

Dispersion of Polyethylene imine-coated chopped fibers in Rubber Matrix

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ABSTRACT

Fibers and fabrics, coated with Resorcinol Formaldehyde Latex (RFL), are traditionally used to reinforce rubbers or polymers for technical applications. Many studies have indicated that the formaldehyde in RFL has potential health and environmental problems. Many research activities are now being dedicated to developing alternative treatments that are formaldehyde-free that can deliver acceptable performance on fibers and rubber. One of the critical goals of these development activities is to use the traditional dipping equipment used in RFL dip coating.

The goal of this study is to evaluate the performance of fibers and fabrics coated with polyethylene imine, an eco-friendly alternative, to reinforce rubbers or polymers for technical applications. An EPDM V-Belt recipe was used to evaluate the effects of RFL-coated and polyethyleneimine-coated chopped fibers on the physical properties of uncured and vulcanized rubber samples. The physical properties evaluated were Mooney viscosity, MDR, durometer, tensile, elongation, modulus, die C tear, trouser tear, compression set, demattia flex crack growth, rotary drum abrasion, DMA strain sweep, and fiber dispersions in the rubber matrix. Results show that the polyethyleneimine - coated fibers and RFL-coated chopped fibers yield similar physical properties, but the polyethyleneimine coating seems to give slightly better dispersion of the chopped fibers in the rubber matrix.

INTRODUCTION

Resorcinol Formaldehyde Latex (RFL) has been used for decades as the coating of choice for fibers and fabrics used for rubber reinforcement. Recently, many studies have indicated that the formaldehyde in RFL has a potential health and environmental problems [1-5]. In addition to the hazards RFL pose to humans, RFL also requires multiple processing steps to produce. These steps require a great deal of effort to prepare and costly time to dip-coat fibers or fabrics for rubber reinforcement.

Recently, many research activities have been focused primarily on developing alternative treatments that are formaldehyde-free systems that deliver acceptable coatings on fibers. For practitioners to readily accept such alternative technology, the goal must be to use the same or similar dipping equipment used in RFL dip coating programs. Louis, et al, discussed formaldehyde-free dip technology introduced by Kordsa Group for reinforcing textile materials [6]. This technology consists of epoxy, polyisocyanate and latex, which were proportionately blended into a dipping solution [9]. The objective was to replace the traditional RFL dipping chemistry and still be able to use the traditional dipping equipment. Gomes, et al, evaluated RFL-free coatings of tire textiles which they compared to RFL system for various fiber materials; the RFL-free coating consisted of Ricobond 7004 from Cray Valley and other ingredients [7]. Ricobond 7004 is a dispersion of a functionalized polymer. The results were reported to be comparable to the RFL system, but with lower peel forces. Bridgestone [8], as part of their broad and comprehensive Eco-Activities program, is involved in the development of RFL-free coating systems. Mehler Engineered Products has recently announced an RFL-free dip coating for various fibers [10].

Different types of fibers, coated with RFL, are generally used to reinforce technical rubber applications. In this instance, technical rubber implies all rubber applications other than tire rubbers. The objectives of this study were to 1) evaluate polyethyleneimine-coated chopped fibers and compare to RFL-coated chopped fibers, and 2) determine if polyethyleneimine can be used as a safer and environmentally- friendly coating replacement for RFL for chopped fibers in technical rubber applications.

An EPDM V-Belt recipe was used to evaluate the effects of RFL-coated and polyethyleneimine-coated chopped fibers. The physical properties of uncured and vulcanized samples were compared.

The physical properties evaluated were Mooney viscosity, MDR, durometer, tensile, elongation, modulus, die C tear, trouser tear, compression set, demattia flex crack growth, rotary drum abrasion, DMA strain sweep, and fiber dispersions in the rubber matrix. Results show that the polyethyleneimine-coated fibers and RFL-coated fibers yield similar physical properties, but the polyethyleneimine coating seems to give slightly better dispersion of the chopped fibers in the rubber matrix.

EXPERIMENTAL

Fiber Preparation and Coating

Polyethyleneimine from BASF Corporation, sold under the tradename “Lupasol®”, was formulated into RFL-free formulation and used for coating the fibers. The general structure is shown in Figure 1. Lupasol® types are cationic molecules whose charge density depends on pH. The molecules consist of branched polymer structure with various degrees of branching. The molecular weights range from 800 g/mole to 2,000,000 g/mole. Lupasol products are multifunctional polyethyleneimine with the following typical branched polymer structure:

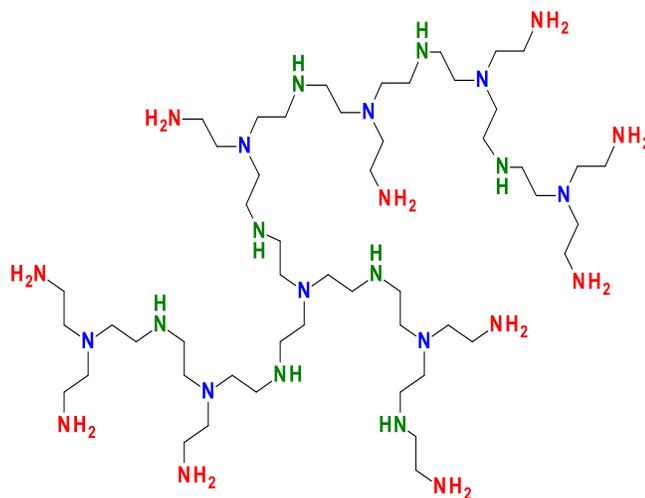
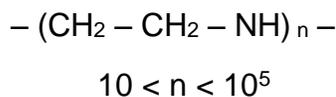


Figure 1: Structure of Polyethylene imine

This structure can be represented by the following formula:



These products have the largest amino group density of any commercial polyamine with Nitrogen to Carbon ratio of appropriately 2:1.

The polyester fibers used in this evaluation were 2000 denier and 492 filaments. Three (3) ends of the untreated polyester yarns were twisted into one construction (2000 /1/3) and subsequently wound into a spool; two spools of the twisted fibers were prepared. The coating was done with a traditional cord dipping system. The polyethyleneimine-coated and RFL-coated fibers were chopped into three (3) millimeters long. For this study, two spools of twisted fibers were treated; one with 5% Lupasol® WF and 0.5% surfactant in aqueous solution and the other spool was treated with a 20% concentration of RFL. The characteristic colors of both RFL and Lupasol coatings are distinctly exhibited.



Figure 2: RFL-Coated Polyester Chopped Fibers



Figure 3: Lupasol-Coated Polyester Chopped Fibers

Table 1 shows the physical properties of Lupasol® WF used in formulating the coating solution for the twisted fibers. A suitable surfactant was optionally included in the composition to lower the surface tension and improve wetting of the coating solution. The coating of the fibers was accomplished in a typical dip coating unit with the RFL and polyethylene imine.

Table 1: Physical properties of Lupasol WF used for coating

Typical Physical Characteristics	Lupasol® WF
Average Weight Molecular Weight (Mw) (g/mol)	25,000
Viscosity at 20 °C (mPa.s)	100,000
Concentration in (wt%)	>99
Water Concentration (wt%)	~1
Pour Point (°C)	-1
Boiling Point (°C)	>>200
Density at 20 °C (g/cm ³)	1.10
pH (1% in water)	10 - 12
pKa Value	7-10
Charge Density	17
Ratio of 1°:2°:3° Amine	1:1.1:0.7

Materials

A model EPDM V-Belt recipe was used to compare the effects of RFL and Lupasol coatings on chopped polyester fibers. Table 2 provides an overview of the key chemical ingredients used in the recipe.

