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Dynamic mechanical analysis of novel polyurethane coating for military applications

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Abstract

Three polyurethane coatings were evaluated using DMA to investigate the relationship between dynamic mechanical properties and durability properties of coated test panels. The current polyurethane solvent-based formulation, used as a chemical agent resistant camouflage top coat on all military tactical vehicles, was investigated along with newly developed water-reducible (WR) polyurethane coatings. The WR coatings offer significantly reduced volatile organic compounds (VOCs) compared to the solvent-based system, and thus represent environmentally compliant coatings. DMA investigations revealed that the two classes of polyurethane coatings exhibit different dynamic mechanical properties, which are attributed to different cross-linking mechanisms involved in film formation. The more uniformly cross-linked solvent-based coating provides the best chemical agent resistance but the poorest mechanical properties. Properties measured using DMA were sensitive to the degree of isocyanate to hydroxyl indexing in the WR formulations as well as the drying time of coatings prior to evaluation. DMA investigations indicated that longer cure times at ambient temperature (6 or more months) may adversely affect the mechanical properties of the solvent-based system and potentially enhance chemical agent resistance of the WR coating. Further studies involving aged coatings are planned. Published by Elsevier Science B.V.

Keywords: DMA; Water dispersible polyurethane; Coating; Chemical agent resistance

1. Introduction

The US Army utilizes polyurethane coatings as camouflage ‘top-coats’ on all Army tactical vehicles and aircraft. These coatings not only serve to camouflage vehicles but also provide protection against chemical warfare agents. The coatings must retain their physical properties over a broad temperature range in widely varying climatic environments. Presently, camouflage top coats used on Army vehicles are comprised of a two-component solvent-based polyurethane. However, in an effort to meet current and anticipated EPA regulations as well as military requirements, the Army Research Lab (ARL), Weapons and Materials Research Directorate at APG, MD, has developed and patented a water reducible, two-component polyurethane coating for military vehicles that exhibits a 50% reduction in VOCs compared to the solvent-based system. The water-reducible (WR) polyurethane maintains required chemical agent resistance and exhibits superior properties compared to the solvent-based formulation.

2. Background

The urethane polymer is formed by the reaction of a hydroxyl terminated polyol with a diisocyanate as shown in Eq. (1).

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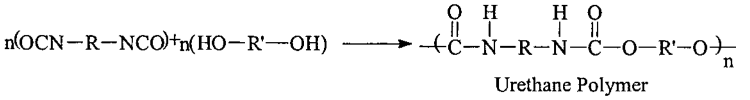
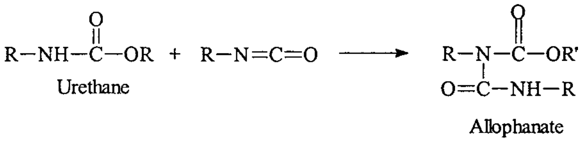


$$n(\mathrm{OCN{-}R{-}NCO}) + n(\mathrm{HO{-}R'{-}OH}) \longrightarrow \left(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}{-}\mathrm{R}{-}\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{O}{-}\mathrm{R'}{-}\mathrm{O}\right)_n \qquad (1)$$

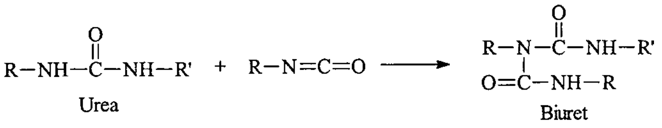
Urethane Polymer

Solvent-based systems are formulated with a slight excess of isocyanate (NCO). NCO to OH ratios approximately equal to 1.1:1.0 are typical for solvent-based polyurethane coating formulations. The excess NCO ensures complete reaction of the polyol and provides optimal film properties. Great care is taken to ensure that excess moisture is not present in non-aqueous, two-component polyurethane formulations due to its undesirable reaction with isocyanate [1,2].

