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High Performance Polyurethane Coatings from Soybean Oil

Abstract

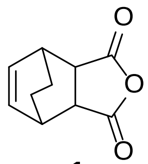
A series of sustainable polyurethane (PU) coatings were developed from polyester polyols based on renewable bicyclic anhydrides derived from soybean oil in conjunction with commercially available isocyanates. Depending on the identity of the isocyanate, coatings ranging from highly transparent rubbery elastomers to rigid glasses (and in-between) could be obtained. These materials appear to be stable towards hydrolysis and UV radiation. Some of these coatings exhibited (qualitatively) very high cut resistance and good thermal stability. The beneficial properties of these coatings is believed to be primarily due to the bicyclic ring in the polyester polyol and is uncommon for PUs derived from natural precursors. Since these materials contain a significant amount of renewable content (ca. 39 wt %) they possess added value as green alternatives to petroleum analogs.

1. Results and Discussion

1.1. Synthesis of Flexible Coatings

Initial attempts to formulate coatings from soybean derived bicyclic anhydride (Chart 1, **1**), glycerol polyester polyols (Chart 1, **2**) focused on reaction with hexamethylene diisocyanate (HMDI; Chart 1, **3**). HMDI was chosen as the first isocyanate to investigate as its aliphatic structure should impart clarity and flexibility to the resultant films. Such films are compliant, hazy materials that are relatively easy to cut with a razor blade (Figure 1, Table 1). The modulus of these materials (Table 1) is directly related to the degree of crosslinking (i.e., [glycerol]) and ranged from 5 MPa down to 1 MPa. The reduction in modulus, which was accompanied by a decrease in thermal stability, may occur due to an increase in the content of flexible components (i.e., glycerol and HMDI) at a constant concentration of polyester polyol **2**. HMDI films were not overly transparent and UV transmittance remained relatively unchanged over the entire glycerol concentration range explored (Table 1, entries 1-3). An attempt to improve film transparency was made using a polyester polyol based on the hydrogenated version of the anhydride **1** (Chart 2, **4**). This did not result in an improvement in clarity (Table 1, entry 4) but did lead to a much stiffer film (~ 10 increase in modulus). The reason for this behavior is not fully understood. Substitution of diglycerol (Chart 2, **5**) for glycerol appears to give films with a higher modulus and better thermal stability when all things else are equal (Table 1, compare entry 5 with entry 3). A few additional interesting observations are:

1. Renewable content up to 38 wt % can be achieved.
2. These materials do not appear to be adversely affected by immersion in water.



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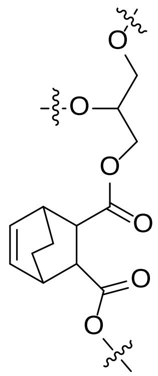

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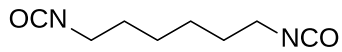

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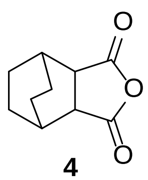
Chart 1. Structures of starting anhydride, its glycerol based polyester polyol, and isocyanate used in the preparation of first generation polyurethane films.



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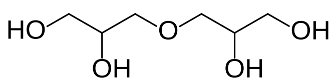

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Chart 2. Structure of alternative anhydride and polyol used in the preparation of first generation polyurethane films.

Table 1. HDMI based films.

Entry	Anhydride/alcohol (mol:mol)	Modulus[a] (MPa) Wt % Renew.	10 Wt % Loss[b] (°C)	% Transmittance at 1100 nm, 700 nm, 400 nm
1	**1**:glycerol 1:4	5.20 38.2	183	4.11, 3.22, 2.51
2	**1**:glycerol 1:5	3.89 36.0	179	13.7, 15.0, 11.5
3	**1**:glycerol 1:6	1.10 34.4	157	20.9, 11.5, 5.49
4	**4**:glycerol 1:6	11.2 34.4	210	1.89, 1.42, 0.87
5	**1**:diglycerol 1:6	6.218 29.7	183	18.8, 15.6, 11.0

a. Young's modulus.
b. Temperature at which 10 wt % is lost. Conditions = N_2, 30-600 °C at 20 °C/min.

