

New Rapid Method for Testing Thermoplastic Elastomers

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Abstract: In the last two decades, thermoplastic vulcanizates (TPVs) and other thermoplastic Elastomers (TPEs) have significantly increased their usage in the rubber industry. New concerns regarding variability in processing characteristics and product performance have emerged and new methods to effectively and quickly predict these differences among different lots or different grades of TPEs have been developed using the Advanced Polymer Analyzer with parallel plate dies. Also this paper explores the advantages of different sample preparation techniques.

Key words: Advanced polymer analyzer (APA) rheometer, thermoplastic vulcanizates, thermoplastic elastomers.

1. Introduction

1.1 Styrenic Block Copolymers (SBC)

In the last forty years, thermoplastic elastomers (TPEs) have been continuously growing in usage throughout the world, in many cases replacing the use of traditional thermoset rubber compounds as well as thermoplastic resins such as flexible PVC. In the 1950s, one of the first TPEs that was developed was the Styrenic Block Copolymers (SBCs), which are based on polymeric blocks of styrene (as hard, glassy domain end blocks) and blocks of butadiene, or isoprene, or butylene, or ethylene (as soft rubbery domain mid blocks) [1]. These blocked polymer TPEs were limited in use by their melt transition for the polystyrenic domains which is around 100 °C. If a product made of one of these styrenic blocked copolymers was heated above 100 °C, even for a very short time span, it would quite literally melt.

1.2 Thermoplastic Polyolefins (TPO)

In the 1970's, thermoplastic polyolefins (TPOs)

came into the market. Commonly TPOs are blends of uncured or partially cured EPDM and polypropylene resin (PP). TPOs are used in rather large volume applications such as automotive bumper fascia and automotive exteriors [2]. While TPOs are used in high volume, they do not have the best compression set, oil resistance, and high temperature properties [3].

1.3 Thermoplastic Vulcanizates (TPV)

Thermoplastic vulcanizates (TPVs) are TPEs that are produced from a process called dynamic vulcanization (*in situ* curing of the rubber phase during mixing in a blend with a thermoplastic resin in a homogenous melt) [4, 5]. Dynamic vulcanization was first discovered by Gessler and Hasslet with Exxon Chemical Co. in 1958 [6, 7]. Further work on this concept was also completed by William Fischer with Uniroyal who developed the first commercial use of TPV based on partial curing of EPDM with polypropylene resin [8, 9]. However, the great commercial breakthrough for TPVs came through the work of researchers at Monsanto, who perfected a new generation of fully cured TPVs through a more efficient dynamic vulcanization procedure [11, 12].

The development of fully cured TPVs has had a

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great impact on the rubber industry. Basically the rubber and plastic used should have similar surface energies to be compatible. The closer that these surface energies are for the chosen rubber and plastic means the size of the droplets in the melted blend will be smaller before the dynamic vulcanization occurs. This also means that when these droplets of rubber become cured solid particles from the DV, these particles will also be small enough to assure relatively high ultimate tensile strength results [12]. Also it was found that crystalline plastic resins work best for strength. As a result, the marketplace found that the EPDM and polypropylene resin gave relatively good tensile strength and compression set for the economics. To a much lesser extent, PP was also used with IIR (butyl rubber) for air permeability resistance and NBR (nitrile rubber) for oil resistance [13]. (Because of the greater compatibility differences between EPDM and NBR, sometimes the resulting rubber particles from dynamic vulcanization for the NBR are not as small as the EPDM particles which could result in the NBR/PP TPV having a lower tensile strength (unless a compatibilizer is used).

1.4 Rheology of TPVs

The rheology of TPVs has been studied thoroughly. It has been reported that EPDM/PP TPVs are very shear thinning, possessing a high level of pseudoplasticity (measured viscosity decreasing rapidly with an increase in applied shear rate). On the other hand these same studies show much less drop in viscosity from a rise in processing or test temperature [14, 15]. Also, unlike the polypropylene resins, there does not appear to be any significant zero-shear plateau region for these TPVs. For the most part, they appear to be smooth extruding with relatively low die swell values [16-18].

