

Wetting and Mechanical Properties of Modified Resins

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ABSTRACT

A series of materials are reacted into epoxy, unsaturated polyester and vinyl ester composite resins. The resultant combined materials are evaluated for improved wetting, hardness, flexibility, tensile strength, impact resistance, and elongation. In particular the effect of using reactive surface tension lowering agents in resins on fiber wetting is examined.

1. INTRODUCTION

Organommodified silicone polymers are used in many markets such as inks and coatings, plastics, personal care, polyurethane foam, oil and gas; but their use in composites products is just beginning. While these polymers also lower surface tension, provide wetting, flow and leveling, and protection in composites, their use is limited due in part to the reputation silicone has for causing problems.

Silicone oil does indeed have a well-earned reputation for causing adhesion and de-wetting problems but the chemically modified organic/silicone hybrid polymers we explore in this study are soluble in organic or aqueous systems. The solubility eliminates these problems normally associated with “pure” silicones. In this work we will show surface tension reduction as well as flow and wetting improvements in some composite resin systems at 1 % use levels and below.

We have also shown in many other systems, using the same resin types used in composites, that higher levels of reactive silicones alter the inherent properties of the resin. [1] The soft, low T_g silicones provide flexibility, elongation and some release properties. Perhaps surprising is that at the right use level, tensile strength and total energy to break properties are dramatically improved. Herein, we also show this effect using reactive wetting agents at around 20 % use level.

2. EXPERIMENTATION

2.1. General

Three epoxy formulations were evaluated in various tests. An epoxy resin, D.E.R. 331 from Dow, is cured with amine hardeners including a solubilized amine functional silicone at 0, 10, 20 and 30 % use levels. Similarly EPON 828/ Epikure W and EPON 863/ Epikure 3300 (all from Hexion) formulations were evaluated with several silicone additives all at 20 % use level.

2.2. Surface Tension Measurement

The sample solutions were mixed until homogeneous and minimal vacuum was applied to degas the solutions before measurement of the surface tension with a KSV Sigma 70 Tensiometer. Ten

individual measurements were taken and recorded by the computer program which reports the average surface tension and the standard deviation for each sample.

2.3. Viscosity Measurement

The viscosity of each test sample was measured using Brookfield Viscometer Model# DV-III. Each test sample was collected and placed into a viscometer. For each viscosity measurement, the motor was set at speeds of 5, 7, and 9 rpm. An average of these values was reported in units of centipoise (cP).

2.4. Rheological Properties and Work Time Measurements

The rheological properties G' , G'' and $\tan \delta$ of each test sample were measured using TA Instruments Rheometer AR-G2. A sample was collected, placed into a rheometer and heat cured. The G' , G'' , and $\tan \delta$ are reported directly from the instrument.

The work time, which is defined as the time required for a sample to double its viscosity, is determined in the rheometer as well. The time required to double the viscosity is reported as work time in seconds.

2.5. Wetting and Relative Contact Angle

A large glass fiber (E Glass, Plain Weave from GlassFiber Supply) was placed on top of a section of aluminum foil laid flat. A few drops of sample were pipetted onto the fiber. The initial diameter of the hemispherical-shaped sample was measured after 1 min.

To determine contact angle a picture was taken of the hemispherical sample and printed out so that a contact angle value could be estimated manually. These contact angles were reported as relative rankings. In the hierarchy, a 1 represents the sample with the highest contact angle and therefore the least wetting.

Once the sample had dried a measurement of after drying diameter was taken.

2.6. Flow

A fresh aluminum foil pan with a glass fiber was inclined at a 45° angle. A sample was applied by pipette and the flow is reported both as the time for the sample to move 20 mm down the ramp and as the distance traveled. A distance of 120 mm indicates the droplet traveled the total test length.

2.7. Gelation Time

Gelation time is measured by placing a sample in a small plastic weighing pan and periodically checking the sample. The time required for a sample to reach this state was then recorded.

2.8. Shrinkage

Shrinkage was determined by oven curing samples in a 40 cm long by 0.5 cm^2 cross section rectangular mold. After curing and cooling to ambient, the shrinkage of the sample was measured and reported as a percentage of the original length.

