Polyurethane Elastomer Hydrolytic Stability: A Comprehensive Review

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Abstract

Some historical PMA literature can be found on polyurethane degradation pertaining to hydrolytic stability, although not very much. In this paper, a comprehensive study is presented comparing multiple backbones, isocyanates, and durometers using not only tensile strength as an indicator of degradation, but also other physical properties. Looking at the trends of the data can give direction of what type of urethane to use in aqueous applications.

Introduction

Hydrolysis is a well know degradation mechanism for all types of chemical species. It literally means a reaction with water in which other products are formed. In polymers, hydrolysis usually leads to a breakdown of polymer chains, lowering the molecular weight and causing a decrease in physical properties. For polyurethane elastomers, resistance to hydrolysis is important in many applications where parts may be subjected to the outdoors elements, humidity in the air, or immersion in aqueous liquids such water, acids, or bases. Acidic solutions compound the problem of hydrolysis as they accelerate the process (1; 2). This paper will focus on the effects of water only.

In polyurethane systems there are three types of bonds that are most susceptible to hydrolysis. They are the urethane and urea linkages formed from the isocyanate/hydroxyl and isocyanate/amine reactions, respectively, and the ester groups that are in the backbone of a polyester based polyurethane. The general order of resistance (with all other things being equal) to hydrolysis by these functional groups is ester<<urea<urethane (1).

Another common bond in polyurethane elastomers is an ether linkage. However, the hydrolytic stability of a polyether group is excellent. In a 1989 study (3), the half-life of a butylurethane of $H_{12}MDI$, which is an aliphatic isocyanate known for excellent hydrolytic stability, was just under 2 years with mild conditions, compared to a half-life of almost 14 years for diethyl ether under highly acidic conditions. This is why polyether polyurethanes are much better suited in an application where moisture is present. The polyethers, typically polypropylene glycol (PPG) or polytetramethylene ether glycol (PTMEG) have only the urea and urethane linkages that present a weak link.

Many factors affect the ability of each of these bonds to resist hydrolysis such as temperature, steric hindrance, water absorption characteristics, and pH to name a few. Small increases in temperature, such as from 50°C to 70°C, have been shown to have large impacts on hydrolysis resistance, decreasing the half-life of a polyether-based system from 2 years down to 5 weeks and a polyester-based system from 4-5 months to 2 weeks (2). The steric hindrance factor not only affects the availability of the group to react with water, but also can affect the polymer's hydrophobicity. In a paper presented at PMA in 2006 (4), polybutadiene-based elastomers were tested against analogous polyether elastomers in 90°C water for 3 weeks. The polybutadiene backbone is extremely hydrophobic, and even though the urea and urethane bonds were still susceptible to hydrolysis, the polymer's resistance to water absorption in general gave the elastomer excellent antihydrolysis properties much better than the polyether. The pH also has a large effect on hydrolysis due to the fact that an acid medium will catalyze the reaction, making it an autocatalytic situation. When polyester bonds break down, they revert to the acid and alcohol groups that created the ester, thus adding more acid functionality to the situation. The urea groups will hydrolyze to a carbamic acid group and amine and the urethane groups to a carbamic acid and hydroxyl group. The carbamic acid isn't stable and decomposes to an amine, giving off carbon dioxide. Thus making the polyester the worse of the three as stated above. A good illustration of this is the pH of the water after the sample immersion was complete. The polyester water should have a lower pH than it started at, since break down of the polyester polymer yields a higher acid content. The polyether water should be at a higher pH due to the more basic amine end groups produced from the breakdown of the urea and urethane bonds. Table 1 has the pH values of some of the water used for the testing. The values corroborate the theory above very well; the water from the polyester materials had a lower pH than the initial water and the polyether material's water had a higher pH than the initial water.

Table 1. pH of Immersion Water

Sample	**pH**
Initial Water	7.76
MDI/PTMEG	8.98
TDI/PTMEG	9.08
H_{12}MDI/PTMEG	9.05
TDI/Polyester	5.47
MDI/Polyester	5.76

When comparing the urethane linkage and the urea linkage directly, it has been shown that in neutral situations the urea linkage will hydrolyze at a rate of 1.68 times faster than the urethane will. In acidic situations, this factor increases to over six times as fast (3). Thus a polyester-based urethane prepolymer cured with an amine would theoretically present the worst hydrolytic stability, all other factors being equal. In a previous study, it was shown that an MDI-based polyester cured with 1,4 butanediol had equivalent hydrolytic stability as a TDI-based polyether cured with MBOCA (2). From a fundamental viewpoint, this doesn't quite seem right as a polyester material should be much less hydrolytically stable than a polyether. A conjecture could be made that since MDI has all polyurethane linkages and the TDI system quite a few urea linkages, that the comparison is not apples to apples.

The main purpose of this study is to compare various isocyanates and backbones at different temperatures and varying hardness. TDI, MDI, and H_{12}MDI were the isocyanates selected since they represent a large piece of the cast elastomer market. PPG, PTMEG, and polyester backbones were chosen for the soft segments for the same reason. As mentioned earlier, the H_{12}MDI is known to have excellent hydrolytic stability due to it being aliphatic. The TDI materials were cured with MBOCA, making them polyurethane-ureas, technically, the MDI materials were cured with 1,4 butanediol, making them polyurethane only, and the H_{12}MDI prepolymers were cured with a DETDA/PTMEG blend (95% DETDA by equivalence), making them also technically a polyurethane-urea.

Experimental

Thirteen unique samples were tested. The nominal hardness values chosen were 85A and 95A. Table 2 lists all the prepolymer types tested along with the curative used. The materials were cast at typical temperatures, and then cured and postcured at 212-230F. After postcure, they were allowed to condition at room temperature for a minimum of 30 days.

Table 2. Prepolymers/Curative Systems Tested

Prepolymer Type (Iso/Polyol)	Curative	Nominal Hardness
TDI/Polyester	MBOCA	85A
TDI/PPG	MBOCA	85A
TDI/PTMEG	MBOCA	85A
LFTDI/PTMEG	MBOCA	85A
H_{12}MDI/PTMEG	DETDA/PTMEG	85A
MDI/Polyester	1,4 Butanediol	85A
MDI/PTMEG	1,4 Butanediol	85A
TDI/Polyester	MBOCA	95A
LFTDI/PPG	MBOCA	95A
TDI/PTMEG	MBOCA	95A
H_{12}MDI/PTMEG	DETDA/PTMEG	95A
MDI/Polyester	1,4 Butanediol	95A
MDI/PTMEG	1,4 Butanediol	95A

The hydrolytic stability testing was carried out in untreated tap water, which was thought to be more applicable and realistic than deionized water from the lab. The samples had split tear (ASTM D1938) and tensile (ASTM D412) test specimens cut from them and they were immersed at 50°C and 90°C. The 90°C specimens were monitored at 3 days, 1 week, 2 weeks, and 4 weeks The 50°C specimens had a five month test period and specimens were tested at 1, 2, 4, and 5 months. At each test point, 3 tensile and 3 tear specimens of each material were tested along with a check of the hardness.

Results and Discussion

With many samples and conditions, there was a lot of data to sort through. All the curves can be found in Appendix A. Overall, it was seen that as expected, polyether backbones were more hydrolytically stable than polyester backbones, regardless of isocyanate. In some situations it was initially observed that an MDI/polyester had better stability than a TDI/polyether, but eventually, the polyether was superior. The aliphatic (H_{12}MDI) materials were, in nearly all cases, the most hydrolytically stable as shown by little change in their properties (negative or positive).

