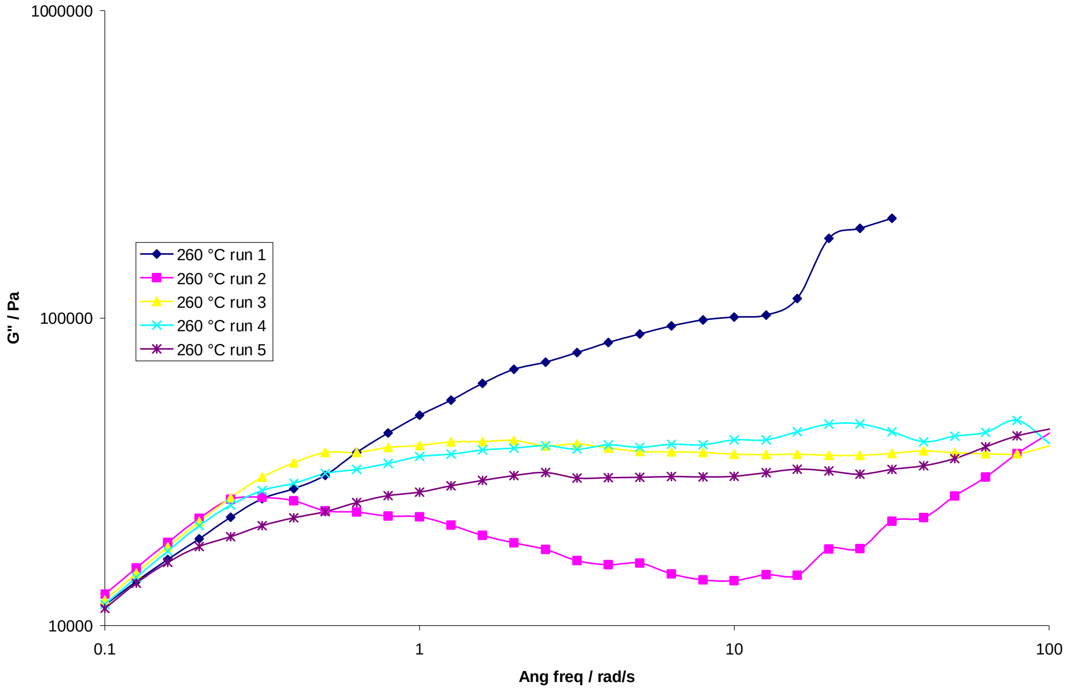

Figure 5-24 – Reverse frequency sweeps of Radel A-100 polymer carried out at 260°C on same sample

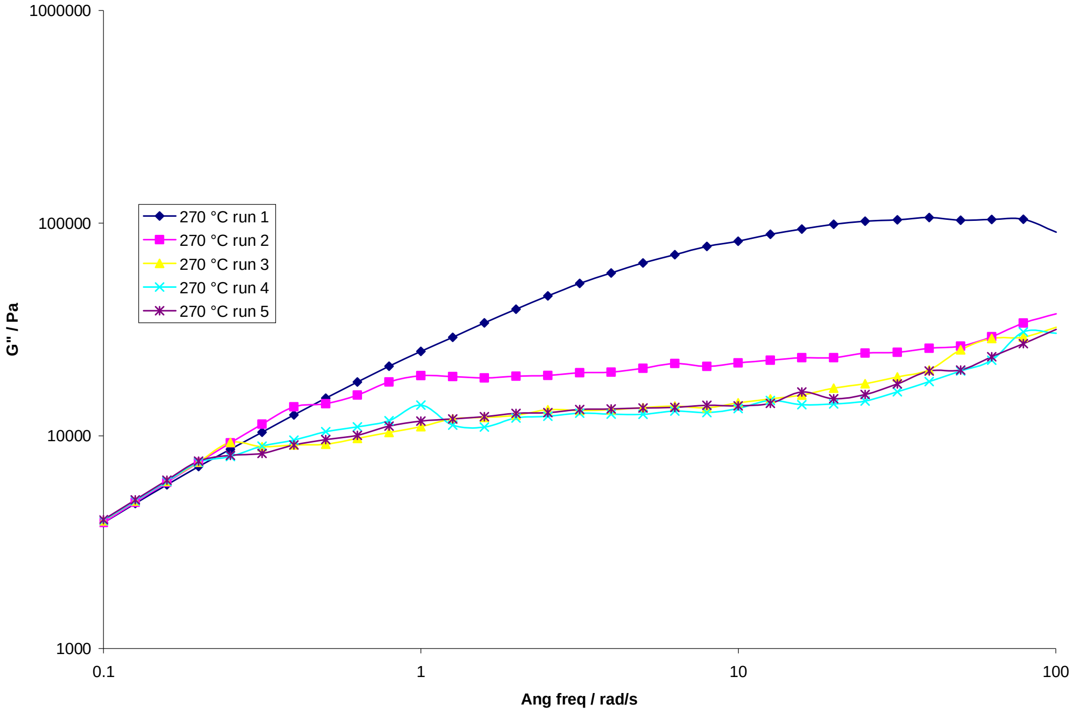

Figure 5-25 – Reverse frequency sweeps of Radel A-100 polymer carried out at 270°C on same sample

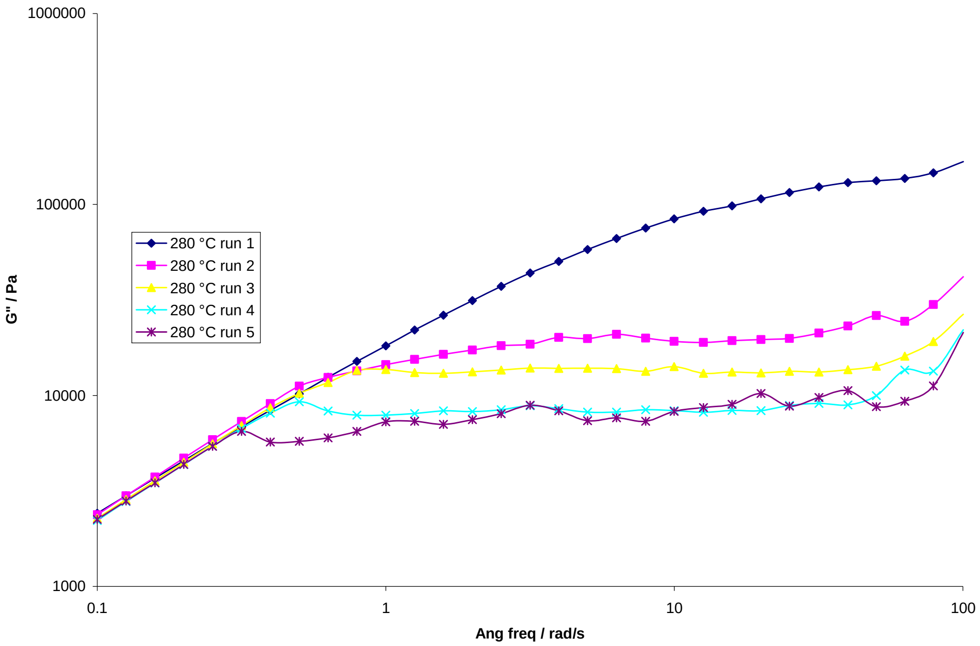

Figure 5-26 – Reverse frequency sweeps of Radel A-100 polymer carried out at 280°C on same sample