1.5 Assignable Causes of of Variation Among TPVs

The TPVs from EPDM and polypropylene are usually complex composites. The following quality variables

can affect either their processing (flow) properties, and/or their solid mechanical properties [19-24].

1.5.1 Variation in the Ratio of EPDM Rubber to Polypropylene Resin

Decreasing this rubber to resin ratio will usually result in a harder solidified TPV at room temperature with a higher moulus and poorer compression set. Also changing this rubber to resin ratio will affect its polymer melt rheology.

1.5.2 Variation in the Curative Concentration for Dynamic Vulcanization

Decreasing the curative concentration for dynamic vulcanization with all other factors remaining constant can result in larger dispersed rubber particle sizes causing a lowering of the processing viscosity and a reduction in ultimate tensile strength.

1.5.3 Variation in DV Temperature

Increasing the temperature during dynamic vulcanization significantly above the optimal temperature can cause a larger particle size for the cured rubber phase because the higher temperature can reduce the shearing forces (lower viscosity) while enhancing the cure kinetics causing the cured particles to form faster while still relatively large.

1.5.4 Variation in the Quality of the Rubber Itself (Such as Variation in Mooney Viscosity, Percent ENB, or Ethylene)

A lower Mooney viscosity (or average molecular weight) rubber or a less reactive rubber (lower ENB content) can result in a lower crosslink density and larger cured particles yielding a lower viscosity TPV.

1.5.5 Variation in the Concentration or Type of Oil Used

Using a higher loading of paraffinic oil may have some effect, but a lesser effect on processing viscosity and solidified hardness. (Commonly EPDMs used to make TPVs may contain up to 50 % paraffinic oil).

1.5.6 Filler Effects

Some economical diluent fillers may have small effects on processing and solidified physical properties.

1.5.7 Resin Effects

Different grades of polypropylene have different average molecular weights and crystallinity, which can effect both the processability as well as the physical properties of the solidified TPV at room temperature.

1.6 The New "Super TPVs"

With the expiration of the original composition patents around the year 2000, a whole new series of TPVs have been marketed. New "Super" TPV series have come to the marketplace. For example, Zeon Chemicals has introduced a new series of polyacrylate rubber / Nylon TPVs with very good oil resistance and high temperature properties [25, 26]. Also ExxonMobil Corp. is introducing a new TPV based on BIMSM (rubber) with Nylon to create a thinner protective barrier for tires in order to eliminate the conventional halobutyl innerliner [27].

1.7 Testing TPEs for Processability

The traditional processability test for TPEs has been the capillary rheometer., The capillary rheometer can be a very effective method for measuring the processability of TPEs; however the capillary rheometer typically takes five times longer to complete a single test compared to the new Advanced Polymer Analyzer (APA) and the VTM Rheometer (for Viscosity, Temperature Transition, and Modulus) which are much faster. A fast and effective way of characterizing TPEs is needed in order to assure consistent quality.

2. Experiments

Much of the testing performed in this study was done with the Alpha Technologies APA 2000® Advanced Polymer Analyzer. The APA is very similar to the RPA 2000® Rubber Process Analyzer, except that it possesses the software and hardware to test with parallel plate dies instead of only biconical dies. The parallel plate dies are used for TPE testing because when cooling the specimen from the hot melt, parallel plate dies allow for even cooling across the interface as the specimen solidifies, which does not happen as well with the biconical dies. Also when testing TPE hot melts, there occasionally are times when the ring procedure needs to be used to assure that sufficient sample pressure is maintained so that slippage does not occur [28]. Fig. 1 gives a profile of the die design for the APA.

The lower die is attached to a high tech robotic motor that is programmed to oscillate sinusoidally against the rubber specimen as shown above. The upper die is connected to a reaction torque transducer and measures the complex torque response (S^*) and the phase angle (δ). These measurements go into a Fourier transform to calculate the pure elastic torque response (S^*) and the pure viscous torque response (S^*). This is illustrated in Fig. 2 below.

