Transport and Related Properties of Paint Films. II. Dynamic Mechanical Properties and Humidity Effects

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Synopsis

A systematic four-stage investigation of eight unpigmented coating formulations, including three vinyl, two polyurethanes, and three epoxy stystems was done to provide baseline structural information upon which an improved understanding and an optimization of protective coatings can be founded. First, the results from dynamic mechanical measurements are provided and discussed for the base polymer component in each coating system. Second, the effects of humidity on the dynamic mechanical properties of these base polymers were determined at room temperature. The extent of property degradation was monitored by calculating the T_g depression with increased humidity, assuming a temperature–humidity superposition. The extent of degradation, as monitored by the T_g, was found to correlate directly with the level of hydrogen bonding in these coatings. Third, the influence of typical coating additives (a TCP plasticizer and a rosin hardener) on the properties of two of the vinyl coating systems was investigated. In the final stage, the synergistic effects of absorbed moisture and these additives on the coatings properties were investigated at room temperature. Increases in the concentration of these additives was found to magnify the degradation effect of increased humidity. This magnified degradation has been assigned to increased water absorption with increases in the concentration of either of these additives.

INTRODUCTION

The practical need to minimize lost service time by extending the effective life of coating systems used to protect transport vechicles is well documented.[1,2] To accomplish this performance extension, an improved understanding of the relations between the structure of the coating system and its corrosion resistive, adhesion, mechanical, and moisture resistive properties is required. In order to examine these structure–property relations on a fundamental basis, well-characterized samples were made from formulations which meet commercial coating specifications.[3,4] In particular, seven different polymer based coating systems were formulated: three vinyl, one polyurethane, and three epoxy based systems. Specific property information, which includes the complete formulations, molecular weight, and infrared spectra, has been previously provided for each coating system.[4]

The complex compositions of many of these coating systems greatly complicates the development of fundamental relations between the properties and structure of the coating system.[4] Furthermore, the development of structure–property relations requires that consideration be given to the various interactions that may occur between the pigments, plasticizers,

polymeric material, and other additives. Although a variety of theoretical and semiempirical models have been proposed to account for these types of interactions,[5] their use is limited, because they require specific information about each additive which is often unavailable in the literature. The need to determine this information has lead us to study the unpigmented formulations of these coating systems. The study and characterization of these simpler unpigmented coating systems should provide the fundamental information necessary to develop structure–property relations in the more complex pigmented systems.

The seven unpigmented coating systems formulated for this study and an unpigmented commercial polyurethane, which was investigated in a previous study,[6] were characterized in this work with dynamic mechanical measurements. This characterization was performed in four stages: First, the dynamic mechanical properties were determined as a function of temperature to provide fundamental baseline information on the transitions exhibited by the base polymer in each coating system. Second, the room temperature dynamic mechanical properties of these base polymers were determined as a function of humidity to elucidate the effects of absorbed moisture. In the third stage, the effects of common coating additives on the prevelant dynamic mechanical transitions were examined for two of the four vinyl systems. Finally, the synergistic effect of moisture and additives on the dynamic mechanical properties of these vinyl systems were investigated. Collectively, this four-stage analysis provides in a rational fashion the fundamental information upon which an improved understanding and optimization of the coating's performance can be founded.

EXPERIMENTAL

Sample Characteristics

A description of the eight unpigmented coating systems investigated in this study is provided in Table I. Further details and specific property information for these coating systems and their components, including infrared and chemical structure, have been provided in a previous publication.[4] In addition to these formulations, a number of special formulations were made for vinyl systems VR3 and VR4, which contained additives in their unpigmented formulations. The composition of these special formulations are also provided in Table I.

Free Films

Free films, which are particularly suitable for the determination of mechanical and vapor-permeability properties, were used for the dynamic mechanical experiments performed in this study. Most commonly, free films are prepared by either (a) the use of a surface which may be amalgamated with mercury or (b) the use of either a water-soluble or a water-sensitive substrate. The free films used in this study were prepared by spray painting a water sensitive decal paper from which the resulting film could be removed by wetting.

To determine the influence of the preparation method used on the mea-

TABLE I
Description of Unpigmented Coating Systems[4]

System	Description[a]
E epoxy	A crosslinked thermoset material formed by curing an epoxy resin mixture and a complex mixture of polyfunctional amines for 16 h at 25°C plus 15 min at 52°C
VR2	A random linear copolymer resin consisting of approximately 80.0% n-butyl acetal, 19.5% vinyl alcohol, and 0.5% vinyl acetate
VR3	A random linear copolymer comprised of 91.0% vinyl chloride 3.0% vinyl acetate, and 6.0% vinyl alcohol which has been plasticized with 9.5% tricresyl phosphate (TCP)
VR3a	System 3 copolymer only
VR3b	System 3 copolymer with 17.2% TCP
VR4	A random linear copolymer comprised of 86% vinyl chloride and 14% vinyl acetate which has been combined with 16% TCP and 42% rosin hardener (Rosin)
VR4a	System 4 copolymer only
VR4b	System 4 copolymer with 15.8% TCP
VR4c	System 4 copolymer with 27.6% TCP
VR4d	System 4 copolymer with 20.0% Rosin
VR4e	System 4 copolymer with 33.3% Rosin
VR4f	System 4 copolymer with 44.7% Rosin
A epoxy	A thermoplastic epoxy resin whose chemical structure is the same as diglycidyl ether of bispenol A with the exception that the epoxy end groups are replaced by phenols and alcohols
K epoxy	A crosslinked material formed by curing an epoxy resin mixture with an ethylenediamine which is released from a ethylenediamine and methyl isobutyl ketone complex by a reaction with ambient moisture
N PUR	A polyurethane which has been cured by reaction of a complex polyester resin with a biuret derived from hexamethylene diisocyanate
O PUR	A commercial polyurethane manufactured by Desoto Inc., Berkely CA., meeting military material specification Mil C-83286

[a] All compositions are given as wt %.

sured coating properties a comparison study was made by Yaseen and Ashton.[7] Their results indicated that mechanical properties (tensile strength and elongation) were not significantly influenced by the preparation method used. In contrast, water permeation and absorption properties were found to depend on the preparation method used. Furthermore, the preparation of a polymer film by evaporation of a solvent from a solution on a phase support results in orientation of the molecular chain segments near the solid interface.[8,9] The effect of this interfacial orientation, which is expected to be different in a free and an attached film, on the properties of coating systems is well documented.[8-10] Consequently, in view of the above observations, caution must be exercised when assigning the properties measured on free films to a film which is attached to a substrate.

Dynamic Mechanical Measurements

The dynamic mechanical properties of these free films were obtained, both as a function of temperature and humidity at a frequency of 11 Hz, using the Rheovibron DDV-IIB.[11] The results reported here are provided in terms of the traditional complex modulus, $|E^*|$, and the tangent of the phase lag angle δ, tan δ, providing a complete description of the viscoelastic char-

acter of the sample being examined. The real (elastic), E', and imaginary (loss), E'', components of the complex modulus were calculated from these quantities when needed.