First Pass		Lupasol	RFL
Material	PHR	PHR	PHR
Royalene 580-HT	100.00	100.00	100.00
N-650 (Carbon Black)	50.00	50.00	50.00
Sunpar 2280 (paraffinic oil)	15.00	15.00	15.00
Zinc Oxide	5.00	5.00	5.00
Vanox CDPA	1.00	1.00	1.00
Vanox ZMTI	1.50	1.50	1.50
Polyester Fibers w/ Lupasol	15.00		
Polyester Fibers w/ RFL			15.00
Total	187.50	187.50	187.50

Final Pass		Lupasol	RFL
Material	PHR	PHR	PHR
Master Batch - 1st Pass	187.50	187.50	187.50
Vanax MBM	1.00	1.00	1.00
Varox DCP-40KE	8.00	8.00	8.00
Total	196.50	196.50	196.50

Table 2: Recipe Formulation (parts per hundred rubber, by weight)

The elastomer used in this study is Royalene 580-HT, an EPDM with Mooney viscosity of 60 (ML (1+4)100°C (milled) = 60) with 53/47 ratio of Ethylene to Propylene and 2.7% ENB content supplied by Lion Elastomers. Additional ingredients such as N650 carbon black, processing oil, antidegradants, zinc oxide, peroxide and co-agent are used in typical proportions.

Processing

The formulas were compounded in a Farrel Model 2.6 BR Banbury Mixer, using a 74% fill factor for the first pass, 73% fill factor for the final pass, and with ram pressure set to 0.28 MPa. A two-stage mixing process was used, as outlined in Table 3, in which elastomers, fillers, processing oil, antidegradants and zinc oxide were added in the first pass. In the first mixing stage the rotor speed was increased after the ingredients were incorporated in order to bring the batch temperature to 138°C. The peroxide and co-agent were mixed with the master batch in the final (productive) pass.

The rubber was sheeted out on a Farrel two-roll mill after each Banbury mixing stage. Cure rate information was determined according to ASTM D 5289-17 using moving die rheometer (Tech Pro rheoTECH MDR, 0.5° arc, 170°C)) [11]. Rubber samples were compression molded with curing temperature equal to 170°C and molding time equal to 15 minutes for test plaques and 20 minutes for compression set buttons, abrasion specimens, and crack growth specimens. The samples were then post-cured in an air oven for 2 hours at 149°C. Processing

properties including Mooney viscosity, ML(1+4) at 100°C, were determined according to ASTM D 1646-17 in a Monsanto MV 2000 Viscometer, using the large rotor [12].

1st Pass Master Batch		Final Pass	
Starting Temp: 38°C		Starting Temp: 38°C	
Starting Rotor Speed: 65-70 RPM		Starting Rotor Speed: 65-70 RPM	
0 min	Add Black, Oil, Remaining Chemicals, and Polymer	0 min	SANDWICH IN CURES
82°C	Sweep	82°C	Sweep
93°C	Sweep	99°C	Dump
110°C	Sweep		
138°C	Dump		

Table 3: Mixing Protocol of EPDM V-Belt Compounds

Physical properties of the compounds were tested for tensile strength, elongation, durometer, tear resistance, compression set, Demattia flex - crack growth, and DIN abrasion (rotary drum).

Tensile properties were tested according to ASTM D 412, Test Method A, Die C [13]. Tear strength was tested according to ASTM D 624-00^{E1}(2012), Die C and Die T (trouser tear) [14]. Five tensile and tear specimens per sample were die-cut from 2 mm thick test plaques using a hydraulic die press. Tensile and tear properties were evaluated using an Instron dual column testing system equipped with a 5-kN load cell and a long-travel extensometer. For tensile strength, the gage length was 25 mm and grip separation velocity was 500 mm/min. For tear resistance, the grip separation velocity was 500 mm/min for die C and 50 mm/min for die T.

Durometer was measured as directed in ASTM D 2240-15^{E1}, type A [15].

Compression set was tested according to ASTM D 395-16^{E1}, Method B [16]. Button specimens were aged 70 hours @ 125°C under 25% deflection and measurements were taken after a 1/2 hour recovery at room temperature.

DIN abrasion (rotary drum) was tested per DIN 53 516 / ASTM D 5963-04 (2015), Method A [17].

Demattia crack growth was tested per ASTM D 813-07 (2014) [18] using grooved and pierced specimens tested at 300 cpm, from a 2mm starting crack until the crack grew to 12.7mm.

Viscoelastic properties were examined using dynamic mechanical analysis (DMA) according to ASTM D 5992-96 (2011) [19]. Storage modulus (E'), loss modulus (E'') and tan δ data were obtained through strain sweeps in tension at 30°C with frequency equal to 1 Hz using a Metravib DMA 150 Dynamic Mechanical Analyzer.

A dispersion analysis was performed using a Nanotronics *nSpec* 3D. A topography scan was performed using a 10X Objective and scan settings of $\Delta Z=0.5$ and Model=0.4. The 3D model was flattened after the scan.

RESULTS AND DISCUSSION

Processing Parameters

The evaluation of key processing parameters provides information about required manufacturing times and constraints. The compounds were evaluated for Mooney viscosity and cure kinetics.

Mooney viscosity at 100°C is used to indicate the ease of processing compounds or the ability of the compounds to flow at processing temperatures. Figure 4 provides a comparison of the effect of Lupasol and RFL coatings on the polyester fibers to the resulting viscosity. There was no significant difference in the viscosities of the two compounds.

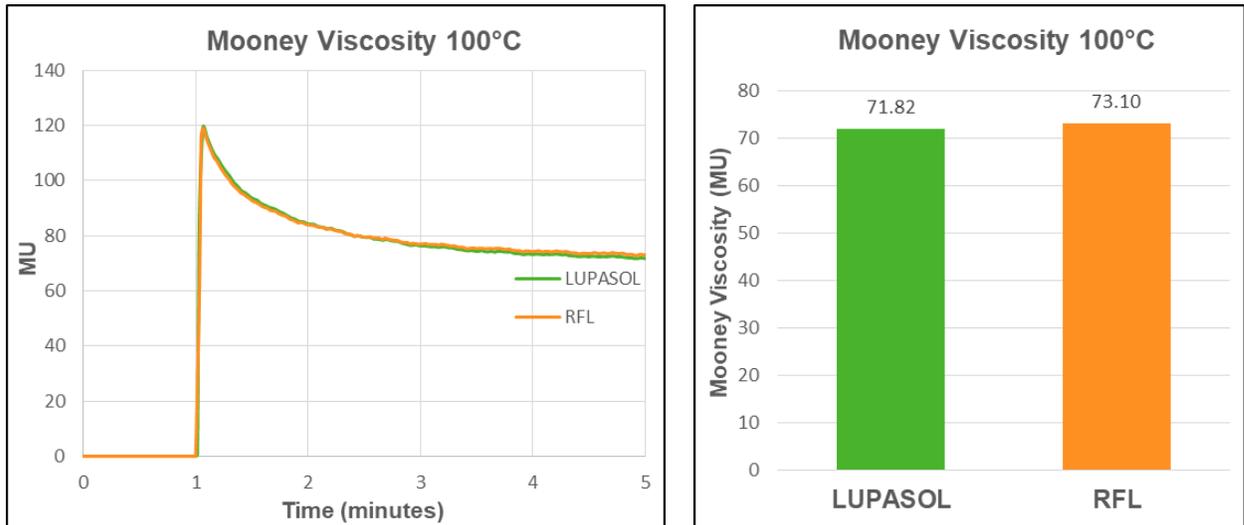


Figure 4: Mooney viscosity at 100°C.

Figure 5 compares the T_{s2} scorch time of the rubber compounds at 170°C. The T_{s2} is the time it takes for the torque to rise 2 points over the minimum torque (ML). Figure 6 compares T_{c90} at 170°C, the time it takes for the rubber compounds to reach 90% of the maximum torque. Figure 7 shows the full rheometer curves for the Lupasol and RFL compounds. As shown by Figures 5 – 7, the Lupasol and RFL compounds exhibit similar cure kinetics.