For parallel plate dies, the relation between torque and shear modulus is shown below.



Fig. 1 APA dies closed.



Fig. 2 Applied sinusoidal strain and resulting stress response.

$$T = \left[\frac{\pi R^4}{2L}\right] G^* \theta \qquad (1)$$

where T = Torque, L = Sample Thickness, R = Die Radius, G^* = Complex Shear Modulus, θ = Strain (radians).

This equation can be rearranged as follows:

$$G^{*} = \frac{T}{\left[\frac{\pi (20.63mm)^{4}}{(2)(2.576 mm)}\right]\theta}$$
(2)

So quite simply shear modulus G (in kPa) can be calculated from the torque (in dNm) if the die gap is set for 2.58 mm by the following simplified equation.

$$G = (54.1 * Torque)/(Strain in Degrees Arc)$$
 (3)

Also every \pm 1.0 degree arc strain is equal to \pm 14% strain. However, the APA/VTM systems have the option to key in the actual sample thickness at the end of a test. This ensures a more accurate viscosity/ modulus calculation.

Much of this work was performed using the so called "105 procedure" for TPE testing. This procedure requires that the sample be quantitatively weighed to \pm 0.02 grams of the target sample weight, which is equal to 105% of the fill factor for the APA die cavity. The 100% cavity fill factor can be empirically determined by simply testing a sample from the sample series that has a weight greater than the 100% fill factor. After completing this APA test, the test specimen is carefully removed from the cavity, the film is carefully removed, and the flash is carefully cut away from this specimen. Then this sample is weighed to the nearest one hundredth of a gram. This weight is then multiplied by 1.05 to determine the target weight for all future tests for this TPE series of materials.

The APA test configurations (test programming) were setup to condition the TPE samples at an appropriate melt temperature, followed by a frequency sweep at 7% strain and a strain sweep at 0.1 Hz, all performed at this same melt temperature. After these polymer melt measurements, the APA was programmed to reduce the temperature quickly, usually

to 60° C in order to measure the solid dynamic properties of the TPE. Sometimes this temperature transition was made with the use of the VTA (Variable Temperature Analysis) subtest which takes more time, however, can provide important information concerning the recrystallization or resolidification rates which is relevant to production molding quality [29].

This APA Technology can also be utilized as the Alpha Technologies VTM[®] Rheometer which is shown in Fig. 3 below.

This VTM is an automated "viscosity, transition, modulus" rheometer. Just as with the APA, the VTM can measure the viscosity, the thermal transition, and the modulus of TPEs and other thermoplastics as well [30].

In addition, testing was also conducted on the Alpha Technologies ARC 2020 capillary rhometer to compare the viscosity measurements from the APA with those measured by the capillary rheometer under conditions of steady state shear.

Three separate series of tests were conducted that included four different commercially available EPDM/polypropylene TPVs of differing hardness, four different styrenic blocked copolymer (SBC) based compounds, and five different acrylic rubber/Nylon TPVs.



Fig. 3 Alpha Technologies VTM® Rheometer.



Fig. 4 Alpha Technologies ARC 2020[®] capillary rhometer.

3. Discussion

A series of measurements were performed on the rheological properties of the TPEs in their melt state and their dynamic properties in their congealed solid state.

3.1 EPDM/Polypropylene Thermoplastic Vulcanizates

Fig. 5 displays the differences in shear thinning profiles observed from the complex dynamic viscosity (η^*) measurements obtained from 10-point frequency sweeps of the polymer melts at 215 °C.

The APA frequency sweep is a very rapid method for measuring differences in shear thinning profiles among grades of TPVs. All TPEs are non-Newtonian, meaning that their viscosity (or resistance to flow) will decrease with a rise in applied shear rate (such as a faster extruder speed, etc.). By using the Cox-Merz Rule, one can assume that 1 radian/second under sinusoidal oscillation is equivalent to 1 s under steady state flow conditions (such as with a capillary rheometer or a factory extruder) [31, 32]. From this study, it can be seen that different grades of EPDM/PP TPVs possess differing degrees of this shear thinning quality (also called pseudoplasticity). As can be observed from the APA data, the D40 TPV has lower viscosity and a flatter shear thinning profile when compared to the other EPDM/PP TPVs studied. However, if one were to extrapolate toward a higher shear rate, one might predict crossover where D40 TPV may actually have the higher viscosity at very high shear rates instead of having the lower viscosity at low shear rate. This extrapolation is further supported from Fig. 6 which shows the real dynamic viscosity (η') plotted against frequency in radians per second.