To obtain the temperature dependence of these dynamic mechanical descriptors, the free film sample was mounted in an environmental chamber which has been described elsewhere.[11] The sample was then cooled with liquid nitrogen to $-140°C$ (for most samples) and held at this temperature until equilibrium had been reached. Using a heating rate of $1°C/min$, measurements were then made approximately once every $4°C$. A dry sample environment was maintained during cooling and heating by continuously purging the chamber with N_2 gas. Measuring the temperature dependence of these properties provides a mechanical spectrum from which structural and compositional information can be inferred.

Dynamic mechanical properties were also measured at room temperature as a function of the percent relative humidity using a Plexiglas humidity chamber. A 0% humidity environment within the chamber was obtained by placing a layer of desiccant on the bottom of the chamber. To obtain other humidity conditions, the desiccant was replaced by water and various saturated salt solutions which produce known relative humidity conditions.[12] Measurements were also made at ambient humidity conditions, for which the relative humidity was determined using a sling psychrometer.

Equilibrium between the coating and its humidity environment was assumed to be reached after 1 h of exposure for the vinyl and polyurethane systems and after 8 h of exposure for the epoxy systems. These times were based on the results of absorption studies presently being completed.

RESULTS AND DISCUSSION

Polymeric Base Components

The base component in these protective coating systems is a polymeric resin which is usually modified with various additives and pigments to obtain the desired coating applicability and appearance. The structural nature of this polymeric resin, which is often complex, gives rise to various viscoelastic transitions (relaxations) that play a significant role in determining the final coating properties. Consequently, a systematic analysis of these coating systems requires that the transitions exhibited by the base polymer component be characterized. The information obtained from this characterization provides the starting point for understanding and improving the performance of protective coating systems.

Vinyl Systems

The dynamic mechanical properties for the base polymer in the three vinyl systems (systems VR2, VR3a, and VR4a) are provided in Figure 1. Two transitions, which are denoted as α and β, were observed in the loss tangent spectrum obtained for each of these vinyl base polymers.

α-**Relaxation.** The large α-relaxation, which was accompanied by a logarithmic decrease in the sample's modulus, was identified as the glass tran-
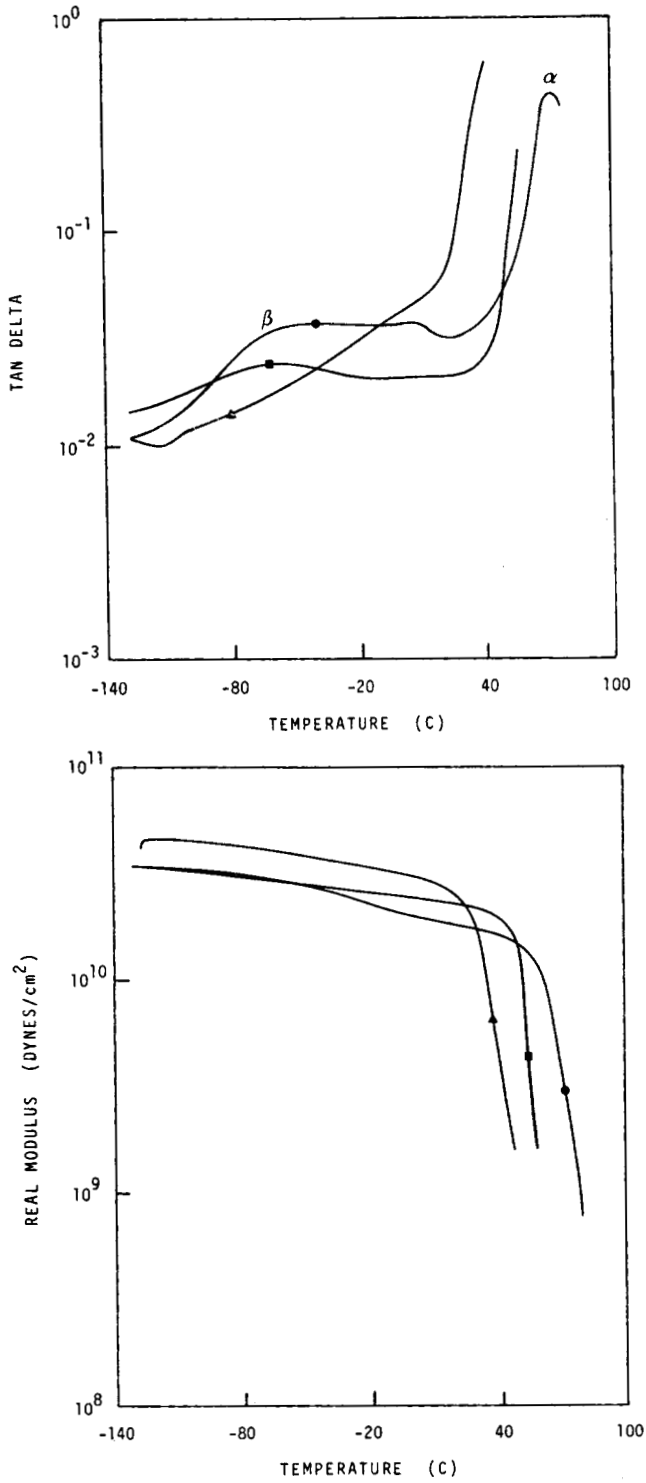
Fig. 1. Dynamic mechanical properties of coating systems VR2 (●), VR3a (■), and VR4a (▲) as a function of temperature at 11 Hz.

sition by comparisons with the results of other investigators.[5,13-15] The glass transition temperature T_g was identified by the maxima exhibited in both the loss tangent and loss modulus spectra (see Table II). When the maximum in the loss tangent peak could not be identified, due to instrument limitations, only the value obtained from the loss modulus spectrum is reported.

An important difference between each of these vinyl systems is the extent of hydrogen bonding which has been determined from infrared measurements.[4] Specifically, system VR2, which due to the character of the acetal and hydroxyl side groups is very polar, was found to have extensive hydrogen bonding. The hydrogen bonding in system VR3a was found to be incomplete with a substantial protion of the —OH and —C=O groups, available from the PVOH and PVAc components, respectively, being observed to be non-hydrogen-bonded. In contrast, only a slight amount of hydrogen bonding was detected in system VR4a. Although other factors play important roles in determing the exhibited T_g, it is of interest to note that the T_g measured for these vinyl systems were found to decrease with decreasing levels of hydrogen bonding (system VR2 > system VR3a > system VR4a).

β-**Relaxation**. The weaker and broader secondary β-relaxation arises from localized motions of either or both the main chain or side groups in the material's glassy state. The magnitude of these kinds of secondary relaxations are thought to be related to the fractional free volume in the glassy state.[14-16] Consistent with this statement is the observation that the β-relaxation is most pronounced for vinyl system VR2, which due to the long butyl side chains would be expected to have a large free volume. The β-relaxation in system VR2 has been extensively discussed by McCrum et al.,[17] who suggested that this relaxation may be due to " . . . local torsional oscillations of the main chain . . . " or " . . . related to the low temperature mechanism in PVOH. . . ."