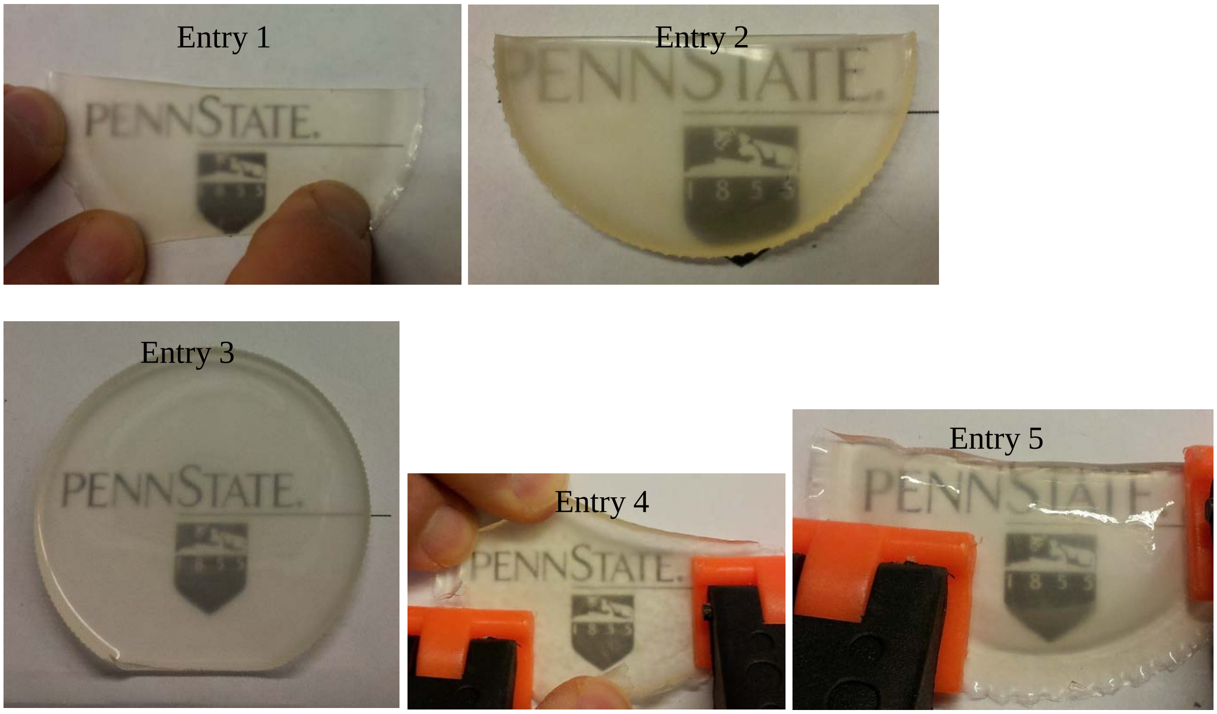

Figure 1. HMDI based films.

Given the initial success with HMDI, a lower volatility aliphatic isocyanate (N3400®) was explored next. These films (Figure 2, and Table 2) were unusual in that they were highly transparent and even more flexible compared to HMDI based materials. Modulus seemed to be little affected by [glycerol] and this may be the result of N3400® being a highly rubbery material which dominates the physical properties of the film. Likewise, no discernable trend in thermal stability as a function of [glycerol] could be ascertained. Since N3400® is safer to work with than HMDI (due to decreased volatility) and because it gives rise to films with high clarity it was selected for use in additional experiments in conjunction with other isocyanate monomers (see below). Although the renewable content of these films is relatively high it is lower than HMDI based films since the molecular weight (MW) of N3400® is larger.

Figure 2. N3400® based films.

Table 2. N3400® based films.