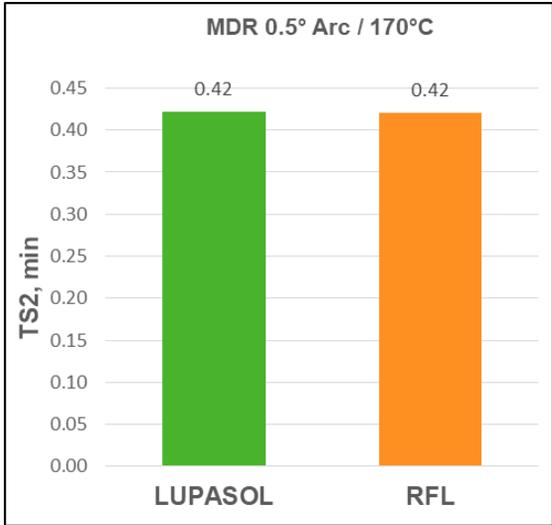


Figure 5: Scorch time (Ts2) by MDR

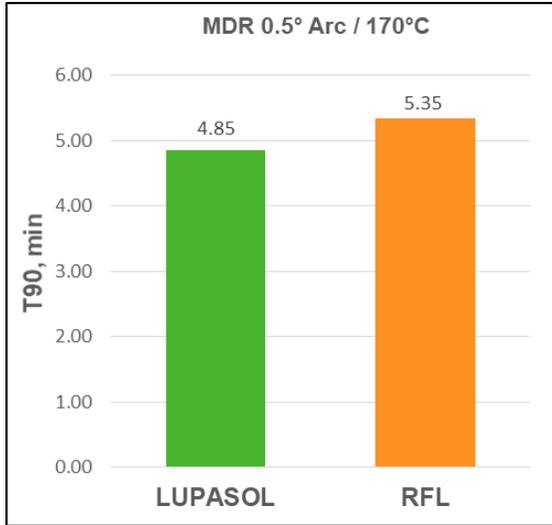


Figure 6: Tc90 (time to 90% cure) by MDR

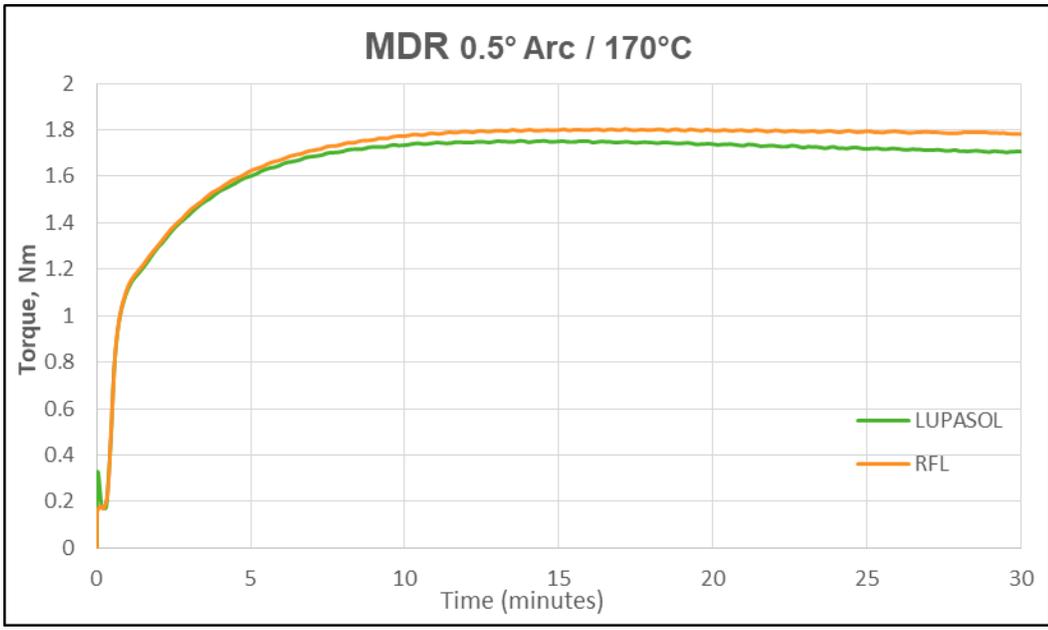


Figure 7: Measured rheometer torque from MDR at 170°C.

Physical Properties

In addition to the processing characteristics, physical properties such as durometer, tensile, elongation, modulus, tear, compression set and abrasion were also evaluated for the Lupasol and RFL compounds. Tensile strength and tear strength were both tested with the grain and against the grain. The grain is imparted on the rubber compound during milling prior to molding. With grain means the fibers are oriented with the direction of strain, which means that the stress increases rapidly as the fibers take the load. In theory, the yield point is where the

bonds between the fibers and the rubber begin to fail. The rubber then continues to stretch until the rubber fails (see figure 8). Against grain means the fibers are oriented perpendicular to the direction of strain, which means that the rubber is stretching as stress is applied. These tensile curves look more typical for a rubber compound because the rubber is primarily taking the load of the stress (see figure 9).

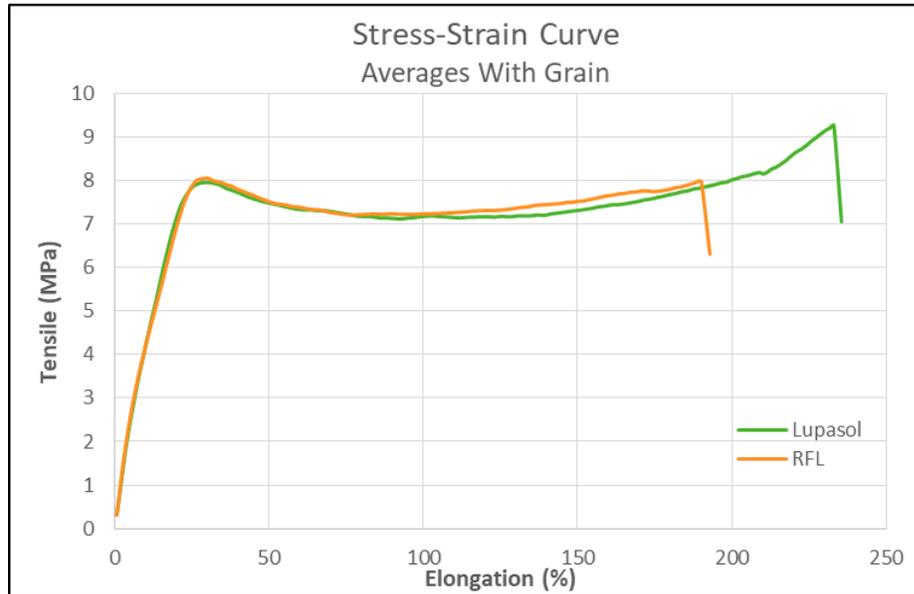


Figure 8: Stress-Strain Curve for Lupasol and RFL Tested With the Grain

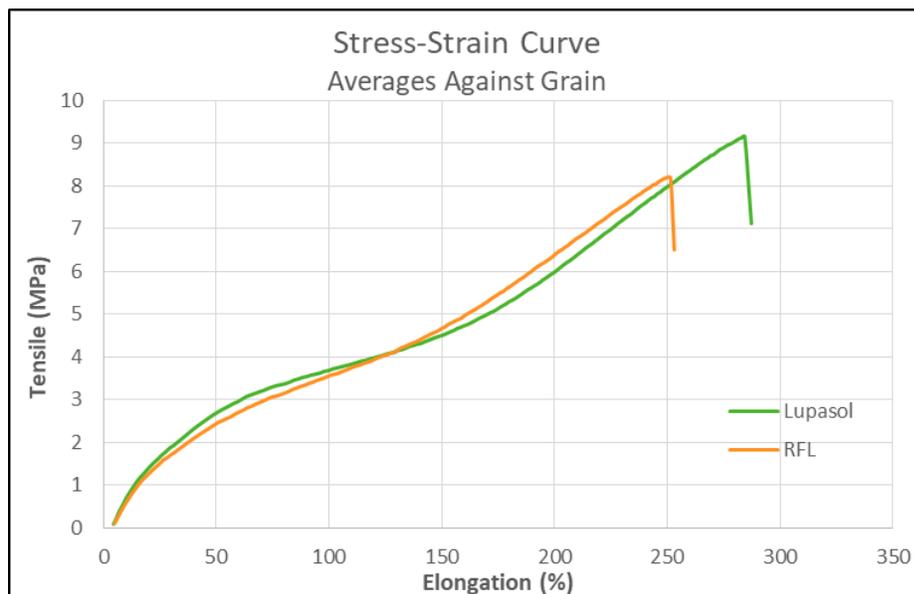


Figure 9: Stress-Strain Curve for Lupasol and RFL Tested With the Grain

Figure 10 compares the tensile strength results for the Lupasol and RFL compounds. The compounds had similar values for the with grain tensile strength at yield which suggests that there is similar bond strength between the polyester fibers and the rubber. The tensile strength at break for both with grain and against grain samples had similar results between the Lupasol and RFL compounds.