Further support for this crossover of the D40 TPV is shown again for these four commercial TPVs in Fig. 7, where they are tested on the ARC 2020 capillary rheometer, which can apply a higher range of shear rates than the APA can apply.

Fig. 7 shows that from comparing the EPDM/PP TPV grades over a wider range of shear rates with the



Fig. 5 EPDM/PP TPV test series APA frequency sweep of melt at 215 °C, 7% strain.



Fig. 6 EPDM/PP TPV test series APA frequency sweep of melt at 215 °C.



Fig. 7 Capillary rheometer ARC 2020 at 210 °C, L/D 20:1, 3/8 inch barrel.

capillary rheometer, the TPV grades which are esigned to impart higher durometer hardness values in their product applications also are higher in viscosity than the other grades at high shear rates, but lower in viscosity than the other grades at low shear rates. In other words these high durometer hardness TPVs are flatter in their shear thinning profiles.

Most commercially available EPDM/PP TPVs are proprietary in nature; however there is a general belief that TPVs with higher durometer hardness values will usually also have higher viscosity as a melt at high shear rates [33]. Also it is generally felt that higher durometer EPDM/PP TPVs usually contain more polypropylene in relation to the EPDM rubber content. If it is true, at low shear rates the polypropylene melt functions somewhat like a "lubricating agent" at low shear rates. Therefore at low shear rates, the particles of vulcanized EPDM rubber are spaced more widely apart and are more free to move, resulting in a relatively lower viscosity. However, these TPVs are actually heterogeneous nanocomposites of vulcanized EPDM particles (representing the discontinuous phase) dispersed in the polypropylene continuous phase. The other "softer" TPV grades contain more of the dispersed, vulcanized EPDM rubber particles which imparts more of a pseudoplastic (shear thinning) effect on the TPV at higher shear rates, causing it to drop its viscosity faster than TPVs (such as the D40 grade), which are not as shear thinning at the higher shear rates. This may explain why the ordinal relationship for ranking of viscosity values becomes inverted when a comparison is made between low shear rate measurements vs. high shear rate measurements. This results in "crossovers" for both the APA profiles as well as the capillary rheometer profiles. However, as discussed in the "Introduction", there are at least six other ways of compounding TPVs to achieve different durometer hardness values as well as other physical properties (besides changing the EPDM/PP ratio). These alternate changes will affect the rheology of the TPV grades differently. Some of these adjustments

might explain the crossovers between TPV A35 and TPV A73 for example. Maybe it is an adjustment in oil content, for instance.

Fig. 8 below compares the elastic quality of the polymer melts for the four EPDM/PP TPV grades tested.

In a broad sense, EPDM/PP TPV grades with a higher weight fraction of vulcanized rubber particles will probably have a higher elasticity in the polymer melt state. Probably TPV D40 has a lower concentration of dispersed particles of crosslinked EPDM rubber.

The tan δ response (G''/G') from the frequency sweep of these four TPVs is shown.

Because TPV D40 has a low elastic response for its polymer melt, it also gives a relatively high tan δ value as well.

In addition to the ten-point frequency sweep, a four-point strain sweep was also performed at only 0.1 Hz (a low shear rate) as shown in Fig. 10.

Here it is clear that at this very low shear rate, the complex viscosity for the TPV D40 is much lower than the other EPDM/PP TPVs tested. This further verifies what we observed in the low frequency region of the frequency sweeps discussed earlier, i.e., that the very high hardness TPV grades show the lowest viscosity at very low shear rate (just the opposite of what happens



Fig. 8 EPDM/PP TPV test series, APA frequency sweep of melt at 215 °C and 7% strain.