Entry	Anhydride/alcohol (mol:mol)	Modulus[a] (MPa) Wt % Renew.	10 Wt % Loss[b] (°C)	% Transmittance at 1100 nm, 700 nm, 400 nm
1	**1**:glycerol 1:4	0.675 35.0	167	86.6, 83.8, 61.7[c]
2	**1**:glycerol 1:5	0.817 32.7	196	86.1, 83.8, 68.4
3	**1**:glycerol 1:6	0.470 31.2	186	88.3, 86.8, 78.2

a. Young's modulus.
b. Temperature at which 10 wt % is lost. Conditions = N_2, 30-600 °C at 20 °C/min.
c. This film had some surface defects that make it appear to not be clear but it is.

1.2. Synthesis of Rigid Coatings

The flexible films described above lacked strength necessary for demanding coating applications (e.g., protective screens for electronic devices). In order to remedy this situation the use of a rigid isocyanate was required; however, clarity demanded that such a monomer also lack chromophores. Isophorone diisocyanate (IPDI; Chart 3, **6**) appeared to be a logical starting point.

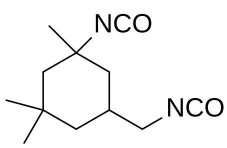

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Chart 3. Structure of isophorone diisocyanate.

Substitution of IPDI for HMDI gave rise to very rigid films (Table 3, Figure 3). The modulus of these materials appears to slightly decrease with increasing [glycerol] and is very high (ca. 1,000 MPa). As a result these materials were extremely difficult to cut; however, once a crack was started it would propagate rapidly. These materials were too brittle to be of great value as coatings yet they were exceedingly clear. In some instances they were so difficult to cut that the razor blade fractured as it was being pounded into the film. Moreover, the thermal stability of these films was superior to HMDI films and again decreased as [glycerol] increased. Substitution of diglycerol for glycerol (Table 3, entry 4) appeared to cause a precipitous drop in modulus but this may be the result of incomplete cure due to problems with solubility. Immersion of IPDI based films in water did not cause degradation to physical properties and these resins also had reasonably high sustainable content.

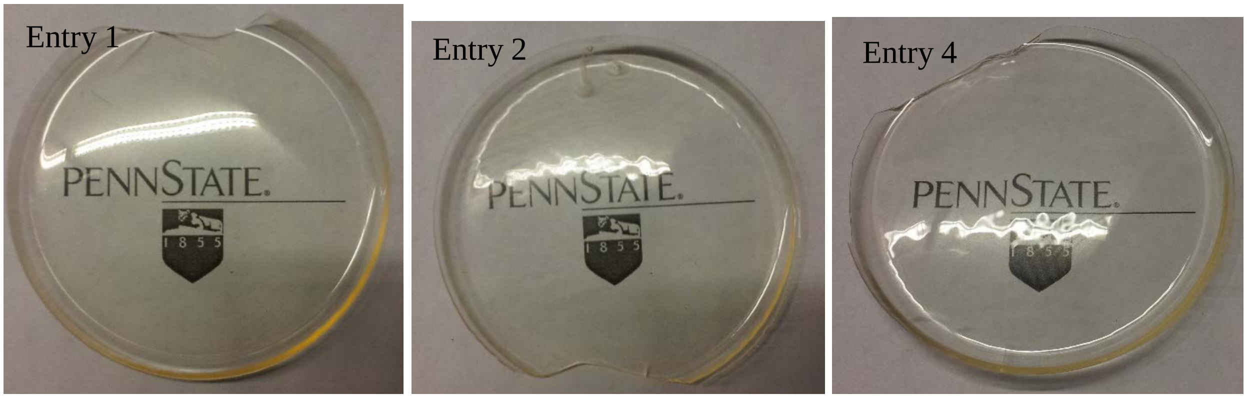

Figure 3. IPDI based films (picture of entry 3 is missing).

Table 3. IPDI based films.

Entry	Anhydride/alcohol (mol:mol)	Modulus[a] (MPa) Wt % Renew.	10 Wt % Loss[b] (°C)	% Transmittance at 1100 nm, 700 nm, 400 nm
1	**1**:glycerol 1:4	1286 32.6	219	88.7, 87.1, 79.4
2	**1**:glycerol 1:5	685 30.5	211	88.9, 87.6, 81.4
3	**1**:diglycerol 1:5	419 25.9	226	89.5, 87,7, 78.5
4	**1**:glycerol 1:6	730 29.0	190	88.7, 86.9, 81.3

a. Young's modulus.
b. Temperature at which 10 wt % is lost. Conditions = N_2, 30-600 °C at 20 °C/min.