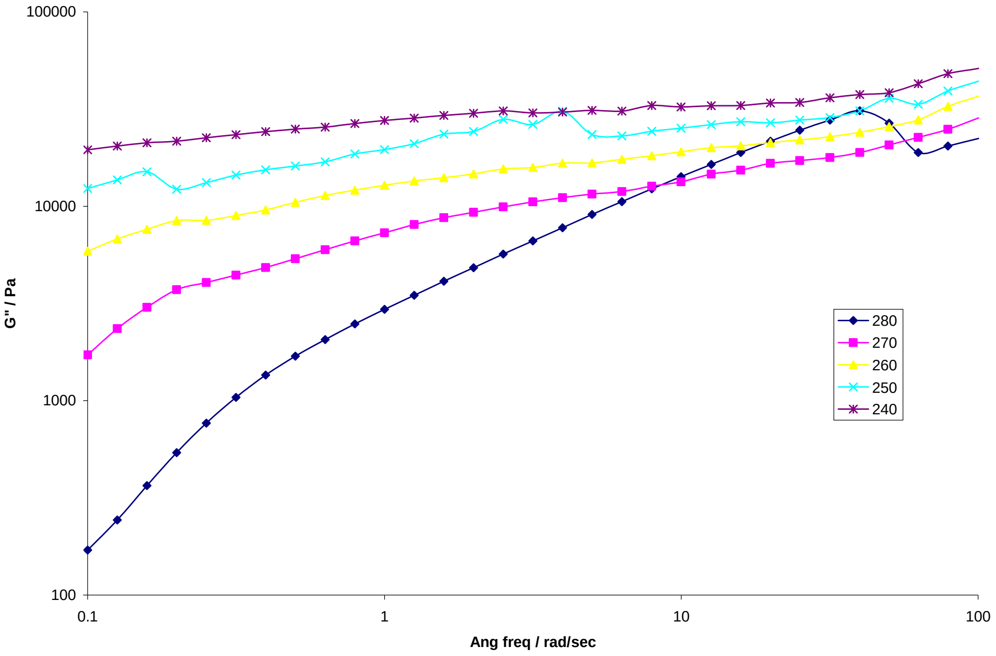

Figure 5-27 – Frequency sweeps of 10 % nanographite in PES-based co-polymer, carried out on same sample

Table 5-3 – G” values for PES-based co-polymer and Radel A-100 at 1 rad s^{-1} for successive runs and increasing temperatures

	G” values at 1 rad s^{-1}				
PES-based co-polymer	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**
240°C	2685	2685	2685	2685	2685
250°C	1359	1474	1569	1682	1970
260°C	1823	1815	1895	2033	2324
270°C	181	242	412	999	2047
280°C	102	190	711	1601	2128
frequency reverse sweep 270°C	990.6	757.4	740.4	765.5	896.5
frequency reverse sweep 280°C	478.2	495.6	642.4	1430	2967
Radel A-100 reverse frequency sweeps	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**
240°C	64470	74980	84660	89970	93250
250°C	61490	103800	20690	40990	43640
260°C	48310	22570	38550	35490	27170
270°C	24950	19180	11040	13950	11740
280°C	18180	14490	13680	7877	7274
10 % nanographite reverse frequency	**Run 1**				
240°C	27610				
250°C	19550				
260°C	12820				
270°C	7309				
280°C	2949				

Upon consideration of Figure 5-15-Figure 5-27 it can be seen that the reproducibility is poorer at the higher temperatures, when the possibility of oxidative effects could be having an effect upon the rheology. When one considers the PES-based co-polymer it is apparent that raising the temperature from 260°C to 270°C leads to a significant drop in viscosity, reflecting a loss of some significant interactions. Similar trends are also observed upon consideration of the Radel A-100, although this transition is less dramatic as the base viscosity is significantly higher than the PES-based co-polymer. The values indicated in red reflect anomalous results and may also be a consequence of incorrect gap filling.

5-3-4 Time Study

In order to study time dependent behaviour at a given temperature, time sweeps were carried out. The PES-based co-polymer and Radel A-100 were each held over a period of time at two separate frequencies – namely 1 rad s^{-1} and 10 rad s^{-1}. The temperatures used were 240-280°C with the sweeps carried out at the higher temperature before moving through to the lower temperatures in sequence. The same sample was used for each time study. It was occasionally seen that at the lower temperatures, in the case of the Radel A-100, the stresses required to reach the specified frequencies were at the limit of the instrument, therefore these data have not been included in the graphs displayed. The resultant graphs are seen in Figure 5-28, Figure 5-29, Figure 5-30 and Figure 5-31. They show the results of the viscous modulus. If one looks at Figure 5-28 which shows Radel A-100 studied at 1 rad s^{-1} it can be seen that as you increase the temperature you decrease G”. This is what you would expect of the material. When one looks at Figure 5-29 it can be seen that at a frequency of 10 rad s^{-1} the PES behaves in a similar way, whereby the G” decreases upon increasing temperature, though the graphs are exhibiting a higher degree of uncertainty reflecting the lack of precision in the measurements.

When one considers the G” graphs of the PES-based co-polymer at 1 rad s^{-1} it is initially seen that the G” values are much less than previously reported for the Radel A-100. The highest value seen for the PES-based co-polymer is just under 5,000 Pa, compared with over 90,000 Pa for Radel A-100. When one considers the PES-based co-polymer at 10 rad s^{-1}, it is seen that the relationship between G” and the temperature is not so clear. The G” value decreases between 240 and 250°C and then increases at 260°C, decreases at 270°C and then increases at 280°C. This relationship is unexpected and shows the rheology to be quite complicated.

As previously discussed, there is a distribution of molecular weights within the material – it may be that the low molecular weight material is phase-separating within the sample. This microphase separation could be leading to inhomogeneity which could, in turn, lead to variations in the viscosity of the material. The samples are being held at an elevated temperature for a significant period of time and are also being subjected to a shear stress; all these factors may be expected to enhance phase-separation.