The β relaxation observed at $-56.0°C$ and 11 Hz for system VR3a is similar to that observed for polyvinylchloride (PVC) at $-50.0°C$ and 1 Hz.[18] This similarity is attributed to the fact that this resin is 91% by weight

TABLE II
Relaxation Temperatures (°C) for the Base Polymer Components

System		Relaxations		
		α	β	γ
	$tan\ \delta_{max}$	E''_{max}	$tan\ \delta_{max}$	$tan\ \delta_{max}$
E Epoxy	95.5	77.5	−51.0	—
VR2	72.0	63.5	−50.0	—
VR3a	—	46.5	−56.0	—
VR4a	—	36.5	—	—
A Epoxy	—	44.5	−56.0	—
K Epoxy	65.0	53.	—	—
N PUR	69.5	43.5	−70.0	< −150.0
O PUR	60.5	36.0	−80.0	< −140.0

PVC and suggests that rough comparisons may be made between data obtained for this system and the vast literature available on PVC.[19] Consequently, one of the many mechanisms proposed for the β-relaxation in PVC, including a crankshaft motion of the main chain,[20] may also be the cause of the β-relaxation observed for system VR3a.

For the base polymer of system VR4 (system VR4a), the β-relaxation appears as a broad shoulder on the low temperature side of the α-relaxation. The lack of a distinct β-relaxation in this system is surprising since its composition is also similar to PVC. Although the mechanism of the β-relaxation was not explicitly identified, it has been proposed that this relaxation may be partially due to an activity of the poly(vinyl acetate) (PVAc) component which has a T_g of 32°C.[5]

Polyurethanes

The dynamic mechanical spectra obtained for the two polyurethane coating systems are provided in Figure 2. Three relaxations, labeled α, β, and γ were observed in the loss tangent spectrum obtained for these coating systems.

α-**Relaxation.** The α-relaxation was assigned to the material's glass transition.[21,22] The T_g for polyurethane block copolymer systems has been found to depend on both the hard segment content[23,24] and the molecular weight and structure of the soft segment component.[25,26] Generally, polyurethane block copolymer systems are composed of alternating low T_g (soft) segments and rigid high T_g (hard) segments. The thermodynamic incompatibility of the flexible soft (usually a polyester or polyether diol) and the hard segments (usually short immobile polyurethane segments) results in the formation of a heterophase domain structure.[27-29] Many of the unique properties of polyurethane block copolymers have been attributed to the heterophase domain morphology. In addition to this heterophase domain structure, hydrogen bonding and other secondary interactive forces are known to make important contributions to the mechanical properties of polyurethanes.[30,31] Although the existence of extensive hydrogen bonding in polyurethane systems N PUR and O PUR has been confirmed with infrared measurements,[4] the extent to which hydrogen bonding influences the viscoelastic transitions observed for these polyurethanes is unclear. The possibility of interactions between like (hard–hard) and unlike (soft–hard) segments complicates the interpretation and explicit assignment of the material's exhibited transitions to hydrogen bonding.[30] Nonetheless, by analogy to the vinyl systems, the higher T_g observed for system N PUR in comparison to system O PUR suggests that the level of hydrogen bonding may be greater in system N PUR than in system O PUR. In addition to these factors, crosslinking in system N PUR, which results from the reaction of a multifunctional isocynate biuret with a linear polyester diol, undoubtedly increases the T_g of this system.

β- **and** γ-**Relaxations.** The secondary β- and γ-relaxations observed in polyurethane systems are primarily associated with interactions and molecular motions in the soft segments. Specifically, the β-relaxation was
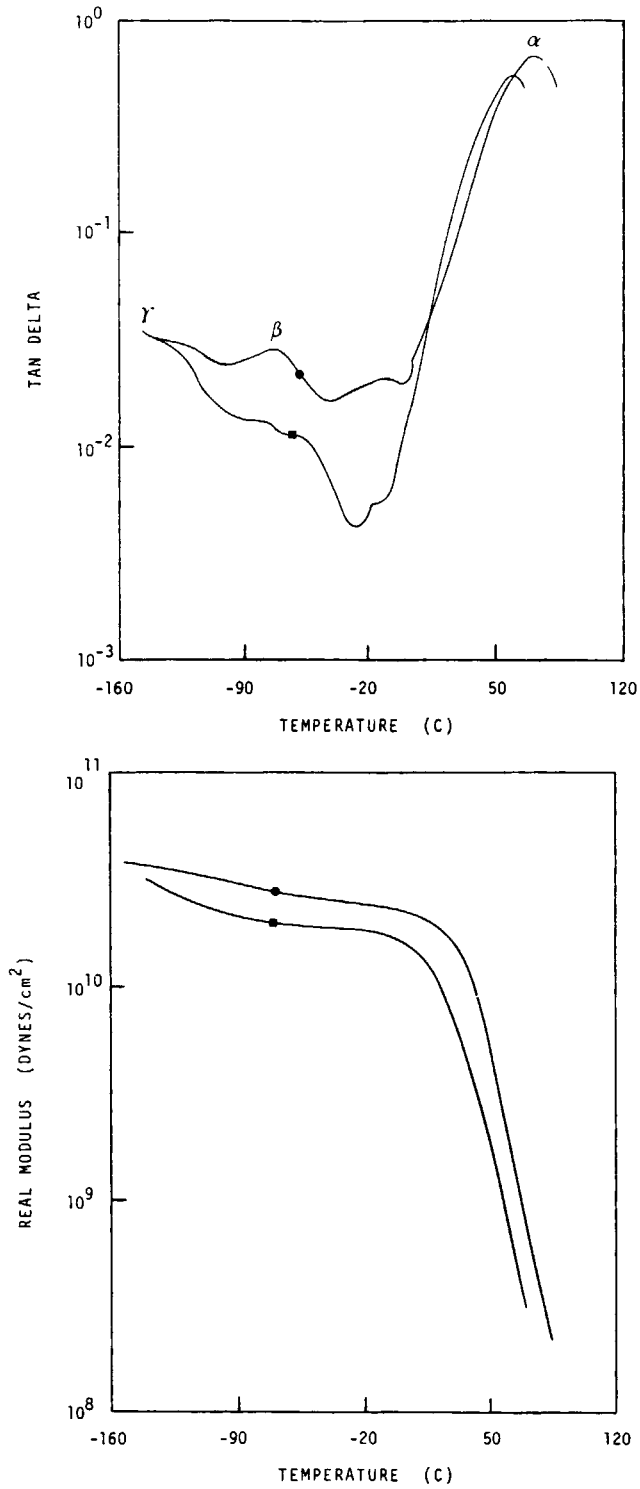
Fig. 2.   Dynamic mechanical properties of coating system N PUR (●) and O PUR (■) as a function of temperature at 11 Hz.

associated with the effects of absorbed water in the polymer,[21,22] and the γ-relaxation was assigned to local motions of the CH_2 chain sequences in the soft domain segments.[21,22] The marked differences in the secondary relaxations observed for these two polyurethane coating systems are a strong indication that the soft segment component in each of these system are substantially different.