Given the promising results with IPDI another rigid aliphatic isocyanate, Desmodur W® (Chart 4, **7**), was also explored. It is worthy to note that these films too were highly transparent and had high modulus values (Figure 4, Table 4). As was the case with IPDI films, those based on Desmodur W® also have the high thermal stability and again, thermal stability appears to decline with increasing [glycerol]. These resins also suffered in that they were brittle despite being very cut resistant. The amount of sustainable content isn't quite as high as films based on IPDI since the MW of Desmodur W® is higher than that of IPDI.

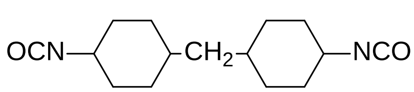

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Chart 4. Structure of Desmodur W®.

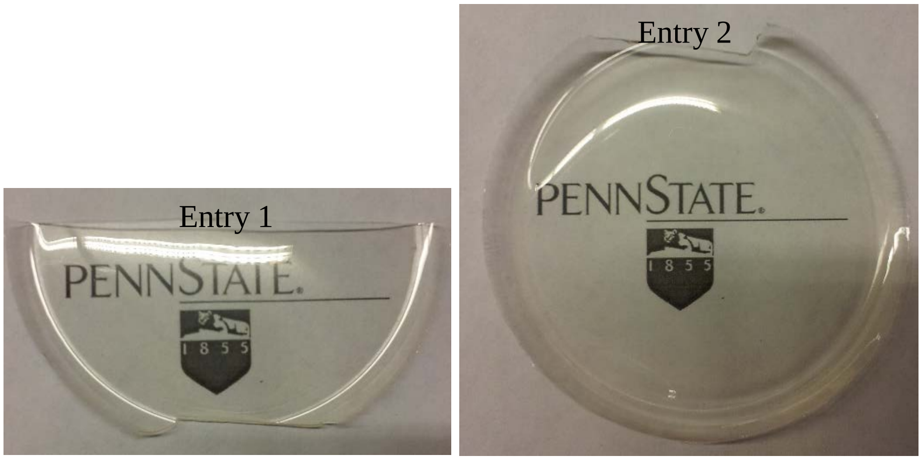


Figure 4. Desmodur W® based films.

Table 4. Desmodur W® based films.

Entry	Anhydride/alcohol (mol:mol)	Modulus[a] (MPa) Wt % Renew.	10 Wt % Loss[b] (°C)	% Transmittance at 1100 nm, 700 nm, 400 nm
1	**1**:glycerol 1:4	620 29.1	251	88.2, 86.4, 79.6
2	**1**:glycerol 1:6	740 25.6	219	87.7, 85.8, 78.1

a. Young's modulus.
b. Temperature at which 10 wt % is lost. Conditions = N_2, 30-600 °C at 20 °C/min.

2.3. Synthesis of Intermediate Coatings

In order to strike a desirable balance of properties it was decided that a mixture of flexible and rigid isocyanates would be useful. The first combination that was explored was an equimolar mixture of HMDI and IPDI. Unlike films based on HMDI alone, those made with a mixture of HMDI and IPDI have very good clarity (Table 5, Figure 5). The modulus of these films was intermediate between those based solely on HDMI or IPDI, respectively. As seen many times before there is an inverse relationship between [glycerol] and modulus; however, thermal stability seemed to be little affected over the concentration entire range explored and falls between that for films based solely on HMDI or IPDI. As such, these films were strong but not brittle and quite difficult to cut. Although these films are not optimized, they can be considered as promising for use in specialty applications. This is impressive since similar to all previously discussed films those based on HMDI + IPDI contain a respectable amount of renewable content. An attempt to improve film clarity was made by substituting polyester polyol based on hydrogenated anhydride **4** for **3** but again this led to a worsening of UV transmittance with concomitant increase in modulus (Table 5, entry 4).