Looking at both the tensile strength retention and the split tear retention gave a unique perspective. Tensile specimens tend to be very sensitive to bubbles or any type of imperfection in the specimen, while split tear specimens are more robust. Having both to look at can maybe rule out any erroneous data from the tensile specimens. Also, split tear is usually more sensitive to stoichiometric changes, which means that changing the polymer molecular weight or the number of crosslinks in the elastomer will have a larger effect on split tear. Split tear will increase with a more linear, less crosslinked system. In this study, for a small period of degradation, the split tear increased, until it reached a peak value and then started to decrease as the sample degraded further. This could be observed with all the systems. In some cases where the degradation was slow, some of the systems were still increasing in split tear and hadn't reached their peak value yet when the test was completed.

HARDNESS RETENTION

The hardness retention at 50°C was very good, especially for the 95A materials (Figure 1). The 85A materials also had fairly flat curves except for the polyesters, which had the largest drop in hardness (Figure 2). At 90°C, the polyesters degraded significantly faster than the polyethers, so it is best to look at each in their own chart. Over the four weeks, the 95A polyether specimens had about a 5 point drop in hardness, while the 85A polyethers varied from 5 to 30 point drops in hardness (Figures 3-4). The polyester specimens, due to their degradation, had inconsistent readings and some of the time the durometer indenter would poke through the material (Figures 5-6). This led to stange looking curves as can be seen in Figure 5. Softer materials degrade faster, in general, and the 85A polyester materials proved that by degrading very quickly. The TDI/polyester materials degraded one week faster than the MDI/polyesters, but both were not testable after three weeks of immersion.

TENSILE RETENTION

Both the 85A and 95A specimens showed the same trends at 90°C. The MDI/PTMEG and the H_{12}MDI/PTMEG had the best stability and were close to equivalent. The TDI/PTMEGs and TDI/PPGs had quite a bit lower stability, and the polyester samples degraded the most and weren't testable at three weeks, as mentioned above (Figures 7-8). The MDI/polyester samples had better retention of tensile strength than the TDI/polyethers at less than one week, but after one week the polyester fell below them and eventually went to zero.

The 50°C immersed samples also had many of the same trends (Figures 9-10). Interestingly, the MDI/polyester specimens (85A and 95A) retained tensile strength very well for about two months, and were better than most of the other samples, including the H_{12}MDI systems and the MDI/PTMEGs. This is counterintuitive. The only thought as to why this occurred is that at 50°C degradation is very slow and since polyesters are the toughest materials, it is possible they have an advantage for a small period of time. It could be due to the amount of hydrogen bonding in a polyester and until there is a certain amount of chain scission, the polyester polymer stays intact to some degree.

After the first two months, however, the polyester's tensile retention dropped dramatically while most of the polyethers stayed at fairly high levels.

ELONGATION RETENTION

Percent elongation or strain data was also plotted in the same fashion as the tensile strength data, but these plots are not included since they illustrated the same trends and reiterated what the tensile data had shown.

SPLIT TEAR RETENTION

The split tear retention is a little more exciting than the tensile data since it gives a good picture how the material is degrading. As the links are undone, the system becomes more linear, thus increasing the split tear, the same as would happen when a part is cast at an increased stoichiometry (OH/NCO or NH/NCO). At some point, however, too many links are broken and the strength starts decreasing. For the samples immersed at 90°C, the stability of the materials really dictated the shape of their retention curve. Being somewhat hydrolysis resistant, the TDI/PTMEGs had huge increases in their split tear in the short term of up to almost 500% for the 85A and almost 250% for the 95A samples (Figures 11-12). The TDI/PPGs had minor increases and then degraded about the same as the TDI/PTMEGs. Since PPGs are low performance materials, it could be that increasing the linearity doesn't have as much of an effect on the split tear as it does for PTMEGs. The polyesters follow the tensile values pretty well in that they degraded to 0% after two weeks. Their split tear didn't have the increases of the PTMEGs since the degradation was so quick. The MDI/PTMEGs don't peak out as high as the TDI/PTMEGs, but they stay stable for a longer period, which is what was observed with the tensile data as well. The peak value was at about three weeks, but since the testing only went for four weeks, the MDI/PTMEGs were still close to or over 200% by the end of the test. The H_{12}MDI materials, being the most hydrolytically stable, stayed very close to the 100% line, with a slight increase at about 2 weeks. Depending on the expected part life, the MDI/PTMEG may be the better choice over the aliphatic taking cost into consideration.

At 50°C, the materials had much slower degradation as expected. The samples with the most degradation at 95A or 85A were the TDI/PTMEGs, which had peaked at about 140-150% retention by the end of the test period (Figures 13-14). The polyester materials looked much different than the 90°C immersion in terms of the shape of the curve. Instead of immediately starting to head to 0% retention, the polyesters started out with a dip and then, as degradation started to increase slowly, the split tear hit a maximum ~125% (85A) and ~105% (95A) before dropping off in both to around 20% tear retention at five months. In both cases, the H_{12}MDI samples were very close to 100% retention of the split tear again indicating little to no hydrolysis.

TENSILE & SPLIT TEAR COMBINED

If the tensile and split tear charts are overlaid, it makes for a good depiction of the degradation reactions taking place. Figure 15 is an overlay of the 95A TDI and MDI polyester curves (50°C immersion) that show this depiction very well. At 60 days, there is an inflection point for both the tensile and split tear where tear is increasing and tensile is decreasing. From 30-60 days, the split tear starts increasing and the tensile is decreasing slightly, which is typical when changing the stoichiometry on an elastomer system. Generally, the tensile doesn't change much in certain stoichiometric ratios, while the split tear might change by a lot. After too much degradation, though, both tensile and split tear start to rapidly fall.

Conclusions

ISOCYANATE COMPARISONS

Comparing the isocyanates, it is obvious that the H_{12}MDI has superior hydrolysis resistance. This was to be expected. Comparing the MDI vs. TDI, the difference isn't as clear. Comparing the polyesters of each, the MDIs appear to be slightly better for a short period of time, especially at 90°C. In the long term, however, the MDI/polyesters break down just as much as the TDI/polyesters.

Regarding the polyethers, most of the data shows that the MDI/PTMEGs degrade slower than the TDI/PTMEGs which degrade slower than the TDI/PPGs. In quite a few cases, the MDI/PTMEGs are even on par with the H_{12}MDIs (Figures 7,8,10). Longer term testing, especially for the 50°C immersion, would be needed to compare the two, and most likely the H_{12}MDI would be the most hydrolysis resistant.

There was no significant difference in the 85A LFTDI/PTMEG and conventional TDI/PTMEG. In some cases, the LFTDI material fared slightly better, but not enough to really conclude that it was more stable.

POLYETHER VS. POLYESTER

It is no surprise that the polyether materials had much better hydrolysis resistance, but an important point that should be made is how big the effect of temperature is. At 90°C, the specimens degrade quite fast, but at 50°C, the polyester samples retained close to 60% or more of their properties for two months. Since polyesters are much tougher to begin with, they might be a viable option in ambient or slightly warm applications where the life span of the part is expected to be short, due to situations of high wear or high stress.

85A VS. 95A

Harder materials, due to more hard segments, inherently are stronger and typically more resistant to degradation. In this study, this was proven true as the 85A materials were less resistant to hydrolysis. In some cases, the difference was small, but the difference in hardness was fairly small as well. It makes sense as a softer material will have more soft segments and less hard segments.

