

Potential Replacement of Toxic PVC Plasticizers with Urea, Its Derivatives, and Related Compounds

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Abstract

The primary plasticizers for the world's most plasticized polymer, poly(vinyl chloride) (PVC), are organic phthalates, this despite being categorized as probable human carcinogens by the EPA. Di-2-ethylhexyl phthalate (DEHP or DOP) is such a typical PVC plasticizer. We sought to find an alternative plasticizer that lowered the glass transition temperature (T_g) and softened PVC, but was not as harmful to the environment and for our health as the currently employed phthalate plasticizers. We recently discovered that urea (U) could complex with amorphous polymers, such as atactic poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc). Compared to neat samples, the T_g s of the PMMA-U and PVAc-U complexes were increased and decreased, respectively. However, when complexed with dimethylurea (DMU), the T_g of the PMMA-DMU complex was lowered. Since T_g s of PMMA and PVAc were lowered by either U or one of its derivatives, this prompted us to investigate whether they could interact and complex with another largely amorphous polymer PVC, that is often plasticized, to soften and lower its T_g . Shifts in the vibrational frequencies observed by Fourier-Transform Infrared spectroscopy and Differential Scanning Calorimetry thermograms indicated that U, its derivative tetramethylurea (TMU)], and the related compound Acetamide (AC) were complexing with PVC. All three complexes (PVC-U, -TMU, and -AC) showed significantly lowered T_g s. Preliminary mechanical property measurements of PVC-U and PVC-AC films showed they were softer and more pliable than PVC films. Consequently, we believe our preliminary results warrant further examination of U, AC, and TMU as potential effective and less harmful PVC plasticizers.

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Introduction

Poly(vinyl chloride) (PVC) is by far the most plasticized polymer, with approximately 90% of all plasticizers used to manufacture PVC products [1-4]. Plasticizers are utilized to reduce the brittleness and increase the flexibility of PVC through the lowering of glass transition temperatures (T_g s). This enables the manufacture of food wrappers, medical products, such as transfusion bags and associated tubing, and many other products, such as toys, electrical insulation, and furniture. Since PVC is thoroughly integrated into the medical and food industries, it is important to use safe materials that will not harm us when medicines and nutrients packaged with plasticized PVC are absorbed and processed by our bodies. Currently, di-2-ethylhexyl phthalate (DEHP), also known as dioctylphthalate (DOP), is the primary plasticizer used to soften PVC. However, DEHP has been associated with wildlife, reproductive, and development concerns, environmental damage, and carcinogenic effects in animals and humans [4-7].

It is imperative that a harmless yet effective plasticizer as an alternative to the phthalates be identified, so that wildlife, humans, and the environment are not subject to the negative effects of current PVC plasticizers like DEHP. A review article has summarized recent attempts to replace the harmful phthalate plasticizers with a variety of plasticizers, some of which may be harmless [8].

We recently discovered that atactic poly(methyl methacrylate) (PMMA) could complex with U and significantly increase its T_g , and PMMA could also complex with dimethylurea, which decreased its T_g [9-11]. In addition, when atactic poly(vinyl acetate) (PVAc) was complexed with U, it acted as a plasticizer and lowered the T_g of PVAc [10]. Since PMMA, PVAc, and PVC are all amorphous polymers, we decided to conduct experiments to investigate whether U or any of its derivatives and related compounds could complex with PVC and lower its T_g .

Urea (U) is used as a fertilizer for enhancing the yields of rice and other crops [12]. Since it is absorbed by vegetation, and vegetables are consumed by humans, it seems safe to assume that U is an environmentally friendly substance. Also, U is used widely in coatings for pools, water parks, and cables. Since humans generate copious quantities of U in their urine, are exposed with minimal protection in the environment to U, and no reports have surfaced to indicate that urea is carcinogenic or in any way unsafe, we have not hesitated to use U in our experiments related to softening PVC.

To determine if PVC and U or its derivatives or related compounds are complexing, and if their T_g s are lower than that of neat PVC, Fourier-Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC) observations were necessary. FTIR uses infrared radiation to identify unknown materials. This is reflected by the peaks seen in the spectra, which are associated with absorption of light of different wavelengths by the vibrations of specific functional groups [13]. If any substantial differences are observed in the vibrational peak frequencies of PVC-complex samples when compared to, in our case, the vibrational peaks in neat PVC and neat U or U related compounds, this indicates that the PVC and U and/or U related

compounds in the sample are intimately mixed and interacting and not just in a phase separated physical mixture.

DSC compares the heat flow between the sample tested and that of an empty reference sample pan, and reveals many thermal characteristics of a sample. The DSC thermal responses of a material that are most important for our research were the identification of a sample's T_g and melting temperature T_m . If the T_g s and T_m s observed are close to those observed in neat PVC and neat U and/or U related compounds, then it is assumed that no complex has formed.

Our past research with amorphous polymers as well as with U derivatives, suggested that implementing similar techniques with PVC might result in promising outcomes [9-11]. Preliminary results from our previous experiments indicated that U did not have a plasticization effect on PVC, yet later more careful and repeated observations partially refuted the earlier results [11], and received further support from our current investigation.

It would be beneficial to perform further research on the effects of different concentrations of U and its related compounds on the PVC-complexes' T_g s, because this could result in the discovery of a more sustainable and less toxic plasticizer. To determine whether our goal of lowering PVC's T_g had been achieved by the complexed PVCs, DSC and FTIR were utilized to analyze the samples made with PVC and U, and/or U related compounds, and mechanical property measurements were made on their films to learn if they were softer than neat PVC.

Previous FTIR and DSC observations of potential complexes of PVC with the U derivatives thiourea and dimethylurea showed that no complexation and associated reductions in T_g s occurred [11]. Consequently, in addition to the potential PVC-U complex, we only describe our observations of the potential PVC-Tetramethylurea (TMU) and PVC-Acetamide (AC) complexes. We attempted to determine whether U and/or its TMU derivative and related AC compound can potentially replace DEHP as PVC's main plasticizer, and if either can, at what concentrations do they most effectively lower the T_g of PVC?

Experimental

Materials

PVC (MW = 80,000 g/mole) and U were purchased from Sigma-Aldrich. TMU was purchased from Alfa Aesar. AC was purchased from Acros Organics, dimethylformamide (DMF) was purchased from Fisher Scientific and methanol was purchased from VWR International. All supplies were purchased from these US manufacturers.