The many complex factors which influence the transitions of these polyurethane systems and the lack of pertinent structural information for commercial system O PUR has prevented quantitative correlation of the observed transitions with the structure of the polyurethanes studied here. Thus, it will be advantageous in future studies to attempt to correlate these transitions with the hard component content by studying special formulations of system N PUR.

Epoxy Systems

The dynamic mechanical properties for the three epoxy systems are provided in Figure 3. Each of these systems displayed a large relaxation denoted by α and a second weaker and broader relaxation denoted by β

α-**Relaxation.** The large α-relaxation was identified as the glass transition temperature by comparison with the results of other investigators.[32–35] As is shown in Table II, and T_g values determined from the maximum in either the loss tangent or loss modulus spectrum for these epoxy systems are very different. This difference may be partially attributed to the fact that the three epoxy systems studied here are unique in both their chemical structure and how they were processed.[4] Specifically, A Epoxy is a linear thermoplastic while both E and K Epoxies are crosslinked network structures. Furthermore, the conditions and mechanism by which E and K Epoxies were crosslinked are very different. K Epoxy is cured at room temperature by a reaction mechanism which requires the absorbance of water to release the amine curing agent. In contrast, E Epoxy is cured for 16 h at 25°C and for 15 min at 52°C. In addition to the use of these different cure conditions, the functionallity of the reaction components is greater in E Epoxy than in K Epoxy. Both the use of a higher cure temperature and the increased functionality of E Epoxy should result in a coating with a higher level of crosslinking. Consistent with this statement is the observation that both the T_g and the rubbery modulus above the T_g are significantly greater for E Epoxy than those found for K Epoxy.[33–35] The T_g value observed for the linear thermoplastic A Epoxy is in good agreement with the results of other investigators.[32]

β-**Relaxation.** The low temperature β transition observed in E and A Epoxy has been attributed to a local crankshaft motion of the hydroxy ether portion of the macromolecular chains.[32,36] The β-relaxation observed in K Epoxy, which appears on the low temperature side of the α-relaxation, may also arise from the same molecular motion. However, due to the overlap of the α- and β-relaxations this assignment cannot be made with certainity.

The nature of the α and β transitions observed for the crosslinked E and K Epoxy may be elucidated further by testing formulations in which the amine content is varied. The successful application of this approach to other
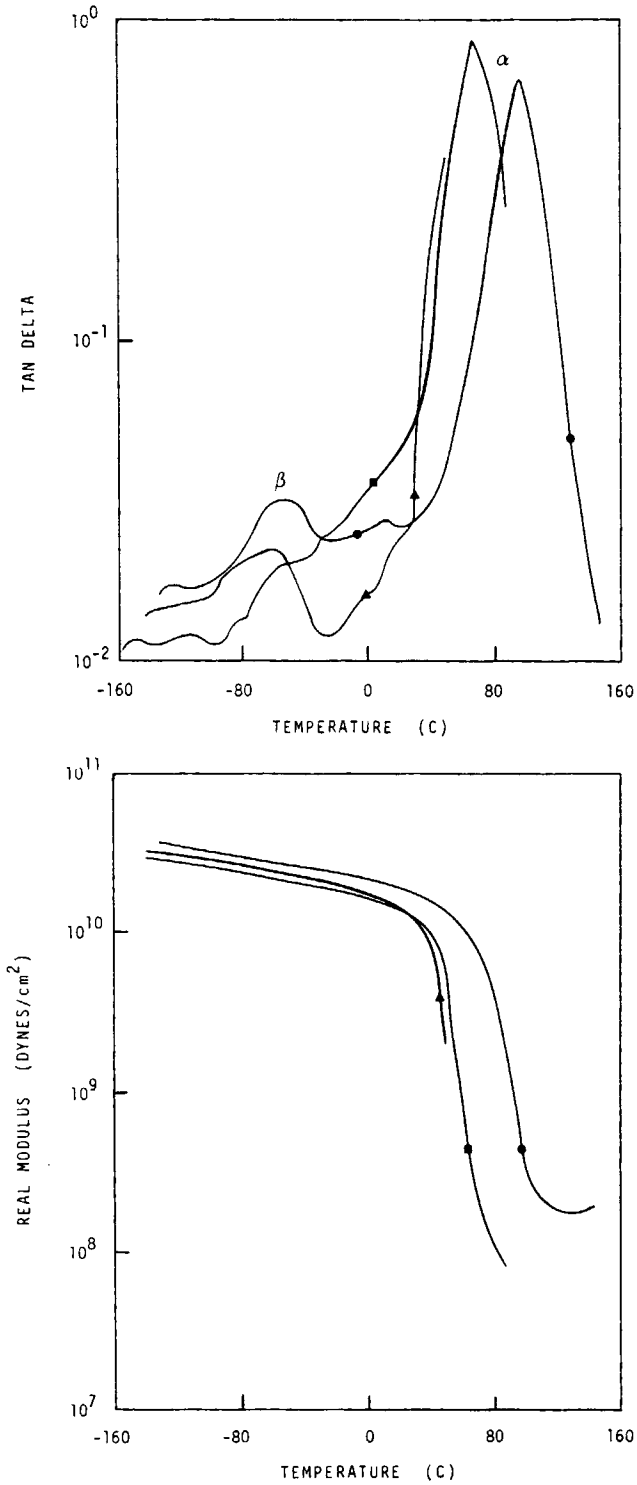
Fig. 3.   Dynamic mechanical properties of the E Epoxy (●), A Epoxy (▲), and K Epoxy (■) coatings as a function of temperature at 11 Hz.

epoxy systems[37] provides a guideline for its future application to these epoxy protective coating systems.

Summary of Base Polymer Transitions

The identification of the viscoelastic transitions exhibited by the base polymer components in the eight unpigmented coating systems provides the starting point for interpretation and improvement of the protective coating performance characteristics. For example, the magnitude and temperature location of these transitions may correlate with the transport, adhesion, sorption, and mechanical properties exhibited by these coating systems. Specifically, the β-relaxation has been found to be sensitive to the absorbed water content in a number of different polymeric materials.[38-40] The low temperature relaxations have been correlated by other investigators to the transport properties in polymeric systems[40,41] and the absorbed water content in a variety of polymeric materials.[37-39,42] Consequently, the marked differences observed in the low temperature relaxations suggest that the transport and sorption properties of the polymeric base component of these eight unpigmented coating systems will be very different. Attempts to develop correlations with the sorption and diffusion data are in progress and should clarify this deduction.

The complex nature and variety of processing conditions used in the formulations of protective coating systems makes *a priori* determination of the baseline dynamic mechanical properties from available structural information and literature data extremely difficult. Consequently, the experimental determination of the baseline properties of the base polymer present in each coating system was necessary. In the sections that follow these baseline spectra are used to interpret the effects of absorbed moisture and other additives on the properties of these unpigmented coating systems.

