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# Compression Set Improvement of Thermoplastic Vulcanizates for High Temperature Tubing

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**Compression Set Improvement of Thermoplastic Vulcanizates for High Temperature Tubing**

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**Honors Research Project**

Submitted to

*The Honors College*

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## Executive Summary:

Despite existing since the 1980s, thermoplastic vulcanizate (TPV) materials have conventionally consisted of only a select few rubber-thermoplastic blends and cannot be used in applications that involve high temperatures or chemically aggressive environments. However, recent investigations at Parker Hannifin Corporation into developing TPV materials for high temperature and chemically aggressive environment applications have proven viable. These newly developed TPVs have the possibility of being a flexible, lightweight alternative to high operating temperature thermoset rubber tubing currently being used for power steering hose. Currently, these TPV materials consistently meet all required material properties for production of high-temperature tubing, except for compression set resistance. The focus of this honors project was determining what TPV compositions, cure systems, and curative levels lead to the lowest compression set values, while still maintaining other necessary TPV material properties.

The first step of this project was to determine the most compatible blends of polyamide thermoplastic (PA) and fluorocarbon rubber (FKM) that were then used for experimenting with different curative systems and curative levels for the TPV system. Sixteen different TPV compositions were investigated, consisting of four different polyamides, and four different FKMs, with attempted 60:40 volumetric ratios of rubber to thermoplastic. These TPV blends were made using a Brabender mixer in order to conserve material. From initial Brabender testing plasticized PA-12 and either a powdered FKM elastomer or a ground FKM elastomer blend were established as the components that should be focused on. Viton Curative (VC-50) was determined to be the best curative for the TPVs being developed since it melted very readily when added to the mixture allowing for more efficient mixing and greater extent of vulcanization of the TPV, along with acting as a processing aid due to its plasticizing properties.

TPV materials made on the Brabender mixer would be ground up and then fed through a single screw extruder that utilized a flat die extruder to make tape extrusion samples. These tapes would then be tested to ensure that density, tensile and proper morphology were being achieved before any compression set testing was to be done. Tape extrusion samples were cut using a hydraulic press and a die to create samples that were then used for tensile property testing in an MTS tensiometer. Proper TPV morphology was determined by using atomic force microscopy (AFM) to image cross-sections of TPV tape extrusion samples that had been cut using a cryomicrotome that utilized a diamond knife to cut the sample at  $-80^{\circ}\text{C}$ . Proper TPV morphology is present when there are discrete droplets of rubber within a continuous thermoplastic matrix. However, these TPVs had inverted morphology and poor physical properties. This was a result of the molten rubber having too low of a viscosity and thus would not break up into droplets when being mixed with the thermoplastic. This issue was corrected through the addition of clay particulate filler to the TPV, which increased the viscosity of the rubber phase, causing it to break up into discrete droplets while maintaining a continuous thermoplastic phase.

With these issues resolved, the processing of TPV materials moved from the Brabender mixer to a 26-mm fully-intermeshing, co-rotating twin-screw extruder. Twin-screw extrusion offered the benefits of a higher intensity mixing and a better representation of how TPV materials are made in manufacturing. Due to feeding limitations because of the number of hoppers available, TPV materials were made in a two-pass process on the twin-screw extruder. In the first pass, all of the components except the curative were blended together and extruded through a three-hole die into a water bath and then fed to a pelletizer. These pellets were then dried in a vacuum oven overnight before being fed through the twin-screw extruder the following day with the curative.

The cured TPV pellets would be dried overnight again before melt flow index (MFI) testing, tape extrusion, AFM imaging, and injection molding were conducted. MFI, AFM, and tape extrusions were used to ensure that physical properties and TPV morphology were still being achieved, while injection molding was done to make buttons that were used for compression set testing. Once these buttons were made and allowed to sit for at least 24 hours, compression set testing was conducted per ASTM D395-03 Method B, by compressing samples between parallel steel plates at a requested elevated temperature of 150°C for 70 hours in forced air convection ovens. After 70 hours, the samples were immediately removed from their compression set devices and allowed to rebound from their compressed state for 30 minutes. The best compression set values were seen in TPV samples that had high levels of curative, but these samples had compression set values of 95%, much higher than the desired value of 75% or less.

Although desired compression set values were not achieved for these new TPVs, this project has laid the groundwork for future studies of PA-FKM TPV systems along with other potential rubber thermoplastic systems. The major points that were identified as being necessary for proper TPV morphology and properties were: 1) having components with compatible surface chemistry, 2) having a significantly more viscous rubber phase than the thermoplastic phase, 3) having high intensity mixing, and 4) having thorough curing of the rubber phase. Using less clay particulate filler, different compounding equipment with higher intensity mixing, and higher levels of curative, all represent future areas of investigation that have the potential to improve the compression set of these PA-FKM TPVs.