Methods

PVC-U and PVC-AC samples were made through a series of steps called solution processing. First, the PVC and U or AC were weighed to obtain their specific molar ratios (moles of PVC repeat units:moles of U or AC), which ranged from ~1:1 to 1:7 (See appendix A:Sample Inventory in the Supplementary Material). Next, 25 ml of DMF was mixed with 1 g or less of PVC, while 35 ml of methanol was used to dissolve U, AC, and TMU. PVC, U, AC, and TMU were placed in different Erlenmeyer flasks, and their corresponding solvents were poured in

along with a stir bar. Since TMU is a liquid no solvent was used. The separate flasks were each placed on a hot plate stirrer and were heated at 60° C and stirred until U and AC dissolved. About 1 ml of the U or AC solution was repeatedly added into the PVC solution with a microliter pipette until all of the U or AC solution was added. The combined solutions were usually left overnight. The precipitates formed were extracted from their solutions through vacuum filtration, which was continued until the precipitate was dry. Next, the precipitate was manually crushed with a mortar and pestle until it was as close to a fine powder as possible and placed into a labeled vial for analysis using FTIR and DSC observations.

Physical mixtures were also created for comparison purposes. A physical mixture was made by combining PVC powder with U or AC powders and mixing them together with a mortar and pestle. PVC-TMU physical mixtures were formulated, but the process used was slightly different. Since TMU is a liquid at room temperature, it was added slowly to the PVC solution while being stirred with a lab spatula in a petri dish. This guaranteed that the PVC would be well mixed with the TMU. The PVC-U and PVC-AC physical mixtures were analyzed with FTIR and DSC, while the PVC-TMU physical mixtures were only analyzed with DSC.

FTIR-ATR spectra were obtained using a Nicolet 510P IR spectrometer with a resolution of 4 cm⁻¹ over the wave number range of 4000-400 cm⁻¹. Signals were averaged over 64 scans for each spectrum. The DSC thermal scans with two heating and intervening cooling steps were recorded on a Perkin-Elmer Diamond DSC-7 instrument. Nitrogen was used as the purge gas and Indium was used for calibration. Samples were first heated from 25 to 150° C, held at 150° C for at least 1 minute, then cooled to 25° C and followed by a second identical heating to 150° C. Both heating and cooling rates were 20° C/min, and their resulting thermograms were analyzed using Pyris software. The onsets of increased heat capacities were taken as T_gs.

2-3 g of finely ground sample powders were placed between Teflon[®] sheets and then placed between the platens of a melt press. PVC was melted at 180° C, pressed at 5,000 kPa for 1 minute, and then further pressed at 10,000 kPa for an additional 45 s. PVC-U and PVC-AC were melted at 120° C, pressed at 5,000 kPa for 30 s, and then further pressed at 10,000 kPa for an additional 30 s. Three dog bone samples were cut from these melt-pressed films, and subjected to mechanical testing.

Film thickness was measured using the Ames Thickness Tester Model: M034/Serial Number: 31152 as described in the ASTM D1777 - Standard Test Method for Thickness of Textile Materials following Option 1 (which uses an applied pressure of 4.14 ± 0.21 kPa (0.60 ± 0.03 psi)). Film Tensile strengths were measured following ASTM D 638 - Standard Test Method for Tensile Properties of Plastics using the MTS Constant-Rate-of-Extension (CRE) tester: Model: Q-Test/5. Serial number: M10181408.

Results and Discussion

FTIR spectroscopy was the first analysis performed, and PVC with U was the first combination of materials observed. Potential complexes with 1:7, 1:3, 1:2, and 1:1.38 PVC:U molar ratios were made and observed. Figure 1 illustrates that the 1:7 PVC:U complex made *via* solution processing contains elements of both PVC and U, and that vibrational shifts from those of neat PVC occur in its spectra. This means some of the U bonds are interacting with PVC.

Vibrational shifts between neat U and the PVC:U complex can also be observed and are between 3435-3440, 1615-1625, and 1594-1597 cm^{-1} . Such vibrational shifts are associated with U N-H bond stretching and bending. A 960-965 cm^{-1} shift between neat PVC and the PVC:U complex can also be identified.

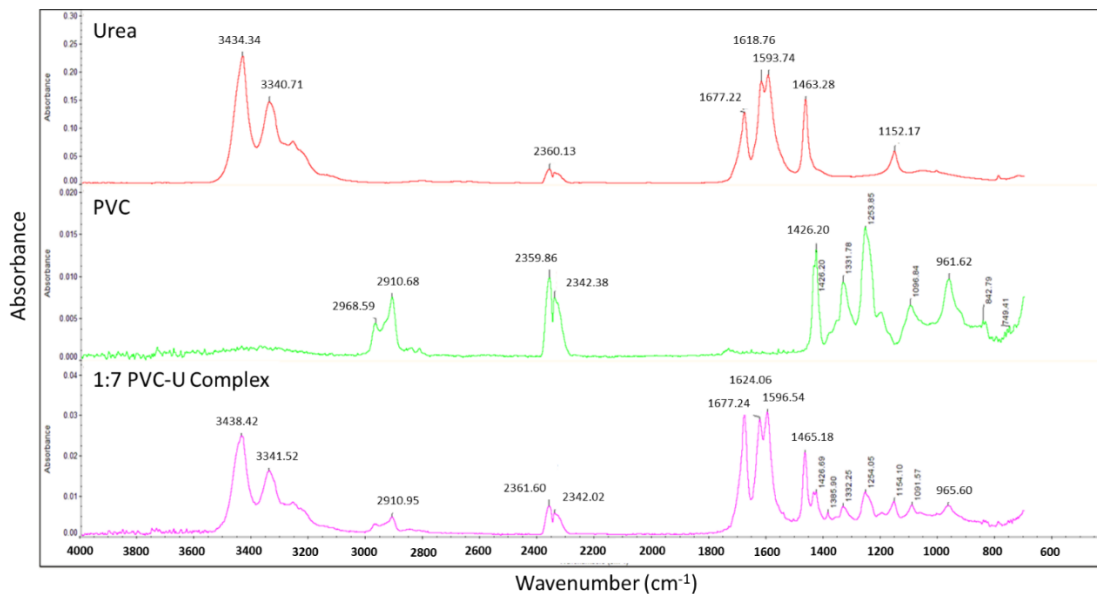


Figure 1. FTIR of U, PVC, and the 1:7 PVC:U Complex (top to bottom).