Fig. 9 EPDM/PP TPV test series, APA frequency sweep of melt at 215 °C and 7% strain.



Fig. 10 Strain sweep of EPDM/PP TPVs at 0.1 Hz, 215 °C.

at high shear rate conditions).

After measuring processability properties of the polymer melt at 215 °C, the APA was programmed to lower the sample temperature to 60 °C, and after a three minute delay (to allow time for the test specimen to completely congeal), a strain sweep was performed. Fig. 11 shows the storage modulus values of the congealed specimen at 60 °C.

It is well known that the durometer hardness scale is logarithmic [34]. So when measured storage modulus values of the congealed specimens are plotted on a log scale vs. applied strain, the resulting plots are evenly spaced apart (as shown above) in relation to their nominal durometer hardness values. These measured APA G' values correlate very well with the durometer hardness rating for these commercial TPV grades examined in this study.

Also Fig. 12 shows the measured tan δ values for the congealed TPV specimens at 60 °C from the same strain sweep.

It can be seen that at the higher strains, the TPV D40 (highest hardness) has a much higher tan δ and is much more hysteretic than the other TPVs. This is probably because this D40 TPV contains a lower concentration of vulcanized rubber particles and a higher concentration of polypropylene (plastic). On the other hand, at very low strains (less than 2%), there is



Fig. 11 The G' response for first strain sweep after congealing of EPDM/PP TPVs at 1 Hz, 60 °C.



Fig. 12 The tan δ response for first strain sweep after congealing of EPDM/PP TPVs at 1 Hz, 60 °C.

crossover where the D40 TPV is actually lower in congealed tan δ . The TPV D40 grades may still be below a "critical strain (at less than 2%) for the continuous polypropylene phase with high hardness grades in the low strain region. This effect is more noticeable with high hardness grades which usually contain higher concentrations of the polypropylene continuous phase. If the strain is below the "critical strain" of the polypropylene phase, then the applied energy is returned more efficiently because of high elasticity that still exists in this low strain region.

Also we ran "back to back" repeat strain sweeps to measure the "strain softening" effects. Fig. 13 shows the measured strain softening effects.

As can be seen, all the EPDM/PP TPV grades possessed some strain softening properties. We quantified both the Payne Effect (the drop in modulus with a rise in strain) as well as the Mullins Effect (the drop in modulus as measured with the second strain sweep immediately afterwards). The TPV A35 TPV appears to have the greatest strain softening effect.

Fig. 14 shows the effects of strain softening on tan δ .

In Fig. 14, it is very obvious that the strain softening effects causes the measured tan δ value to rise significantly with the second "back-to-back" strain sweep. On the second strain sweep, the EPDM/PP TPVs are actually more hysteretic (more energy absorbing. This is another method for quantifying the Payne and Mullins effects.

Fig. 15 is a master G' modulus curve showing the overall relationship of these modulus values from the polymer melt stage at 215 °C with the frequency sweep and strain sweep, followed by the congealed modulus values at 60° C from two back-to-back strain sweeps.

Fig. 16 gives an estimate of the statistical test sensitivity and repeatability from replicate testing for processability measurements of the polymer melt at 215 °C vs. the dynamic property measurements of the congealed specimens at 60 °C

The instrument repeatability was measured by calculating the coefficient of variation (CV) from the



Fig. 13 Strain softening effect from first and second "back to back" strain sweeps congealed EPDM/PP TPVs at 1 Hz, 60 °C.



Fig. 14 Strain softening effect from first and second "back to back" strain sweeps congealed EPDM/PP TPVs at 1 Hz, 60 °C.



Fig. 15 Master curve of the G' response from the polymer melt at 215 °C to congealed solid at 60 °C.