It is important to note that although urethane formation occurs in the water dispersible formulations, other reactions producing amine and ureas are also prevalent [1,2]. Additionally, because of the excess isocyanate present in these systems, additional cross-linking reactions resulting in the formation of allophanate and biuret are also likely. Cross-linking reactions of urethanes and ureas with isocyanate are shown schematically in Eqs. (2) and (3).



$$\underset{\text{Urethane}}{\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}OR}} + \mathrm{R{-}N{=}C{=}O} \longrightarrow \underset{\text{Allophanate}}{\mathrm{R{-}\underset{O{=}C{-}NH{-}R}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OR'}} \qquad (2)$$



$$\underset{\text{Urea}}{\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R'}} + \mathrm{R{-}N{=}C{=}O} \longrightarrow \underset{\text{Biuret}}{\mathrm{R{-}\underset{O{=}C{-}NH{-}R}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R'}} \qquad (3)$$

Recent developments in water-borne polyurethane technology have enabled high performance coatings to be formulated using water-dispersible polyisocyanates and hydroxyl-functional polyurethane dispersions [3]. Hegedus et al. recently proposed a mechanism for film formation of two component water-borne polyurethane systems which suggests that the reaction between the isocyanate and water is sluggish compared to the reaction between isocyanate and the hydroxyl terminated polyol, therefore enabling urethane formation to take place [4,5]. In water-borne formulations, greater excess of NCO is required to account for the competing reaction between isocyanate and water. Typically, water-borne formulations are indexed using excess NCO ranging from 1.5 to 3.5. ARL presently utilizes NCO to OH indexing of 5.0:1.0 in order to meet the stringent chemical agent resistance test requirement. However, experimental coatings with NCO to OH indexing of 3.5:1.0 are currently being studied.

It is a likely assumption that the cumulative effect of the side reactions occurring during film formation of the water dispersible coatings, results in films with less uniform or more heterogeneous cross-links compared to the solvent-based films. The likelihood of numerous reactions occurring during film formation of WR coatings has been discussed by Hegedus et al. [4,5]. DMA was utilized to investigate the mechanical properties of the different systems in an effort to further understand the structure/property relationships of these complex coatings.

3. Experimental

DMA and was performed on non-supported coating films. These films were prepared by spraying the coating onto release paper. The films were dried for varying lengths of time at ambient temperature (25±2°C) before separating them from the release paper. Coating film thickness varied between 160 and

280 μm. Data was normalized according to individual sample dimensions.

DMA of the non-supported films was performed using an Imass autovibron (automated Rheo-200 rheovibron, Toyo Instruments). The samples were evaluated between −100 and +150°C at a heating rate of 2°C/min. Data was collected at 1.1 Hz.

Formulations reported in this paper were pigmented conforming to color number 34094 (green 383) as stated in MIL-C-46168D, the US Army specification for two-component polyurethane coatings. WR formulations are followed by the specific NCO indexing. The solvent-based system is designated as 'SOL'. Tests on coated panels were conducted according to MIL-C-46168D.

4. Results and discussion

A complete evaluation of the coating properties and test methodology according to MIL-C-46168D has been previously reported [6]. WR 3.5 and 5.0 both pass all of the specification requirements with the exception that WR 3.5 does not meet the necessary requirement for chemical agent resistance (CAR). Both WR formulations exhibit vastly improved VOC compared to the conventional solvent-based system. Additionally, the WR formulations exhibit significantly improved impact resistance and low temperature flexibility. These properties, determined in accordance with MIL-C-46168D, are shown in Table 1.