None of these shifts are visible in Figure 2 for the 1:7 PVC:U physical mixture, so we can conclude that in the 1:7 complex PVC and U are interacting on a more intimate molecular level when solution processed as described here.

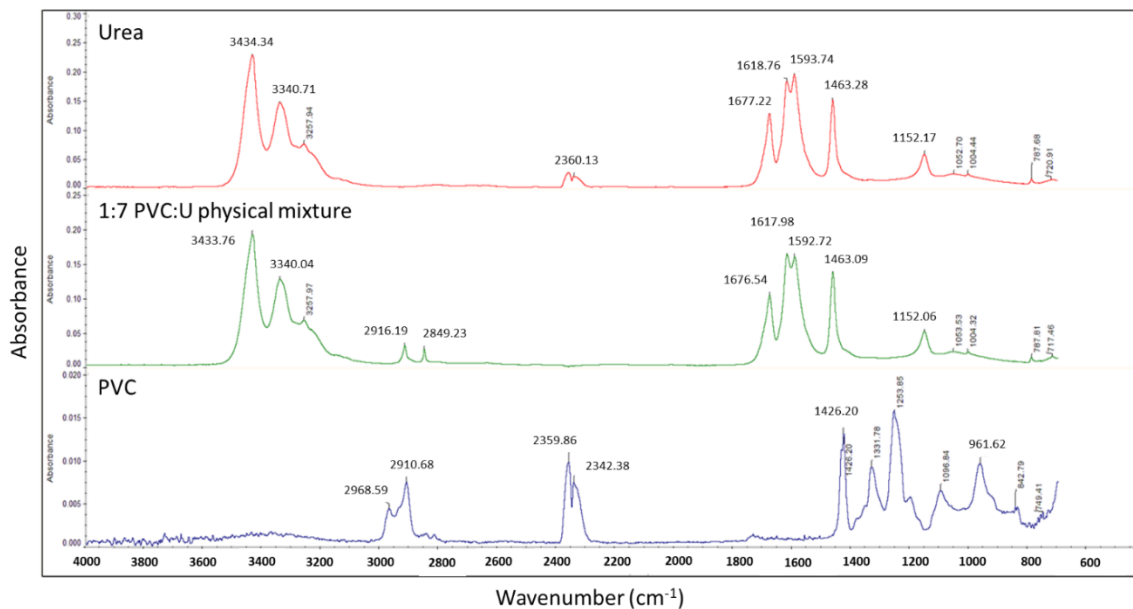


Figure 2. FTIR of urea, 1:7 PVC:U physical mixture, and PVC (top to bottom).

Also note from Figures 1 and 2 that the U vibrational peaks below 1700 cm^{-1} are closely similar in neat U, the 1:7PVC:U complex, and the 1:7 PVC:U physical mixture. This is a result of the crystallization of the excess uncomplexed U in the 1:7 PVC complex. This observation is confirmed by DSC observations, as we shall see.

The shifts observed in the 1:7 PVC-U complex are similar to those observed in the 1:3, 1:2, and 1:1.38 PVC-U complexes, though those with less urea exhibited even more significant shifts than the 1:7 PVC-U complex, indicating that all the U was complexed with PVC. Their FTIR spectra are found in Appendices B-D in the Supplementary Material and are summarized in Tables 1-3. It is evident that PVC can successfully complex with U, and this was also reflected in the DSC thermograms of the various PVC:U complexes.

Table 1. 1:3 PVC:U complex FTIR peak wavenumbers compared to pure U and PVC.

Wavenumber of 1:3 PVC-U peak (cm^{-1})	Urea Peak	PVC Peak	Difference	Bond Movement
3438.16	3434.34		3.82	Urea's N-H stretching
3343.22	3340.71		2.51	Urea's N-H stretching
2916.43		2910.68	5.75	PVC's C-H stretching
1624.40	1618.76		5.64	Urea's N-H bending
1091.17		1096.84	5.67	Associated with C-O...
964.29		961.32	2.67	PVC's C=C bending

After performing FTIR on the PVC-U complexed samples, they were examined by DSC. For comparison, pure PVC was first analyzed with DSC and its thermogram illustrated that the PVC used in our samples has a T_g between $85\text{-}88^\circ\text{ C}$ (Figure 3). Next, we analyzed a physical molar mixture of 1:1.4 PVC:U. Its T_g dropped very little to 82° C . When 3 moles of U were solution processed and combined with 1 mole of PVC, this PVC:U complex's T_g dropped to 51° C . However, a 1:3 PVC:U physical mixture did not alter the T_g of PVC (Figure 4).

Referring to Figure 5, an interesting trend was found, which refuted the expectation that "the more plasticizer used, the more T_g will be lowered." DSC revealed that the sample, with a 1:7 PVC:U molar ratio, which evidenced a clear melting peak for the uncomplexed excess U, had an average T_g of 63° C , which is higher than that of both the 1:3 and 1:2 complexes. It can be concluded that the most effective molar ratio in PVC:U complexes is between 1:2 to 1:3,

since their T_g s are both in the low 50° Cs (See Figure 5 and Appendices E, F, and G in the Supplementary Material).

Table 2. 1:2 PVC:U complex FTIR peak wavenumbers compared to pure U and PVC.

Wavenumber of 1:3 PVC-U peak (cm ⁻¹)	Urea Peak	PVC Peak	Difference	Bond Movement
3438.16	3434.34		3.82	Urea's N-H stretching
3343.22	3340.71		2.51	Urea's N-H stretching
2916.43		2910.68	5.75	PVC's C-H stretching
1624.40	1618.76		5.64	Urea's N-H bending
1091.17		1096.84	5.67	Associated with C-O...
964.29		961.32	2.67	PVC's C=C bending

Table 3. 1:1.38 PVC:U complex FTIR peak wavenumbers compared to pure U and PVC.

Wavenumber of 1:1.38 PVC-U peak (cm ⁻¹)	Urea	PVC	Difference	Bond Movement
3447.27	3434.34		12.39	Urea's N-H stretching
2915.97		2910.68	5.29	PVC's C-H stretching
1635.71	1618.76		16.95	Urea's N-H bending
1596.87	1593.74		3.13	Urea's N-H bending
964.19		961.62	2.57	PVC's C=C bending

It should be noted that there are no observed neat U or U-IC melting peaks expected at ~135° C in the PVC:U DSC scans except for the 1:7 sample which apparently has excess U that is not complexed with PVC and has crystallized [14]. Complexes with less U show endothermic peaks at ~110° C indicating decomplexation or melting of the PVC-U complexes.