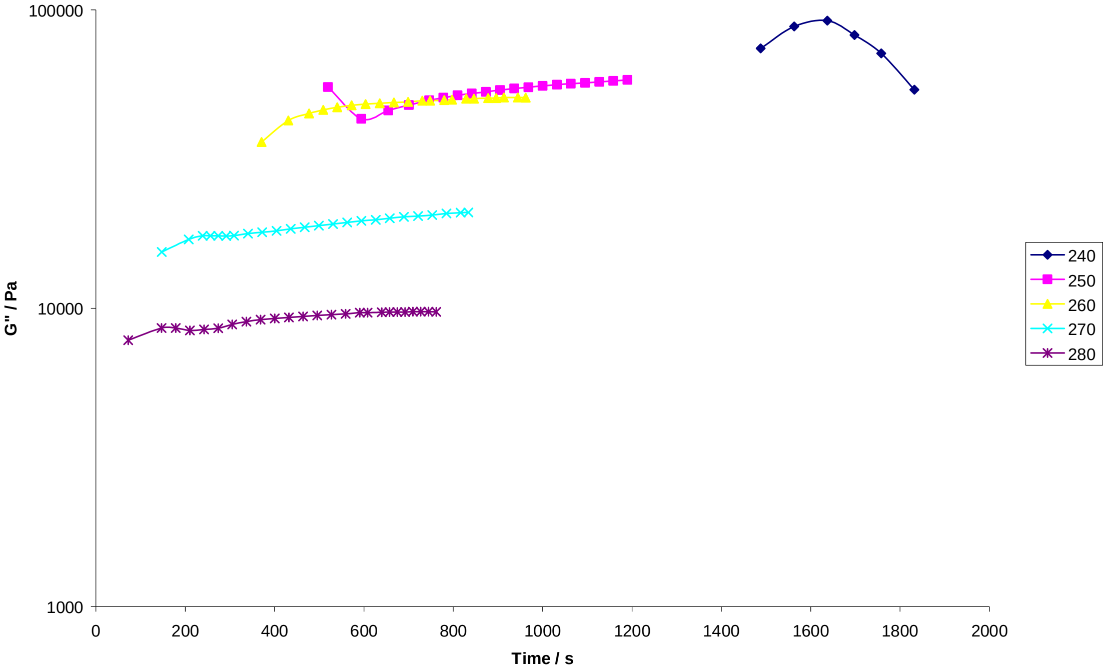

Figure 5-28 PES G" graphs at 1 rad s^{-1}

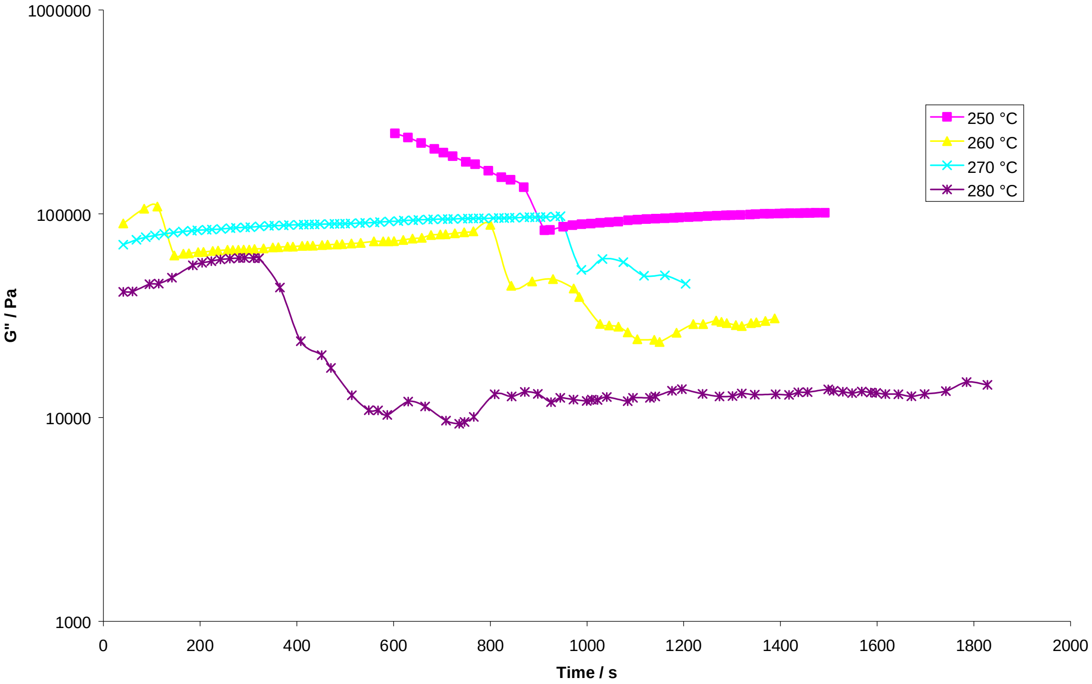

Figure 5-29 - PES G” graphs at 10 rad s^{-1}

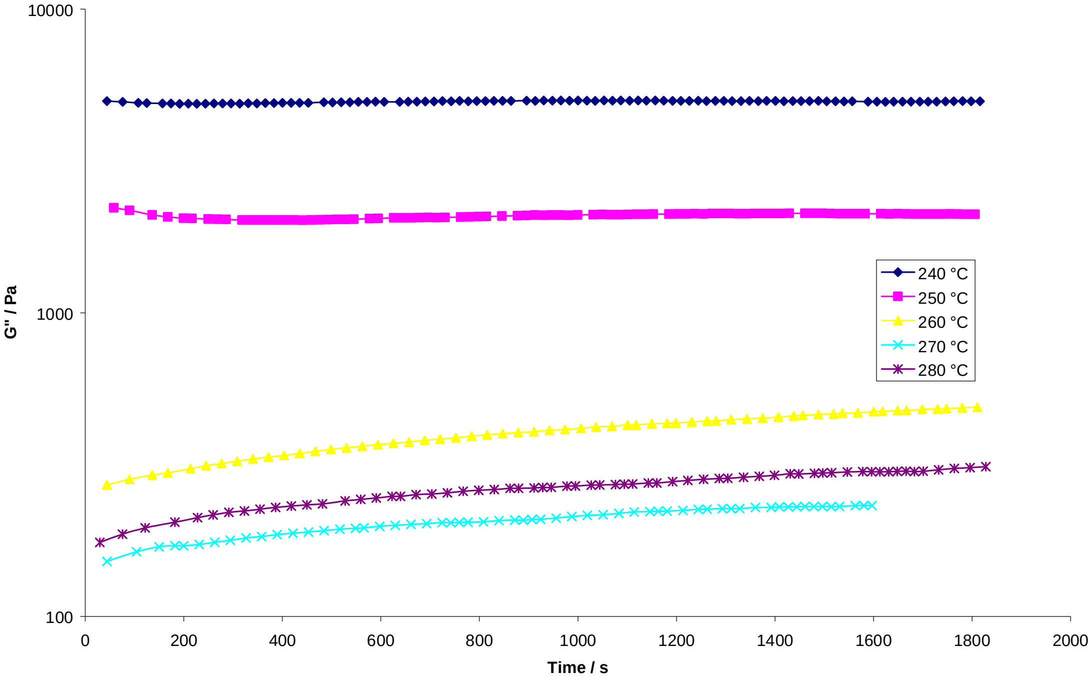

Figure 5-30 – PES-based co-polymer G” graphs at 1 rad s^{-1}

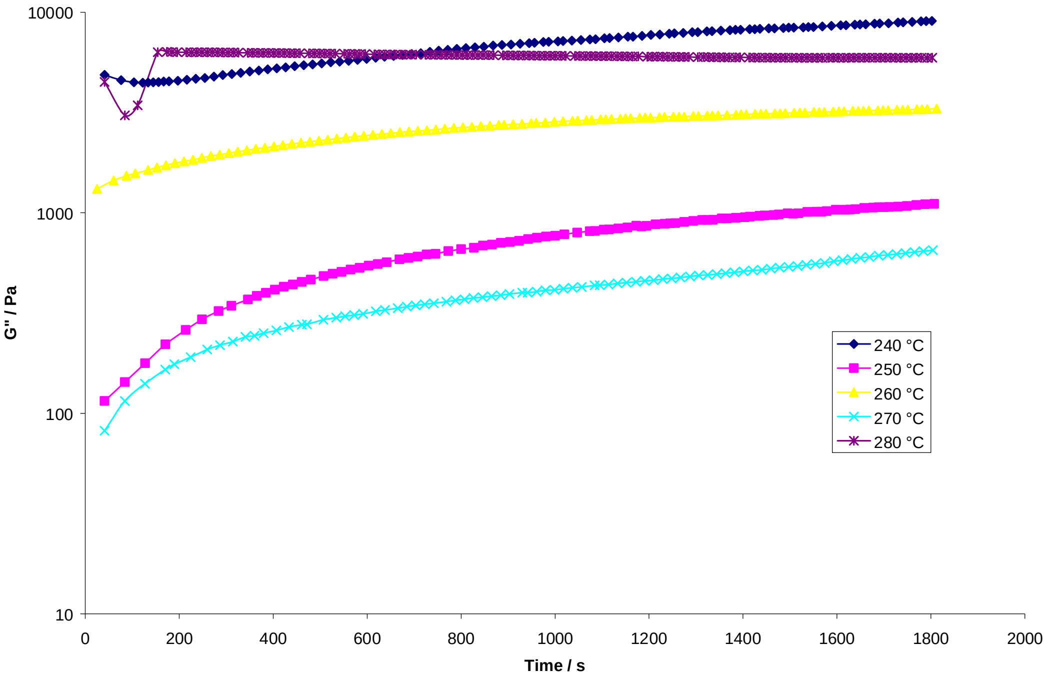

Figure 5-31 – PES-based co-polymer G" graphs at 10 rad s^{-1}

5-3-5 Flow Studies

In order to further study time dependent behaviour a fixed shear stress was applied to the polymers at a fixed temperature of 280°C. The stresses utilised to study the behaviour of the PES-based co-polymer were 100-900 Pa. The resultant graph can be seen in Figure 5-32. In all cases a fresh sample was used to study each stress. It can be seen that over time the viscosity increases. It can also be seen that the application of a higher stress also results in a higher viscosity. In order to determine if the results at each stress are reproducible a stress of 100 Pa was applied to a fresh PES-based co-polymer sample for four repeat runs. The resultant graph can be seen in Figure 5-33. It is seen here that there is a high degree of variation between the samples, with the viscosity varying between 168 Pa s to over 1000 Pa s. Again, the differences in the profiles are attributed to is the potential of microphase separation occurring within the sample, meaning that with the small sample sizes used it may not be possible to obtain the same molecular weight distribution of polymer molecules every time. In addition, it can be seen that there is a distinct ‘wobble’ to the graphs. After testing it was determined that this was not due to the misalignment of the plates, although the working of the entire instrument could not be fully tested to rule out instrument instability.