## Introduction:

Customer demands have requested flexible, lightweight alternatives to high operating temperature thermoset rubber currently being used for power steering hose. Despite high component immiscibility, recent investigations at Parker Hannifin Corporation into manufacturing dual rubber thermoplastic vulcanizate (TPV) materials for tubing in such hoses, have proven viable. These TPVs are considered to be dual rubber since they consist of a polyamide thermoplastic, a vulcanized fluorocarbon rubber (FKM), and vulcanized hydrogenated acrylonitrile-butadiene rubber (HNBR). Currently, these TPV materials consistently meet all required material properties for production of high-temperature tubing, except for compression set resistance. The focus of this honors project was determining what TPV compositions, cure systems, and curative levels lead to the best compression set values, while still maintaining other necessary TPV material properties.

This project involved the use of several  $2^k$  factorial design of experiments (DOEs). 16 different TPV compositions were investigated, consisting of 4 different polyamides, and 4 different FKMs, with attempted 60:40 volumetric ratios of rubber to thermoplastic. It should be noted that although the final TPVs are dual rubber, the second rubber component, HNBR, was not investigated or used in TPV formulations as it was beyond the scope of this honors project. The second rubber will be used to make the final TPV tubing for power steering hose. Viton Curative (VC) 20, VC 30, and VC 50 were the main cure systems being investigated. The level of curative added varied from 2 parts per hundred rubber (PHR) to 6 PHR. TPV materials were made using a Brabender mixer and a 26-mm fully-intermeshing, co-rotating twin-screw extruder, while compression set buttons used for testing were made through injection molding. Compression set testing was conducted per ASTM D395-03 Method B, by compressing samples

between parallel steel plates at a requested elevated temperature of 150°C for 70 hours in forced air convection ovens.

### Background:

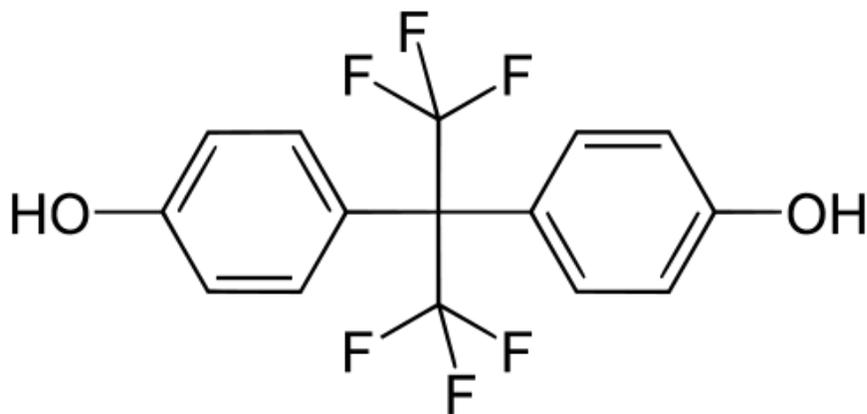
TPVs are blends of a thermoplastic and a vulcanized (cured) elastomer (rubber), where droplets of cured elastomer are homogeneously dispersed within a continuous thermoplastic matrix.<sup>1</sup> Thermoplastics are much easier to process than thermoset rubber and can be reprocessed if product quality specifications are not achieved during manufacturing, reducing overall waste.<sup>2</sup> However, thermoset rubbers tend to have better overall physical properties than thermoplastics, specifically temperature and environmental degradation and creep resistance, TPVs are desirable because they combine the physical properties of their component rubber with the reprocessable manufacturing capability of thermoplastics.<sup>2,3,4</sup>

TPVs were invented in the 1980s through a joint venture between Monsanto and ExxonMobil Chemical via Advanced Elastomer Systems, which is now completely owned and operated by ExxonMobil Chemical.<sup>2,4</sup> Although extensively patented during the time of their initial invention, nearly all of these early TPV patents have since expired. TPVs are often referred to by their commercial names, with some of the most popular TPVs being Santoprene™ (ExxonMobil Chemical), Zeotherm® (Zeon Corporation), ETPV (DuPont Performance Elastomers), and TPSiV® (Dow Chemical Company). The specific chemical formulations of each TPV are patented by their respective companies.<sup>4</sup>

The particular TPV formulation being investigated at Parker Hannifin Corporation is unique because of the utilization of a Bisphenol AF (2,2-bis(4-hydroxyphenyl) hexafluoropropane) cure for FKM either exclusively or in combination with other cure systems,

along with a second cured elastomer component, which in this case is cured HNBR. The less chemically aggressive nature of the Bisphenol AF cure system, relative to other cure systems, enables greater compatibility between the FKM and the thermoplastic.<sup>1</sup> The cure system can also be adjusted to increase the compatibility of different thermoplastics and FKM. The concept of adjustable cure systems for different thermoplastic and FKM blends is another unique characteristic of the TPV formulations being investigated.