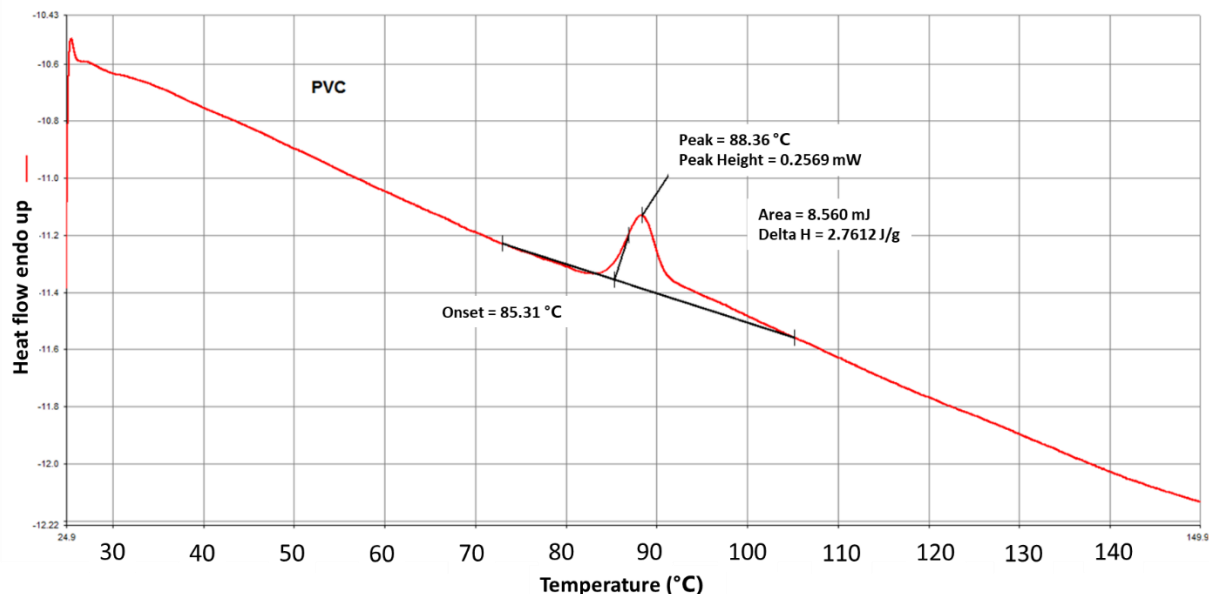


Figure 3. DSC of Pure PVC.

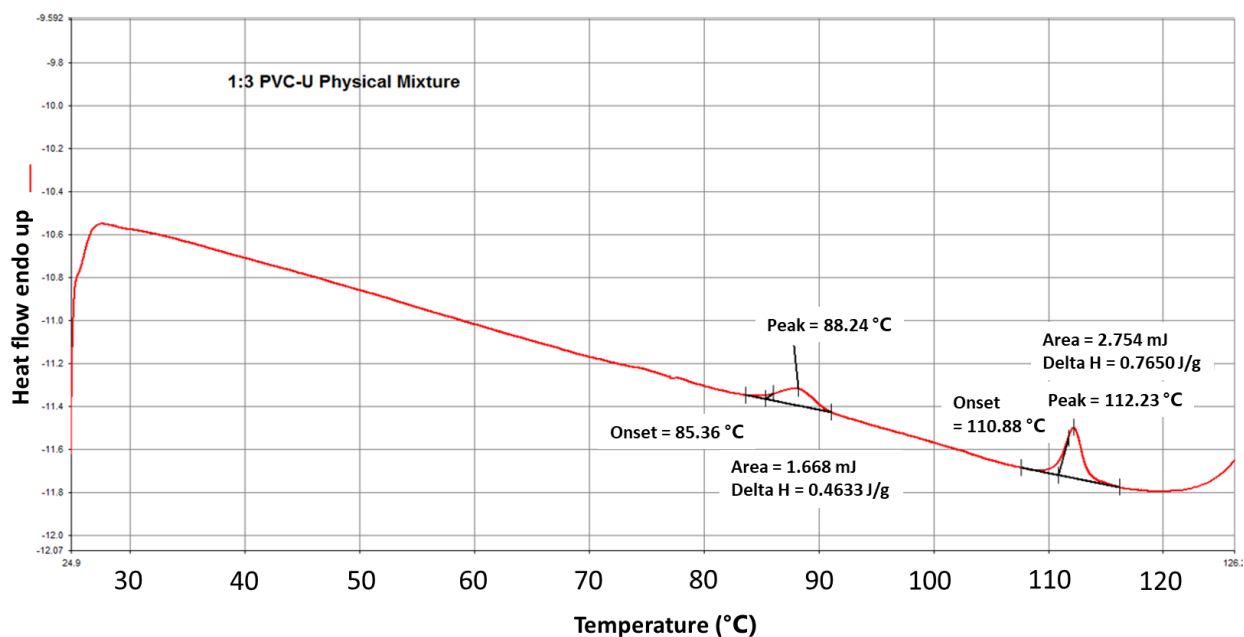


Figure 4. DSC of a 1:3 PVC-U Physical Mixture Sample.

After experimenting with U as a plasticizer for PVC, its TMU derivative and the related compound AC were considered next. Potential complexes were created with 1:2 and 1:1.38 PVC-AC mole ratios. FTIR and DSC analyses were performed on both samples and showed promising results. Significant shifts were seen in the 1:2 PVC-AC sample's FTIR spectrum, especially in the region between 3400 and 3200 cm^{-1} and around 1300-1400 cm^{-1} (See Figure 6). The difference between the 1:2 PVC-AC peaks and peaks in those regions from neat AC vary from 11- 46 cm^{-1} and even reached 94 cm^{-1} .