It has been suggested that a polymer can still be affected by its thermal history even up to 70°C above the T_g. Even though we are working at 80°C above the T_g, a study of the flow behaviour was also carried out at 290°C. In order to produce the same initial shear rate that was found for the material studied at 280°C, slightly lower stress were applied; 45, 140, 200, 400 and 525 Pa were used. In all cases, fresh samples were used to study each stress. The resultant graph can be seen in Figure 5-34. It can be seen, again, that the viscosity increases over time and also with the application of higher stresses.

It is important to determine if the huge sample variation behaviour seen up till now, was apparent when a larger gap was used. Therefore a study was undertaken where all experimental conditions were maintained, but a gap of 500 µm was utilised instead of the usual 250 µm. The stress applied was 100 Pa and three repeats were carried out on fresh samples. The resultant graph can be seen in Figure 5-35, where it can be seen that two repeats have very similar behaviour, with one sample having much lower viscosities. It is also seen that these two samples have an apparent drop in viscosity. This is attributed to inhomogeneity in the sample, and the loss of transient structure, rather than a shear thinning effect. It was anticipated that the effects of inhomogeneity in the sample would be less pronounced if a larger sample of material is used, unfortunately this was not found. This inconsistent behaviour, with an increase in viscosity followed by a break down of the structure, followed by a gradual rebuilding is consistent with stretching of the polymer, creating more interactions and therefore structure in the system.

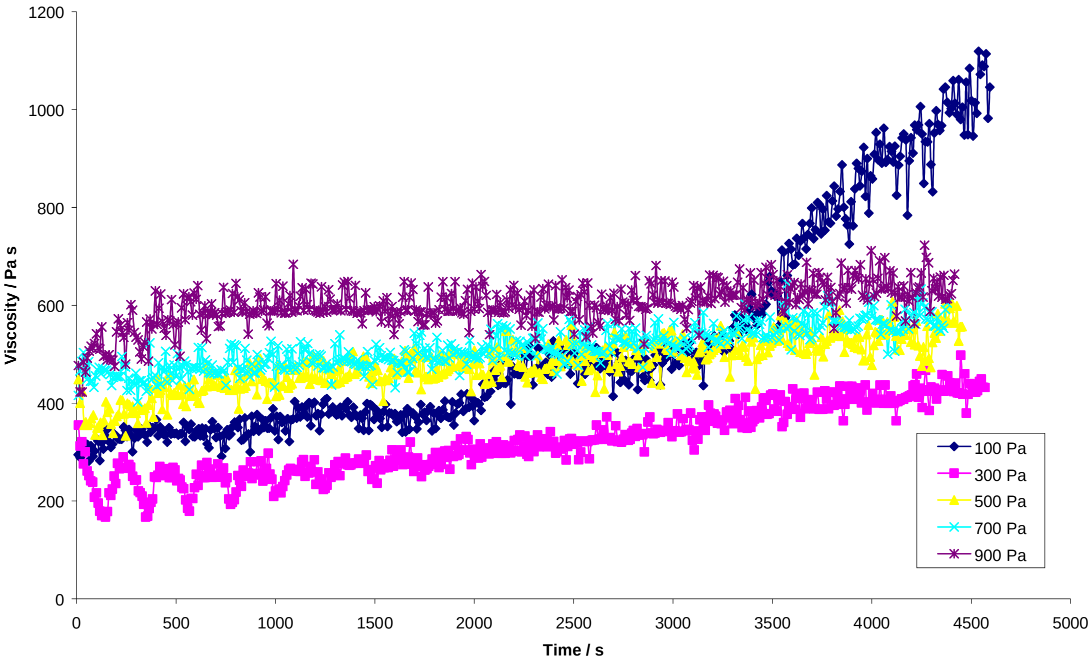

Figure 5-32 - Viscosity variance over time with various stresses applied at 280°C for the PES-based co-polymer