Humidity Effects

The exposure to temperature and humidity variations can have a devastating effect on the properties of polymer based protective coating systems. Accordingly the effects of humidity on the dynamic mechanical properties of the base polymer component were investigated at 22°C. In the discussion that follows, these room temperature results are provided for the vinyl, polyurethane, and epoxy coating systems.

Vinyl Systems

The dependence of the dynamic mecahnical properties of the base polymer in the three vinyl systems on humidity are provided in Figure 4. As is shown, the dynamic mechanical properties for these base polymers were affected by humidity to various extents. Specifically, the real modulus of the VR2 coating system was substantially decreased while the loss tangent was increased with increasing levels of relative humidity. These results imply a strong plastcization effect of moisture for this system. In contrast, coating systems VR3a and VR4a were only slightly plasticized as is demonstrated by the small changes in their real modulus and loss tangent properties with relative humidity.
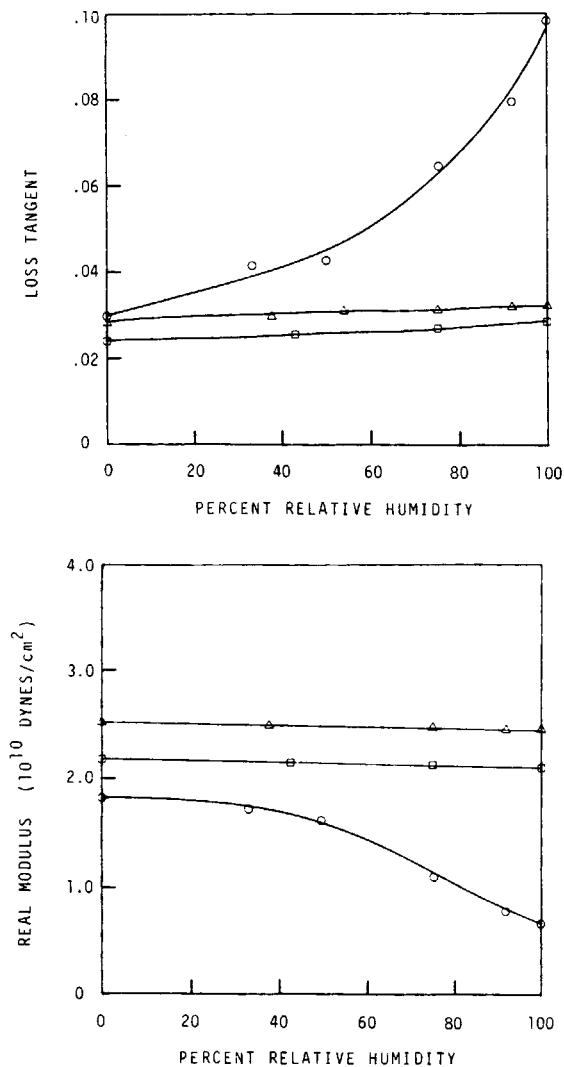
Fig. 4. Dynamic mechanical properties of coating systems VR2 (○), VR3a (□), and VR4a (△) as a function of relative humidity at 11 Hz and 22°C.

Polyurethanes

The effects of humidity on the dynamic mechanical properties for both polyurethane coating systems are provided in Figure 5. Both the real modulus and loss tangent measured for these coating systems exhibited a strong dependence on humidity. Displaying a typical plasticization effect, the real modulus was substantially decreased while the loss tangent dramatically increased with increasing relative humidity levels.

Epoxy Systems

The effect of humidity on the dynamic mechanical properties of the three epoxy coating systems were also measured. Both the modulus and loss tangent were slightly affected by changes in the relative humidity condi-
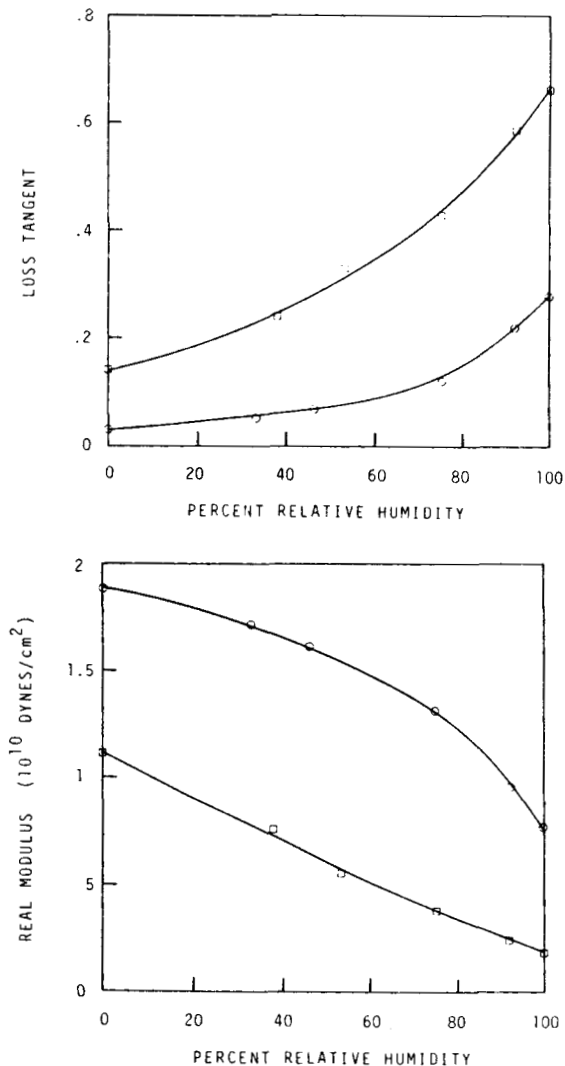
Fig. 5. Dynamic mechanical properties of coating systems N PUR (○) and O PUR (□) as a function of relative humidity at 11 Hz and 22°C.

tions for the E and K Epoxy systems, indicating a moderate plasticization effect by absorbed moisture. In contrast, these properties were significantly affected by changes in relative humidity for the A Epoxy system.

Summary of Plasticization Effect

It is apparent from the results discussed above that moisture plasticizes all of the base polymers examined to different extents, depending on their structure. The magnitude of the plasticization effect due to absorbed moisture can be monitored by measuring the corresponding decrease in the polymer's T_g.[38-40,43,44] Most of the methods used for the determination of the T_g of the polymer, however, involve taking the sample through a temperature cycle during which the sample may be both heated and cooled. The water content, which is identified at room temperature conditions prior to

the T_g measurement, is assumed to remain unchanged during this temperature cycle. Thus, water loss from the sample during measurement, which can ocurr if the polymer is tested under nonequilibrium conditions, may result in incorrect correlations of the T_g's changes with water content.