The preferred curative for gum FKM is Bisphenol AF, an aromatic dihydroxy compound, the structure of which is illustrated in **Figure 1**. Other curative compounds such as Bisphenol S, Bisphenol A, VC 20, VC 30 and VC 50 were also investigated.<sup>5,6</sup> It should be noted that VC 20, VC 30, and VC 50 are all different types of Bisphenol AF cure systems. The curing process results in the crosslinking of FKM chains using an ionic curing mechanism. This crosslinking process takes place in three steps. The first step is the formation of a soluble bisphenol monophosphonium salt. The subsequent reaction of FKM and the bisphenol monophosphonium salt creates diene functionalities in FKM. Thirdly, the bisphenol monophosphonium salt reacts with fluorine atoms next to the double bonds, resulting in crosslinking.<sup>7</sup>



**Figure 1.** Molecular structure of Bisphenol AF (2,2-bis(4-hydroxyphenyl) hexafluoropropane).

### Experimental Methods:

This project focused on using DOEs to improve compression set resistance of TPVs, through varying TPV composition, type of elastomer cure system, and level of curative. First, TPV samples were made on a small scale using a Brabender mixer to identify promising TPV compositions and curative systems for TPVs that were later produced using the twin-screw extruder. Twin-screw extruder samples, in turn, focused on varying levels of curative for these promising compositions to determine the effects of curative level on compression set values. This type of testing was done to save material since Brabender mixing requires less material (50 g) to make an experimental sample than the twin-screw extruder (1-5 kg). Personal protective equipment (PPE) for making TPV materials on these machines includes safety goggles, steel-toe shoes, heat resistant gloves, and heat resistant clothing. Safe operating procedures were always followed when operating these machines, especially when feeding materials into the Brabender mixer or adding materials into the hoppers that fed the twin-screw extruder. Ventilation units and vacuum systems were used for the Brabender and twin-screw extruder respectively in order to contain hazardous volatiles that may be created during the compounding process. Operators were also aware to keep their hands away from pullers and rubber pelletizers during operation and followed proper shutdown and cleaning procedures.

After these samples were collected and allowed to dry in a vacuum oven overnight at 60°C, melt flow index (MFI) testing was conducted to determine the rate at which the materials would flow in a molten state at 230°C. This rate of flow gives a general idea about ease of processability of a given TPV material, with easier to process materials having higher MFI values. All Brabender and twin-screw extruded materials were extruded into tapes using a single-

screw extruder that utilizes a flat die attachment with a flat narrow opening. Tensile property and density testing were conducted on the samples die-cut from the tapes. Injection molded samples were also made from twin-screw extruded TPV pellets, allowing for flexural modulus, impact strength, and compression set testing. Temperature, pressure, screw speed, and torque were recorded for all compounding equipment in order to ensure that materials were being made within reasonable machine processing tolerances, that could be later transitioned into production machinery. Complete physical property testing was carried out to ensure that necessary material properties are still being achieved while attempting to improve compression set resistance.

Compression set testing was conducted per ASTM D395 B standards by having samples compressed between parallel steel plates with spacers in between them at a requested elevated temperature of 150°C for 70 hours in forced air convection ovens. The initial thickness of the compression set samples made by injection molding (compression set buttons) was measured before the samples are placed in the compression set device, shown in **Figure 2**. Compression set buttons are compressed between parallel steel plates by screwing down nuts on the opposite sided of the plates until the plates are flush with the spacers. Compression set devices are placed in the ovens for testing within 1 hour of having samples compressed in them. After testing compression set buttons are immediately removed from the compression set devices and given at least 30 min to cool and rebound from their compressed state, at which point the thickness of the samples is remeasured and the compression set is calculated. Compression set values were calculated using the following equation:

$$C_B = \left( \frac{(t_0 - t_i)}{(t_0 - t_n)} \right) * 100$$

Where:  $C_B$  = compression set (percentage),  $t_0$  = original sample thickness (in inches),

$t_i$  = final sample thickness after recovery (in inches),

$t_n$  = thickness of spacers between compression plates (0.376 inches)



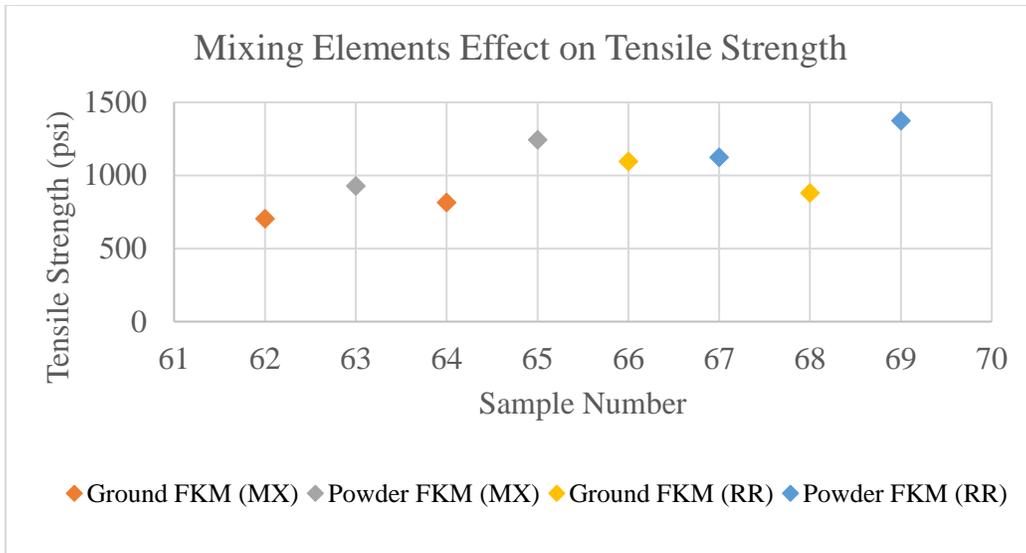
**Figure 2.** A picture of a compression set device with a similar design to the ones that were used in this project. The spacers, compression plates, nuts, and bolts that make up the device are easily visible.