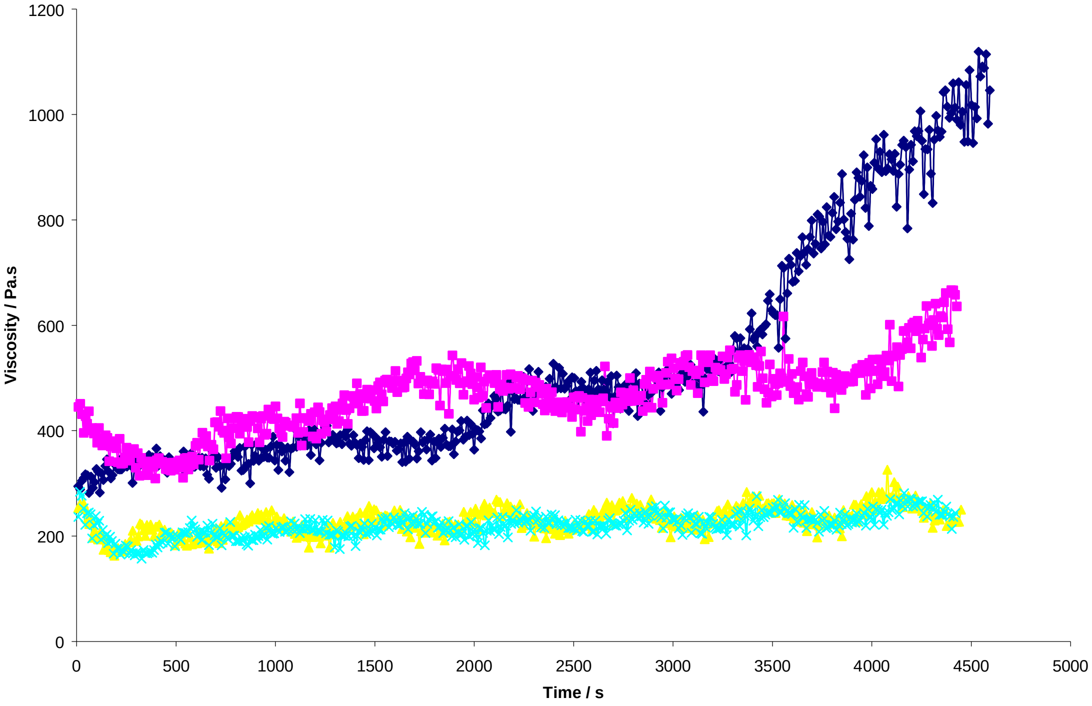

Figure 5-33– PES-based co-polymer repeats at 100 Pa

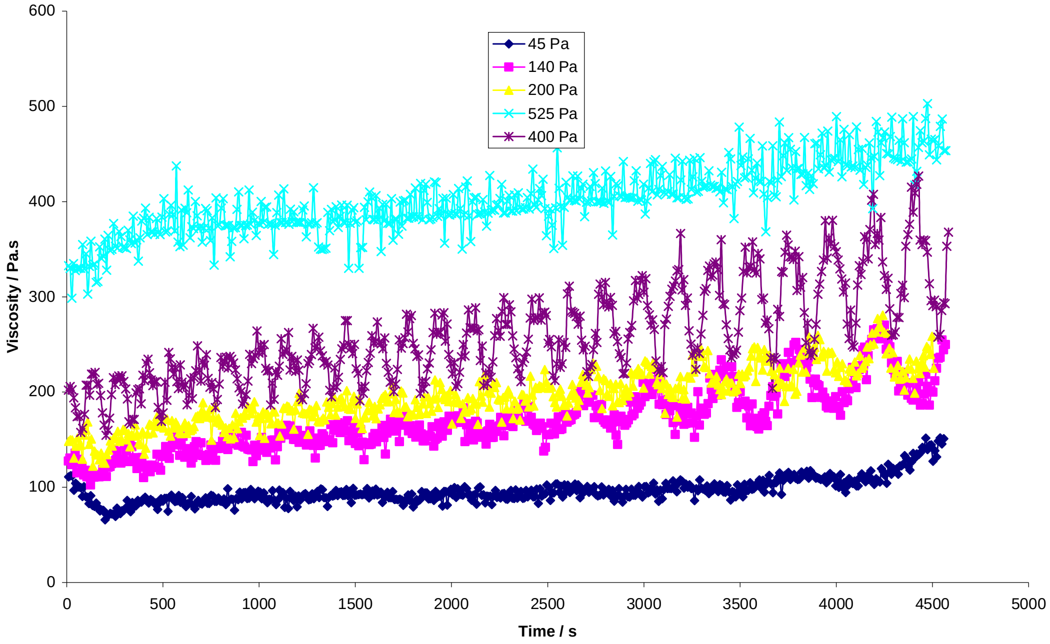

Figure 5-34 – Viscosity variance over time with various stresses applied at 280°C for the PES-based co-polymer

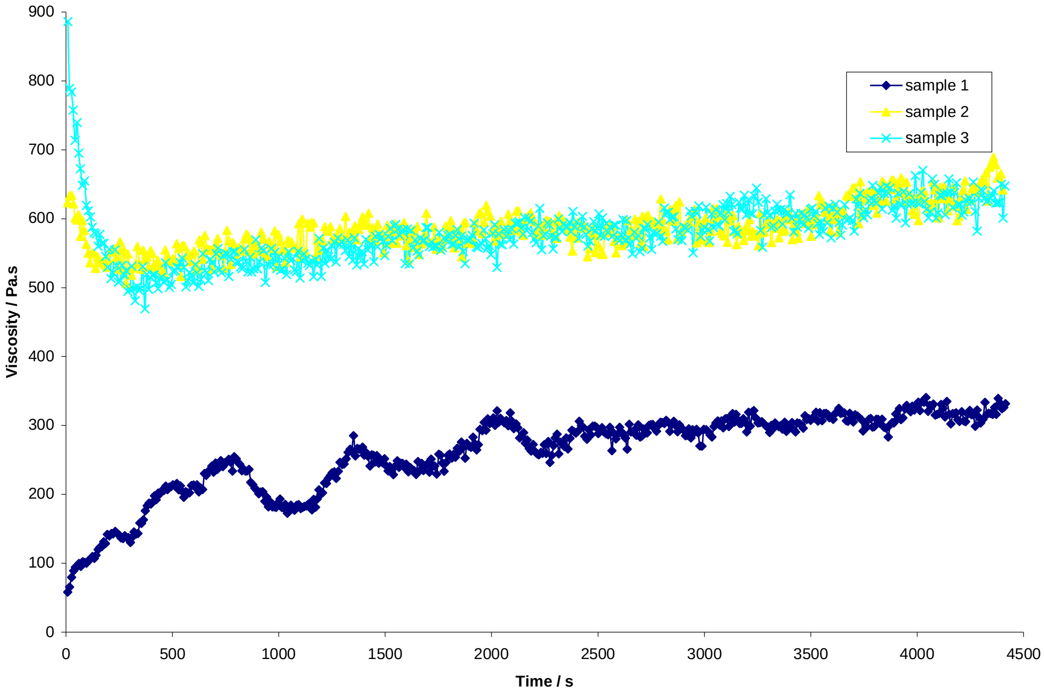

Figure 5-35 - Viscosity variance over time for the PES-based co-polymer at 100 Pa and 280°C – 500 µm gap was used in this case

The time dependent behaviour of the Radel A-100 was also studied at 280°C, see Figure 5-36. It was decided to try to maintain the same shear rates for both PES materials. With this in mind stresses were chosen to get shear rates of 0.35 and 1 s^{-1}. In this case 6,000 and 8,000 Pa were the necessary stresses; this is in comparison to 100 and 300 Pa which were the necessary stresses used in the case of the PES-based co-polymer. It can be seen, again, that much higher viscosities are produced, 4,000-19,000 Pa s.

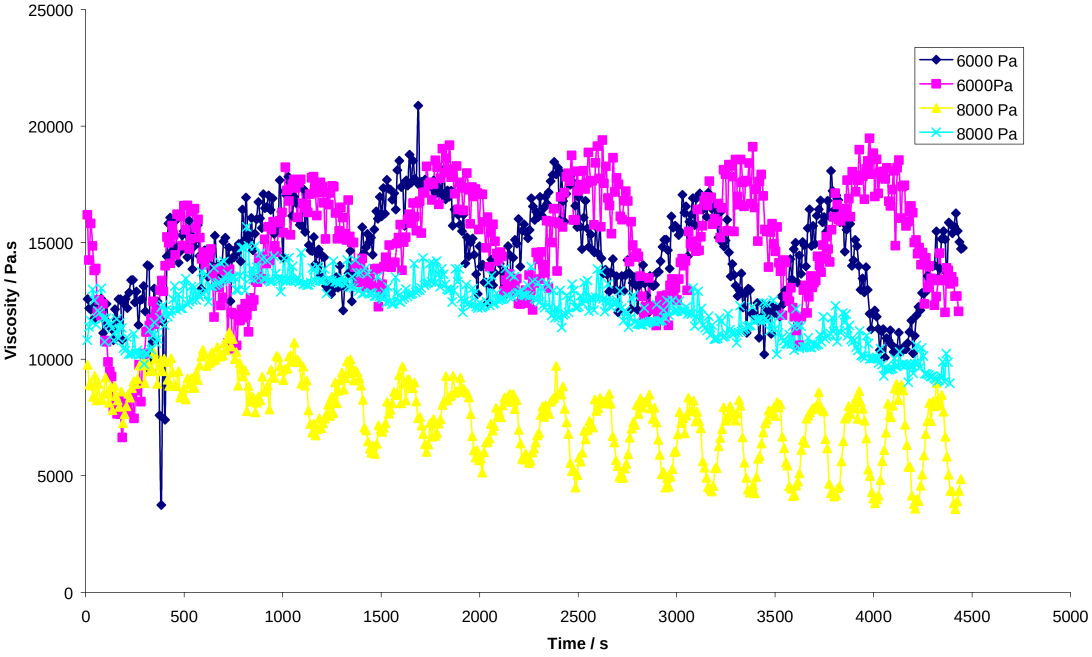

Figure 5-36 - Viscosity variance over time with various stresses applied at 280°C for Radel A-100

In order to further determine if the Strathclyde instrument was fully functional, it was decided to have the sample analysed by Anton Parr. The resultant graphs can be seen in Figure 5-37 and Figure 5-38. The data obtained by the Strathclyde instrument was showing erratic behaviour, which could be a consequence of instability in the sample, or of the instrument. The Anton Parr instrument uses a different control mechanism and may therefore be expected to behave in a different manner during the rheological measurements. In the case of the PES-based co-polymer it can be seen that as time increases the viscosity increases. The viscosity can also be seen to decrease with the application of increasing stresses.