To obtain an estimate of the T_g depression with humidity, from the room temperature dynamic mechanical measurements provided for these coating systems, a temperature–humidity superposition of the properties was assumed. The use of this superposition was based on the successful application of a time–humidity superposition by other investigators.[45-48] Their results suggest that the T_g depression can be estimated by determining the temperatures at which the dry sample modulus measured at a heating rate of 1°C/min are identical to the 0% ($T_{RH=0\%}$) and 100% ($T_{RH=100\%}$) relative humidity moduli values measured at 22°C. The difference between these values ($T_{RH=100\%} - T_{RH=0\%}$) provides an estimate of the depression of the material's T_g, based on 1°C/min dynamic mechanical measurements, caused by changing from a 0% to a 100% relative humidity environment. The results from this calculation, which can be easily extended to estimate the T_g change between any two humidity conditions, are provided in Table IIIA for each base polymer examined. It should be emphasized that this procedure assumes that the effects of heating rate on the T_g for the 0% and 100% relative humidity sample are the same and that the possible need for a vertical shift[49,50] of the properties can be neglected. Nonetheless, these results were found to compare well with literature results[39,40,43,44] when put on a T_g shift per percent absorbed water basis using sorption data presently being obtained.

As is shown in Table IIIA, the largest T_g depressions were observed for systems with extensive hydrogen bonding (systems VR2, N PUR, and O PUR), while the lowest T_g depressions were measured for the hydrophobic vinyl systems which exhibit low levels of hydrogen bonding (systems VR3 and VR4). In comparison, the T_g depression for the epoxy systems (i.e., E, A, and K Epoxy), which have a high level of hydrogen bonding,[4] were intermediate to the values obtained for these systems with the highest T_g depression being observed for A Epoxy, the linear epoxy system. The lower T_g depressions measured for the amine-cured epoxy systems (i.e., E and K Epoxy) were attributed to their crosslinked structure which counteracts the degradation effects of absorbed moisture.

A second measure of the plasticization effect due to the absorbed water was obtained by calculating the relative modulus, E'_{rel} (%RH), which was defined as:

$$E'_{rel} (\%RH) = E'_{RH}/E'_{RH=0\%} \qquad (1)$$

where $E'_{RH=0\%}$ is the modulus value measured at 0% relative humidity and E'_{RH} is the modulus at the humidity condition of interest. In Table IIIB the room temperature relative modulus at 100% relative humidity is given for the eight base polymers. Other than the trend reversal observed for systems VR2 and O PUR, these results are in excellent agreement with the T_g depression trends.

TABLE IIIA
Glass Transition Depression with Humidity for the Base Polymer Components at 22°C

System	$T_{RH=100\%}$	$T_{RH=0\%}$	$T_{RH=100\%} - T_{RH=0\%}$
E Epoxy	28.0	14.0	14.0
VR2	63.0	15.0	48.0
VR3a	27.0	21.0	6.0
VR4a	22.0	19.5	2.5
A Epoxy	35.5	16.5	19.0
K Epoxy	25.0	16.0	9.0
N PUR	46.0	22.0	24.0
O PUR	54.5	19.0	35.5

TABLE IIIB
Relative Modulus at 100% Relative Humidity Conditions for the
Base Polymer Components at 22°C

System	E_{rel} (RH = 100%)
E Epoxy	0.88
VR2	0.39
VR3a	0.97
VR4a	0.97
A Epoxy	0.74
K Epoxy	0.91
N PUR	0.41
O PUR	0.17

The above observations agree well with the results of Takayanagi,[51] who studied the effect of moisture on poly(vinyl alcohol) and concluded that the plasticization effect in this system was caused by the breakage of intermolecular hydrogen bonds by the absorbed water. The lessening of these intermolecular interactions results in increased chain mobility as indicated by the depression of the materials T_g and the observed increase in the loss tangent.

Additive Effects

Vinyl systems VR3 and VR4 both contain a polar liquid plasticizer tricreysl phosphate (TCP) in their unpigmented formulations.[4] The incorporation of plasticizers to both improve flow properties and decrease the polymer's brittleness is a common commercial practice with polyvinyl chloride type polymers.[19] In addition to this plasticizer, coating system VR4 also contains a rosin hardener which is largely abietic acid with other related compounds.[4] The effects of these additives on the dynamic mechanical properties of vinyl system VR3 and VR4 are detailed in the following discussion.

To investigate the influence of the TCP plasticizer on the dynamic mechanical properties of coating system VR3, measurements were made on

the three formulations described in Table I. Increasing the TCP plasticizer content shifted the material's T_g to lower temperatures. The depression of the T_g by the addition of the TCP plasticizer can be described with the following relation[14]:

$$T_g = T_{gu} - kW''_1 \qquad (2)$$

where W_1 is the weight fraction of the plasticizer, T_{gu} is the glass transition of the nonplasticized polymer, and K is a coefficient which depends on both the polymer and the plasticizer. As is shown in Figure 6, the coating's T_g, which was identified by the maximum in the loss modulus spectrum, was found to decrease linearly with the weight fraction TCP plasticizer as predicted by eq. (2).

The secondary β-relaxation observed in the loss tangent spectrum of system VR3a was completely damped out by the addition of the TCP plasticizer. This observation is consistent with the results of Pezzin,[18] who reported complete elimination of the β-relaxation peak with the addition of 12 parts diethylhexyl phthalate plasticizer (DOP) per hundred parts polyvinyl chloride. Pezzin attributed the decrease in the β-relaxation to interactions (such as polar attractions) between the plasticizer molecules and the polyvinyl chloride chains which hinder the motions that cause the β-relaxation. Since the TCP plasticizer is very polar, like the DOP plasticizer studied by Pezzin, and the copolymer in system VR3 is 91% PVC by weight, it seems reasonable to conclude that this explanation also applies to the observations described above.

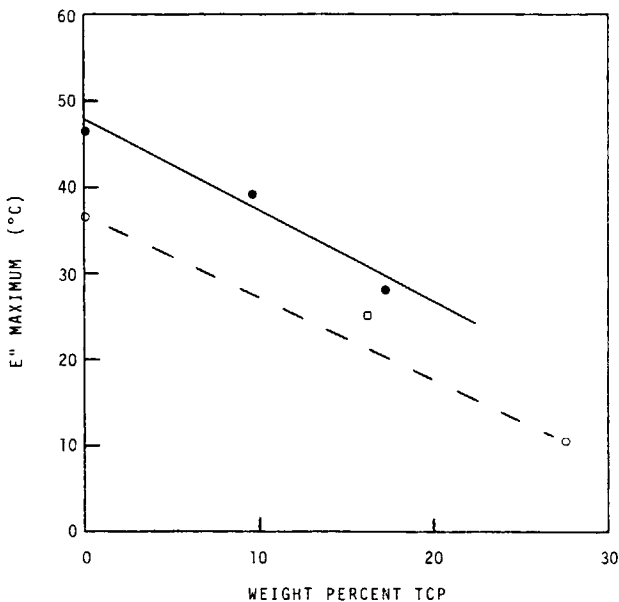The effect of TCP content on the dynamic mechanical properties of coating

Fig. 6. The glass transition temperature as determined from the maximum in the loss modulus spectrum for systems VR3, VR3a, and VR3b ($\bullet$), systems VR4a and VR4c ($\bigcirc$), and system VR4 ($\square$) as a function of wt % TCP plasticizer.

system VR4 were investigated by examing systems VR4a and VR4c. The T_g for system VR4, which was identified by the maximum in the loss modulus spectrum, was decreased with increased TCP content in a manner which paralleled the effect observed in system VR3.