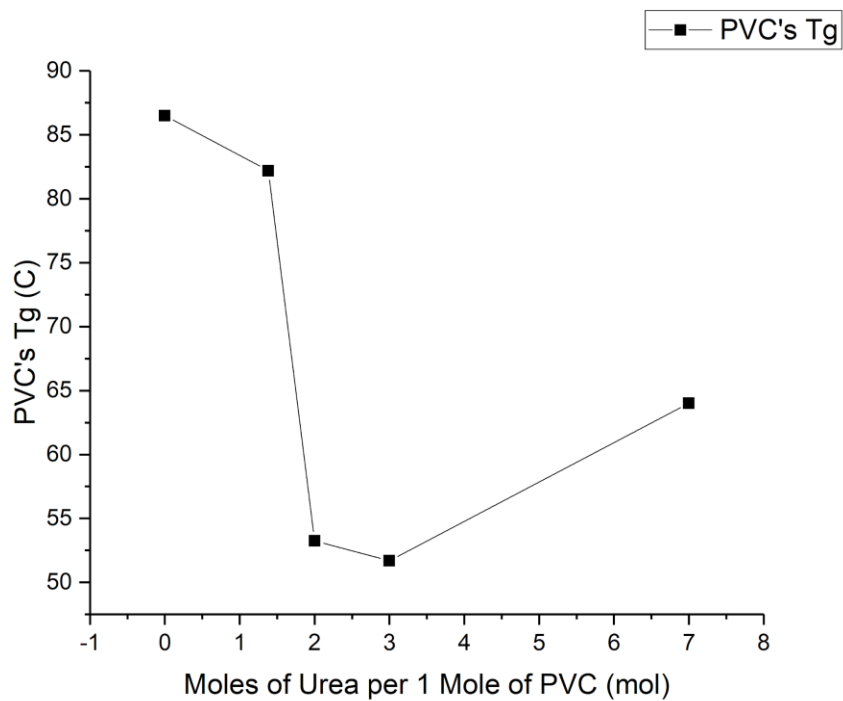


Figure 5: Accumulated DSC results illustrating the effect of the U:PVC molar ratio on the T_gs of the PVC-U complexes.

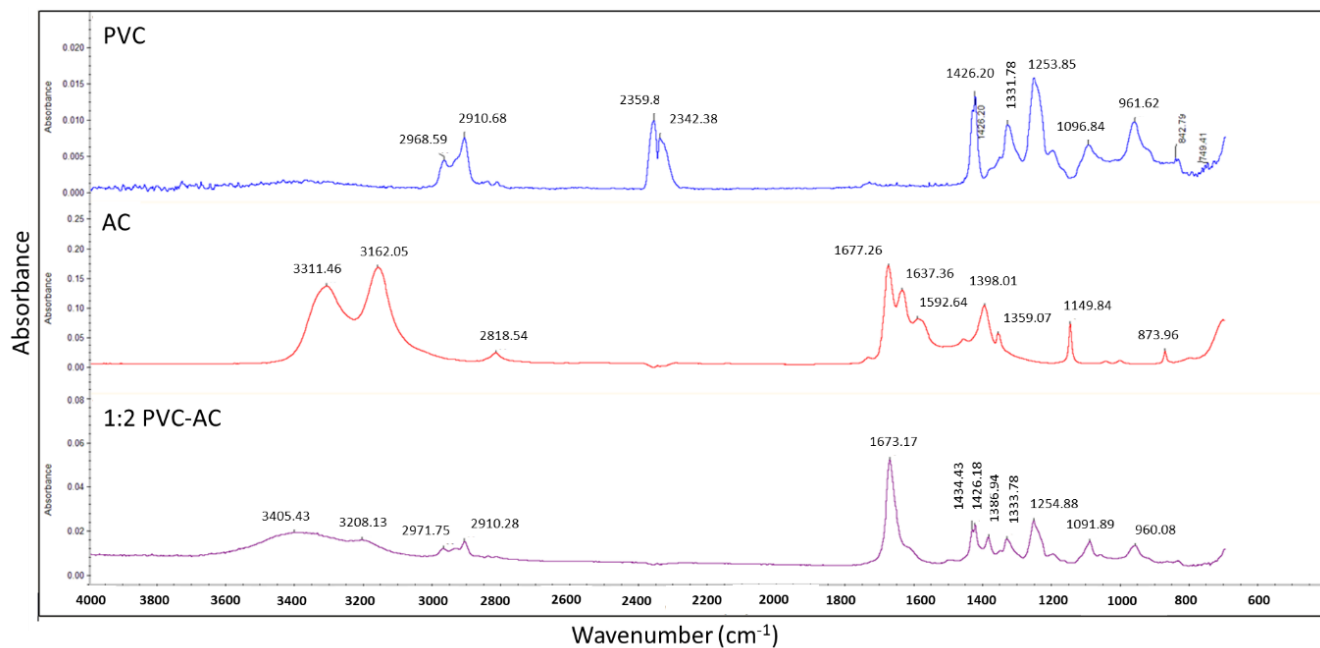


Figure 6: FTIR of PVC, AC, and 1:2 PVC-AC Complex (top to bottom).

By comparison, the 1:1.38 PVC:AC complex spectrum had smaller shifts, but they were still indicating that PVC was complexing with AC. That sample had noticeable shifts in the 3300- 3340 cm^{-1} and 1385-1680 cm^{-1} regions. The shifts between the 1:1.38 PVC:AC peaks and AC peaks in those two regions varied from 4, 12, and up to 27 cm^{-1} as seen in Figure 7.