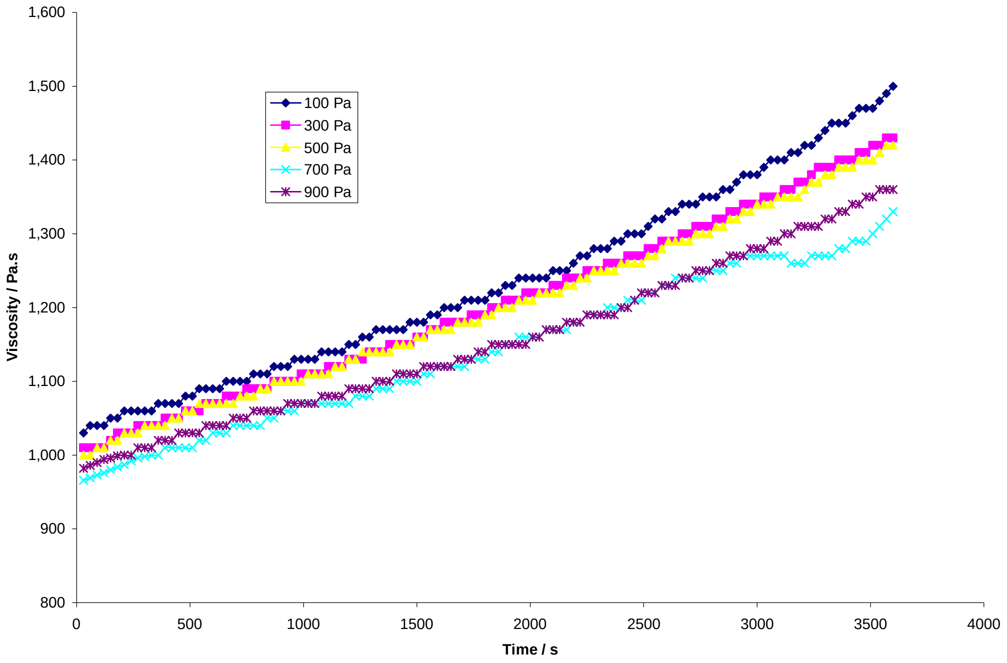

Figure 5-37– Viscosity variance over time with various stresses applied at 280°C for PES-based co-polymer (carried out at Anton Parr)

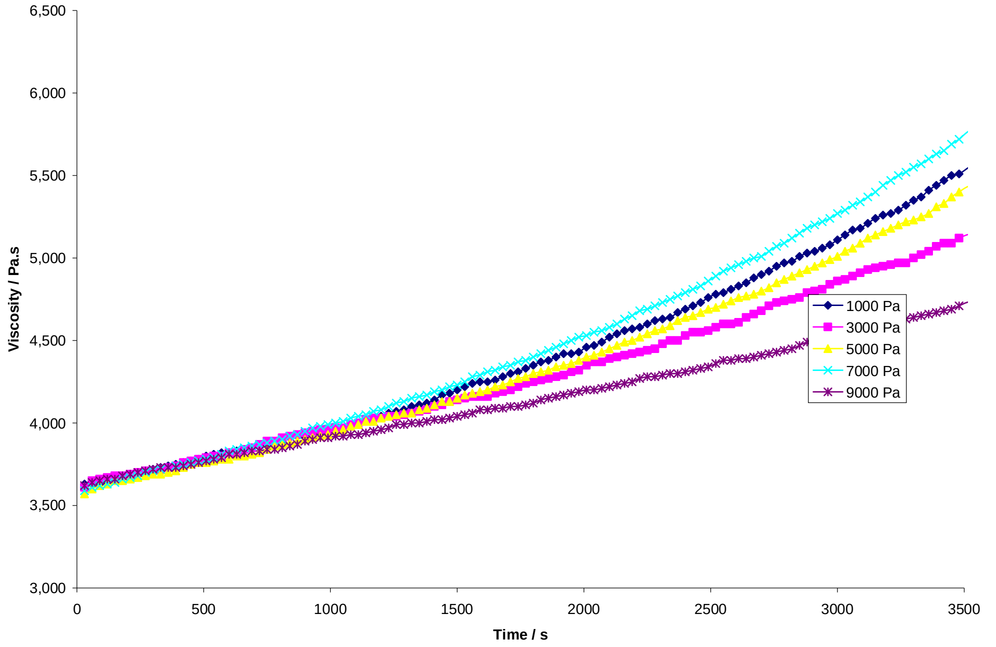

Figure 5-38 – Viscosity variance over time with various stresses applied at 330°C for Radel A-100 (carried out at Anton Parr)

When analysing the Radel A-100 sample at 280°C, it was observed that the sample was not in a fully flowing state; therefore the experiment had to be carried out at 330°C. This may be indicative of a problem with measurement of the highly viscous material with this type of instrument. Looking at the resultant graph it was again found that the viscosity increased with time, although there was not a steady decrease in viscosity at increasing stresses as would be expected. This is another indication that the rheology associated with the polymers is quite complex. The oscillatory behaviour reported in these measurements is clearly unreal and reflects possible resonance behaviour within the instrument, which is a consequence of the high values of the viscosity.

Increasing viscosity with time can often be a reflection of some form of chemistry occurring in the system. Oxidation can induce crosslinking, and this will be evident in a slowly increasing viscosity of the type observed. There is, however, also the possibility in these systems that the end functionality in the PES-based co-polymer can undergo reaction, increasing the molar mass; this increase in molecular weight was seen from GPC results.

In the case of Radel A-100; if the terminal chlorine were to be hydrolysed then coupling with a significant increasing in molar mass could occur, which would lead to increased viscosity of the melt. The changes which are occurring, however, are sufficiently small that they are unlikely to be detectable in terms of the molecular weight distribution of the polymer material.

For purposes of comparison, a sample of 10 % nanographite was also studied using the Strathclyde instrument; stresses of 300, 400 and 550 Pa were applied and the resultant graph can be seen in Figure 5-39. In addition a study was carried out to determine the effect of applying higher stresses, of 500-3,000 Pa; with the resultant graph seen in Figure 5-40.

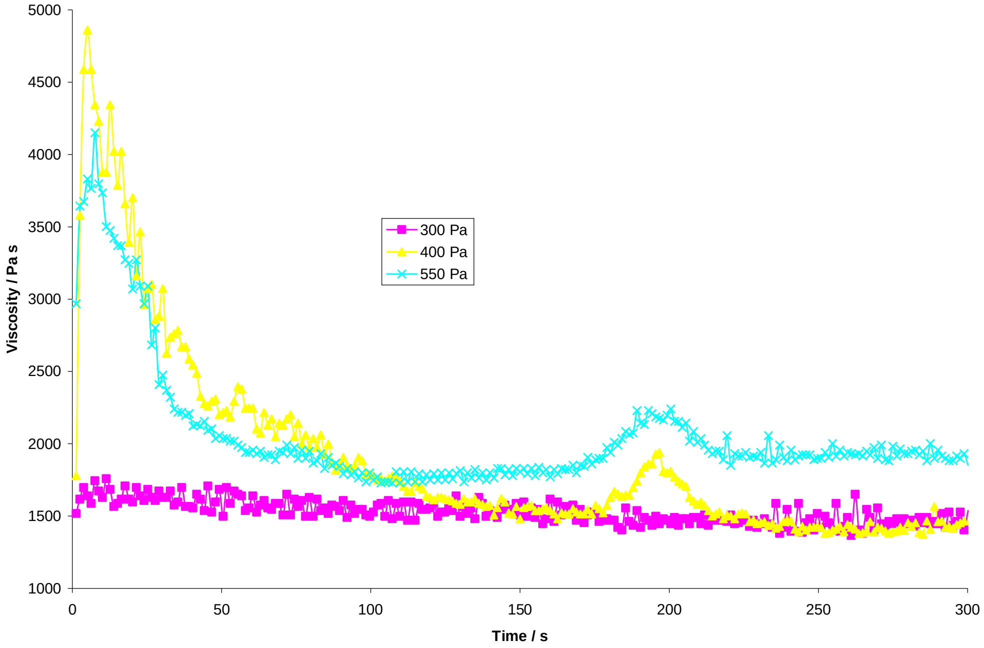

Figure 5-39 Viscosity variance over time with various stresses applied for 10 % nanographite / PES-based co-polymer