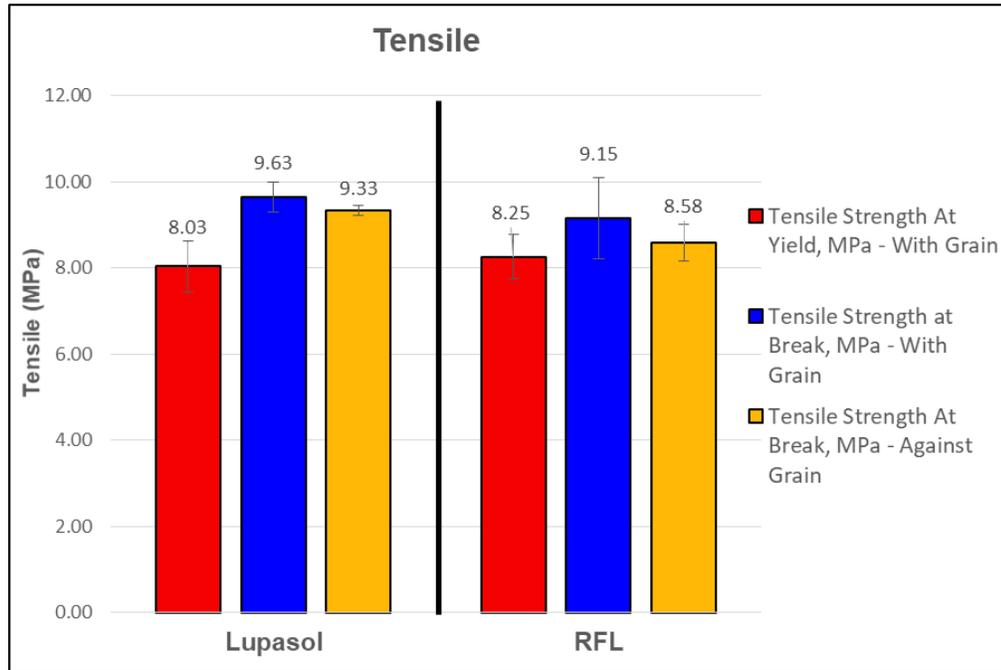


Figure 10: Tensile Strength of Lupasol and RFL Compounds

Figure 11 compares the percent elongation results for the Lupasol and RFL compounds. The compounds had similar values for the with grain elongation at yield which suggests that there is similar bond strength between the polyester fibers and the rubber. The Lupasol compound had slightly higher elongation at break than the RFL for both with grain and against grain samples. This may suggest that the Lupasol compound has slightly better dispersion than the RFL compound.

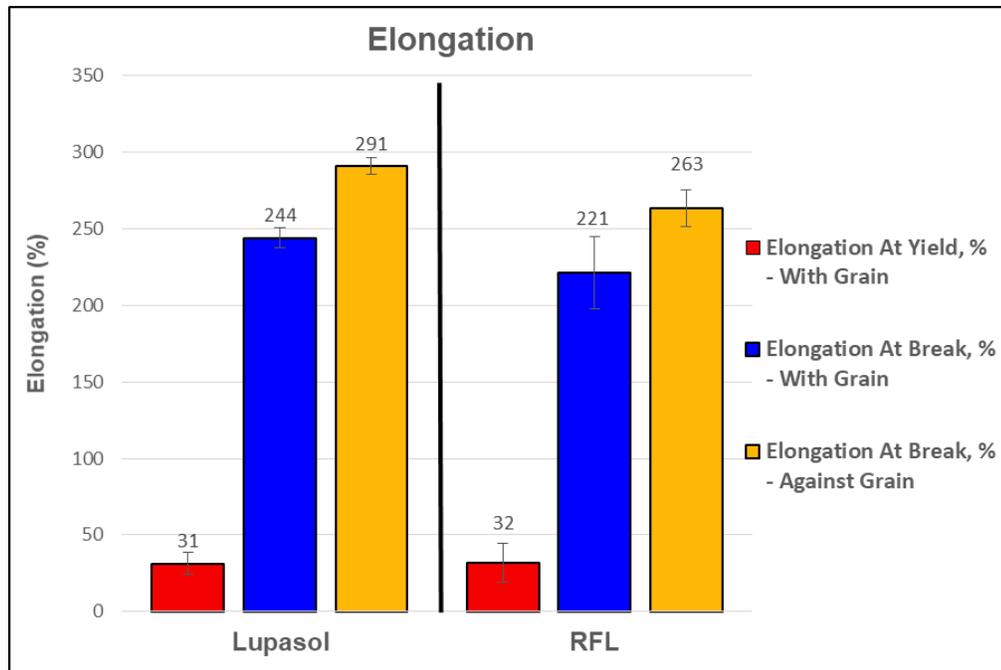


Figure 11: Percent Elongation of Lupasol and RFL Compounds

Figures 12 & 13 compare the Die C and Die T tear strength results for the Lupasol and RFL compounds. Die C Tear Resistance is the force required to cause a rupture (tear initiation) at the stress concentration (90° apex) of the die C test piece. Die T or trouser tear strength is the force required to propagate a tear in a die T (trouser) test piece in a direction parallel to the length of both legs. The Lupasol compound had slightly better die C tear resistance than the RFL compound. For trouser tear resistance, the RFL compound had lower with grain tear and higher against grain tear than the Lupasol compound. The RFL also had a much higher standard deviation in the against grain tear than the Lupasol compound. This suggests that the fibers coated with the RFL may not be as well dispersed as the Lupasol coated fibers.

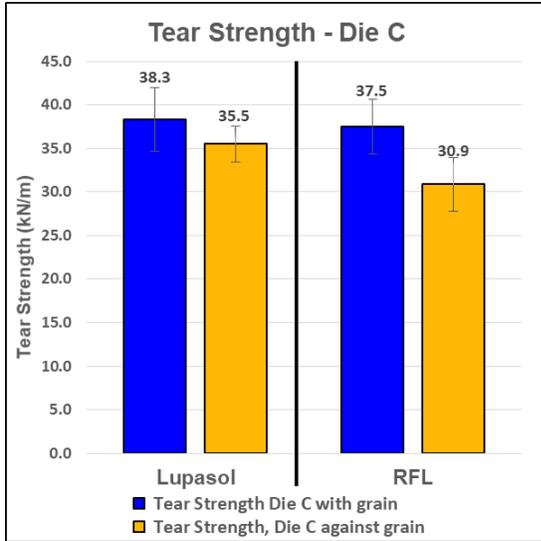


Figure 12: Die C (Trouser) Tear Strength

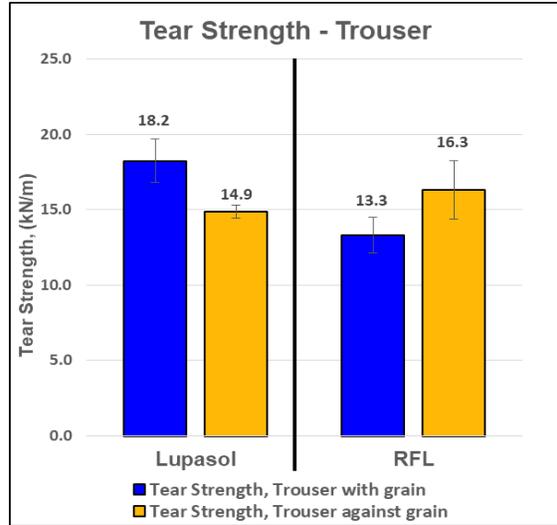


Figure 13: Die T (Trouser) Tear Strength

Figure 14 compares the durometer (type A) results for the Lupasol and RFL compounds. The compounds had similar durometer values.