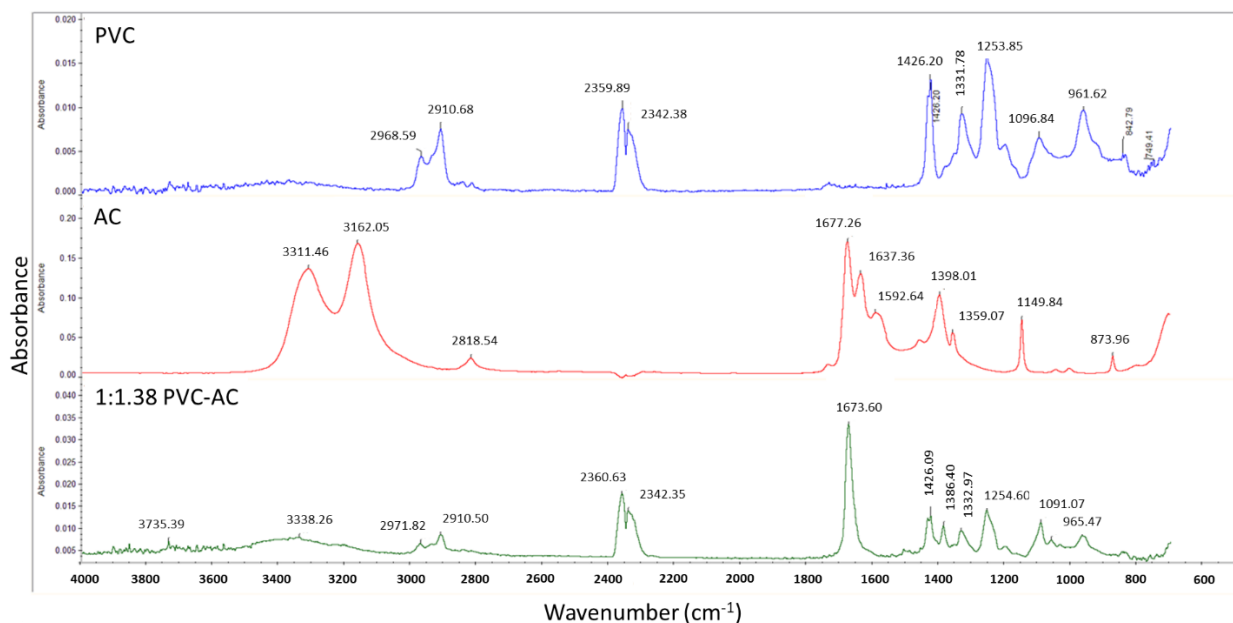


Figure 7. FTIR of PVC, AC, and 1:38 PVC-AC Complex (top to bottom).

Their DSC results were consistent with the magnitudes of their observed vibrational peak shifts, because the T_g of PVC (85-88° C) was dramatically lowered to 45° C in the 1:2 PVC:AC complex, while the T_g of the 1:1.38 PVC:AC complex was about 50° C (See Figures 8 and 9). This 5° C T_g difference (50 to 45° C) is not large, but it appears to be consistent with that found for the 1:2 and 1:3 PVC:U complexes. The 1:2 molar ratio of PVC:U or AC seems to be the most effective in lowering their T_g s. There is also an indication for decomplexation or melting of neat AC in the DSC scans of the 1:2 PVC:AC sample (See Figure 8).

The last urea derivative investigated was tetramethylurea (TMU). Only one sample was made using solution processing, because TMU is a liquid. Nevertheless, the single solution processed sample was acquired with a 1:1.38 PVC:TMU molar ratio. FTIR and DSC were also utilized to analyze that sample. Not many shifts were observed in that sample's FTIR spectrum, and most of the spectrum was dominated by PVC.

Only two notable shifts were recorded. One PVC shift occurred from 2965 to 2970 cm^{-1} and one TMU shift from 1630 to 1640 cm^{-1} (Figure 10). Both of these shifts are not major at ~5-10 cm^{-1} . It is known that TMU evaporates, so when vacuum filtration was performed, most of the TMU might have left the precipitate. Nevertheless, TMU did also affect the T_g of PVC, as

illustrated in Figure 11, where PVC's T_g was lowered by roughly 30° C degrees to a range between 50-61° C.

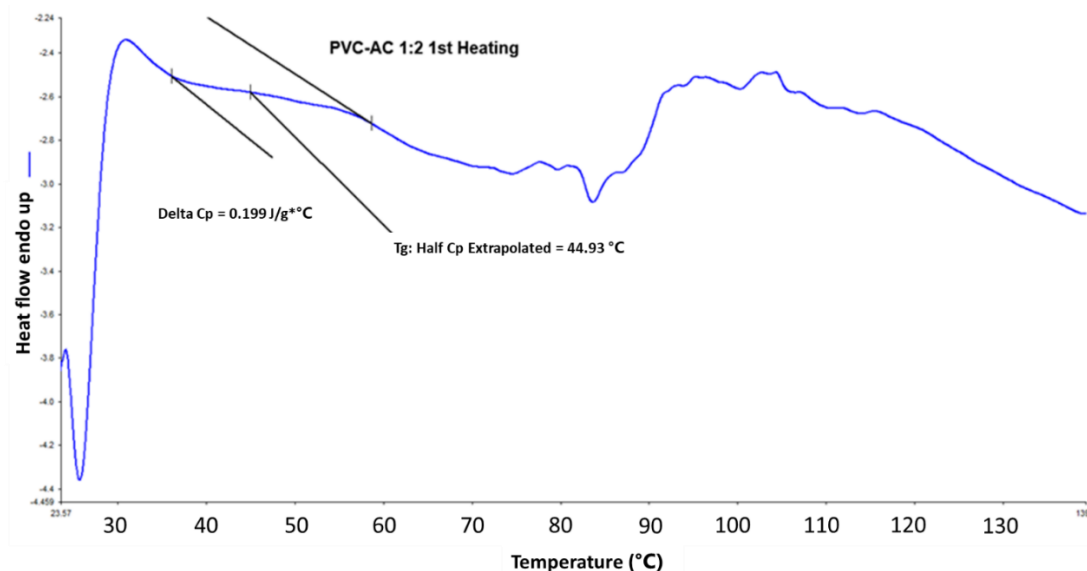


Figure 8. DSC of a 1:2 PVC:AC Complex Sample.

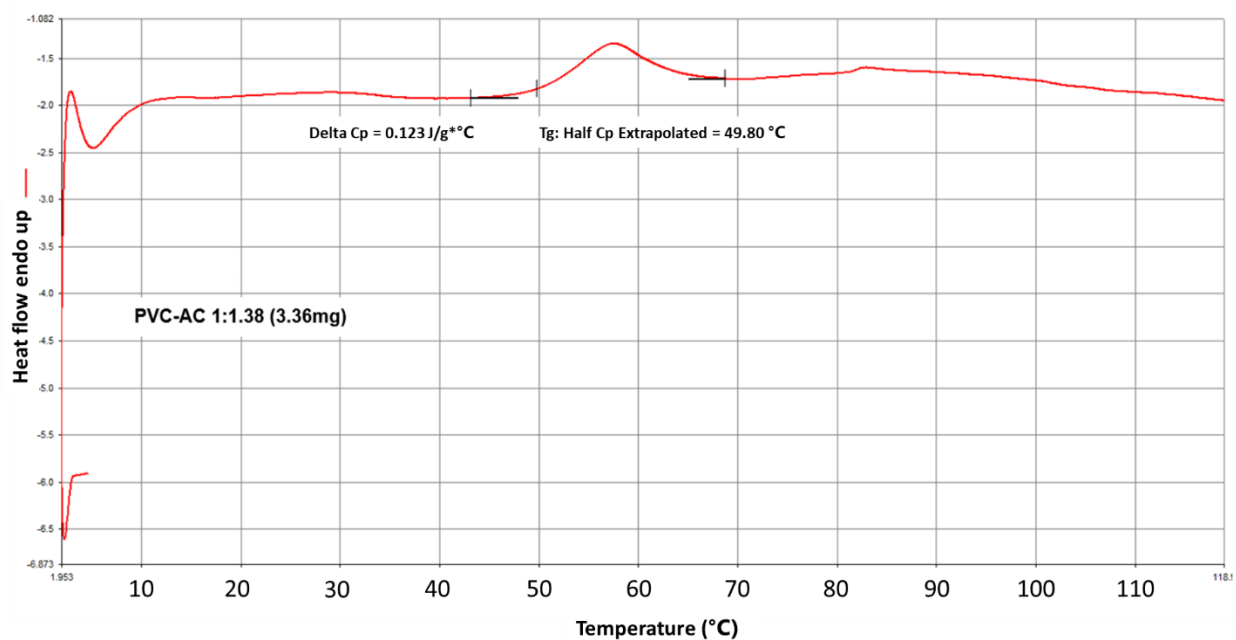


Figure 9. DSC of a 1:1.38 PVC:AC Complex Sample.