In a polyester, the soft segments are its weak link, thus softer polyesters will degrade faster than harder ones. In a polyether, less hard segments means it takes less urethane/urea bonds to break until the polymer is totally degraded.

OTHER STUDIES

An immersion test at room temperature would be good to run to compare polyesters and polyethers. As stated in the previous section, the 50°C immersion testing was much less severe to all samples. It would be interesting to see what the long term stability of a polyester would be at room temperature, not only in water, but also in an acidic environment as well. Depending on the expected part life, a polyester might last the needed amount of time and be quite okay. However, a study such as this might take a year or years to see any meaningful results. Non-immersion tests in high humidity at varying temperatures would also be helpful data, but again the testing period might need to be quite a bit longer, depending on the temperature used.

Another test that is currently being ran, but will be beyond the submission of this paper, is comparing an MDI/PTMEG polyurethane-urea (amine-cured) to a TDI/PTMEG polyurethane (diol-cured). This was done by taking an MDI/PTMEG and curing it with MBOCA and taking an LFTDI/PTMEG system and curing it with 1,4 butanediol. One problem with this is that the TDI system doesn't create a good hard segment with the 1,4 butanediol, thus giving a much softer part. As mentioned above, softer parts are less resistant to hydrolysis, but this should give some kind of indication as to whether the MDI/PTMEG is superior to the TDI/PTMEG because of the isocyanate structure or because of it being an all urethane system.