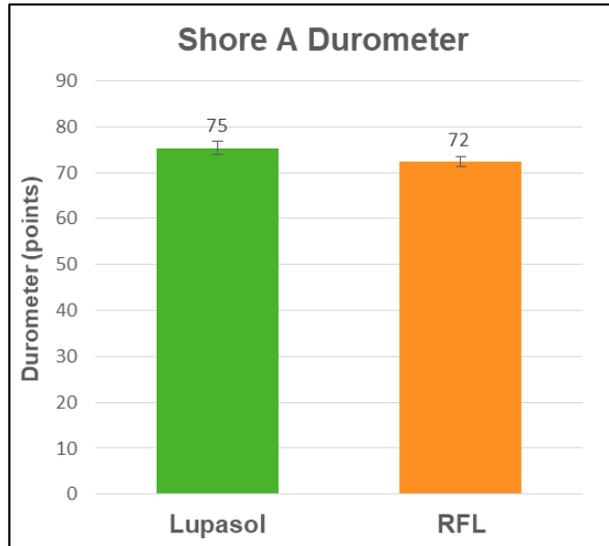


Figure 14: Durometer (type A)

Figure 15 compares the compression set results for the Lupasol and RFL compounds. The test specimens were aged 70 hours @ 125°C under 25% deflection. The compounds had similar compression set values.

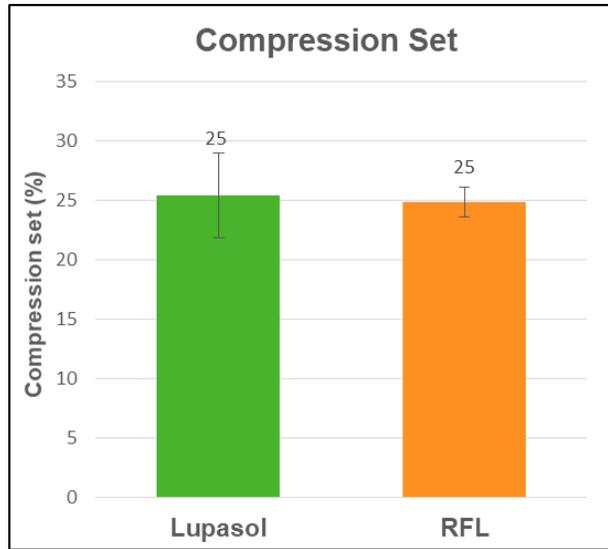


Figure 15: Compression Set After 70 hours @ 125°C under 25% deflection

Figure 16 compares the DIN abrasion (rotary drum) results for the Lupasol and RFL compounds. The test was performed following method A of DIN 53 516 / ASTM D 5963-04 (2015). The compounds had similar abrasion properties.

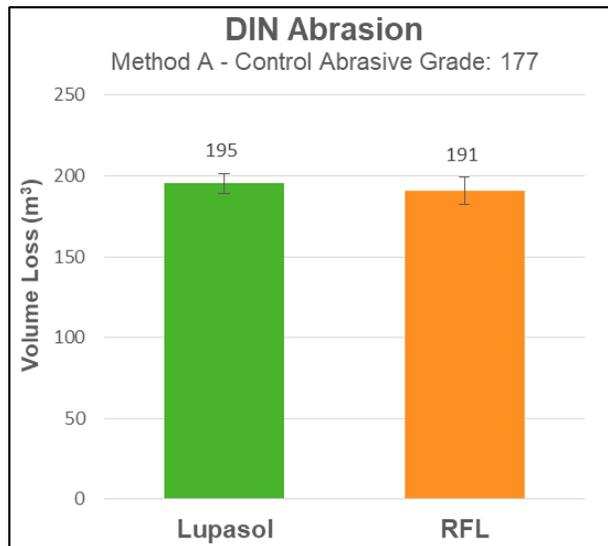


Figure 16: DIN Abrasion – Method A

Table 4 shows a summary of the physical property data. Most of the physical properties are similar between the Lupasol and RFL compounds. The slight differences suggest that the fibers with the Lupasol coating may be more thoroughly dispersed than the RFL coated fibers.

	Lupasol with grain	RFL with grain	Lupasol against grain	RFL against grain
Tensile Strength at Break, MPa	9.63	9.15	9.33	8.58
<i>Standard Deviation</i>	0.35	0.95	0.12	0.43
Tensile Strength at Yield, MPa	8.03	8.25	No Yield Point	No Yield Point
<i>Standard Deviation</i>	0.60	0.52		
Elongation Strain at Break, %	244	221	291	263
<i>Standard Deviation</i>	7	23	6	12
Elongation Strain at Yield, %	31	32	No Yield Point	No Yield Point
<i>Standard Deviation</i>	7	13		
50% Modulus, MPa	7.49	7.46	2.70	2.43
<i>Standard Deviation</i>	0.46	0.28	0.43	0.20
100% Modulus, MPa	7.14	7.26	3.69	3.55
<i>Standard Deviation</i>	0.27	0.07	0.43	0.17
200% Modulus, MPa	8.08	7.07	5.99	6.38
<i>Standard Deviation</i>	0.13	2.81	0.33	0.17
Tear Strength Die C, kN/m	38.31	37.51	35.53	30.87
<i>Standard Deviation</i>	3.65	3.15	2.06	3.09
Tear Strength Die T, kN/m	18.23	13.31	14.86	16.31
<i>Standard Deviation</i>	1.44	1.20	0.42	1.96
Shore A Durometer, points	75	72		
<i>Standard Deviation</i>	1.3	1.1		
Compression Set, %	25	25		
<i>Standard Deviation</i>	3.6	1.3		
Abrasion Avg. Vol. Loss (mm³)	195	191		
<i>Standard Deviation</i>	5.9	8.7		

Table 4: Summary of Physical Property Data

Dynamic Testing

Dynamic properties including Demattia crack growth and Dynamic mechanical analysis (DMA) were also evaluated for the Lupasol and RFL compounds. Figures 17 & 18 show that the Lupasol and the RFL had similar performance for Demattia crack growth.