Table 5. HMDI + IPDI based films.

Entry	Anhydride/alcohol (mol:mol)	Modulus[a] (MPa) Wt % Renew.	10 Wt % Loss[b] (°C)	% Transmittance at 1100 nm, 700 nm, 400 nm
1	**1**:glycerol 1:4	459 35.3	177	83.6, 80.9, 78.8
2	**1**:glycerol 1:5	349 33.0	241	88.2, 86.9, 84.5
3	**1**:diglycerol 1:6	304 31.4	191	85.6, 82,6, 78.0
4	**4**:glycerol 1:6	490 26.9	220	72.8, 61.3, 48.7

a. Young's modulus.
b. Temperature at which 10 wt % is lost. Conditions = N_2, 30-600 °C at 20 °C/min.

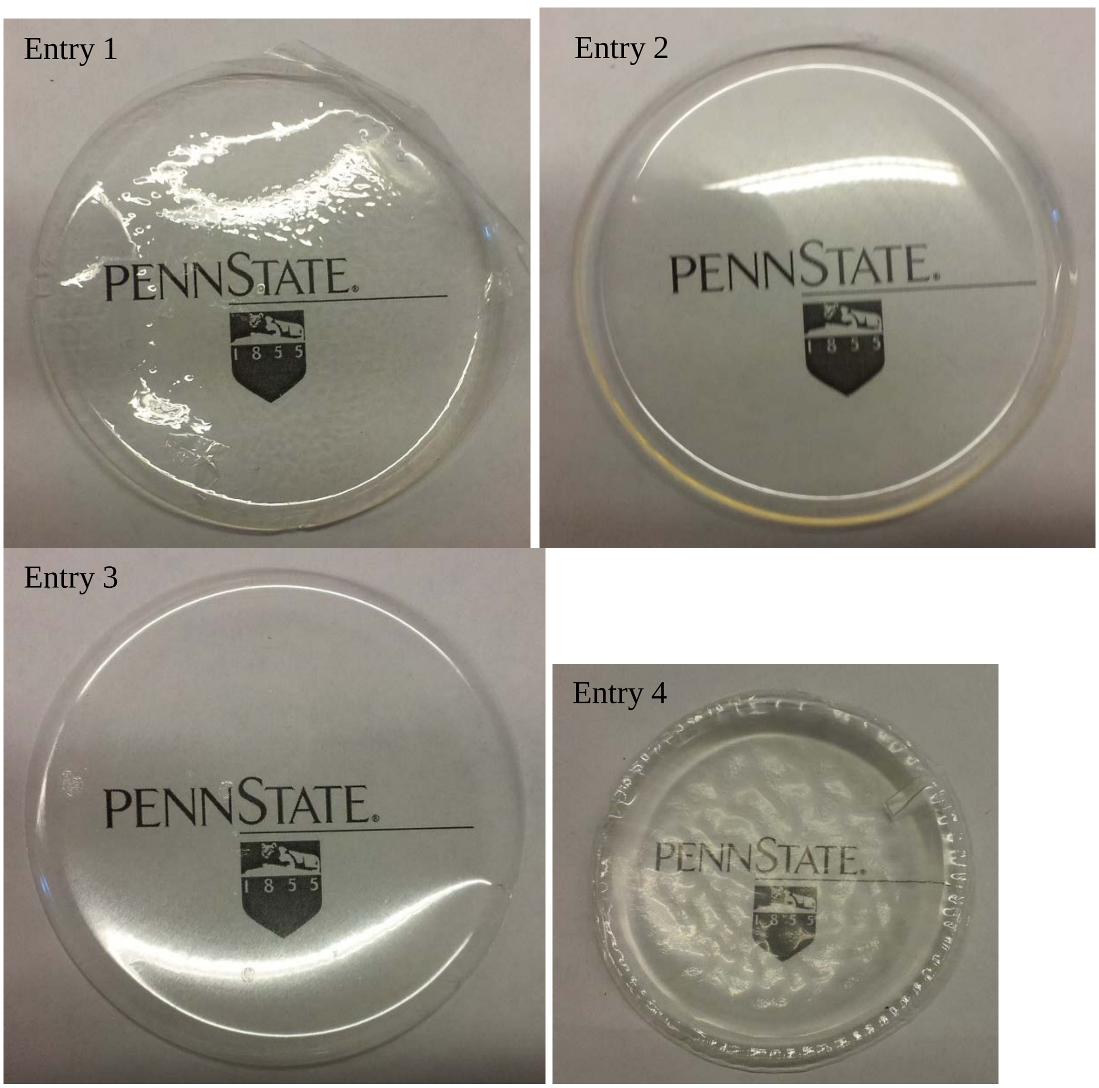


Figure 5. HMDI + IPDI based films.

A final foray was made in the area of a mixture of flexible and rigid isocyanates, this time a mixture of N3400® and Desmodur W®. In this series of experiments the [N3400®]/[Desmodur W®] ratio was varied for resins based on a specific glycerol content (Table 6, Figures 6-8). As with HMDI + IPDI films those based on a mixture of N3400® + Desmodur W® had high clarity, reduced brittleness, and were quite tough. In general, as the [N3400®]/[Desmodur W®] ratio decreases modulus increases and thermal stability either remains unchanged or slightly increases. These films represent a promising first generation of coatings that may be of value in specialty applications.

Table 6. N3400® + Desmodur W® based films.

Entry	Anhydride/alcohol (mol:mol)	N3400®/**7** (mol:mol)	Modulus[a] (MPa) Wt % Renew.	10 Wt % Loss[b] (°C)
1	**1**:glycerol 1:4	7/3	1.21 33.2	193
2	**1**:glycerol 1:4	1/1	10.8 31.9	185
3	**1**:glycerol 1:4	3/7	15.7 30.8	189
4	**1**:glycerol 1:6	7/3	3.79 29.6	192
5	**4**:glycerol 1:6	3/2	1.97 28.9	218
6	**1**:glycerol 1:6	1/1	63.0 28.5	210
7	**1**:glycerol 1:6	2/3	234 27.8	210
8	**1**:glycerol 1:6	3/7	398 27.3	221

a. Young's modulus.
b. Temperature at which 10 wt % is lost. Conditions = N_2, 30-600 °C at 20 °C/min.