The effects of processing conditions on TPV morphology were also analyzed using an atomic force microscope (AFM). AFM microscopy works by using a probe that scans the surface of a sample by passing back and forth over the sample and responding to variations in hardness of the material. The lighter the region is on the AFM image the higher its hardness. This identification of variations in hardness shows where all the components are in the TPV since nylon, FKM, filler particles, and curative components all have different hardness values, and can thus be identified on an AFM image. Ideally, AFM images will show a continuous thermoplastic matrix with homogenous drops of cured FKM than are less than 2  $\mu\text{m}$  in diameter. This sort of AFM image shows an ideal TPV morphology which has been identified to be likely to result in desirable material properties. Deviations from this morphology indicated that compounding

conditions may be incorrect and that temperature, screw speed, or even a screw redesign may be necessary to achieve proper TPV morphology and desired material properties. These images are crucial when identifying what needs to be modified when promising TPV formulations are producing materials that have subpar properties.

### Results:

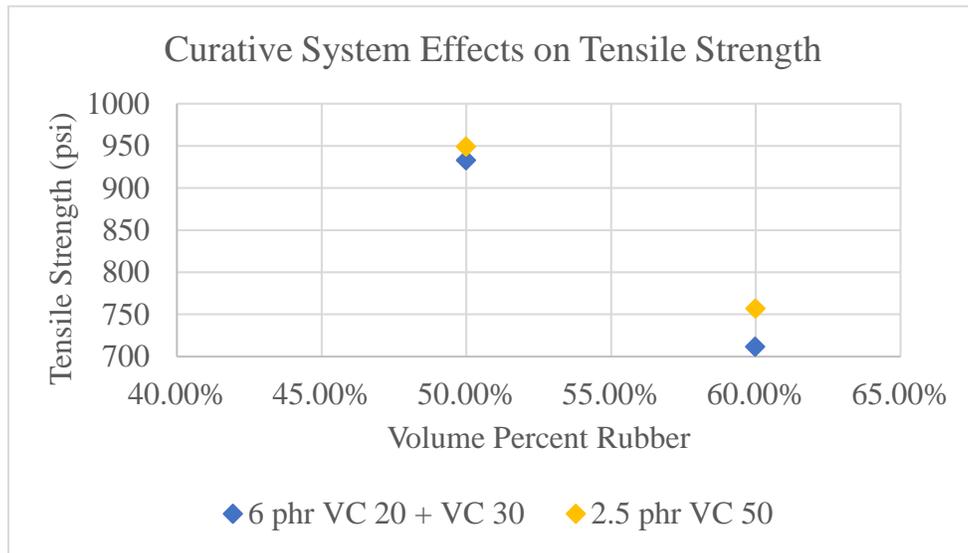
As previously explained, initial Brabender TPV samples sought to identify what TPV formulations had the most promising traits which would be focused on later in the project. This proved problematic for several reasons. Firstly, the formulations themselves were highly immiscible since they contained only thermoplastic, elastomer, and a cure system. This resulted in an inverted TPV morphology where the rubber phase was continuous, and the thermoplastic formed individual droplets. These TPVs had no mechanical strength and would immediately fall apart when trying to make tape extrusion samples. The addition of a small amount of a thermoplastic compatibilizer, use of higher intensity mixing elements, and increasing Brabender rotor speed resulted in being able to produce a tape sample but was not able to achieve proper TPV morphology or desired material properties. The improved tensile strength of TPVs made using higher intensity mixing elements can be seen in **Figure 3**.



**Figure 3.** The above plot show how TPV tensile strength improved with the switch to higher intensity mixing elements. TPV samples 62 – 65 were made using standard rotor mixing elements (MX) on the Brabender mixer, while TPV samples 66 – 69 had the same respective chemical compositions and processing conditions, with the only difference being the use of high intensity tri-lobe rotor mixing elements. This change in mixing elements improved TPV tensile strength but did not achieve the target tensile strength of 3,000 psi.

Despite not being able to achieve proper morphology or properties on the Brabender mixer initially, some general conclusions were able to be drawn from this testing. Firstly, from these experiments the list of suitable TPV components was narrowed down to one thermoplastic and two possible elastomers. A plasticized nylon 12 and either a powdered FKM elastomer or a ground FKM elastomer blend was established as the components that should be focused on. Secondly, the proper cure system was established from the three different systems investigated. VC 50 (Fluorocure 5) was concluded to be the best curative system because when it was added to the Brabender mixer it melted very readily allowing for more efficient mixing and greater extent of vulcanization in the TPV, which was confirmed with the better tensile properties of materials made using this cure system, as seen in **Figure 4**. This curative melting also had the added benefit of having a plasticizing effect on the TPV mixture, dropping the torque on the Brabender mixer when initially added, effectively acting as a minor processing aid. It should be

noted that in order for the cure system to work safely and effectively, varying amounts of magnesium oxide and calcium hydroxide were also added to the TPV along with VC 50 as part of the cure system.