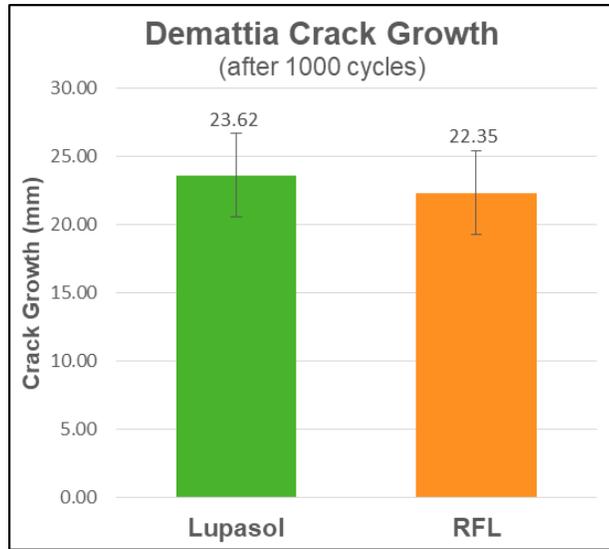


Figure 17: Demattia Crack Growth after 1000 Cycles

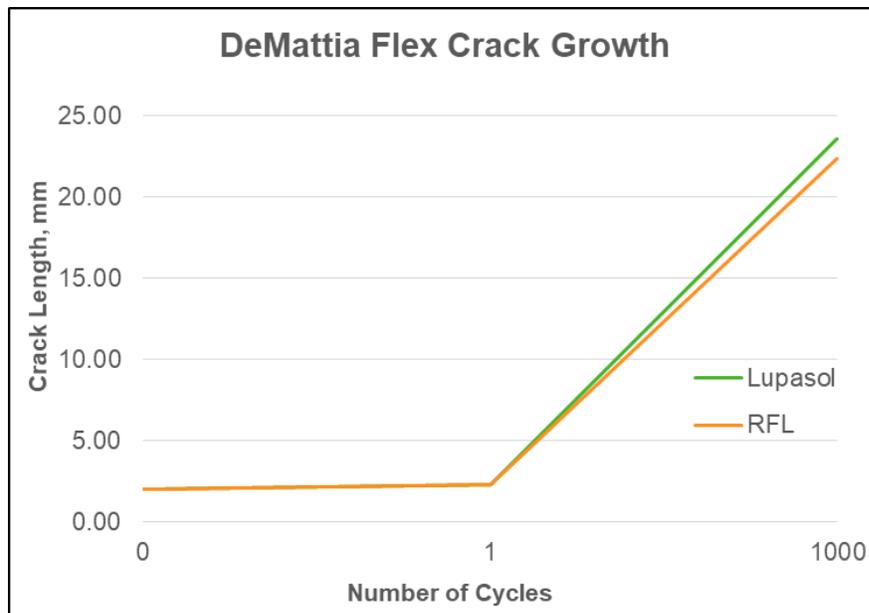


Figure 18: Demattia Crack Growth versus Number of Cycles

Storage modulus (E'), loss modulus (E'') and $\tan \delta$ data were obtained through strain sweeps in tension at 30°C with frequency equal to 1 Hz. The range of dynamic strain was selected to ensure that the bonds between the rubber and the polyester fibers were not broken. Figures 19 – 21 show the storage modulus (E'), loss modulus (E'') and $\tan \delta$ data of the compounds respectively. The Lupasol compound has slightly higher storage modulus values than the RFL, which suggests that the Lupasol compound is more reinforcing possibly due to better dispersion of the fibers or better bonding of the fibers to the rubber. The Lupasol compound has slightly higher loss modulus values than the RFL, which also suggests that the Lupasol

compound is more reinforcing than the RFL compound. The tan deltas of the Lupasol and the RFL are very similar despite the differences in the storage and loss modulus profiles.