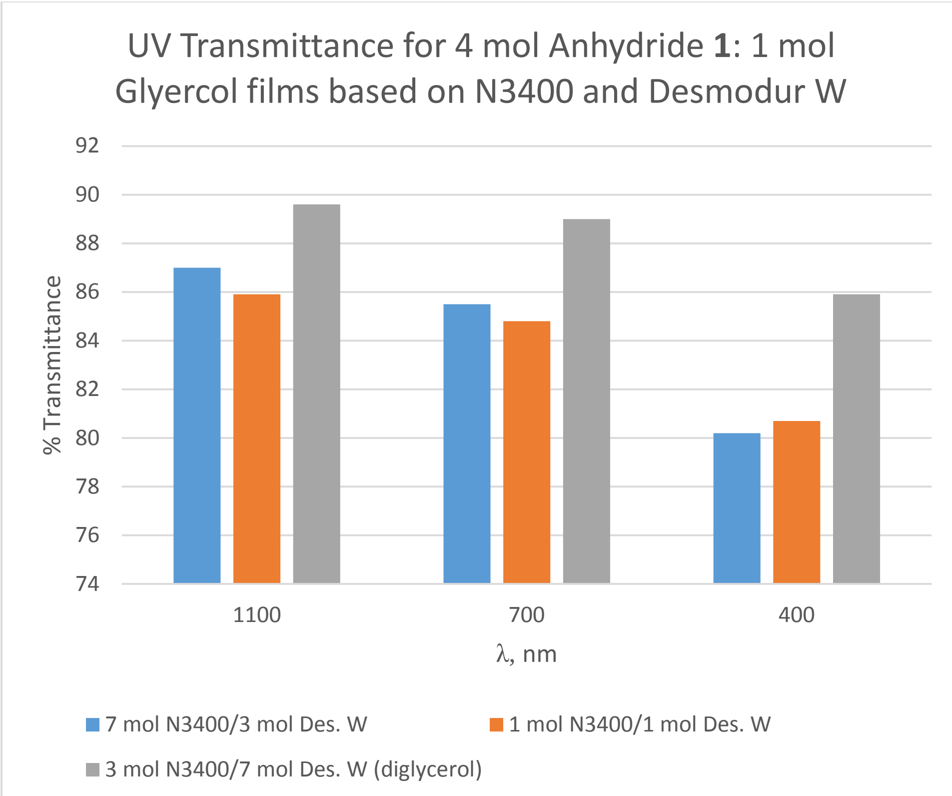


Figure 6. Variance of transparency of films based on 4 mol anhydride **1**: 1 mol glycerol