Fig. 1 shows the storage modulus, E', versus temperature for the three polyurethane coatings. WR 3.5 exhibits the highest values for E' in the rubbery plateau region of the curve. E' is a measure of material stiffness and can be used to provide information regarding polymer molecular weight, degree of cure and cross-link density [7–9]. The difference between the storage modulus ($\Delta E'$) in the plateau regions before and after the glass transition is related to the degree of cross-link density. A smaller $\Delta E'$ is associated with greater cross-link density [7,8]. Measurements of $\Delta E'$ for the three polyurethane coatings indicate that WR 3.5 and 5.0 have slightly higher cross-link densities (smaller $\Delta E'$) compared to the solvent-based system. These experiments were performed on coatings allowed to dry for 10 days prior to evaluation.

Tan δ of the polyurethane coatings is shown in Fig. 2. The solvent-based coating exhibits a much larger and sharper tan δ peak compared to the WR coatings. The temperature associated with the peak magnitude of tan δ is defined as the glass transition temperature (T_g). The solvent-based system exhibits a significantly lower T_g (43°C) compared to the WR coatings (73°C) following a 10-day dry time. The sharper tan δ transition observed for the solvent-based coating, suggests more uniform cross-links compared to the WR coatings. WR 3.5 exhibits the broadest tan δ transition of the three coatings, suggesting the greatest degree of heterogeneity of cross-links. These results were also observed in the loss modulus (E'') versus temperature curves as shown in Fig. 3. WR 3.5 exhibits a very broad E'' transition that is notably high over a broad temperature range (−98 to +80°C). E'' of WR 5.0 is also broad compared to that of SOL. High values of E'' suggest greater mobility of the

Table 1
Selected properties of coated panels

Sample	VOC (≤420 g/l)	CAR (≤180 μg)[a,b]	Forward impact resistance (lb)	Low temperature flexibility[b,c]
SOL	∼420	∼20	52[d], 48[e], 28[f]	F
WR 3.5	∼180	∼510	160[d], 148[e], 148[f]	B
WR 5.0	∼180	∼98	148[d], 84[e], 100[f]	P

[a] MIL-C-46168 requirement shown in parenthesis.

[b] Data reported after 7-day dry time.

[c] P=pass, B=borderline/pass, F=fail, failure is indicated by visible cracking in the coating after bending the coated panel around a cylindrical mandrel at 0°C.

[d] Data reported after 10-day dry time.

[e] Data reported after 17-day dry time.

[f] Data reported after 24-day dry time.