The results of our preliminary mechanical property measurements performed on PVC, PVC U, and PVC-AC films are presented in Table 4. With respect to the neat PVC films, it is clear that the PVC-U and PVC-AC complexed films are softer. It should be noted that no segregation of U or AC from PVC was observed in the complexed films tested for mechanical properties.

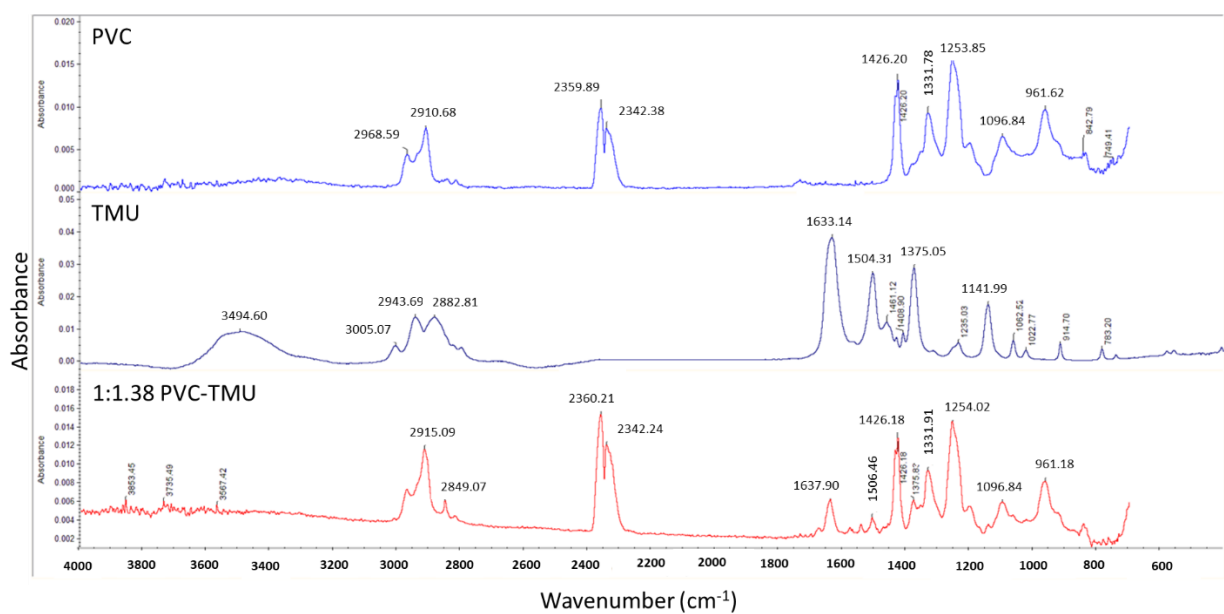


Figure 10. FTIR of PVC, TMU, and the 1:1.38 PVC-TMU Complex (top to bottom).

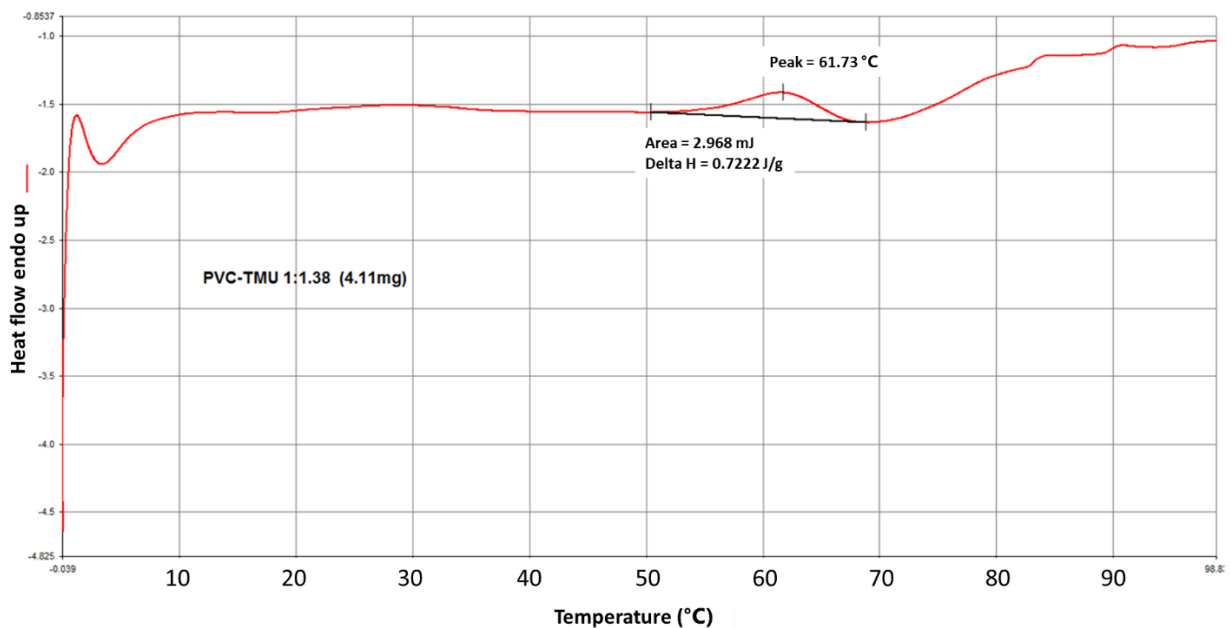
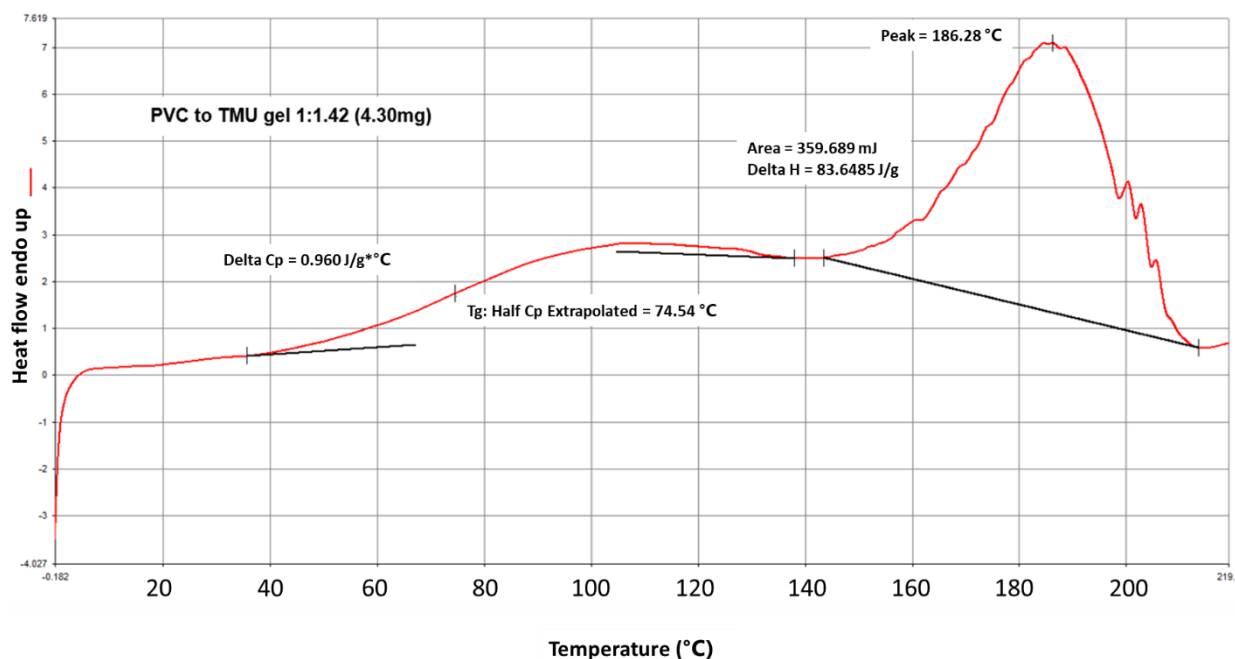