as a function of [N3400®] and [Desmodur W®].

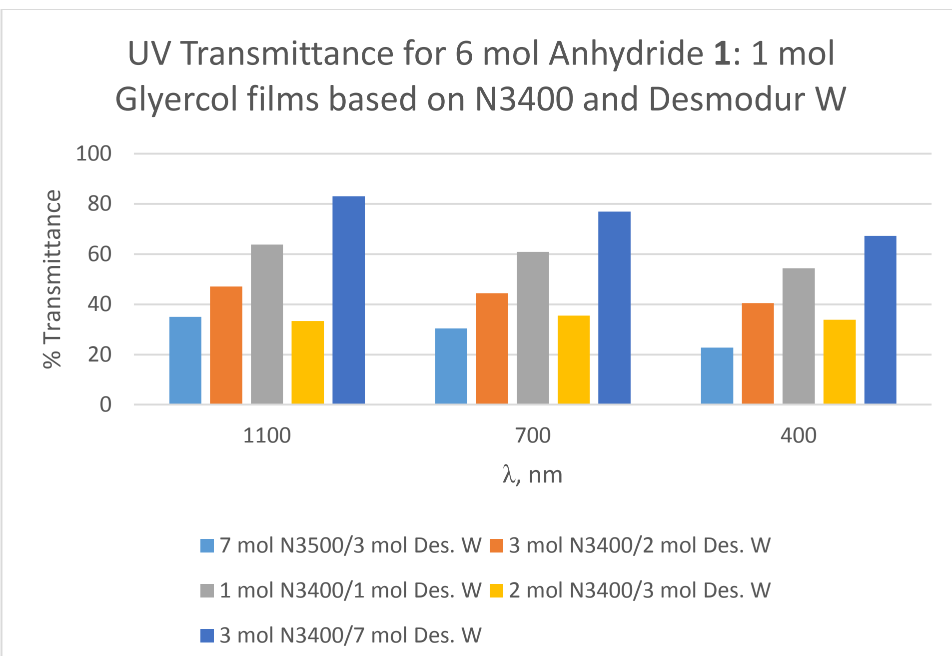
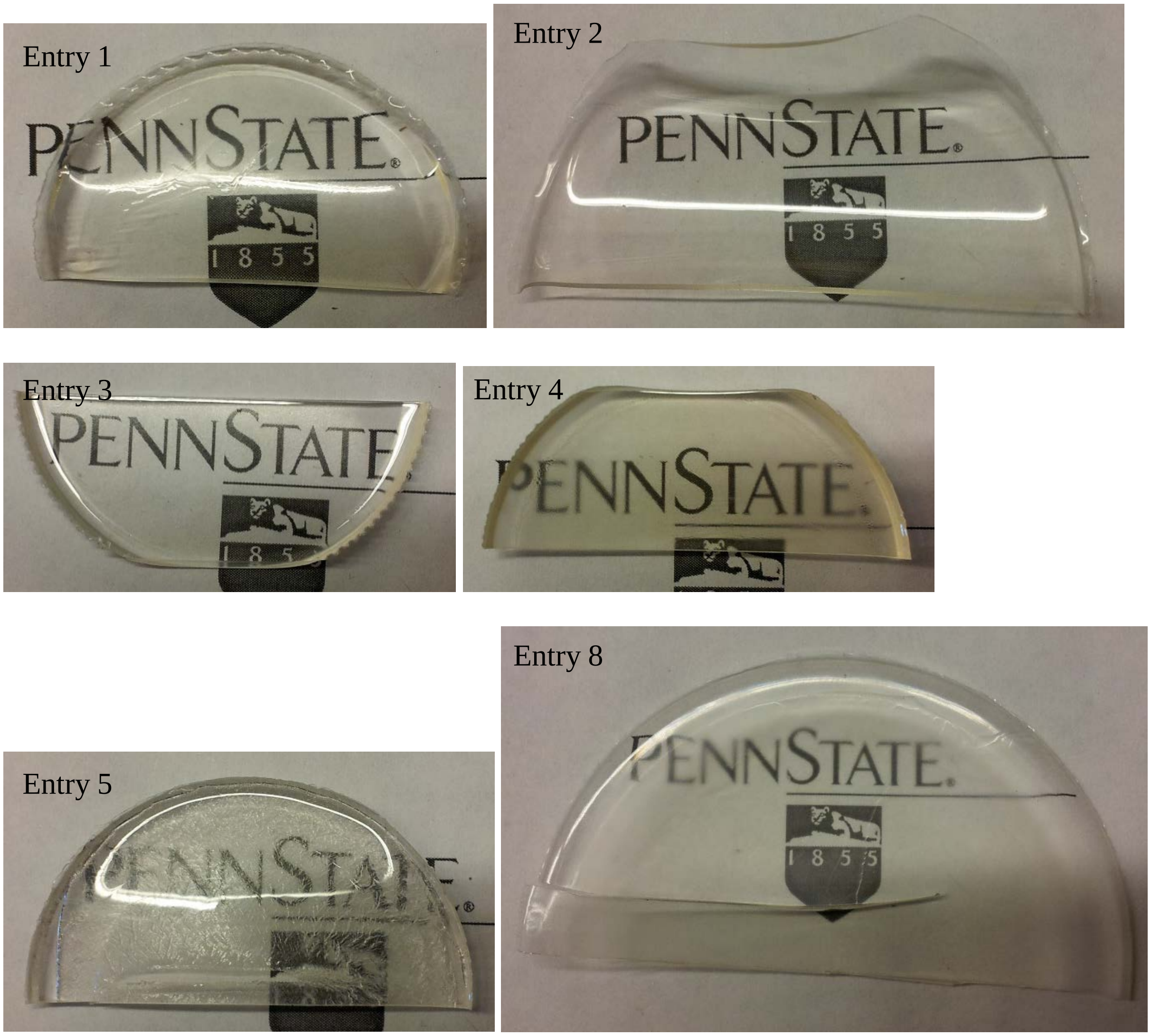