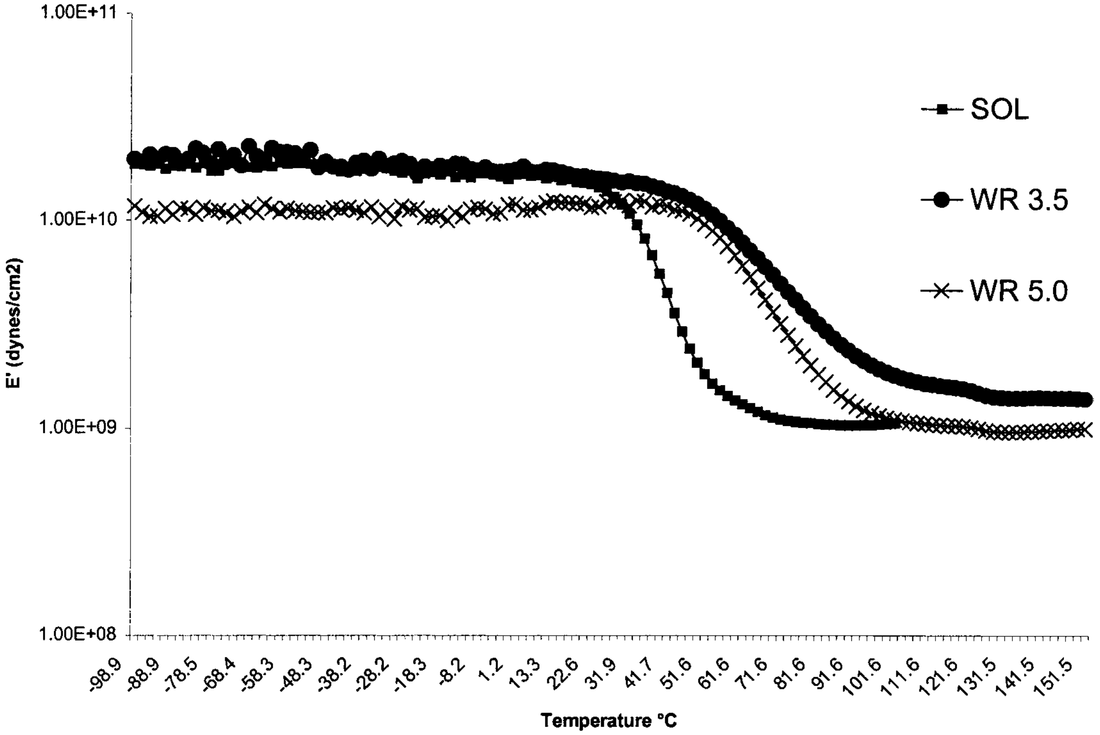


Fig. 1. E' at 1.1 Hz after 10-day dry time.

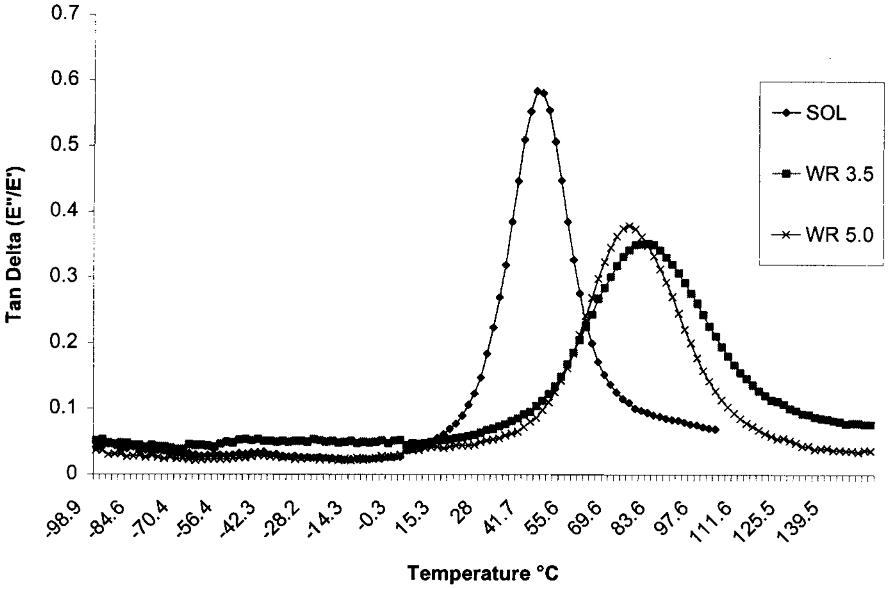


Fig. 2. Tan δ at 1.1 Hz after 10-day dry time.