Figure 11. DSC of the 1:1.38 PVC:TMU Complex Sample.

Table 4. Mechanical Properties of PVC, PVC/U (1/1.3), and PVC/AC (1/1.3) Films

Sample	Thickness (mm)	Peak load (lbF)	Stress (MPa)	Strain (%)	Break load (KgF)	Stress (MPa)	Strain (%)	Yield load (KgF)	Modulus (MPa)
PVC	0.66	38.1	43.4	5.5	9.8	25.3	14.7	17.3	1530
PVC/U	0.57	12.3	15.0	1.4	11.4	13.9	1.5	12.3	1280
PVC/AC	0.60	10.9	13.8	1.1	5.0	13.8	1.1	3.5	1380

Physical mixtures of PVC and TMU were produced and resulted in novel observations. One gram of PVC powder was weighed and TMU (a liquid U derivative) was slowly added and manually mixed. This process created a clear colorless gel, which seemed to have vastly different mechanical properties than our other more rigid solution processed PVC:U, AC, and TMU samples. FTIR was not performed, instead DSC was utilized, and an “apparent T_g ” for the 1:1.38 PVC:TMU physical mixture was measured to be about 75°C , $\sim 10\text{--}15^\circ\text{C}$ degrees below the T_g of pure PVC (Figure 12). Other ratios of PVC to TMU physical mixtures were analyzed with DSC, but none of them evidenced a T_g lower than pure PVC (See Appendices H, I, and J in the Supplementary Material).

**Figure 12.** DSC of the 1:1.4 PVC-TMU Gel Sample.

DSC might not be the best method for analyzing these gels, because the samples are PVC gels swollen with TMU. At room temperature (23°C), the PVC-TMU gel was probed with a glass rod and exhibited reversible elastic deformation upon extension. Consequently, the swollen PVC chains are able to change their conformations and are moving, though not irreversibly, as is

usually assumed to be the case for neat amorphous polymers above their glass transition temperatures. Clearly the thermal signature seen in Figure 12 at $\sim 75^\circ\text{C}$ cannot be attributed to the typical softening observed in neat amorphous polymers at and above their T_g s. The mechanical properties of the PVC-TMU gel samples are vastly different from pure rigid PVC. They are non-flowing after their creation, and remained soft and reversibly elastically deformable.

Though exciting, a concern for these gels was raised from experiments that showed TMU slowly evaporates from the gels, making them potential environmental pollutants. This is confirmed by the DSC scan in Figure 12 showing the boiling off of TMU at $\sim 185^\circ\text{C}$. Appropriate toxicological investigations of TMU's environmental effects are lacking, but hopefully future experiments will reveal that its effects on wildlife in general and on humans in particular are less severe than DEHP. For now, however, this cannot be concluded. Nevertheless, some specialized applications for the PVC-TMU Gels may be envisioned, especially if they are coated with a polymer film insoluble in and impermeable to TMU.

Conclusions

Urea, its derivative TMU, and its related compound AC, have the ability to lower PVC's T_g some $30\text{-}40^\circ\text{C}$. The largest PVC T_g reduction was accomplished by AC. A 1:2 PVC-AC complex showed a T_g of 45°C , which is an $\sim 40^\circ\text{C}$ drop from the T_g of pure PVC. It was also evident that 2-3 moles of U added to 1 mole of PVC lowers the T_g of the PVC-U complexes the most. PVC-U and PVC-AC complexed films were also softer and more pliable.

In addition, an unprecedented gel was created between PVC and TMU. This gel could be of industrial importance, so more research would have to be conducted to determine how useful the gel is. In addition, more quantitative analyses would be of value to characterize more completely the PVC-TMU gels, including their mechanical properties.

Though requiring further studies to determine whether U or any of its derivatives and related compounds can be effectively integrated into PVC's many manufacturing processes to replace DEHP and other currently used phthalate plasticizers, we have nevertheless presented some promising preliminary results.

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