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Appendix A

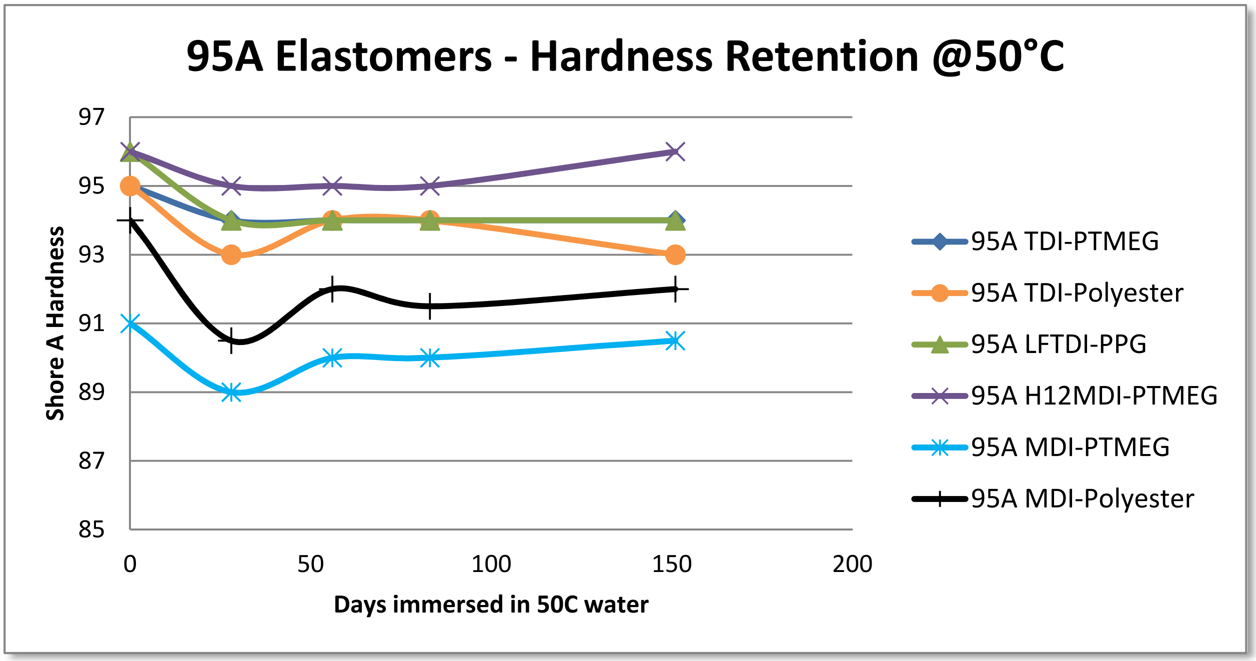


Figure 1

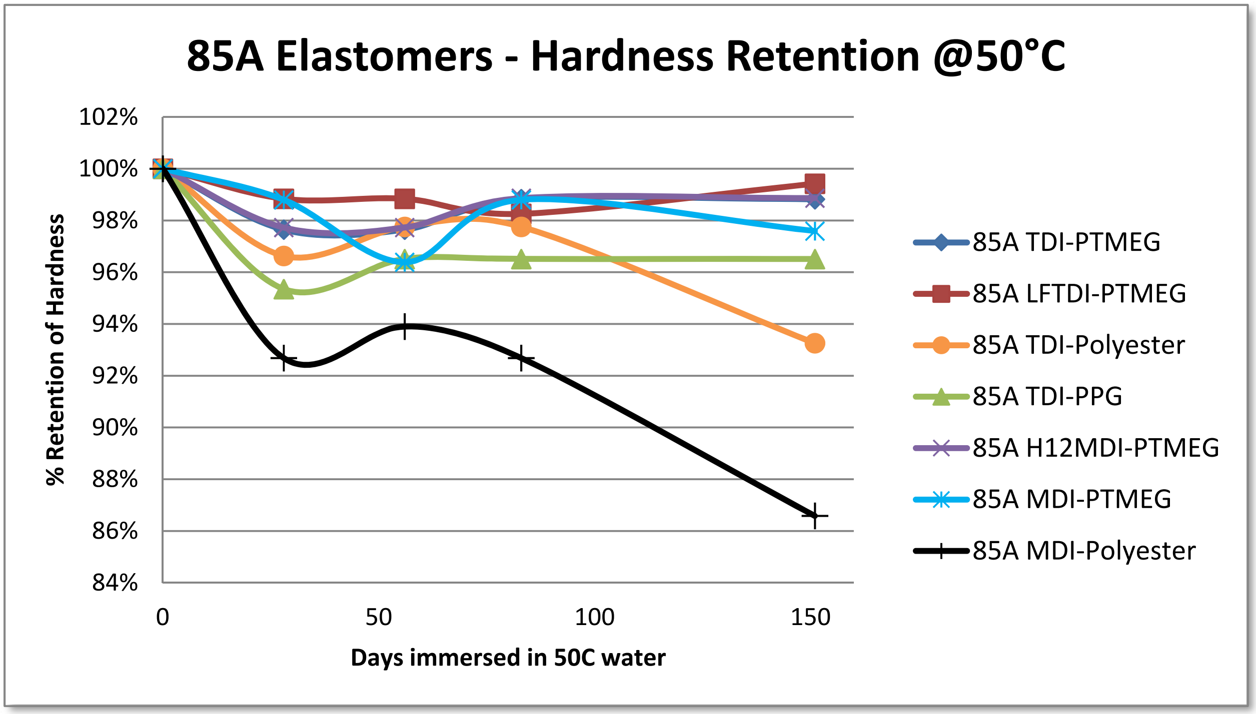


Figure 2

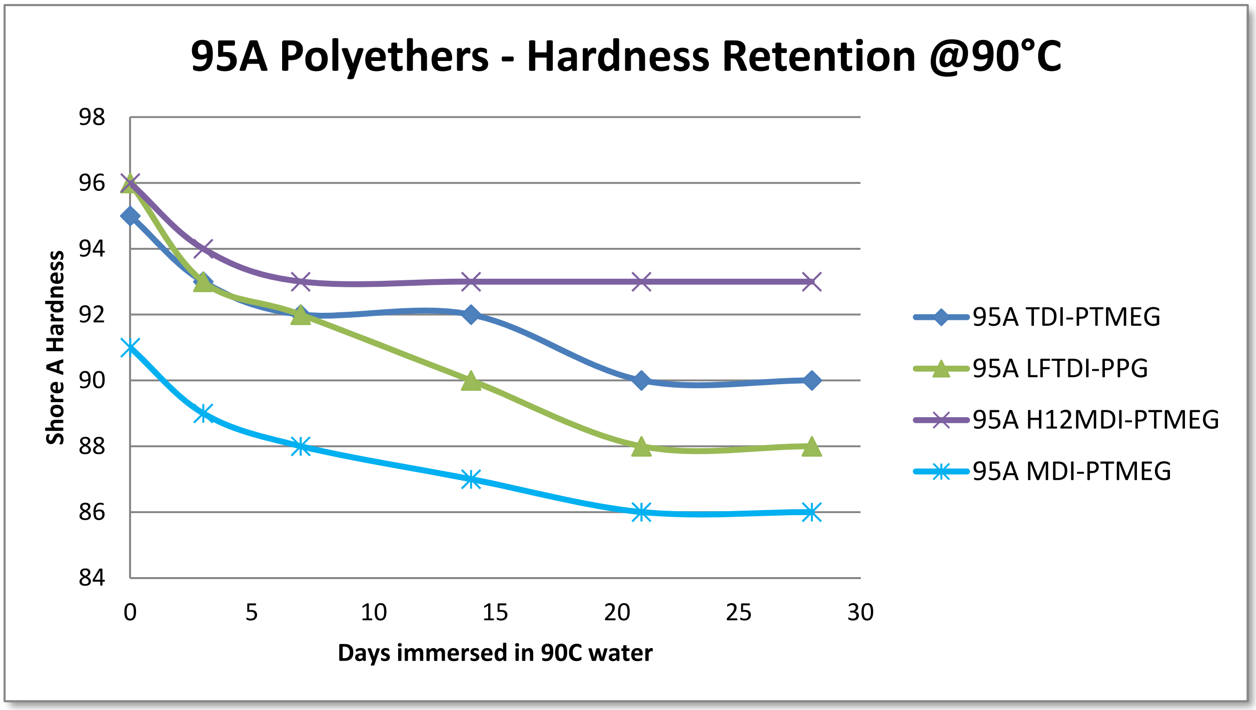


Figure 3

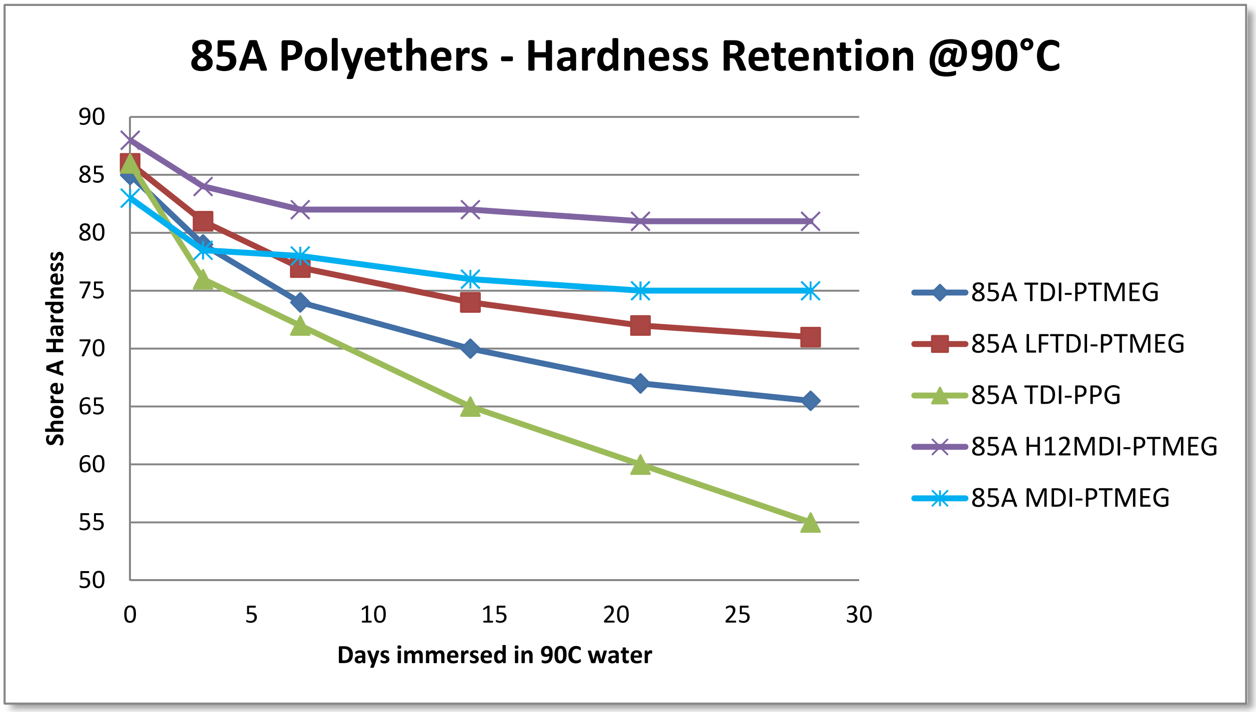
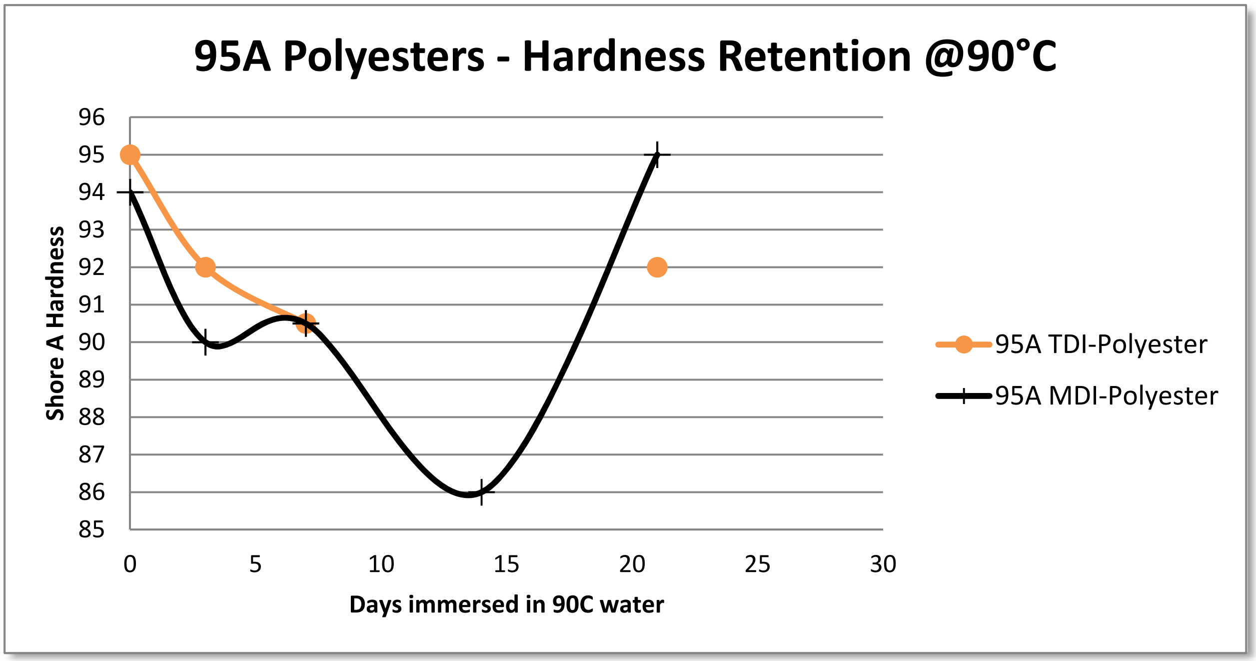