Fig. 16 (a) 105% fill factor APA method frequency sweeps at 7% strain at 215 °C for repeats of EPDM/PP TPVs, (b) 105% fill factor APA method frequency sweeps at 7% strain at 215 °C for repeats of EPDM/PP TPVs at 60 °C with repeats.

replicate tests. CV is equal to 100 times the pooled standard deviation Sp (from replicate tests) divided by the grand average. As can be seen, the complex viscosity measurements of the polymer melts at 215 °C (to quantify processability) gave a CV of 4.0 % compared to a CV of 2.4% for the congealed modulus measurements at 60 °C.

On the other hand statistical test sensitivity measurements in accordance with ASTM D6600 Standard Practice were carried out. This is a traditional way to measure the sensitivity of an instrument and is calculated from the signal-to-noise ratio (S/N). A higher S/N value means the greater the discriminating power of the APA test parameter. The signal is calculated from the difference between the highest average and the lowest average value. The noise is calculated from pooling the standard deviations of each of the replicate tests performed. For a test parameter to be effective at discerning real differences among a group of TPVs tested, it should have a S/N equal to or greater than 6. In our experiment with the four different EPDM/PP TPV grades, we calculated a S/N equal to 26.8 for the processability viscosity differences at 215 °C for the polymer melt, and a S/N equal to 156 for the congealed modulus values at 60 °C for these same TPV samples. So for both processability and congealed physical property measurements, the APA gave very good statistical test sensitivity.

3.2 Styrenic Block Copolymer Thermplastic Elastomers

Fig. 17 shows the complex dynamic viscosity η^* profiles from APA frequency sweeps of the styrenic blocked copolymer TPE grades with nominal hardness of Shore A values of 46, 58, 60, and 91.

These SBC TPE grades are composed of differing proprietary formulations of polymer and fillers, but no oil. The polymer base is either a hydrogenated midblock of ethylene/butylene with styrene end blocks (SEBS), or a midblock of butadiene with styrene end blocks (SBS). Through compounding, these polymers are formulated to a specific hardness target. As can be seen from Fig. 17, these different compounds possess differing degrees of shear thinning quality as polymer melts (the decreasing of viscosity with a rise in shear rate). It may also be noted that this comparison with the SBC TPE grades does not show directly any crossover as was observed with the EPDM/PP TPVs in Fig. 5.

Fig. 18 shows the differing degrees of melt elasticity that these SBCs possess.

As can be seen, even though SEBS 60A and SEBS 58A have about the same durometer hardness, the elasticity of their respective polymer melts is quite different. The SBS grade has the lowest melt elasticity.

Fig. 19 compares the tan δ values of the polymer melts.

These comparisons by tan δ can be used to predict differences in the ease of processing , extruding or injection molding.

Fig. 20 compares the SBC TPE grades by a high strain test to compare the viscosity values under low shear rate conditions (only 0.1 Hz in frequency).

This strain sweep of the polymer melts verifies the same ordinal relationship for viscosity noted in Fig. 17.

After the cool down and delay, Fig. 21 shows the measured G' elastic modulus values for the congealed SBC TPE specimens at 60 °C.

Since durometer hardness is on a logarithmic scale, the different hardness grades of SBC TPEs are better



Fig. 17 Thermoplastic styrenic block copolymers APA frequency sweep of melt at 200 °C, 7% strain.



Fig. 18 Thermoplastic styrenic block copolymers APA frequency sweep of melt at 200 °C, 7% strain.



Fig. 19 Thermoplastic styrenic block copolymers APA frequency sweep of melt at 200 °C, 7% strain.



Fig. 20 Thermoplastic styrenic block copolymers APA frequency sweep of melt at 200 °C, 0.1 Hz.



Fig. 21 The G' response for thermoplastic styrenic block copolymers APA strain sweep of congealed sample at 60 °C, 0.1 Hz.



Fig. 22 The tan δ response from thermoplastic styrenic block copolymers APA strain sweep of congealed sample at 60 °C, 0.1 Hz.

compared when the y-axis is logarithmic. Also the slight difference in hardness between the SEBS 58A and SEBS 60A is measured more effectively at the lower applied strains (> 2%). Therefore, lower strain measurements might be more sensitive to subtle differences in durometer hardness [35].