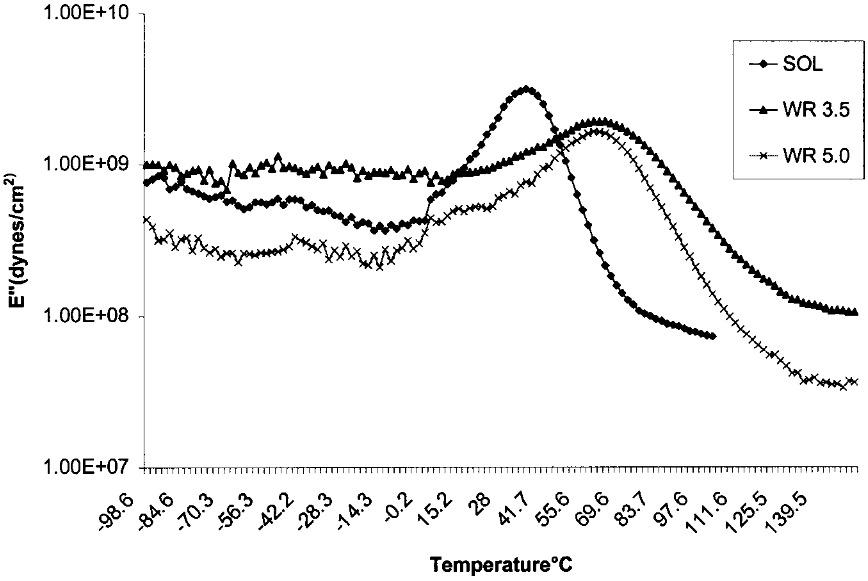


Fig. 3. E'' at 1.1 Hz after 10-day dry time.

polymer chains associated with dissipation of energy when the polymer is subjected to deformation [10]. Thus, coatings exhibiting a high and broad E'' transition have the ability to absorb energy associated with impact. Therefore, the DMA data helps to explain the superior impact resistance of WR 3.5 and 5.0 compared to the solvent-based system. Although impact resistance was measured at ambient temperature (25±2°C), the DMA data suggests that WR 3.5 in particular may also exhibit superior low temperature impact resistance. The DMA data suggests that while broad loss transitions indicate superior mechanical properties such as impact resistance, sharper loss transitions, such as those exhibited by SOL appear to be related to superior chemical agent resistance. Broad E'' and tan δ transitions suggest non-uniformity of cross-links in the WR system [7,8,10,11]. Broad loss transitions have been previously observed in WR system [10,12,13]. Thus, research by Hegedus [4,5] that indicates the potential for side reactions in addition to polyurethane formation, is further explained by the broad loss transitions observed in the present study. It is speculated that such non-uniformity during film formation may introduce voids in the polymer matrix allowing greater amount of chemical agent to penetrate and become trapped in the WR coating compared to solvent-based systems. Therefore, DMA provides some insight into the fact that differences in cross-linking as a result of film formation in the solvent-based and WR coatings result in optimization of different properties. The authors are unaware of other findings that qualitatively relate chemical agent resistance of paint to DMA loss properties.

While WR 5.0 currently provides the best balance of chemical and mechanical properties, WR 3.5 exhibits the most enhanced mechanical properties. Additionally, WR 3.5 requires less isocyanate for formation of the coating, which is an important cost consideration for full scale production. It is interesting to note that while SOL exhibits a significantly lower T_g than the WR coatings, SOL exhibits poorer low temperature (0°C) flexibility. At 25°C, all three polyurethane coatings exhibit acceptable flexibility as measured by bending the coated panel over a cylindrical mandrel (specified in ASTM D 522 Method B). The enhanced low temperature flexibility of WR 3.5 and 5.0 is believed to be the result of the broad loss transitions shown in Figs. 2 and 3.

DMA was also used to study the effect of coating dry time on mechanical properties. The dynamic mechanical properties of SOL were found to be much more sensitive to coating dry time compared to the WR coatings. After all dry times, E' in the rubbery