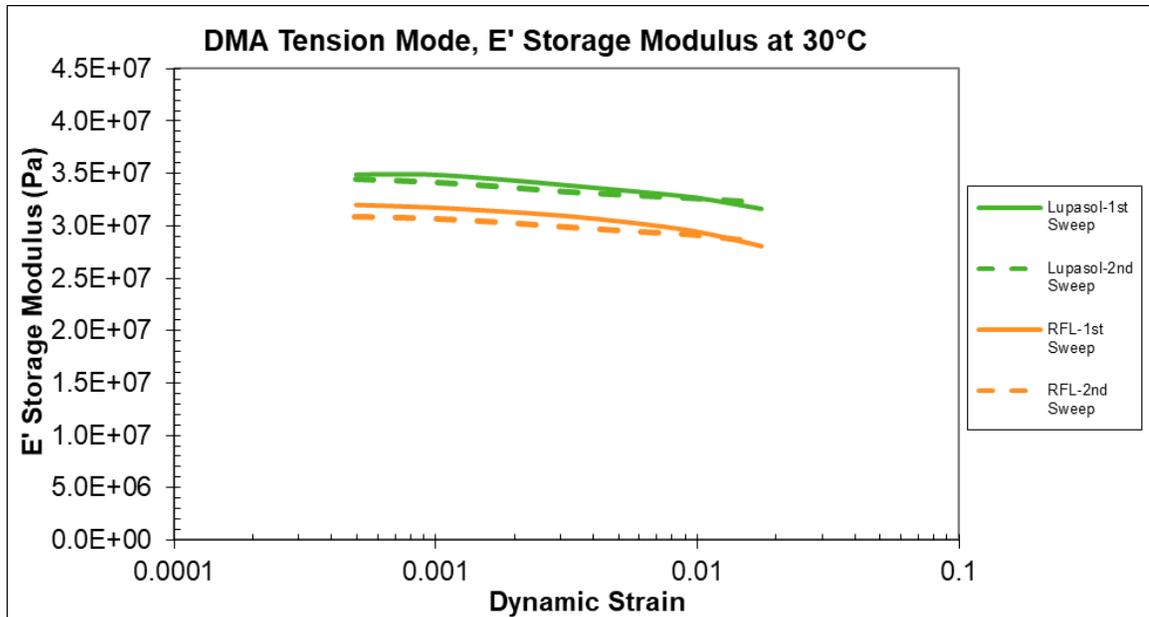


Figure 19: Storage Modulus from Strain Sweep at 30°C

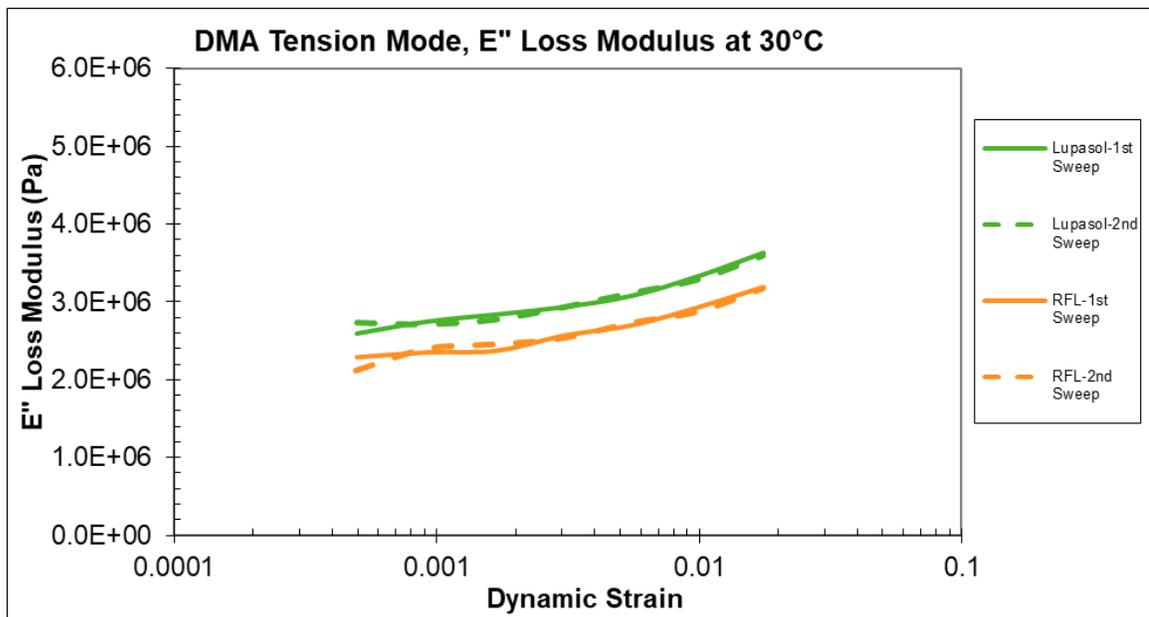


Figure 20: Loss Modulus from Strain Sweep at 30°C

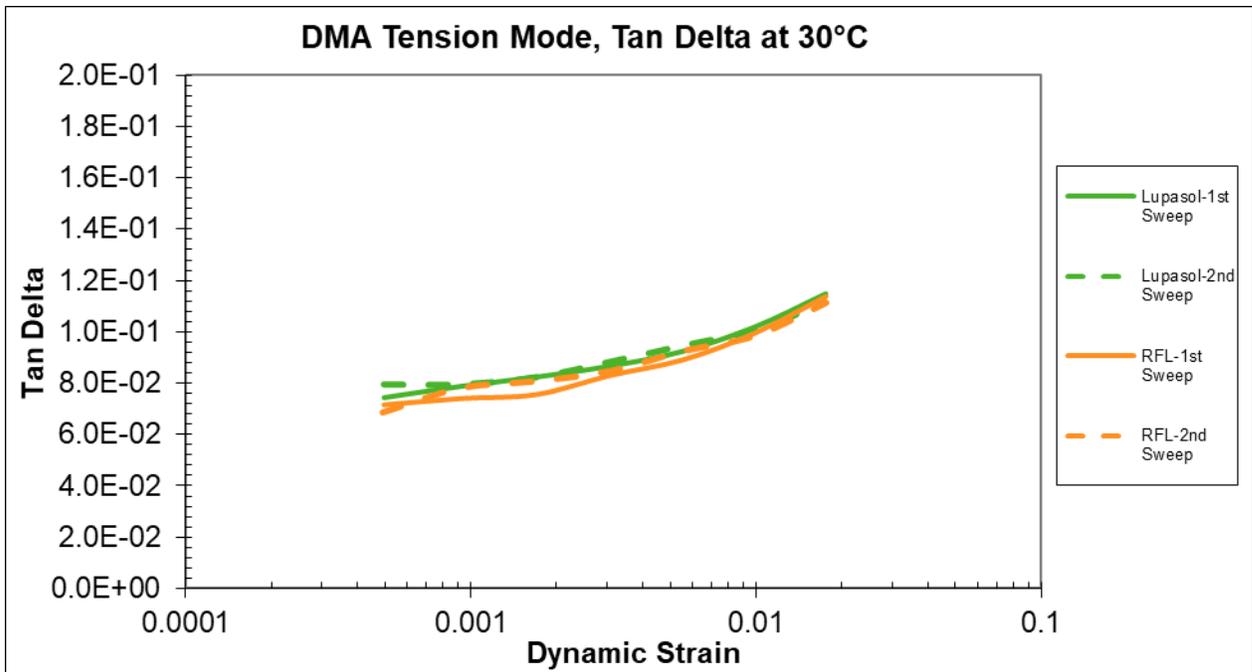


Figure 21: Tangent Delta from Strain Sweep at 30°C

Figures 22 & 23 show the Payne effect and Mullins effect of the Lupasol and RFL compounds. The Payne effect is the drop in E' as the dynamic strain is increased. The Payne effect is attributed to the filler-filler interaction, the breaking and recovery of weak physical bonds linking adjacent filler particles. Better filler dispersion gives lower Payne effect. The Mullins effect is a measure of the dynamic stress-softening (the drop in E') that is observed between the first and second strain sweeps due to the polymer-filler matrix being pulled apart during the first strain sweep and not having time to re-agglomerate. A lower Mullins effect would indicate stronger polymer to filler interaction. The Lupasol compound has a slightly lower Payne effect than the RFL, which suggests that the Lupasol compound has better dispersion of the fibers. The Lupasol compound has a lower Mullins effect than the RFL compound, which suggests that the Lupasol coated fibers have better bonding to the rubber matrix than the RFL coated fibers.

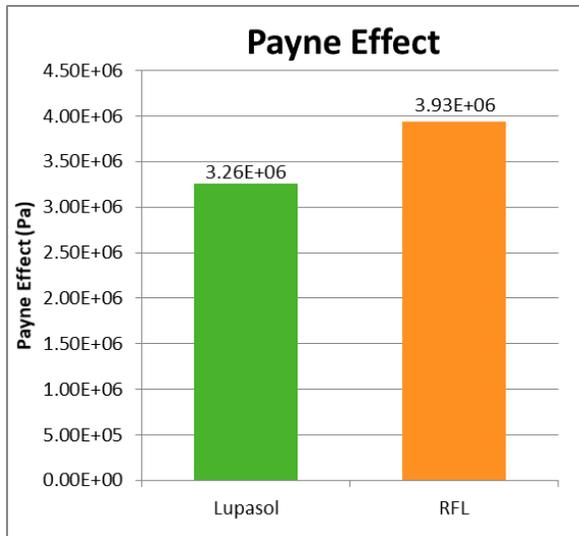


Figure 22: Payne Effect from Strain Sweep at 30°C

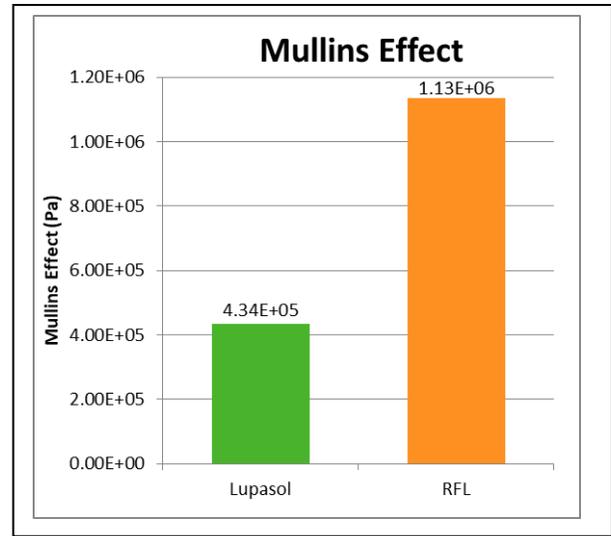


Figure 23: Mullins Effect from Strain Sweep at 30°C

Dispersion Analysis

A 3D topography scan was performed on the Lupasol and RFL compounds looking at cuts that were made with the grain (looking at the sides of the fibers) and against the grain (looking at the ends of the fibers). Table 5 shows a summary of the data collected from the topography scan. In this analysis a peak or a valley was identified as a fiber (either the end of it or the side of it depending on the view).

	3D Topography Scan Summary			
	Sample ID	Lupasol	RFL	Lupasol
Orientation	With Grain	With Grain	Against Grain	Against Grain
Avg Volume of Peaks+Valleys, μm^3	4880.3	6419.3	5776.2	9013.1
Sa (Surface Roughness), μm	3.65	6.92	6.61	6.56
Sq (Roughness Deviation), μm	53.95	71.19	82.15	63.86
Number of Peaks+Valleys	105	189	264	164

Table 5: Summary of Data from nSpec 3D Topography Scan

Sa – arithmetical mean roughness value (area): The arithmetical average of the absolute values of the profile height deviations from the mean surface plane, recorded within the evaluation area.

Sq – root mean square deviation (area): The root mean square average of the profile height deviations from the mean surface plane, recorded within the evaluation area. It is equivalent to the standard deviation of heights.

Lupasol & RFL - With Grain

The with grain data from Table 5 along with the images in Figures 24 – 27 suggest that the fibers with the RFL have a larger volume than the Lupasol coated fibers. Since the same polyester fibers were used (only different coatings) in both compounds, this may indicate that the RFL fibers are clumped together instead of individually dispersed.