Fig. 22 shows the tan δ values of the congealed SBC specimens at 60 °C.

Compounding techniques have a large effect of the physical properties of these SBCs. For example, while the SEBS 5A and SEBS 60 A are very similar in hardness and the measured G' values in the

congealedstate, their respective tan δ values for the congealed state are quite different. Because of proprietary compounding differences, SEBS 60 A has a significantly higher tan δ (is more hysteretic) than the SEBS 58A.

Just as we discussed with EPDM/PP TPVs, these SBC TPEs are also subject to strain softening effects or Payne effects as discussed earlier with Figs. 14a and 14b. In the case of these SBC compounds, strain softening effects were observed as shown in Fig. 23.

As measured earlier, straining the congealed polymer TPEs the first time disrupts existing networks somewhat. So with the second strain, the tan δ is noticeably greater (more hysteretic than measured during the first strain). Just as with the TPVs, higher durometer SBCs tend to display more of this Payne Effect when compared to the lower durometer SBCs. As can be observed, the 91 durometer SBC shows a very significant rise in tan δ from the 2nd strain sweep vs. its value with the 1st strain sweep. On the other hand, the lower durometer (more "rubbery") SBC compounds show much less of this effect.

Fig. 24 is a master G' modulus curve showing the overall relationship of these modulus values from the polymer melt stage at 200 °C with the frequency sweep and strain sweep, followed by the congealed modulus values at 60 °C from two back-to-back strain sweeps.



Fig. 25 gives an estimate of the statistical test

Fig. 23 Strain softening effect from first and second "back to back" strain sweeps congealed SBC TPEs at 1 Hz, 60 °C.



Fig. 24 Master curve of the G' response from the SBC polymer melt at 200 °C to congealed solid at 60 °C.



Fig. 25 (a) 105% fill factor APA method frequency sweeps at 7% strain at 200 °C for repeats of SBC TPEs, (b) 105% fill factor APA method frequency sweeps at 7% strain at 200 °C for repeats of SBC TPEs at 60 °C with repeats

sensitivity and repeatability from replicate testing for processability measurements of the SBC melt at 200 °C vs. the dynamic property measurements of the congealed SBC specimens at 60 °C.

Test sensitivity and repeatability measurements for the EPDM/PP TPV grades were discussed earlier (reference Fig. 16). The same applies for the APA's performance when testing SBC thermoplastic elastomer based compounds shown in Fig. 25. By comparing Fig. 16 directly with Fig. 25, similar melt and congealed (solid) test sensitivity and repeatability parameters are observed.

3.3 ACM / Nylon Thermoplastic Vulcanizates

Five different commercially available acrylic rubber/Nylon thermoplastic vulcanizates were also selected for APA testing by the 105 fill factor method. Four of these commercial TPVs were injection molding grades with nominal Shore A hardness values of 60, 70, 80 and 90. The fourth one was an extrusion grade with a nominal target Shore A hardness of 90. Because Nylon has a much higher melt temperature (Tm) compared to polypropylene or polystyrene, the standard APA melt measurements were conducted at 250 °C. Also because nylon melts are known to be relatively low in viscosity, a strain of 50 % was applied in the initial frequency sweep instead of the 7 % used for the EPDM / PP TPVs and The SBC TPEs.

Fig. 26 gives the shear thinning profiles of the ACM/Nylon based TPV melts at 250 °C.

As can be observed, the extrusion grade has a flatter shear thinning profile than the injection molding grade of "equal" hardness. In some cases there is "crossover" among the grades of ACM/Nylon TPVs studied.

Fig. 27 compares the tan δ values for the polymer melts at 250 °C.

As can be seen, these different grades of ACM / Nylon TPVs display very different rheology caused by their different chemical compositions. Differences in the melt tan δ can lead to large differences in processing characteristics such as injection rates and



Fig. 26 ACM/Nylon TPV test series APA frequency sweep of melt at 250 °C, 50% strain.