Figure 7. Variance of transparency of films based on 6 mol anhydride **1**: 1 mol glycerol as a function of [N3400®] and [Desmodur W®].

Figure 8. N3400® + Desmodur W® based films.



2. Conclusions

A broad range of coatings based on soybean derived 1,4-CHD have been synthesized. These range from flexible to rigid coatings. Depending on the identity of the isocyanate, transparency can be quite high. These PUs appear to be unaffected by moisture and since they lack chromophores they could possibly be used in harsh environments. Furthermore, films with relatively high temperature stability can be made. Renewable content of these materials is respectable and could potentially be further increased if multifunctional isocyanates with functionality of 3 or higher are used. The most promising materials are those based on a mixture of flexible and rigid isocyanates as these materials appear to possess a good blend of desired properties. These materials may find use as coatings for optics, displays, windows, etc. and could prove to be superior over more traditional polymers in terms of cut/scratch resistance. In particular, solvent free systems that give rise to similar or better coatings may be very attractive in niche areas where high performance, sustainable coatings are required.

Abbreviations

CHD = cyclohexadiene
DesW = Desmodur W® {hydrogenated methylene diphenyl diisocyanate (MDI)}
HMDI = Hexamethylene diisocyanate
IPDI = Isophorone diisocyanate
MPa = Mega Pascals
MW = Molecuar weight
N3400® = (a proprietary HMDI based polymer)
PU = Polyurethane