Figure 4



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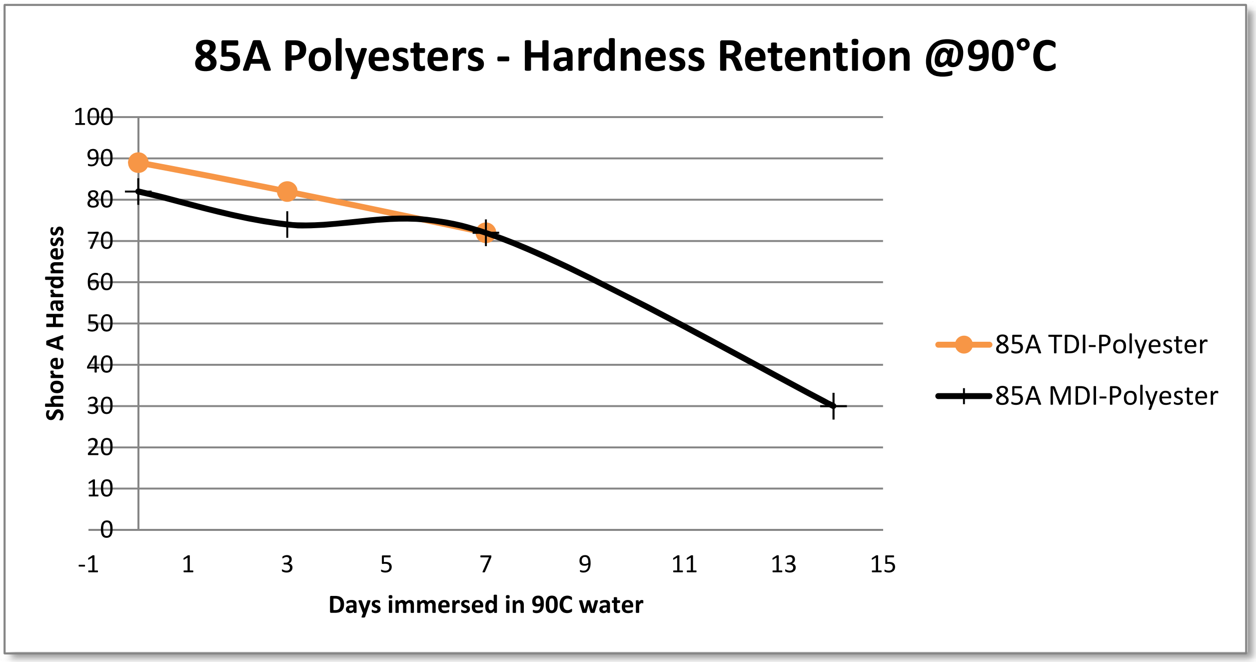


Figure 6

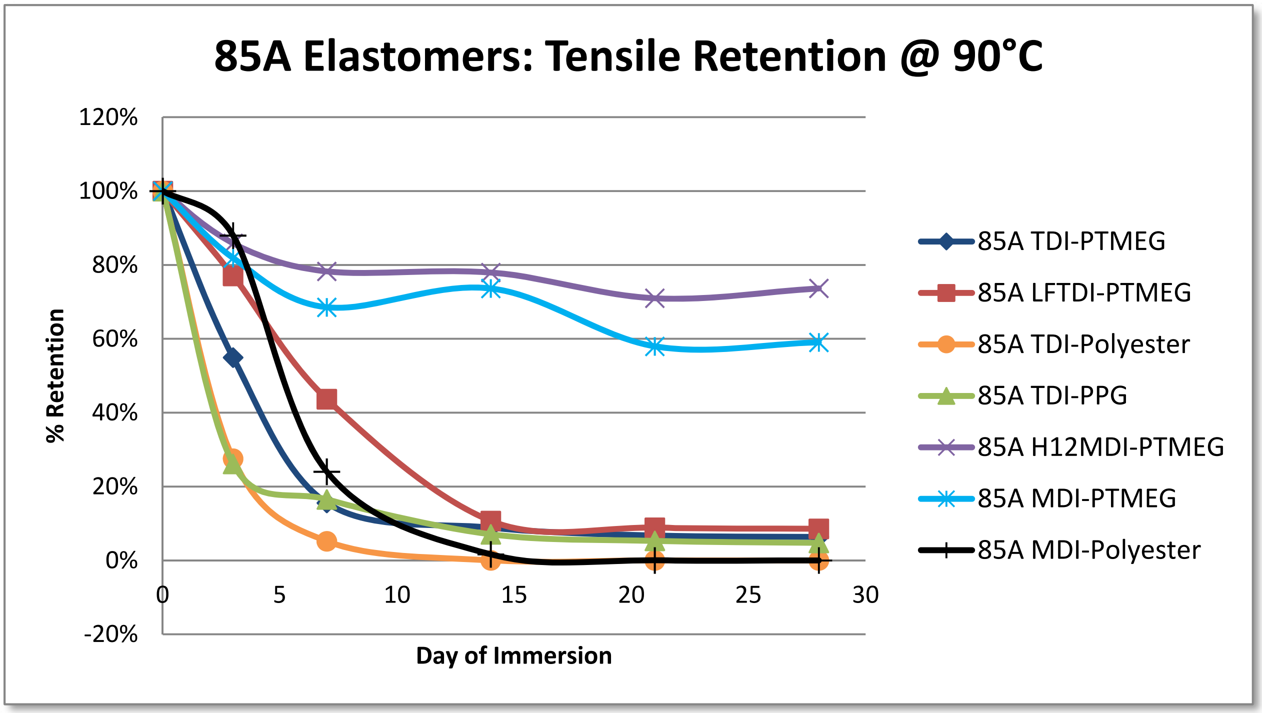
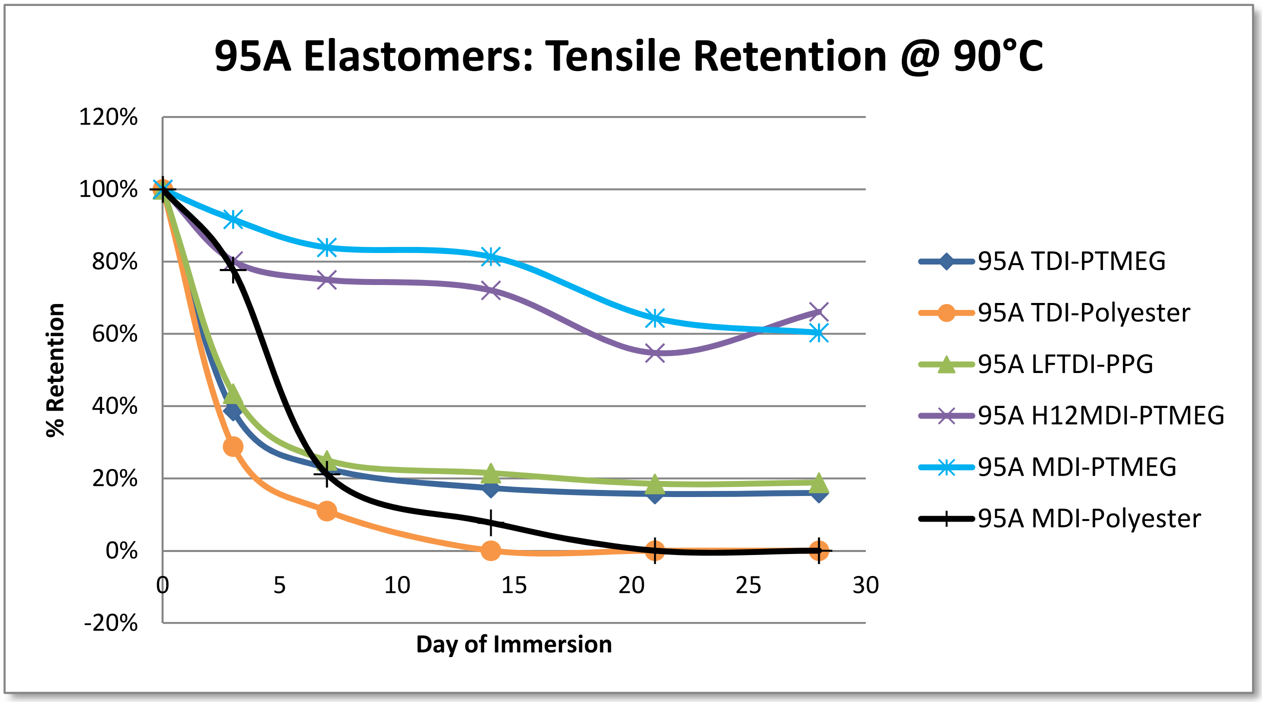