2.9. Bending

Bending is measured to determine the flexibility of the test samples after oven-curing. A molded dog bone is cured and attached to a flat surface with half of its length unsupported. Weights are applied at 90°.

It is important to note that the majority of test samples in this study produced a brittle, glass-like cured structure. All of these control materials were found to not be able to bend without cracking or breaking. Five of the additive modified samples were found to be able to withstand bending to 45°. These samples were compared with one another and ranked according to their ability to withstand bending with 1 being the highest bending or most flexible and 10 being no bending.

2.10. Tensile Strength and Elongation

Once the dog bones were developed and cooled to room temperature, they were measured for tensile strength and elongation properties using the INSTRON 1122 and ASTM D412 Die C standard test method.

2.11. Hardness Measurement

Cured dog bone molded samples were evaluated with a Shore D Durometer. Three readings were taken and reported as an average.

2.12. Silicone Structures

Various silicone structures were used in this paper (Table 2). Variations include molecular weight (MW); linear compared to pendant architecture; type of organic modification (for solubility in the formulation); and the number and type of reactive groups. While the most commonly used materials were polyether modified silicones, a few aliphatic hydrocarbon types were screened as well.

Table 1. Silicone Additives

Code	Modification	Architecture	Reactive Group
A1	Hydrocarbon	Pendant	None
VE1	Alkylvinylester	Pendant	Vinyl ester
E1	Cycloaliphatic Epoxy	Pendant	Epoxy
E2	Cycloaliphatic Epoxy	Pendant	Epoxy
H1	Alkylalcohol	Pendant	Hydroxyl
H2	Alkylalcohol	Pendant	Hydroxyl
H3	Alkylalcohol	Pendant	Hydroxyl
H4	Alkylalcohol	Pendant	Hydroxyl
H5	Alkylalcohol	Pendant	Hydroxyl
N1	Alkylamine	Pendant	Amine
N2	Alkylamine	Pendant	Amine
PE1	Polyether	Pendant	Hydroxyl
PE2	Polyether	Pendant	Hydroxyl
PE3	Polyether	Pendant	Hydroxyl
PE4	Polyether	Pendant	Hydroxyl

PE5	Polyether	Pendant	Hydroxyl
PE6	Polyether	Pendant	Hydroxyl
PE7	Polyether	Pendant	Hydroxyl
PE8	Polyether	Pendant	Hydroxyl
PE9	Polyether	Pendant	Hydroxyl
PE10	Polyether	Pendant	Hydroxyl
PE11	Polyether	Pendant	Hydroxyl
PE12	Polyether	Linear	Hydroxyl
PE13	Polyether	Linear	Hydroxyl
PE14	Polyether	Linear	Hydroxyl
PE15	Polyether	Linear	Hydroxyl
PE16	Polyether	Linear	Hydroxyl
PE17	Polyether	Linear	Hydroxyl
PE18	Polyether	Linear	Hydroxyl
PE19	Polyether	Pendant	Hydroxyl
PE20	Polyether	Pendant	Hydroxyl
PE21	Polyether	Pendant	Hydroxyl
PE22	Polyether	Pendant	Hydroxyl
PE23	Polyether	Pendant	Hydroxyl
PE24	Polyether	Pendant	Hydroxyl
PE25	Polyether	Pendant	Hydroxyl
PE26	Polyether	Pendant	Hydroxyl
PE27	Polyether	Pendant	Hydroxyl
PE28	Polyether	Pendant	Hydroxyl
PE29	Polyether	Pendant	Hydroxyl

3. RESULTS

Figure 1 shows the surface tension of the AME 6001 T-25 (Ashland) epoxy vinyl ester resin with varying concentrations of a polyether modified silicone, designated PE9. This well-known concentration effect is expected for surface tension reduction. Further screens were conducted at 1 %, well above the minimum needed to see an effect.