**Figure 4.** The above plot show how TPV tensile strength was better for TPVs made using VC 50 as the curative system, rather than VC 20 and VC 30. In addition to having better tensile properties, the VC 50 cure system only required 2.5 parts per hundred rubber to achieve similar tensile strength, while the VC 20 and CV 30 curative system required 6 parts per hundred rubber.

Even after scouting mixing experiments and material testing, the appropriate material properties were not achieved. When the AFM imaging of the TPV samples were done, the inverted TPV morphology was found where rubber was the continuous phase and thermoplastic was dispersed within this phase. It is theorized that this inverted morphology happened because of the low viscosity of molten FKM relative to molten nylon. It was found that the viscosity of the FKM at processing temperatures was less than the viscosity of nylon, causing the break up of the more viscous nylon component into droplets dispersed in FKM. Previous nylon-FKM TPV systems that had achieved the desired TPV morphology, used pre-compounded FKMs that contained both fillers and curatives. By introducing fine clay filler into the current TPV

formulations, which utilized unfilled FKM, the viscosity of the FKM was increased, the material properties were closer to desired values, and the morphology was more like ideal TPV. Filler was used in a ratio of 1 part filler to 10 parts FKM elastomer by weight in order to keep the overall amount of powder added to the TPV low. This was imperative as too much filler could not only hinder proper TPV morphology, but could also result in worse compression set values, which was the failure of the first PA-FKM study. The compression set values for the TPVs samples tested are shown in **Table 1**.

**Table 1.** The compression set values for TPV samples FCG 016-115 to FCG 016-118. Sample FCG 0016-115 has the lowest average compression set value ( $C_B$ ) at 95%, but is much greater than the target compression set value of 75%.

Process Parameter	FCG 016-114	FCG 016-115	FCG 016-116	FCG 016-117	FCG 016-118
<b>Sample 1</b>					
$t_0$		0.4820	0.4820	0.4830	0.4860
$t_i$		0.3760	0.3760	0.3760	0.3760
$t_n$	0.3760	0.3760	0.3760	0.3760	0.3760
% Compression	#DIV/0!	22.0%	22.0%	22.2%	22.6%
$C_B$	0.00	100.00	100.00	100.00	100.00
<b>Sample 2</b>					
$t_0$		0.4820	0.4820	0.4820	0.4850
$t_i$		0.3890	0.3760	0.3760	0.3760
$t_n$	0.3760	0.3760	0.3760	0.3760	0.3760
% Compression	#DIV/0!	22.0%	22.0%	22.0%	22.5%
$C_B$	0.00	87.74	100.00	100.00	100.00
<b>Sample 3</b>					
$t_0$		0.4820	0.4820	0.4820	0.4850
$t_i$		0.3800	0.3760	0.3760	0.3760
$t_n$	0.3760	0.3760	0.3760	0.3760	0.3760
% Compression	#DIV/0!	22.0%	22.0%	22.0%	22.5%
$C_B$	0.00	96.23	100.00	100.00	100.00
Median $C_B$	0.000	96.226	100.000	100.000	100.000
Average $C_B$	0.000	94.654	100.000	100.000	100.000
Standard Deviation $C_B$	0.0000	5.1288	0.0000	0.0000	0.0000

With an understanding of how to achieve proper material properties and TPV morphology gained largely through small scale mixes, scale-up studies with the twin-screw

extruder commenced. Due to limited hopper feeding capacity, TPV materials were made on the twin-screw via a two-pass process. In the first pass, nylon, FKM, magnesium oxide, calcium hydroxide, and filler were compounded at a total rate of 50 lb/hr and a screw speed of 250 RPM. This material exited the die of the twin-screw extruder as three strands that went into a water bath, exited the bath and had the water blown off using compressed air, and was then fed into a pelletizer. These pellets were then collected, weighed, and dried overnight in preparation for the second pass. In the second pass, the pellets made in the first pass, were then fed into the extruder along with the curative VC 50, which had been ground up into a powder to achieve consistent curative feeding rates. Feed rate was reduced to 20 lb/hr to avoid an over-torque shutdown of the extruder, since material viscosity drastically increased while curing. While operating the extruder, atmospheric vents and vacuum ports were periodically checked in order to make sure that polymer had not plugged them while running.