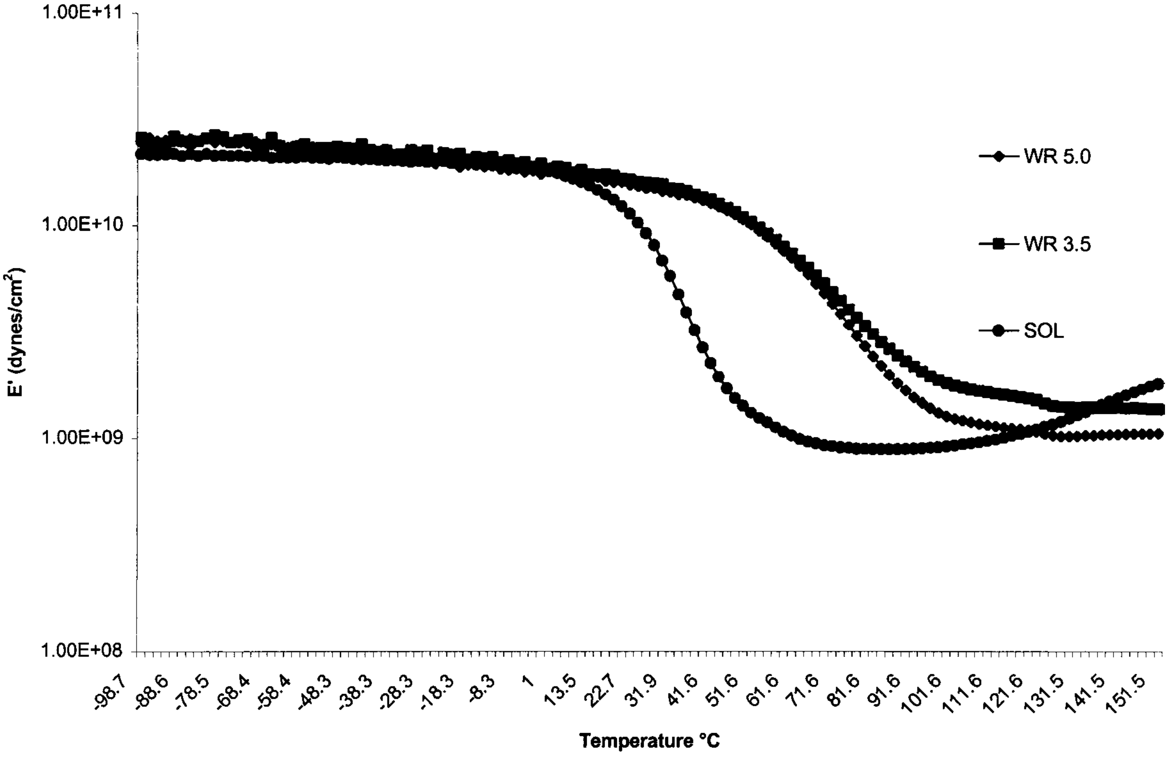


Fig. 4. E' at 1.1 Hz of SOL after dry time of 24 days.

plateau was observed to increase with increasing temperature for SOL while the WR coatings exhibited a flat rubbery plateau throughout the experiment. This was most pronounced after 17- and 24-day dry time and less pronounced after the 6-month dry time for SOL. The observation of increased E' versus temperature is shown in Fig. 4 after a 24-day dry time. This data indicated that SOL was not fully cross-linked at dry times less than or equal to 24 days at ambient temperature.

The cross-link density, determined by measuring $\Delta E'$ between plateaus, is significantly increased for SOL after 6-month dry time as shown in Fig. 5. Tan δ peak magnitude for the SOL coating was also significantly reduced when allowed to dry at ambient temperature for 6 months. The increase in E' and decrease in tan δ peak magnitude strongly suggests a notable increase in cross-link density after 6-month dry time for the SOL coating. Although WR 5.0 also exhibited increased E' after drying for 6 months, a negligible change in tan δ peak magnitude was observed. However, WR 5.0 exhibited a significant increase in T_g after the 6-month dry time. WR 3.5 was not evaluated after 6 months. DMA data for SOL and WR 5.0 coatings is shown in Table 2. The data suggests that while SOL may undergo increased cross-link density with respect to dry time, the changes in WR 5.0 are notably different. It is speculated that observed changes in DMA data for WR 5.0 after 6 months, may indicate a densification occurring in the coating. Densification in coatings as a result of physical aging has been observed by other researchers [8,14]. The DMA data indicates increased cross-link density of SOL after longer dry times that may actually result in reduced mechanical performance due to brittleness associated with cross-linking. Evidence of densification observed for WR 5.0 may lead to enhanced chemical agent resistance without further compromise of mechanical properties. Tests on coated panels after longer dry times are necessary to confirm the DMA results. Although the chemical agent resistance associated with SOL is desirable, chemical