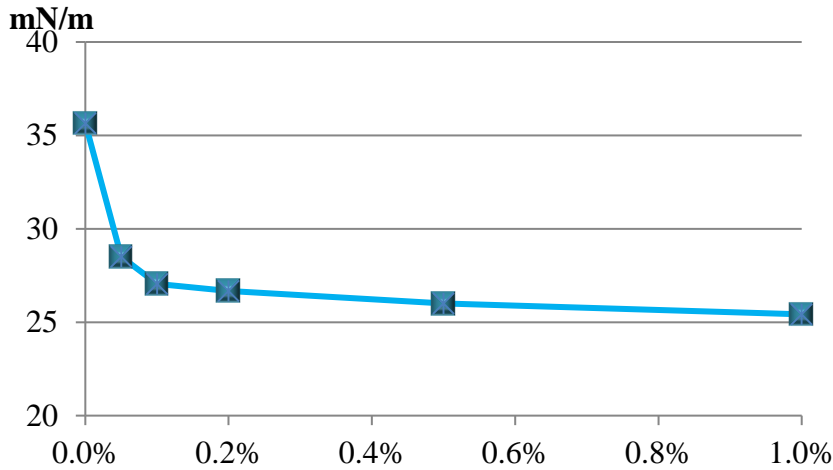


Figure 1: Surface Tension of PE9 in AME 6001 T-25 by concentration.

Next, a large group of organomodified silicones were screened at 1 % use level for surface tension reduction in Aropol Q 67700 T-30 (Ashland), an unsaturated vinyl ester, and in AME 6001 T-25 (Ashland) epoxy vinyl ester. Referring to Figure 2, the results show that all of these materials reduced surface tension. Some of the materials were very effective, reducing surface tension into the 25-28 mN/m range where the resin will wet most fibers.

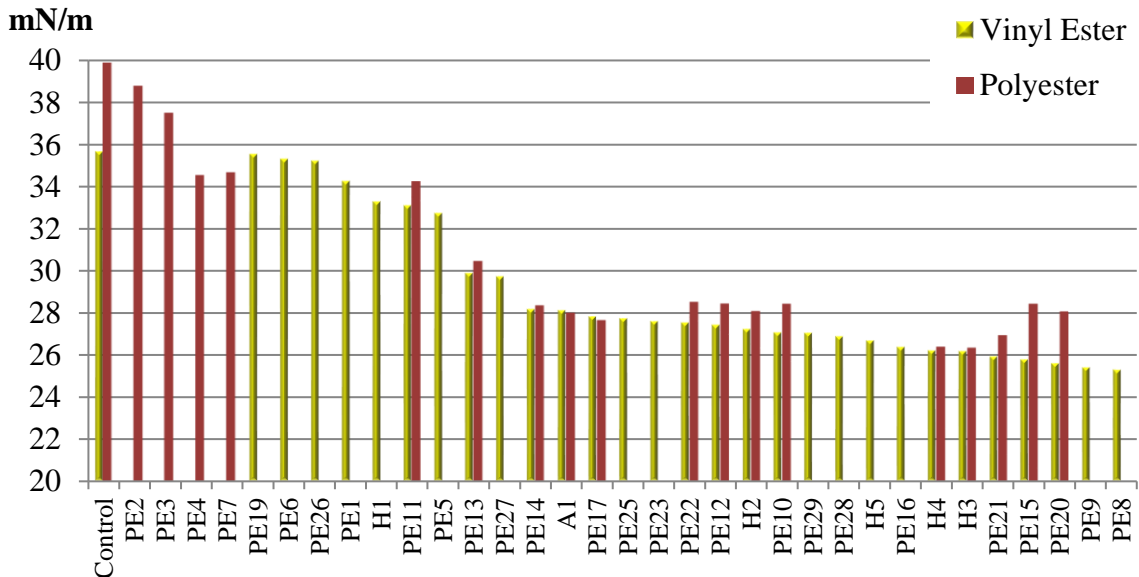


Figure 2: Surface Tension at 1% Additive in Two Resins.