The effect of the rosin hardener on the properties of system VR4 were investigated using special formulations for system VR4 (systems VR4d, VR4e, and VR4f) which have different levels of rosin concentration (see Table I). As is illustrated by the results provided for system VR4f in Figure 7, two relaxations were observed in the dynamic mechanical spectra of the special formulations of coating system VR4. The α-relaxation, as can be seen by comparing the results of systems VR4a and VR4f, was essentially unchanged by the addition of the rosin hardener. In contrast, the β-relaxation was both increased in magnitude and shifted to lower temperatures as the rosin hardener content was increased. From these observations it was concluded that the β-relaxation was due to an activity associated with the rosin hardener additive.

The dynamic mechanical properties obtained for the normal formulation of vinyl system VR4, which contains both the TCP plasticizer and the rosin hardener (see Table I), are also provided in Figure 7. As is shown, the α- and β-relaxations observed in the loss tangent spectrum obtained for this coating, were both shifted to lower temperatures and increased in magnitude as a result of the combined effects of the TCP plasticizer and the rosin hardener. Although the combined effects of these additives have not been decoupled, it is of interest to note that the T_g determined for system VR4, which contains 16% TCP, 42% rosin hardener, and 42% base polymer by weight, is approximately the same as that which should be observed in a system which contains 16% TCP and 84% base polymer by weight (see Fig. 6).

Synergistic Humidity and Additive Effects

In addition to the TCP and rosin additives in the unpigmented formulations of coating systems VR3 and VR4, depending on both the environmental conditions and the composition of the coating system, varying amounts of water are absorbed by these vinyl systems. To investigate the influence of this absorbed water on the dynamic mechanical properties of these vinyl coating systems, measurements were made as a function of composition and humidity at 22°C.

The results obtained for both systems VR4a, VR4b, and VR4c, and the three formulations of system VR3 were similar. Increases in either the TCP content or the relative humidity resulted in increasing the loss tangent and decreasing the real modulus measured for these formulations of system VR4. The results obtained for systems VR4a, VR4b, and VR4c and systems VR3a and VR3c are compared in Figure 8 on a relative modulus basis. These results clearly show that the extent to which the modulus properties were decreased with increased relative humidity was magnified by increases in the TCP content. This magnification of the modulus property degradation was partially attributed to the increased water absorption (on a wt % basis)
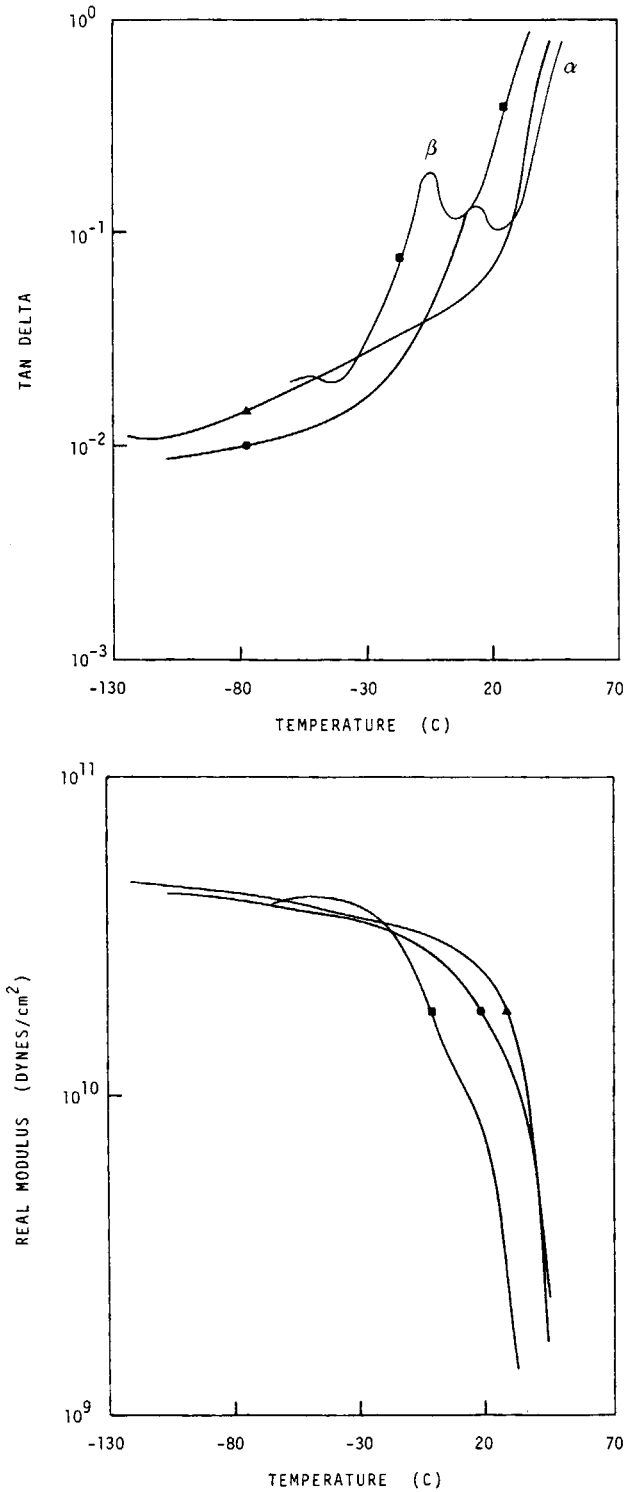
Fig. 7.   Dynamic mechanical properties of coating systems VR4 (■), VR4a (▲), and VR4f (●) as a function of temperature at 11 Hz.
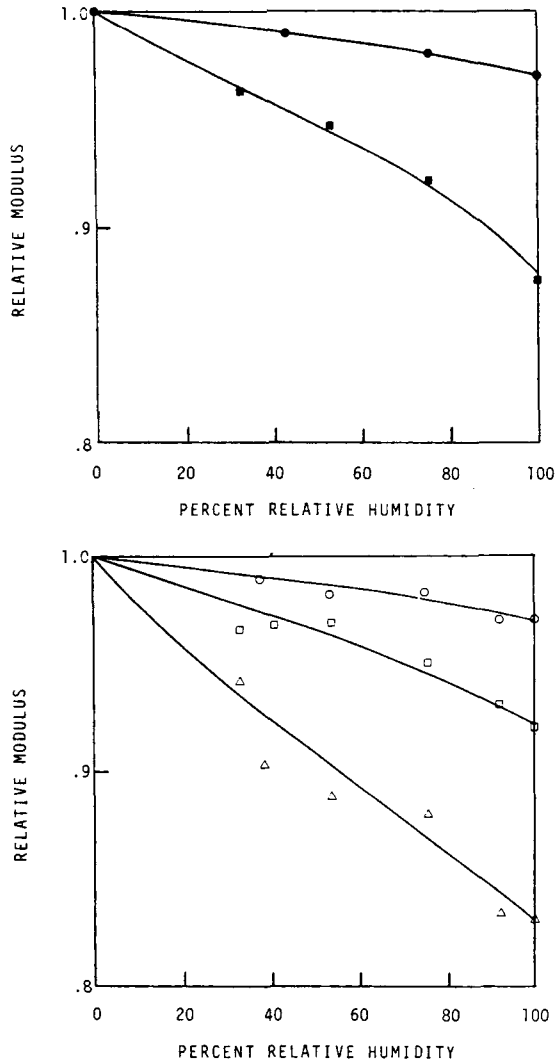
Fig. 8. Relative modulus of coating systems VR3 (■) and VR3a (●) and coating systems VR4a (○), VR4b (□), and VR4c (△) as a function of relative humidity at 11 Hz and 22°C.