Figure 5-40 – 10 % nanographite viscosity variation at higher stresses

It is observed that, generally speaking, the viscosity of the samples decreases with the application of higher stresses, as would be expected. Viscosities of 10 % nanographite and the PES-based co-polymer were compared after 500 seconds, at the same temperature of 280°C, in order to determine if significant differences were seen. It was found that the viscosity of the PES-based co-polymer was 417 Pa s; when 10 % nanographite was added the viscosity was seen to rise significantly to 1,724 Pa s.

It is noted at this point that a comparison study was carried out to determine the mass of the PES-based co-polymer which can be extruded over a 1 minute period, with, and without the inclusion of nanographite. It was seen that the average mass of polymer which could be extruded, with a drive speed of 50 rpm was 7.5 g. With the addition of 10 % nanographite the average mass extruded, at the same drive speed, was 1 g. This is obviously a direct result of the increased viscosity which becomes apparent with increasing quantities of nanographite. In order to extrude a higher mass of sample it would be necessary to use a higher temperature, a higher drive speed or a larger die.

5-3-6 Creep

Creep tests are an easy way to determine the zero–shear viscosity of a sample. The test involves the application of a constant low stress to a material and the monitoring of the resulting deformation or strain, over the period of the test. The procedure followed required fifteen minutes of polymer retardation, followed by fifteen minutes of polymer relaxation, at 240°C. The retardation curves for the PES-based co-polymer are shown in Figure 5-41. Stresses of 1 Pa through to 20 Pa were carried out on the same sample. It can be seen from this graph that the curves are all close together, more so at the lower times, indicating that the material is in the viscoelastic region. It is also seen that both the initial elastic response and the delayed elastic response are very small. The material is exhibiting a stronger viscous response which is echoed in the relaxation curves displayed in Figure 5-42, where it is seen that there is no initial elastic recovery.

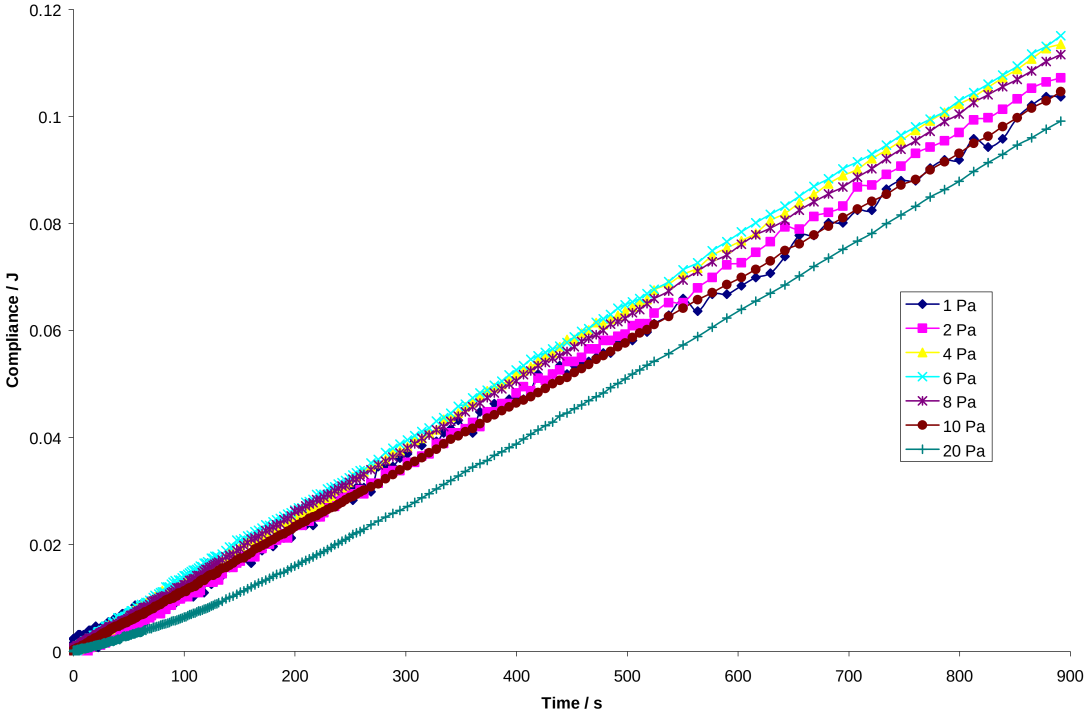

Figure 5-41 – PES-based co-polymer creep curves 15 minute retardation

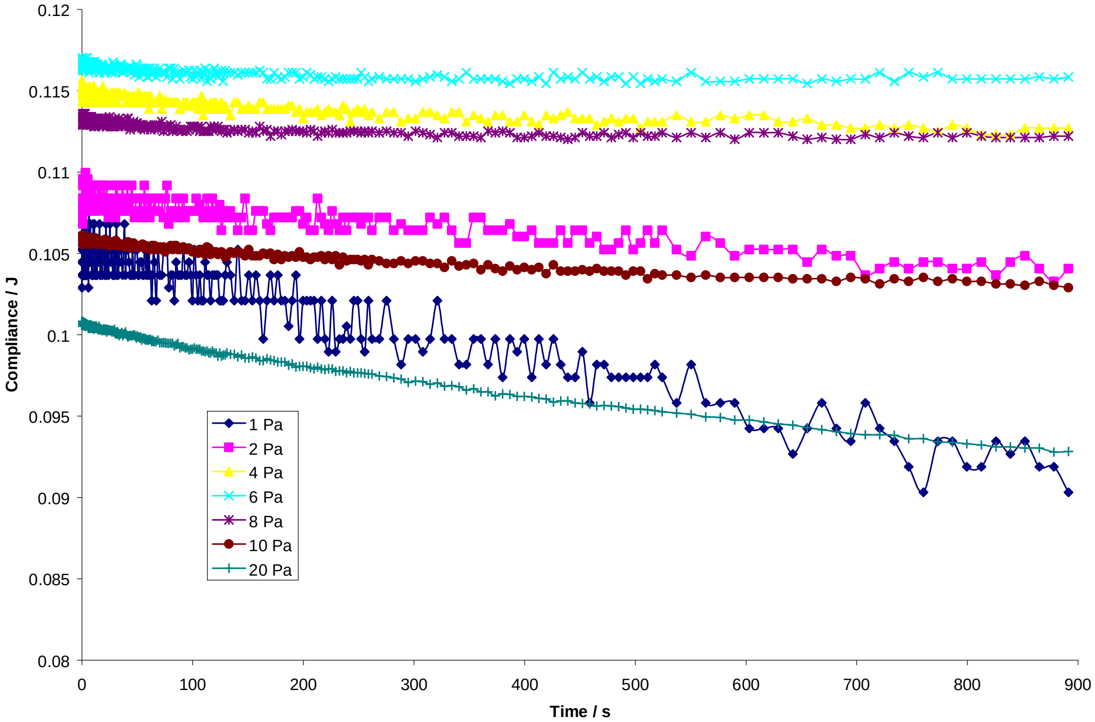

Figure 5-42 – PES-based co-polymer creep curves 15 minute relaxation

From the retardation curve of the PES-based co-polymer, is seen that at higher stresses (8-20 Pa) the curves reached equilibrium before the 15 minutes were finished. It should be noted that the higher stresses were measured first as the instrument was not able to reach the lower stresses in the first instance. There is a huge variation in the creep curves obtained at the various stresses, where one would expect them, in principle, to follow the same curve; thus indicating that the material is not in the viscoelastic region. The possibility of solvent evaporation must therefore be considered, as this would also lead to an increase in the viscosity of the material.