Vinyl ester functionalized versions of PE11, PE12 and PE22, referred to as VE1, VE2 and VE3 respectively, were used to demonstrate the impact of reacting the wetting agents into the resins at higher concentrations. These materials were reacted into AME 6001 resin at 24 % using the very simple formula shown in Table 2. The mechanical properties are shown in Table 3 with key properties plotted in Figure 3.

Table 2: Basic Vinyl Ester Formula

Component	Weight Percent
Reactive Wetting Agent	24.00 %
AMF 6001	73.85 %
MEKP	1.98 %
Duroct Co 12%	0.05 %
DMA	0.12 %
Total	100.00 %

Table 3: Mechanical Properties of Vinyl Ester Formula with 24 % Reactive Additives.

Maximum Tensile	Control	VE1	VE2	VE3
Tensile Str. (MPa)	4.92	61.1	43.47	46.35
Elongation (%)	1.23	5.09	3.88	4.04
Total Energy (mJ/mm)	1.86	9.98	6.11	9.76
Hardness (Shore D)	89	82	81	83
G' (MPa)	13.48	4.25	3.46	3.92
G'' (MPa)	1.1	0.72	0.59	0.45
Tan(δ)	0.08	0.17	0.17	0.12

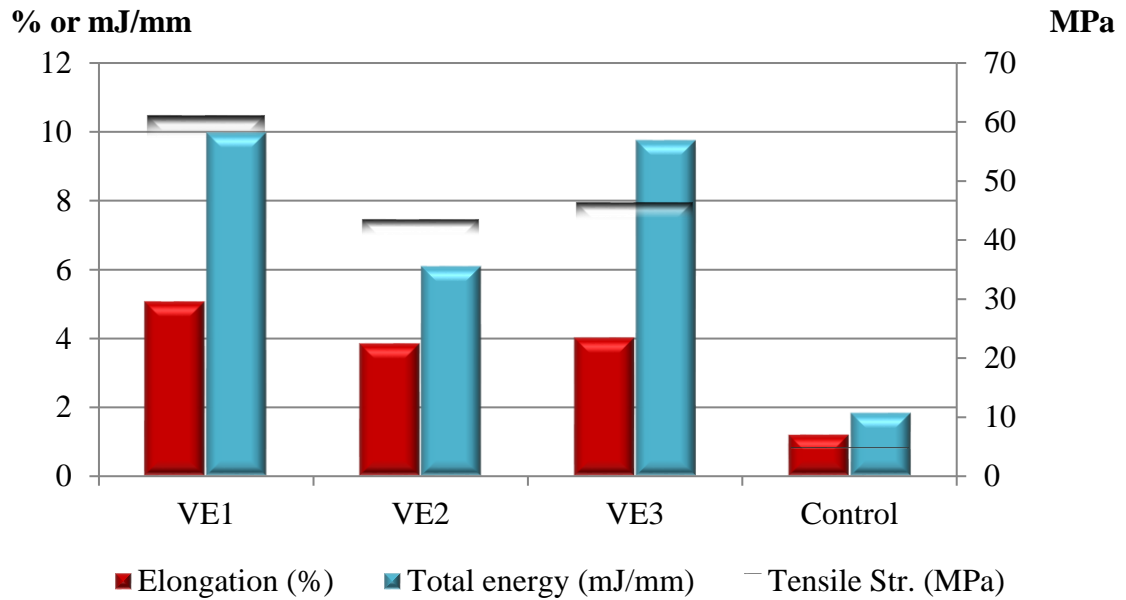


Figure 3: Key Properties of Vinyl Ester with 24 % Reactive Additives.

It is important to note, that the elongation and strength are dramatically increased when the wetting agents are reacted into the resin at a high use level. Normally the maximum in these properties occurs around 20-25 % of the silicone by weight. [1]

Next three epoxy formulations were used to demonstrate wetting and reaction into the same system. A standard system that we often use was run as a positive control. This uses DER 331 (Dow), silicone designated as N2 at 20 % loading, Ancamine 1618 (Dow) and AMI-1 catalyst. The amine to epoxy ratio was 1:1. The reactive amine group is very effective at reacting into the epoxy resin and is a system we have published before. [2]

In addition, formulations were evaluated based on EPON 828 cured with Epikure W and EPON 863 cured with Epikure 3300 (all from Hexion). Table 4 shows these formulations which used a variety of reactive wetting agents at 20 %.