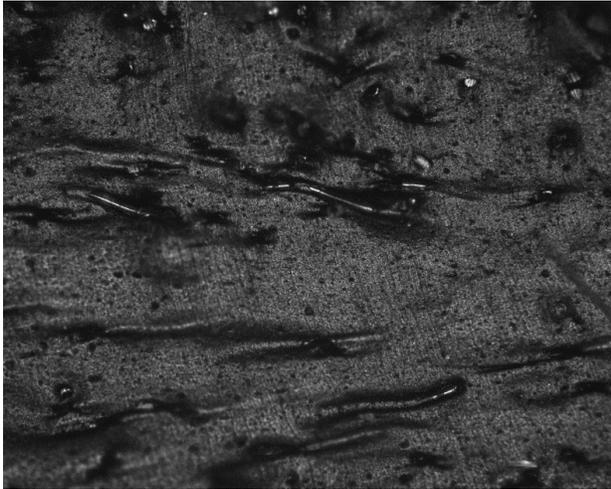


Figure 24:
Image at 10x Magnification of Lupasol With Grain

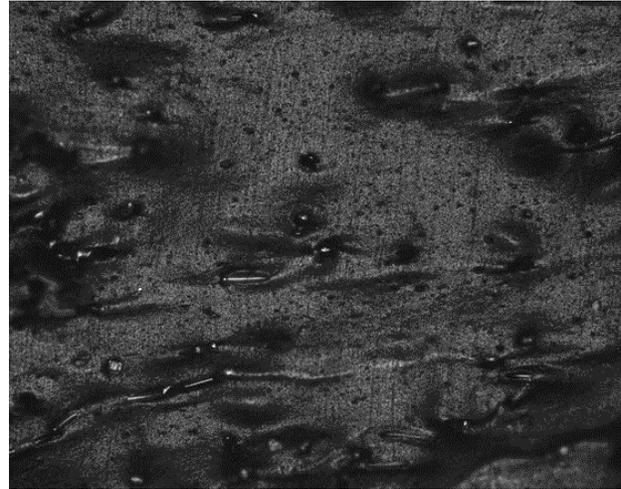


Figure 25:
Image at 10x Magnification of RFL With Grain

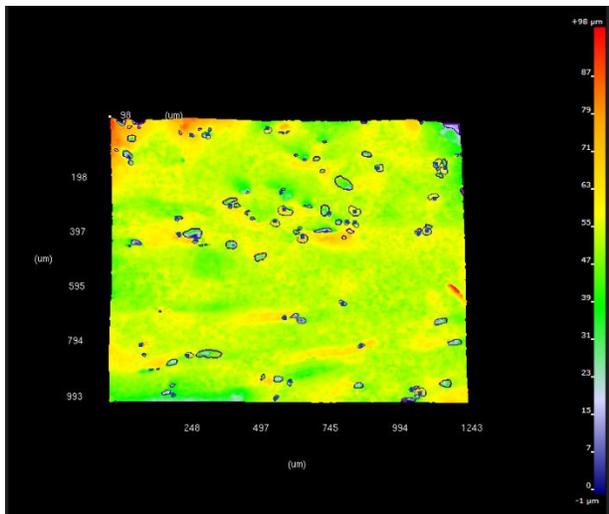


Figure 26:
3D Model of Surface of Lupasol With Grain

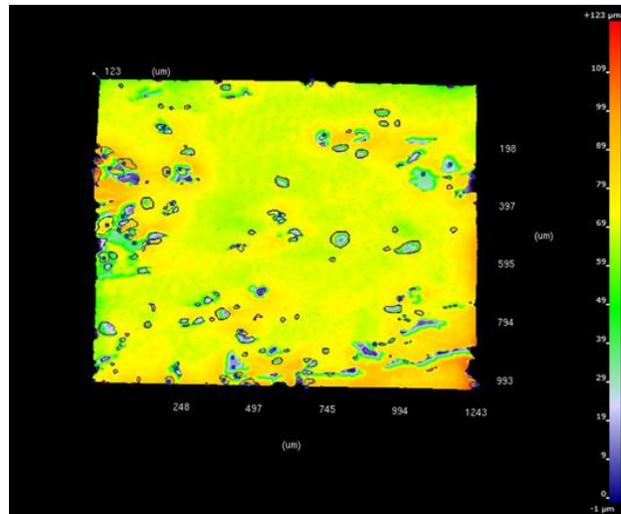


Figure 27:
3D Model of Surface of RFL With Grain

Lupasol & RFL – Against Grain

The against grain data from table 5 along with the images in figures 28 – 31 also suggest that the fibers with the RFL have a larger volume than the Lupasol coated fibers. The camera images below (figures 28 & 29) as well as the number of peaks and valleys shown in the table show that there are many individual fibers visible in the compound with the Lupasol coated fibers, while the RFL coated fibers seem to be grouped together in a lower number of clumps. This dispersion analysis supports other evidence (such as the physical property data and the DMA data) that suggests that the Lupasol coated fibers achieved better dispersion in the polymer matrix than RFL coated fibers.

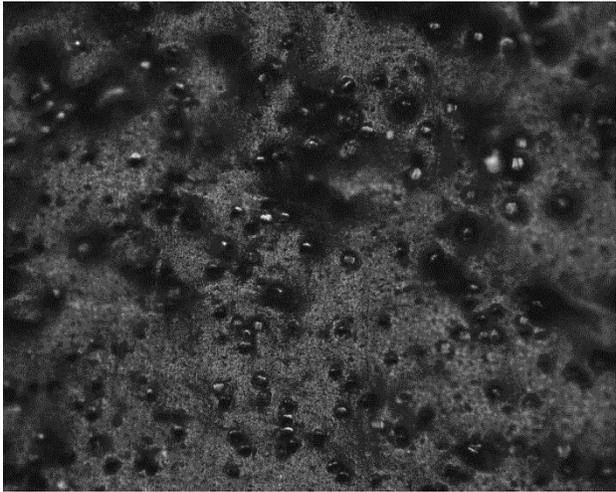


Figure 28:
Image at 10x Magnification of Lupasol Against Grain

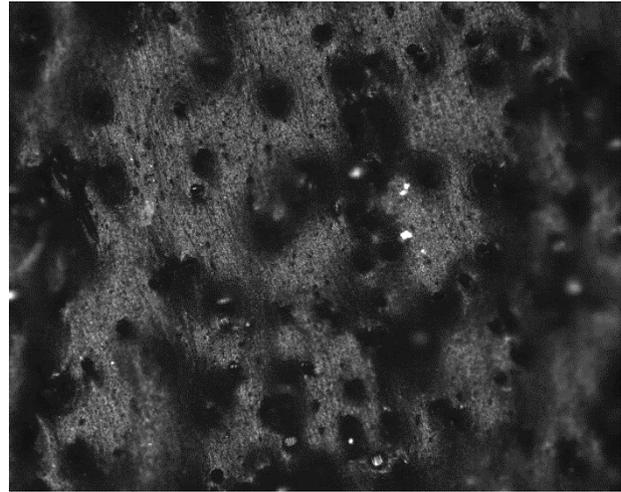


Figure 29:
Image at 10x Magnification of RFL Against Grain

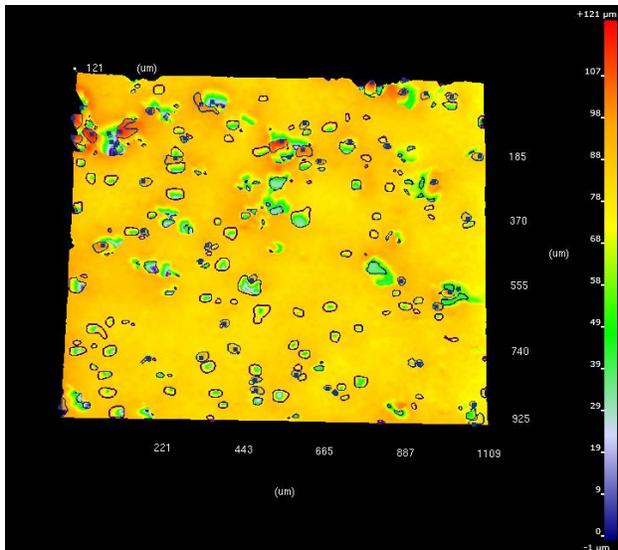


Figure 30:
3D Model of Surface of Lupasol Against Grain

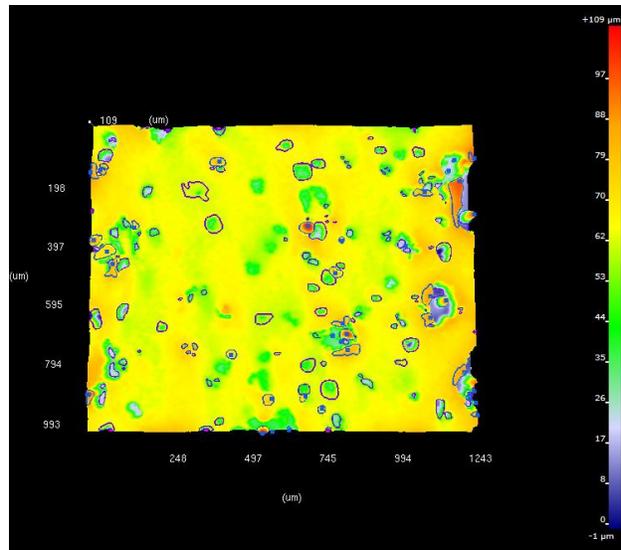


Figure 31:
3D Model of Surface of RFL Against Grain

CONCLUSIONS

Most of the physical properties of the Lupasol & RFL compounds are very similar. The slight differences in properties such as elongation and tear resistance suggest that the fibers with the Lupasol coating may be more thoroughly dispersed than the RFL coated fibers.

The Dynamic Mechanical Analysis showed that the Lupasol compound has slightly higher storage modulus and loss modulus values than the RFL, while maintaining similar tangent deltas. This also suggests that the Lupasol compound is more reinforcing possibly due to better dispersion of the fibers or better bonding of the fibers to the rubber.

The dispersion analysis of the against grain compound showed both visually and numerically that there are more individual fibers in the compound with the Lupasol coated fibers, while the RFL coated fibers seem to be grouped together in a lower number of clumps.

All the data indicates that the Lupasol coated fibers achieved better dispersion in the polymer matrix than RFL coated fibers while maintaining the physical properties of the compound.

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