The PES-based co-polymer is showing yield stress behaviour, as exemplified by the increase in the compliance up to a given yield level and then a progressive decrease. The rate of decrease of the compliance with time also reflects a change in the nature of the relaxation processes occurring in the system. This may be a reflection of the end group effects on the rheological behaviour. In the case of the Radel A-100 where entanglement is likely to be the dominant factor a smoother and progressive change is observed over the range of conditions used in the study.

An exponential decay was fitted to the relaxation curves in order to determine the relaxation times of the polymers. The times can be seen in Table 5-4. It can be seen from this table that when one considers the Radel A-100, the relaxation times vary from 4,025-8,482 seconds, with a tendency for the time to increase with increasing stresses. One would expect that, within the linear viscoelastic region, the time would be essentially constant. When considering the PES-based co-polymer, it is seen that there is a huge variation in the reported relaxation times – going from 6,330-69,238 seconds. Again this suggests that the material is not within the linear viscoelastic region.

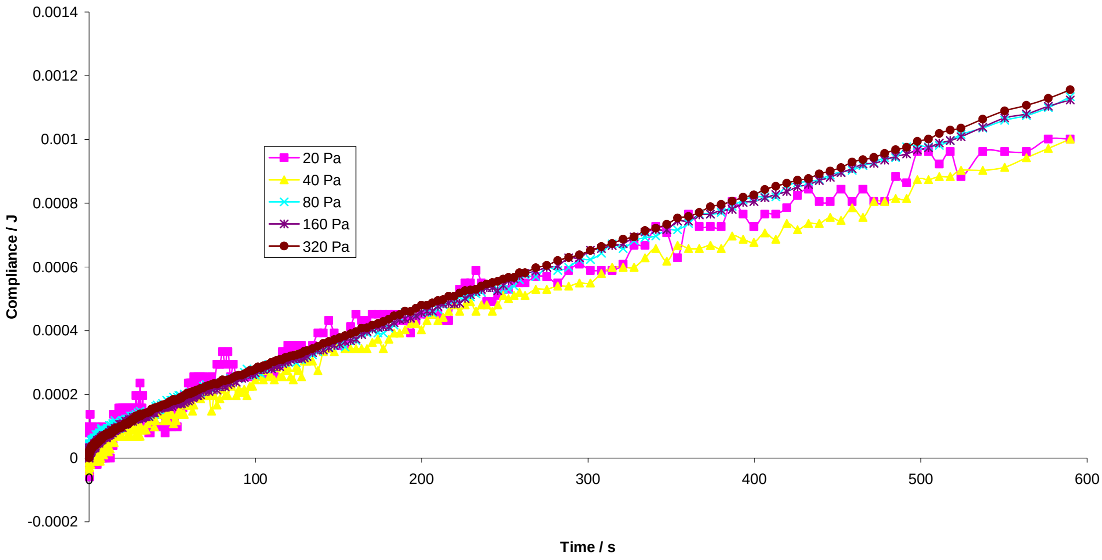

Figure 5-43 – Radel A-100 creep curves fifteen minute retardation

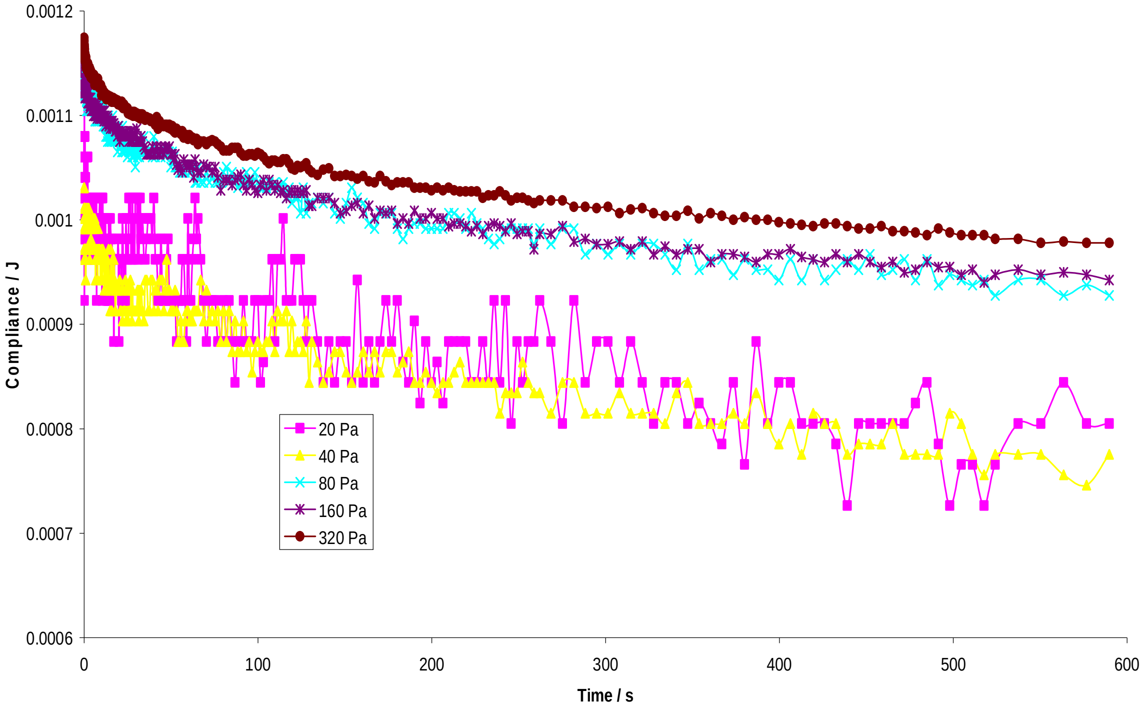

Figure 5-44 – Radel A-100 creep curves fifteen minute relaxation

Table 5-4 – Relaxation times of Radel A-100 and PES-based co-polymer

	Stress (Pa)	**Relaxation Time (s)**
Radel A-100	20	4,025
	40	3,438
	80	7,072
	160	8,482
	320	8,354
PES-based co-polymer	1	6,330
	2	19,579
	4	49,606
	10	69,238
	20	13,578

5-4 Conclusions

The rheological studies carried out indicate that the materials are showing a high degree of viscsoelasticity and are also unstable as a consequence of a number of factors; the effects of entanglement, possible further polymerisation and transient aggregation in the melt. It is known that close to the melt temperature, transient aggregates enhanced by end group interactions can be formed which will act rather like entanglements and can be sensitive to the level of the shear stress. It is possible that this may partly explain some of the transient behaviour observed with these materials. In addition, there would appear to be significant rheological variations in samples which are caused by molecular weight affects and, in the case of the PES-based co-polymer, the possibility of end group reactions. The possibility of reactions occurring at these elevated temperatures cannot be eliminated, and these rheological studies indicate there may be serious implications when considering extrusion as a potential processing technique. There exists the possibility that even fibre flow may not be possible as the polymer goes to a fine thread, with this effect becoming increasingly more apparent with the inclusion of nanographite.

5-5 References

1. R.A. Pethrick, *Polymer Structure Characterisation - From Nano to Macro Organisation.* 2007, RSC Publishing