Table 4: Epon 828 and 863 Formulations

		EPON 828	Epikure W	EPON 863	Epikure 3300	Additive
EPON 828	Control	80 %	20 %	-	-	-
Epikure W	Test	64 %	16 %	-	-	20 %
Epon 863	Control	-	-	80 %	20 %	-
Epikure 3300	Test	-	-	64 %	16 %	20 %

The products were cured at 170°C. Table 5 shows the wetting properties and Table 6 reports the mechanical properties of these systems. Table 7 shows the work time properties.

Table 5: Wetting Properties of Epoxy Formulations

Resin	Additive	ST (mN/m)	Wetting Diameter (mm)	Dry Wetting Diameter (mm)	Flow Time (s)	Distance (mm)	Rank of Contact Angles 1=High
DER331/Ancamine 1618/AMI-1	N2	24.3	18.6	39.8	120	28	4
	control	50.8	17.1	82.0	132	38	1
	PE14	32.1	21.2	46.7	9	120	8
EPON 828/ Epikure W	N1	26.5	20.8	30.5	55	31	3
	PE24	32.5	18.5	44.6	8	120	6
	PE12	27.7	26.8	89.7	14	43	11
	E1	25.7	21.9	50.3	27	37	9
	N2	25.2	18.5	32.3	7	120	6
EPON 863/ Epikure 3300	control	35.2	12.7	13.1	2	120	7
	PE14	37.0	24.9	83.7	7	120	7
	N1	23.3	19.1	22.1	4	120	4
	PE24	30.4	19.6	35.7	13	104	5
	PE12	25.6	21.7	34.5	10	54	10
	N2	23.4	13.7	29.3	27	120	5

Table 6: Mechanical Properties of Epoxy Systems

Resin	Additive	Shore D	Bend Rank 1=most	G' (Pa)	G'' (Pa)	Tan (δ)	Tensile Strength at		
							Absolute Peak (kPa)	Elongation (%)	Tear (N/mm)
DER331/Ancamine 1618/AMI-1									
	N2	73	3	6.30E+05	2.57E+03	3.93E-03	40,318	4.82	36.09
	control	88	10	3.55E+06	3.70E+04	1.05E-02	2,730	0.59	2.09
EPON 828/Epikure W									
	PE14	75	1	3.14E+05	6.29E+04	2.19E-01	11,181	1.54	12.83
	N1	83	9	2.51E+06	2.87E+05	1.15E-01	12,109	1.35	21.03
	PE24	70	5	6.24E+05	7.05E+03	1.10E-02	15,645	15.58	38.41
	PE12	73	8	4.11E+05	1.15E+03	2.32E-03	17,029	2.28	10.96
	E1	80	8	5.99E+05	8.42E+02	1.40E-03	12,790	1.39	0
	N2	76	9	2.42E+06	1.08E+05	4.46E-02	4,368	0.83	4.89
	control	87	10	4.22E+06	9.24E+04	2.19E-02	59,750	1.26	NA
EPON 863/Epikure 3300									
	PE14	53	8	N/A	N/A	N/A	N/A	N/A	N/A
	N1	64	9	N/A	N/A	N/A	N/A	N/A	N/A
	PE24	70	8	2.79E+06	6.65E+04	2.39E-02	30,166	3.31	56.68
	PE12	73	2	4.03E+05	2.61E+04	7.57E-02	N/A	N/A	N/A
	N2	73	4	N/A	N/A	N/A	23,633	2.21	33.6

Table 7: Working Properties of Epoxy Formulations

Resin	Additive	Work Time		
		(min)	Gel Time (min)	Shrinkage (%)
DER331/Ancamine 1618/AMI-1				
	N2	34	261	<0.1
	control			<0.5
	PE14			<0.3
EPON 828/Epikure W				
	N1			<0.3
	PE24	No Reaction at Room Temperature		<0.3
	PE12			<0.3
	E1			<0.3
	N2			<0.1
EPON 863/Epikure 3300				
	control	17	180	<0.5
	PE14	60	180	<0.3
	N1	20	120	<0.3
	PE24	30	210	<0.3
	PE12	33	135	<0.1
	N2	33	180	<0.3