with increased TCP content. This increased moisture absorption, which has been observed in initial sorption studies, was attributed to the polar nature of the TCP plasticizer.

The effect of relative humidity and rosin content on the dynamic mechanical properties of system VR4 was determined by making measurements for systems VR4d, VR4e, and VR4f. The magnitude of the loss tangent at 22°C increased with increased rosin content at all humidity conditions. In contrast, the trend of the loss tangent with humidity was very sensitive to the rosin content. At low rosin concentrations the loss tangent increased as the relative humidity was increased, while at high concentrations the opposite behavior was observed. Both of these observation are consistent

with the increased magnitude of the β-relaxation and its shift to lower temperatures with increased rosin content. Specifically, the increase of the loss tangent with relative humidity at low rosin content results because the β-relaxation maximum occurs above the 22°C test temperature. In comparison, the decrease of the loss tangent with relative humidity at high rosin content results because as the rosin content is increased the β-relaxation is shifted below 22°C. In contrast to the loss tangent results, both increased rosin content and increased relative humidity resulted in decreased modulus values for these samples. Replotting these modulus values on a relative basis in Figure 9 clearly shows that the degradation effect of humidity is magnified with increased rosin content. Initial sorption measurements indicate that this magnified degradation effect is due to increased water absorbence with increased rosin content.

To illustrate the combined effects of TCP plasticizer, rosin hardener, and absorbed water measurements were also made for system VR4. Comparison of systems VR4 and VR4f, which differ only by their TCP content, showed that the further addition of TCP plasticizer increases the loss tangent while reducing the real modulus. Comparing the relative modulus results for system VR4 and VR4f provided in Figure 9 shows that the further addition of TCP magnifies the degradation effects of humidity. The complexity of the interactions between the additives and the absorbed water has prevented quantitative interpretation of these results at this time. Further investigations to decouple the interactions of these additives are planned.

CONCLUSIONS

The dynamic mechanical properties of eight unpigmented coating systems were examined in a fundamental and systematic four stage investigation. First, the dynamic mechanical properties of the polymeric base component
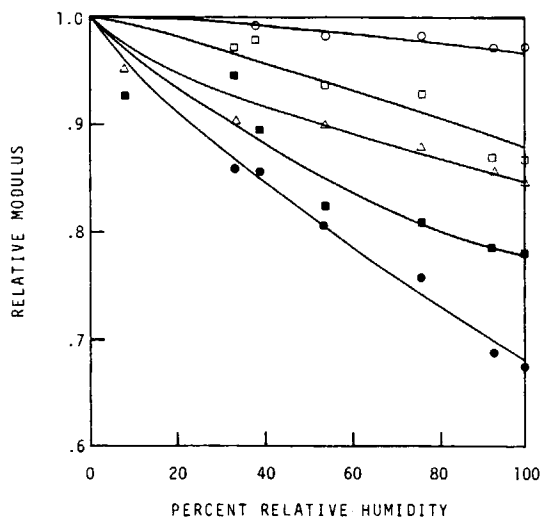
Fig. 9. Relative modulus of coating systems VR4 (●), VR4a (○), VR4d (□), VR4e (△), and VR4f (■) as a function of relative humidity at 11 Hz and 22°C. The lines are provided for clarity.

in each coating system were determined to provide a baseline for the comparison and interpretation of the effects of temperature, moisture, and additives on the coating's dynamic mechanical properties. A common feature observed for all of these systems was the relatively low T_g which, as determined from the maximum in the loss modulus spectrum, ranged between 36.0 and 77.5°C. In addition to the T_g relaxation, at least one low temperature transition was observed in the loss tangent spectrum obtained for each of these systems. The mechanisms of these secondary relaxations were identified by comparisons with literature results.

Second, the short term effects of absorbed moisture on the dynamic mechanical properties of these base polymer components were investigated at 22°C. The effect of humidity was monitored by the T_g shift, which was calculated assuming a temperature–humidity superposition, and by monitoring changes in the relative modulus. The dynamic mechanical properties of the base polymers were found to be degraded to varying extents with increasing humidity. The most drastically affected base polymers were those which exhibited extensive hydrogen bonding while the least effected were the vinyl systems which exhibited little or no hydrogen bonding. The degradation of the epoxy systems, which exhibited T_g depressions intermediate of these values, was counteracted by the crosslinking in the amine-cured systems. Sorption data presently being obtained should allow for a more quanitative interpretation of the effects of moisture on the dynamic mechanical properties of these base polymers.

Third, the compositional effects of the various additives were investigated for vinyl system VR3, which contains TCP plasticizer in its unpigmented formulation, and system VR4, which contains both TCP and a rosin hardener in its unpigmented formulation. The addition of the TCP plasticizer was found to lower the T_g of these vinyl systems. Furthermore, the addition of TCP resulted in the complete damping of the low temperature β-relaxation observed in the loss tangent obtained for the base polymer component in vinyl system VR3. The effects of the rosin hardener on the properties of system VR4 were investigated by studying samples with different rosin concentrations. From the investigation of these samples the β-relaxation observed in the loss tangent spectrum for system VR4 was attributed to interactions between the rosin hardener and the polymer base component. Also, in contrast to the effect of TCP, the T_g of system VR4 was found to be unaffected by the addition of rosin hardener.

In the final stage, the interactions between the various additives and the absorbed moisture were investigated at room temperature. The addition of either the TCP plasticizer or the rosin hardener was found to magnify the degradation effect of increased relative humidity. This magnification of the effect of humidity was attributed to an increase in the wt % absorbed water caused by the addition of these additives.

The systematic and fundamental approach taken in this study has provided baseline information which can be used to interpret and correlate the structural properties of the complete pigmented formulations with their adhesion and transport properties. Continuation of this systematic approach incorporating each additive in a systematic manner was demonstrated to be essential if an understanding of the structural nature of these complete

coating systems is to be achieved. Furthermore, combining the results presented here with the diffusion, adhesion, and sorption data presently being obtained should allow for correlation of the dynamic mechanical properties of these coating systems with these other performance properties.

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