The initial test results from the TPV materials made from the twin-screw extruder were better than those achieved from the Brabender mixer, but they were still not meeting desired property targets. Tensile strength was below the 3,000 psi value that had been set as a good bench mark to reach. Although TPV morphology was greatly improved, it was still closer to co-continuous rubber and thermoplastic phases, rather than discrete rubber droplets in a continuous thermoplastic phase. In order to achieve proper morphology, the screw element configuration was redesigned, which switched out several conveying sections of the screw with high intensity mixing sections in order to break up FKM droplets more effectively. This redesigned screw had the desired effect, resulting in a much better TPV morphology that matched exactly what was trying to be achieved. The material properties also improved greatly, with tape extrusion samples having tensile strength of over 3,000 psi, modulus of 19,000 psi, and processing parameters

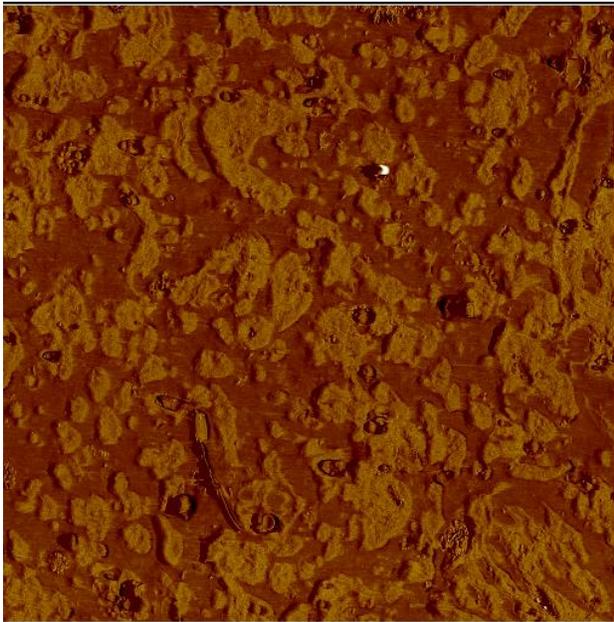
where tape extrusion screw speed was 50 rpms, with torque ranging from 4,100 – 7,200 Gm, all of which is within acceptable ranges. The physical properties and processing parameters for these improved TPVs can be found in **Table 2**. The surfaces of the tapes were also smoother than before, which was an improvement over prior nylon-FKM TPV formulations.

**Table 2.** The physical properties and processing parameters for 2<sup>nd</sup> pass cured TPVs made on the twin-screw extruder. Only sample 115 has tensile strength greater than 3,000 psi, but all samples had stronger tensile strengths than those previous TPVs.

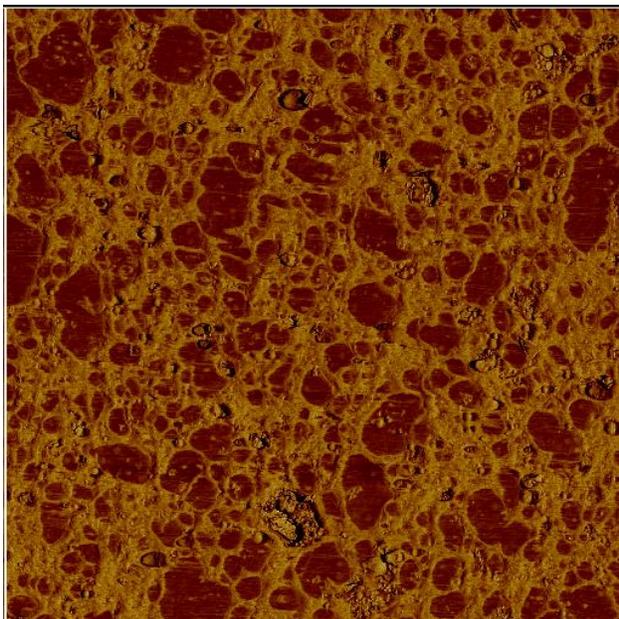
Properties	Units	109	114	115	116	117	118	
ZSK 26mm TSE: Feed Rate	lb/hr	20	20	20	20	20	20	
ZSK 26mm TSE: Screw Speed	rpm	250	250	250	250	250	250	
ZSK 26mm TSE: Torque	%	80.00%	69-73%	70-73%	78-81%	74%	80%	
ZSK 26mm TSE: Melt Pressure	psi	285	532-651	395-530	389-435	460-540	460-541	
ZSK 26mm TSE: Melt Temp	C	242	257	241	240	247	246	
		109	114	115	116	117	118	
Melt Flow Index (230C, 22kg)	g/10min	17.21	0.05	0.72	0.18	0.10	0.14	
		109	114	115	116	117	118	
Tape Extrusion: Screw Speed	rpm	50	50	50	50	50	50	
Tape Extrusion: Torque	Gm	3427	7167	5350	4053	4442	4306	
Tape Extrusion: Melt Pressure	psi	879	3122	1314	1465	1387	1511	
Tape Extrusion: Melt Temp 1	C	201	206	191	204	199	198	
Tape Extrusion: Melt Temp 2	C	249	248	247	248	249	248	
		109	114	115	116	117	118	
Tape Extrusion: Tensile Strength	psi	2182.5	2265.9	3688.8	1530.5	2375.7	2070.2	
Tape Extrusion: Strain at Break	%	148.5	119.3	245.5	57.4	90.5	98.9	
Tape Extrusion: Modulus	psi	1492.0	1595.2	1994.5	1376.5	1897.1	1670.8	
Tape Density	mean	g/cc	1.404	1.465	1.443	1.389	1.459	1.453
% Theoretical Density	%		94.87%	99.50%	98.01%	94.63%	98.72%	98.60%