4. CONCLUSIONS

Overall, the data show that the additives lower the surface tension of resins at 0.2-20 % use levels. More than half of the additives evaluated lower the surface tension of the resins below 28 mN/m at 1 % use level. This surface tension reduction improves wetting and flow over the fibers as shown by contact angle and flow data. The expectation is that the improved wetting of the fibers by resins will translate to strength and adhesion improvements in fully formulated composite systems.

The surface and wetting effects at the higher use levels (20 %) needed to modify the mechanical properties significantly are shown in Figures 4 and 5. In each example, both surface tension and contact angle is improved over the control. In flow measurements all samples improved the flow time while most improved or equaled the flow distance in the EPON 828 system. The EPON 863 system showed excellent flow with the control alone.

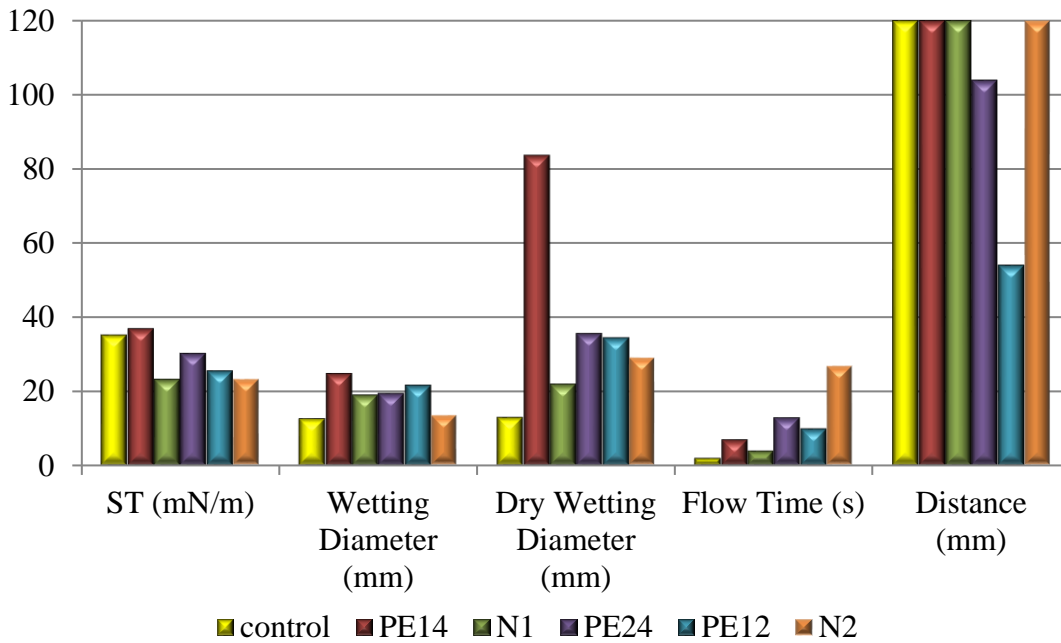


Figure 4: Surface and Wetting Properties of Reactive Wetting Agents EPON 863 System.