Figure 7



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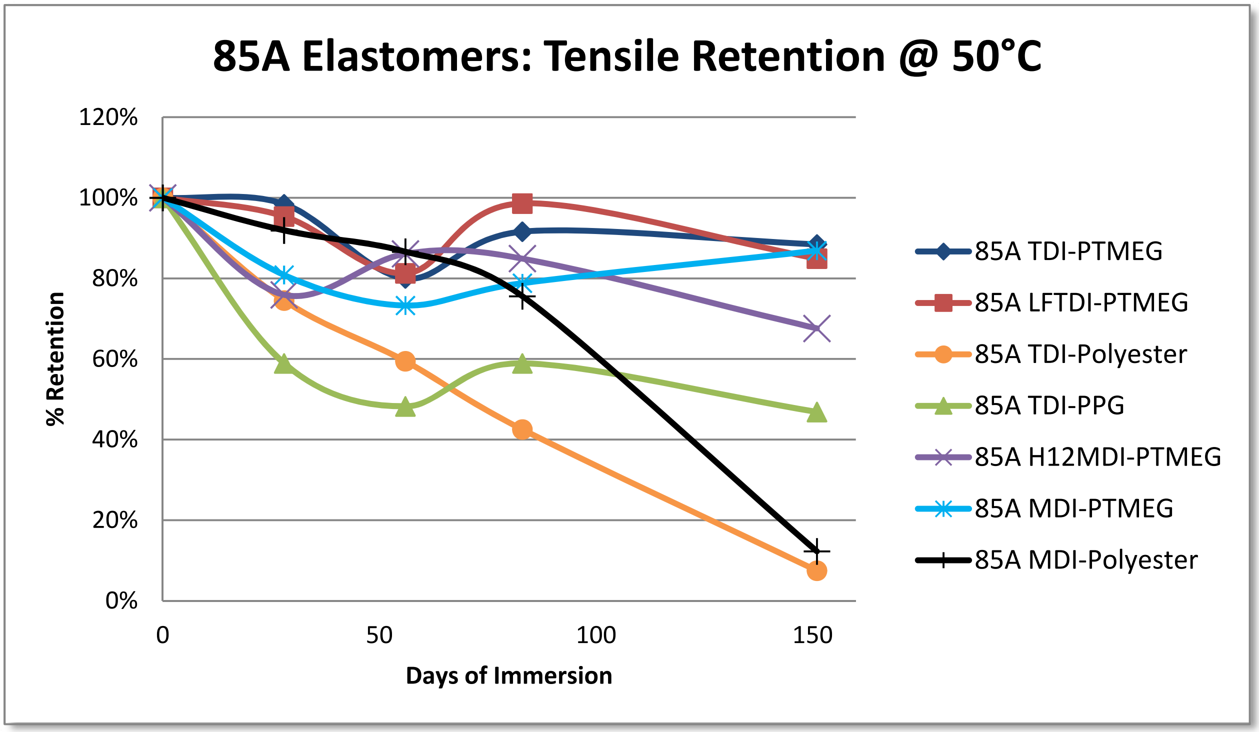