To examine morphology of TPV materials produced on the twin-screw extruder, AFM analysis was conducted on tape extrusion samples. AFM analysis was not done on a lot of tape extrusion samples that were made from Brabender-mixer, due to the preliminary nature of Brabender mixing and the time intensive nature of AFM imaging. It was found that TPVs that had proper morphology had better physical properties overall than TPVs that had either co-continuous rubber and thermoplastic phases or inverted phase morphology (continuous rubber and droplets of thermoplastic). These different TPV morphologies can be seen in **Figures 5-7**.

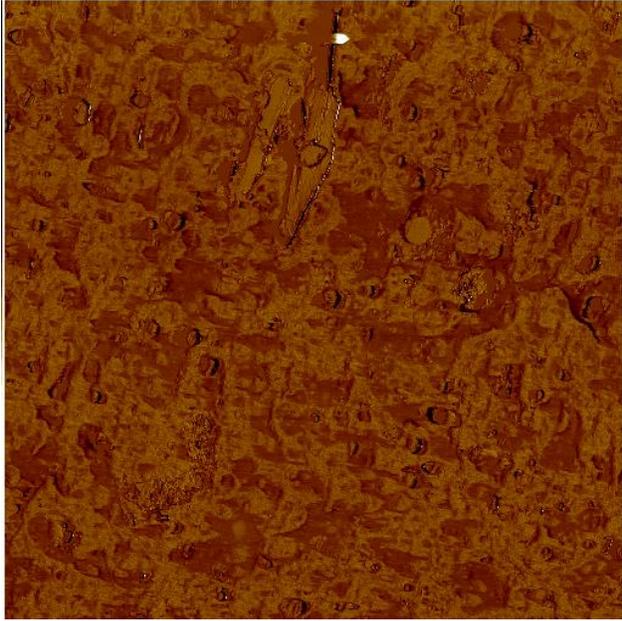
With the nylon-FKM TPVs showing good morphology and achieving all necessary material properties, compression set buttons were made via injection molding to find out if there was any noticeable improvement in compression set values with the new cure system. Unfortunately, the compression set resistance of these new TPV materials did not show any improvement, with compression set values averaging around 95%.



**Figure 5.** The picture to the left is an AFM image 10  $\mu\text{m}$  x 10  $\mu\text{m}$  in size that shows the morphology of TPV sample FCG016-115, made through twin-screw extrusion that utilized a high intensity mixing screw design. This TPV consisted of a ground FKM rubber blend and a low viscosity, plasticized nylon. The morphology is ideal with a continuous thermoplastic matrix (light colored material) and discrete droplets of FKM (dark colored material).



**Figure 6.** The picture to the left is an AFM image 10  $\mu\text{m}$  x 10  $\mu\text{m}$  in size that shows the morphology of TPV sample FCG016-105, made through twin-screw extrusion that utilized a moderate intensity mixing screw design. This TPV consisted of a ground FKM rubber blend and a low viscosity, plasticized nylon. The morphology is inverted with a continuous rubber phase (dark colored material) and droplets of thermoplastic (light colored material).



**Figure 7.** The picture to the left is an AFM image 10  $\mu\text{m}$  x 10  $\mu\text{m}$  in size that shows the morphology of TPV sample FCG016-118, made through twin-screw extrusion that utilized a high intensity mixing screw design. This TPV consisted of a ground FKM rubber blend and a high viscosity, plasticized nylon. The morphology is co-continuous with a continuous rubber phase (dark colored material) and continuous thermoplastic phase (light colored material) both being presents in the TPV.

#### Discussion and Future Work:

Compression set values of the new TPV formulations investigated for this project did not achieve the target value of 75% or less. However, this investigation has laid the groundwork for future studies of PA-FKM TPV systems along with other potential rubber thermoplastic systems. The major points that were identified as being necessary for proper TPV morphology and properties were: 1) having components with appropriate chemical compatibility, 2) having a significantly more viscous rubber phase than the thermoplastic phase, 3) having high intensity mixing, and 4) having thorough curing of the rubber phase.

The identification of the TPV components with appropriate chemical compatibility is a key aspect of TPV development. Tape extrusions of TPV materials made using Brabender mixing proved this hypothesis, with TPV samples with less compatible components crumbling upon extrusion from the die as the materials had no structural integrity. These materials had components that would rather exist as separate rubber and thermoplastic phases, and could not be extruded as one solid tape sample. TPVs that had more compatible rubber and thermoplastic

components were able to be extruded as solid tape samples that may have had significant surface roughness or ribboning effects around the edges of the tapes, but were able to be extruded continuously to create a solid piece of material.