Fig. 28 The G' response for ACM/Nylon TPV test series APA frequency sweep of melt at 250 °C, 50% strain.

extrusion die swell differences.

Fig. 28 compares the melt elastic modulus for the ACM/Nylon TPV grades studied.

Fig. 28 shows directionally that the higher the nominal hardness of the ACM/Nylon TPV usually means the lower the melt elasticity (probably because there is less rubber content). Also there is a very large difference in the amount of elasticity in the melt of the injection molding grade vs. the extrusion grade for the same durometer hardenss target.

Fig. 29 shows low shear rate complex viscosity measurements made through high strain sweeps at low frequency.



Fig. 27 The tan δ response for ACM/Nylon TPV test series APA frequency sweep of melt at 250 °C, 50% strain.



Fig. 29 ACM/Nylon TPV test series APA strain sweep of melt at 250 °C, 0.1Hz.

At these relatively low shear rates, the high durometer TPVs (probably containing more Nylon resin) show lower viscosity values.

Fig. 30 compares the G' elastic modulus values for the ACM/Nylon TPV grades after congealing. These measurements are made at 60 $^{\circ}$ C

As can be seen, the higher nominal hardness grades of ACM/Nylon TPVs impart higher congealed G' elastic modulus values at 60 °C. Also the measured elastic modulus values decrease somewhat when going from low strain to high strain.

Fig. 31 compares the congealed tan δ values at 60 °C.



Fig. 30 First strain sweep congealing of ACM/Nylon TPV at 0.1 Hz, 60 °C.



Fig. 32 Strain softening effect from first and second "back to back" strain sweeps ACM/Nylon TPVs at 1 Hz, 60 °C.



Fig. 33 Strain softening effect from first and second "back to back" strain sweeps ACM/Nylon TPVs at 1 Hz, 60 °C.



Fig. 31 First strain sweep congealing of ACM/Nylon TPV at 1 Hz, 60 °C.

Probably because of the higher nylon resin content, the higher durometer grades tend to have higher tan δ values (more hysteretic) at the higher strains than grades with lower nominal hardness.

After the first strain sweep was performed on the congealed specimens at 60 °C, a second strain sweep followed immediately. Fig. 32 shows the differences in elastic modulus from the first strain sweep and the second strain sweep (called strain softening).

As can be observed, there is a significant strain softening effect between the first and second strain sweeps for the congealed specimens. In fact the extent of strain softening for these ACM/Nylon TPV grades appears to be greater than what we observed for the EPDM/PP TPVs measured at the same temperature (60 °C). Also the strain softening effect appears to be more consistent for the ACM/Nylon TPV grades, whether they are of a low durometer grade or a high durometer grade.

Fig. 33 shows the strain softening effects as measured with the tan δ .

As can be seen with each grade, the tan δ value increases significantly from the first strain sweep to the second strain sweep because of the Payne effect discussed earlier. From observing the changes in tan δ , it appears that the strain softening effects are rather



Fig. 34 Master curve of the G' response from the polymer melt at 250 °C to congealed solid at 60 °C.

large for these ACM/Nylon TPVs, especially for the grades with higher nominal hardness values.

Fig. 34 shows the master curve of the G' response which includes measurements from the polymer melts at 250 °C and the measurements of the congealed solid at 60 °C.

Unlike the earlier master curves, this one for the ACM/Nylon TPV grades in the polymer melt stage was measured in a frequency sweep at 50% strain instead of the 7% strain.

4. Conclusions

A consistent test configuration and test method was established which has broad applicability across a broad range of thermoplastic elastomers.

This test procedure displayed very good statistical test sensitivity (discerning power) regarding TPE quality differences in both the melt state and congealed state, and very good test repeatability for both the melt state and the congealed state.

This system can measure changes in shear thinning profiles due to TPE compositional changes. Changes in melt elasticity caused by TPE compositional changes were effectively measured as well. The elastic modulus of the congealed TPE could be effectively measured by this test procedure. Hysteretic differences of the congealed specimens were also effectively measured. Differences in strain softening profiles of the congealed specimens were also effectively measured as well.

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