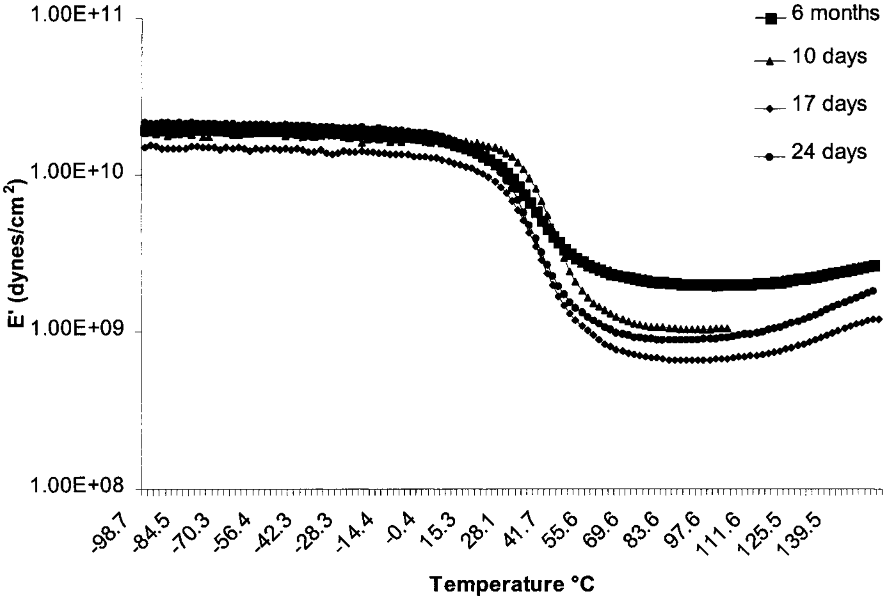


Fig. 5. Effect of dry time of rubbery plateau modulus of SOL.

Table 2
DMA data measured at 1.1 Hz of SOL and WR 5.0 with respect to coating dry time

Sample	T_g (°C)	Tan δ peak magnitude	E' (dyn/cm^2) at 100°C
SOL 10-day dry time	43	0.584	1.06×10^9
SOL 6-month dry time	37	0.336	2.00×10^9
WR 5.0 10-day dry time	73	0.379	1.13×10^9
WR 5.0 6-month dry time	91	0.384	1.96×10^9

agent resistance is obviously irrelevant if the mechanical properties of the material can not meet minimum durability requirements.

5. Conclusions

The US Army Research Laboratory, Weapons and Materials Research Directorate, has successfully developed a WR, chemical agent resistant coating which meets MIL-C-46168D specifications and exhibits a significant reduction of VOC compared to the currently used solvent-based polyurethane coating. The WR coating formulation exhibits superior mechanical properties compared to the solvent-based system. While WR 5.0 meets chemical agent resistance requirements, WR 3.5 exhibits optimal mechanical properties which are important for long term durability under broadly varying environmental conditions observed in service. DMA provided insight into the different chemistries associated with film formation of the solvent-based and water dispersible formulations, and the affect of dry time on the dynamic mechanical properties of the coatings. It was determined that the type of cross-linking required for superior chemical agent resistance is different for that required to optimize mechanical properties. WR 5.0 may exhibit improved chemical agent resistance and therefore sharper loss transitions compared to WR 3.5 because of the additional cross-linking associated with the excess isocyanate present in the WR 5.0 formulation. The more highly cross-linked film may exhibit fewer voids that can trap chemical agents. The dynamic mechanical properties of SOL was shown to be much more sensitive to dry time compared to the WR coatings which may adversely affect coated panel properties of the solvent system in service. Future work is planned to evaluate both WR and SOL coated onto test panels, to determine the mechanical properties such as impact resistance and low temperature flexibility and chemical agent resistance with respect to aging.

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