The identification of the necessity of having a higher viscosity rubber phase than the thermoplastic phase resulted in improved physical properties and morphology for compatible rubber-thermoplastic TPV blends. Unfilled gum FKM on its own has a viscosity similar to that of plasticized PA-12 when molten. This is an issue because in order to break up the rubber phase into discrete droplets and maintain a continuous thermoplastic phase when mixing, the rubber phase must be more viscous than the thermoplastic when molten. To increase the viscosity of the rubber, 5 wt% clay particulate filler was added to existing compatible TPV formulations. This resulted in improved material properties, appearance, and morphology, as these TPVs were now achieving a more ideal morphology. The drawback of using clay particulate filler to increase the rubber phase viscosity this way is that as the clay particulate filler enters the rubber phase of the TPV it hinders the ability of the cured rubber to rebound after compression, resulting in higher compression set values. A future potential area of investigation would be to analyze how much clay particulate filler needs be added to the TPV to produce proper morphology without compromising compression set resistance. Other ways of increasing rubber viscosity in order to achieve proper morphology while not hindering the rubber components ability to rebound should also be investigated.

Higher intensity mixing is necessary when working with PA-FKM TPV systems in order to achieve proper morphology and properties. This was first noticed on the Brabender mixer when increasing rotor speed (RPM) resulted in TPV materials that had better overall properties. These TPVs resulted in tape extrusion samples that had less surface roughness and better

physical properties. Changing the rotor style in the Brabender mixer to higher intensity tri-lobe rotors further improved these properties. The same trends were seen on the twin-screw extruder, with TPV materials using higher intensity mixing elements showing the same improvements in morphology, surface roughness, and physical properties. Screw design optimization for higher intensity mixing, or compounding of TPVs on higher intensity mixing equipment, such as a reciprocating continuous kneader, are potential areas of interest for future TPV development. Improved blending and compounding has the potential to lead to lower compression set values, and may permit the removal of clay particulate filler from the formulations.

Thorough curing of the TPV's rubber phase components was identified as being necessary for achieving rubber-like rebound characteristics. This is consistent with trends reported in the literature as greater levels of curative lead to lower compression set values. It is postulated that VC 50 allowed for more thorough curing of the rubber phase since at processing temperatures it was molten, allowing for more even dispersion of curative during mixing and thus better overall curing of the rubber phase. Future testing with higher levels of curative should be investigated using the twin-screw extruder. Increasing curative levels in the TPV formulations may lead to lower compression set values, but could also approach the operating limits of the processing equipment. Experimentation with appropriate processing conditions will be needed to pursue more thoroughly cured TPVs.

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Appendices:

Appendix A: Equipment



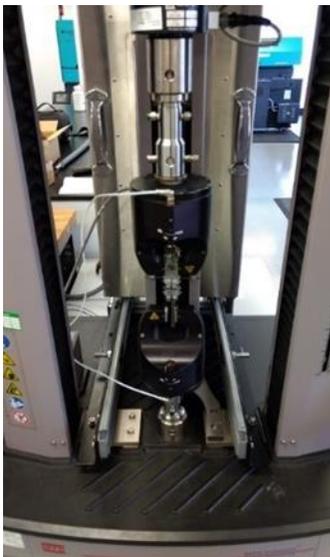
**Figure 8.** The above figure is a picture of the Brabender mixer that was used to identify promising TPV formulations.



**Figure 9.** The above figure is a picture of the 26 mm fully intermeshing, co-rotating twin-screw extruder, water bath, and rubber pelletizer that was used to determine the ideal amount of curative and cure system for TPV samples.



**Figure 10.** The above figure is a picture of the single screw extruder tape extrusion line that was used to make tape extrusion samples for tensile testing and other material characterization.



**Figure 11.** The above figure is a picture of the mts tensiometer that was used for tensile testing of TPV samples. Samples were cut into standard size tensile bar samples using a die and a hydraulic press before testing.



**Figure 12.** The above figure is a picture of the Melt Flow Indexer that was to determine the flow rate of TPV samples at 230°C. These flowrates served as general viscosity measurements and helped determine TPV processability.



**Figure 13.** The above figure is a picture of the Injection Molding Machine that was used to make TPV compression set button samples that were used for compression set testing.

### Honors Abstract Addendum:

It was hypothesized that increasing the curative level of the fluorocarbon rubber (FKM) used in manufacturing of thermoplastic vulcanizate (TPV) materials would decrease the compression set values of the TPV enough for it to be suitable as a flexible, lightweight alternative to high operating temperature thermoset rubber tubing currently being used for power steering hose. First, promising TPV formulations were identified by varying the polyamide (PA) and FKM used in a Brabender mixer. Four different types of polyamide and four different types of FKM were investigated, with two of the FKM types and one polyamide type identified as being promising. A compounding twin-screw extruder was used to determine the ideal amount of curative and cure system. Materials made on the twin-screw extruder were made into compression set buttons through injection molding, with compression set testing being conducted per ASTM D395-03 Method B. These TPV materials had compression set values of 95%, much greater than the desired value of  $\leq 75\%$ . Further experimentation using higher curative levels or modified screw designs for the twin-screw extruder should be conducted to achieve the desired compression set resistance for the PA-FKM system.