Figure 9

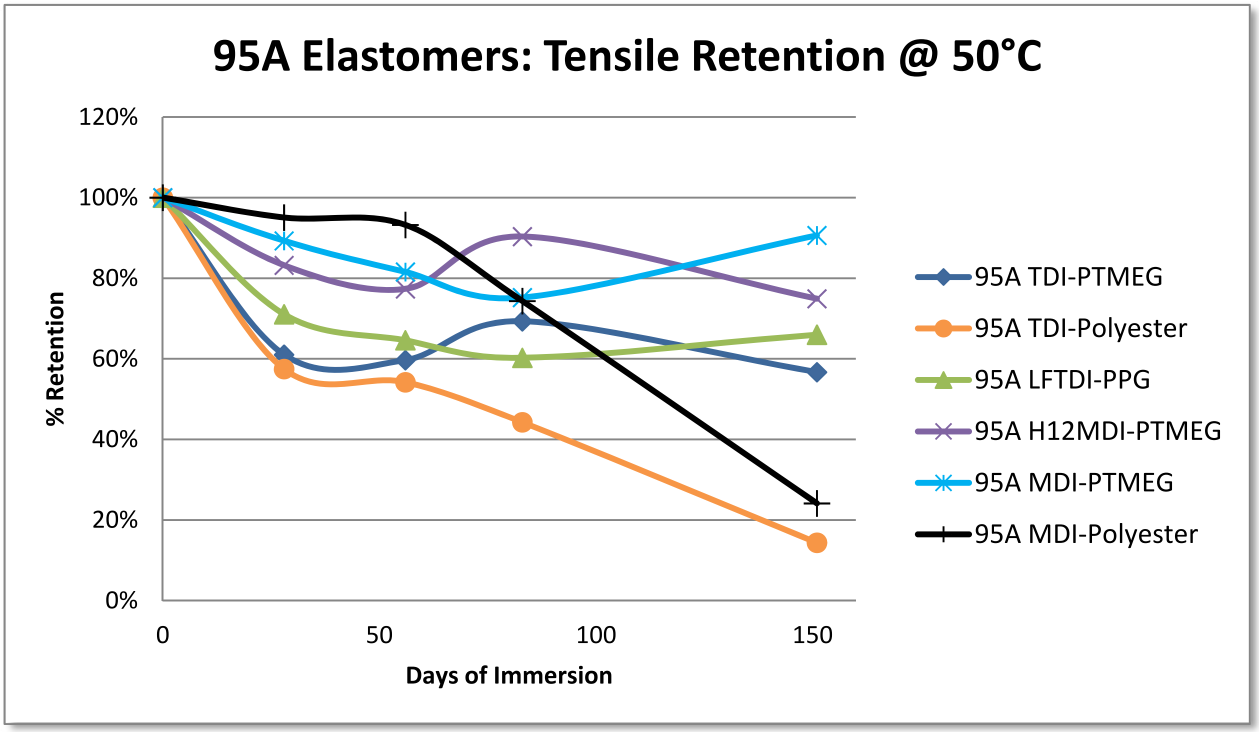


Figure 10

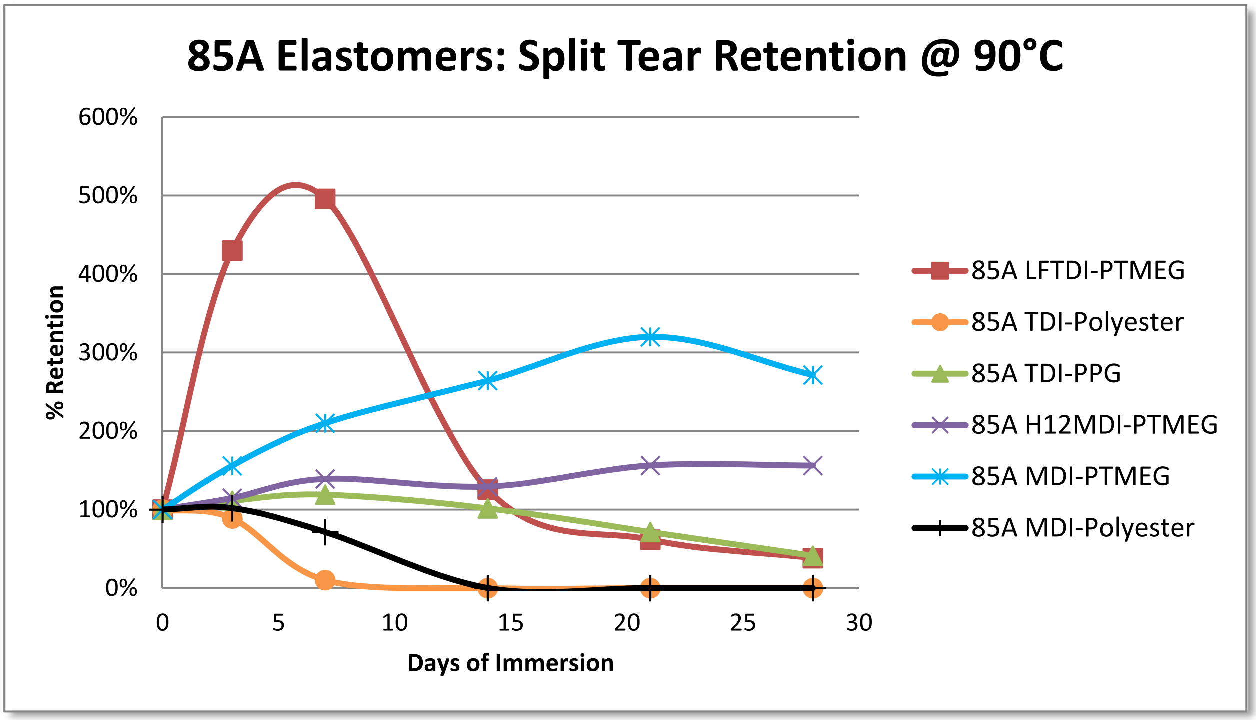
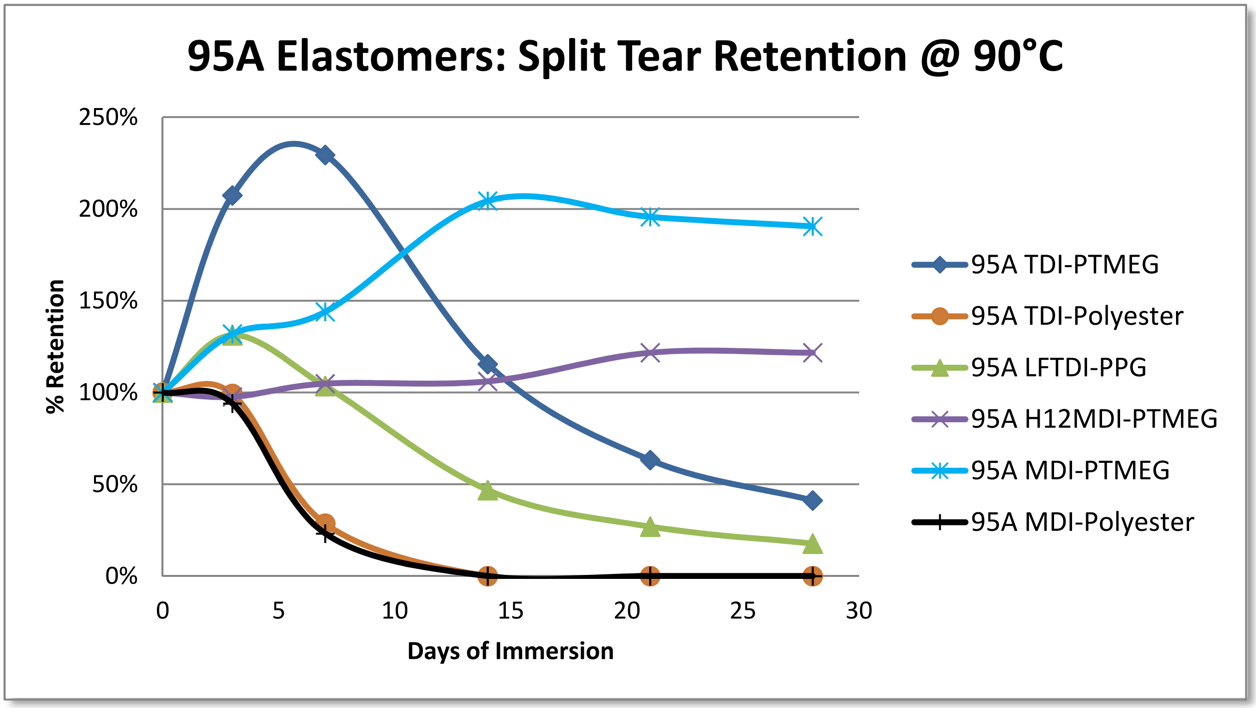