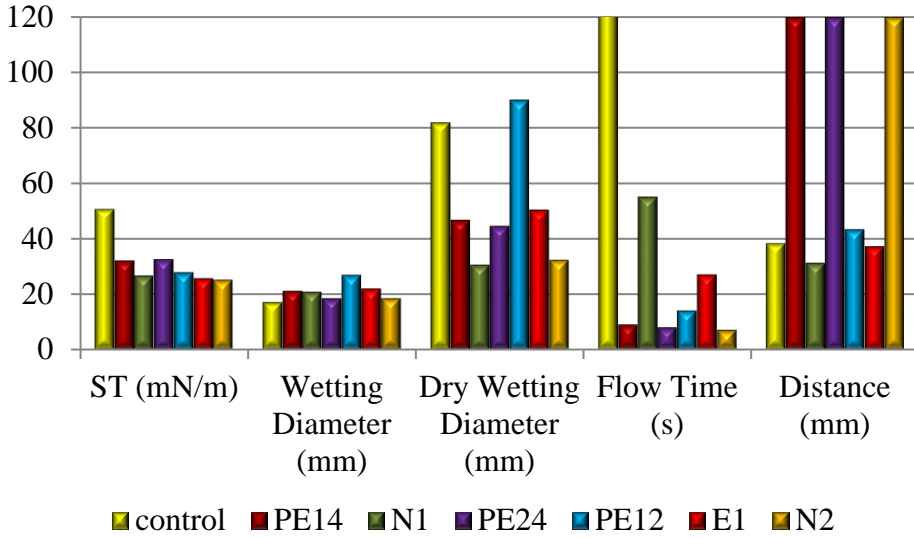


Figure 5: Surface and Wetting Properties of Reactive Wetting Agents EPON 828 System.

In addition, the reactive materials provide altered the mechanical properties of the resins. Referring to Figure 5, one can see that relative to the controls hardness is reduced and flexibility is increased. Elongation and bending are increased in this study relative to the very hard and brittle controls.

Strength and toughness are increased as well. Although not demonstrated in this study, we designed these experiments using a use level of the additives which should give us near the maximum improvements of strength and toughness.

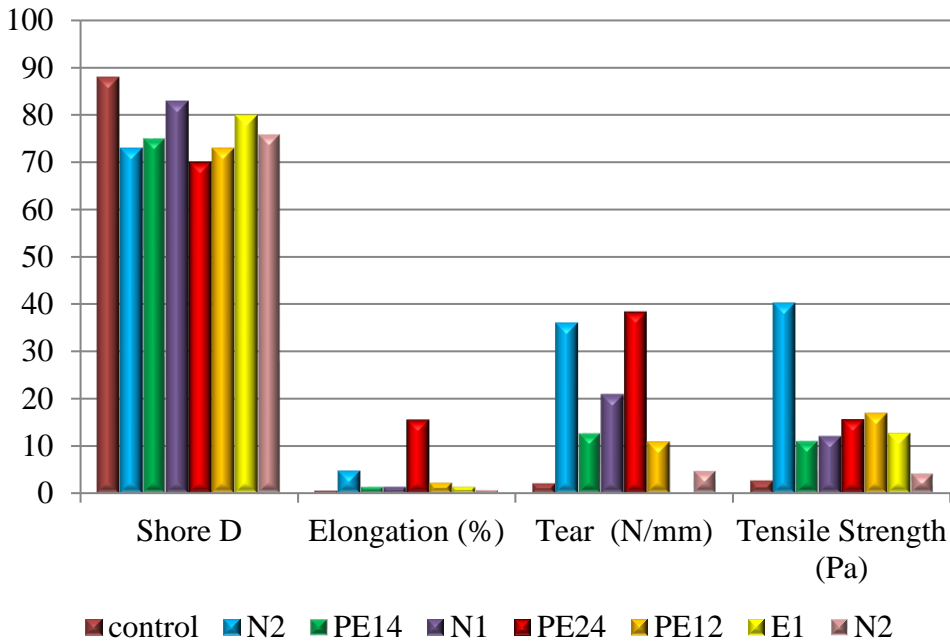


Figure 6: Mechanical Properties of Reactive Wetting Agents in EPON 828 System.

Processing times such as work time, and gel time are not significantly affected. Shrinkage is perhaps slightly reduced over the control formulations.

5. REFERENCES

1. Cheung, Tom., Ruckle, Robert., "Properties of Silicone Modified Films.", *Proceedings of the Waterborne Symposium*. New Orleans, LA, February 6-8, 2013. University of Southern Mississippi.
2. Cheung, Tom., Ruckle, Robert. "A Structure Property Study Of Epoxy Resins Reacted With Epoxy Silicones. ", *Proceedings of the Sampetech*, Baltimore, MD, May 18-21, 2015. Society for the Advancement of Material and Process Engineering.