Figure 11



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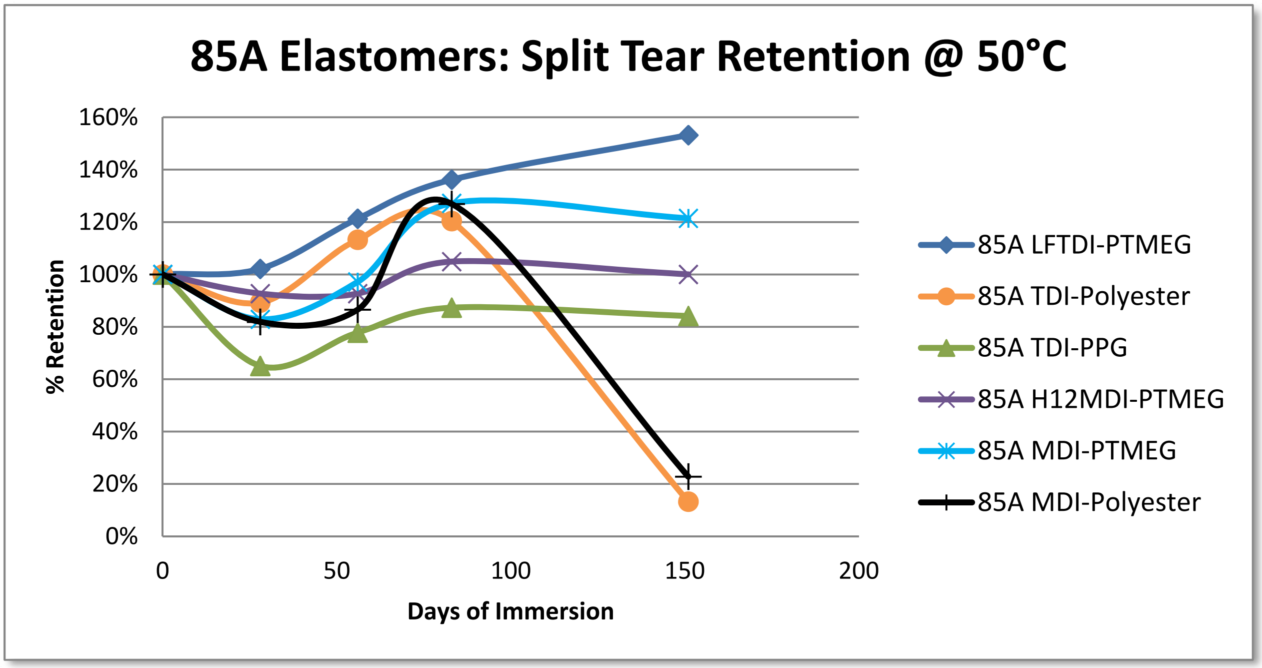

Figure 13

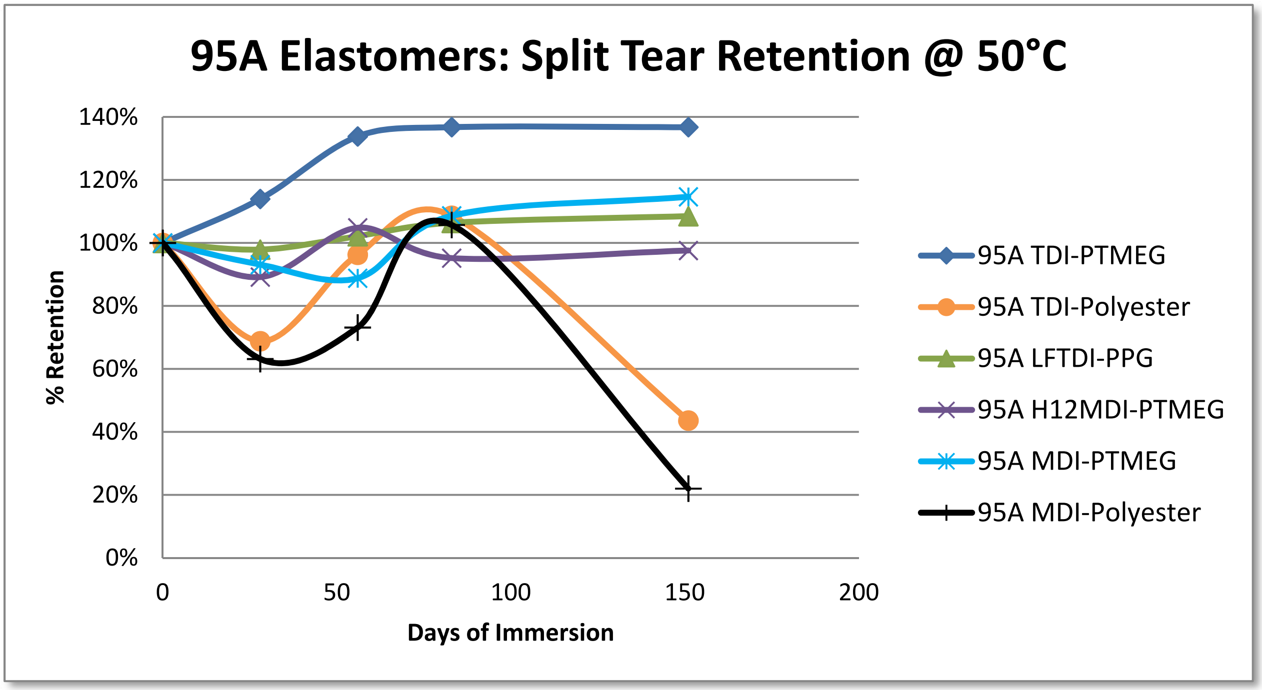

Figure 14

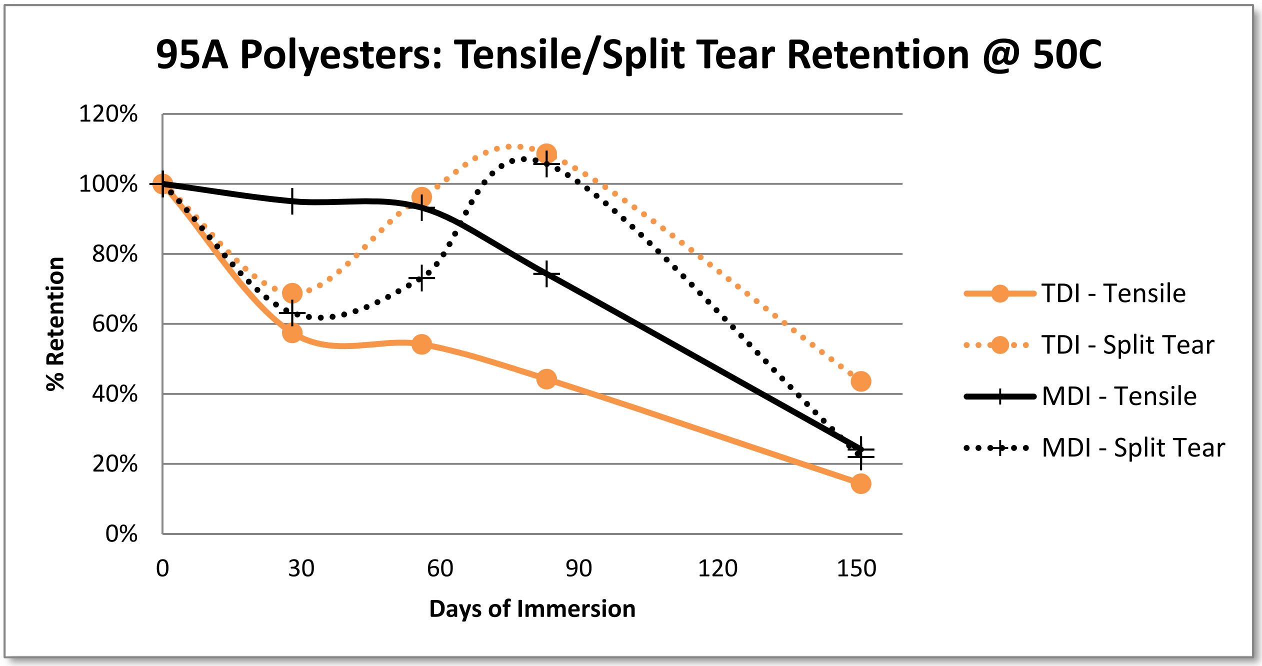
95A Polyesters: Tensile/Split Tear Retention @ 50C
120%
100%
80%
60%
40%
20%
0%
% Retention
0
30
60
90
120
150
Days of Immersion
TDI - Tensile
TDI - Split Tear
MDI - Tensile
MDI - Split Tear

Figure 15