“It’s all in the chemistry...”
-Shelby F. Thames

The Waterborne Symposium

Proceedings of the Forty-First Annual International Waterborne, High-Solids, and Powder Coatings Symposium

Robson F. Storey
James W. Rawlins

New Orleans, LA
February 24 - 28, 2014

School of Polymers and High Performance Materials
The University of Southern Mississippi

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Proceedings of the Forty-First Annual International Waterborne, High-Solids, and Powder Coatings Symposium

Chairmen

Robson F. Storey
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A Symposium Sponsored by
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The Waterborne Symposium

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PREFACE

In this, the 41st year of The Waterborne Symposium, we have organized a collection of papers into six topical sessions related to various aspects of surface coatings: opening, general, waterborne, additives, pigments, and powder coatings. In the opening session, our plenary speaker, James Rawlins of The University of Southern Mississippi, will present a talk entitled "The World of Surface Coatings is Centered Around the Glass Transition Temperature, But Which One?" Featured guest speakers are Joe Lichtenhan of Hybrid Plastics whose talk is entitled "POSS® Surfaces: How They Impact Biological and Industrial Polymers and Coatings" and Steve & Beth McDaniel who will jointly present a lecture from their monthly contribution "iPaint, uPaint, We All Paint!" in Coatings World. The third annual Sidney Lauren Memorial Lecture will be presented by Christopher Howard of Evonik Corporation, speaking on "From Evolution to Innovation".

In addition to the main technical program, the Waterborne Symposium also includes a three day Technology Showcase. The Showcase, now in its 17th year, is a multiday coatings program focused on emerging technologies, new materials, innovative services, and state-of-the-art equipment in an exhibit type format. The Showcase opens during symposium registration on Tuesday afternoon and continues with the Tuesday Evening Opening Reception. The Showcase remains open through the evening on Thursday. New this year, our Showcase has added an exhibitors product showcase to be held during show hours.

USM students will present their research in the form of twenty-two student posters. The posters will be open for viewing and visiting with the students on Thursday afternoon.

This year the Symposium will present several awards: the ***Shelby F. Thames Best Paper Award***, the ***Siltech Innovation Award***, the ***SSCT Best Student Paper Award***, and the ***Eastman Student Poster Awards***.

Premiering this year, we are excited to add a new format with our Automotive Coatings panel discussion session. Coordinated by Dale Pritchett of Coatings World Magazine, this panel will feature the following experts:

- Mark Nichols, Technical Leader, Paint Research | Materials Research Department, Ford Research and Advanced Engineering, Ford Motor Company
- Bill Eibon, Director, Global Color Technology, PPG Industries
- Scott Kubish, Manager, Toyota Motor Engineering & Manufacturing North America
- Russell J. Schwartz, Chief Technology Officer, Sun Chemical Corporation

Of the 41 papers presented at the 2014 symposium, 30 are published in this volume. It is our hope that this collection will prove interesting and stimulating to the many polymer and coatings scientists working in our field. We sincerely thank the many authors, speakers, their employers, and the various sponsors who have contributed to the success of this symposium.

All proceeds from The Waterborne Symposium are used to fund our students and Polymer Science program at USM. Continuing support and participation at our symposium helps ensure the FUTURE of the polymer science industry.

Robson F. Storey & James W. Rawlins
Hattiesburg, Mississippi
February 2014

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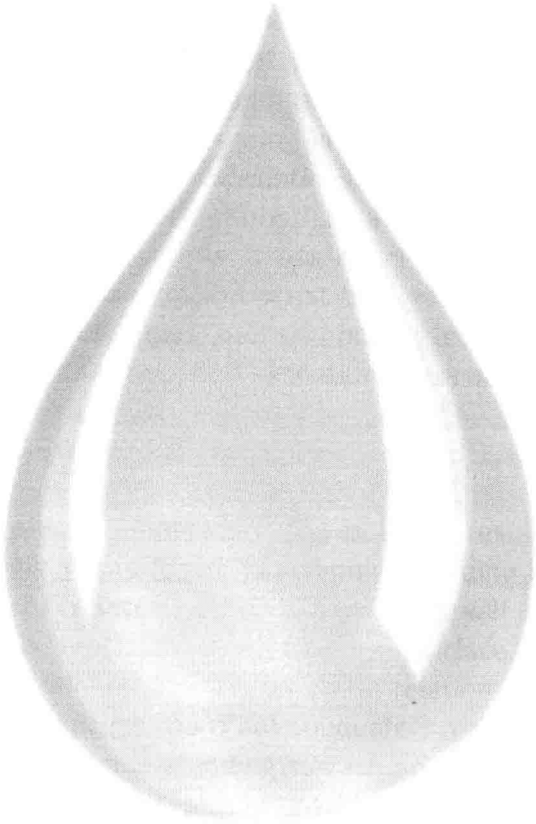

THE WORLD OF SURFACE COATINGS IS CENTERED AROUND THE GLASS TRANSITION TEMPERATURE, BUT WHICH ONE?

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Abstract

Polymeric materials are employed in a wide variety of applications, and whether the desired performance is a mechanical response, specific permeability, chemical reactivity, or general response to any given stimuli, the target properties are strongly affected by the molecular dynamics of all blended materials and reactants. The molecular dynamics of amorphous materials are controlled by the resulting glass transition temperature (T_g). This article reviews the importance of T_g in polymeric coatings, and emphasizes the shifting nature of a material's T_g throughout the service lifetime. In attempting to simplify a complex combination of material dynamics, a polymer's T_g has often been utilized as a single value parameter throughout history. While correlations exist between the T_g and many important material properties, a single T_g value does not communicate the multifaceted material dynamics involved in formulation, application, film formation, cure, or *in-service* use.

Introduction

Each coating's glass transition temperature (T_g) is a net result of the effects of its constituents, and the compositions and ratios of its polymeric building blocks. In many cases, T_gs correlate with performance parameters. In this paper, we will limit our discussion to amorphous polymers and matrix materials used to form surface coatings (intentionally excluding semi-crystalline and crystalline polymers, as these relationships become even more complex). The T_g is a very intricate concept and is not adequately represented by a single value, albeit, an excellent starting point for understanding surface coating dynamics. A number of methods are available to measure T_g that typically provide a range of values with subtle to significant differences. Furthermore, the T_g range, e.g., the difference between dry and wet T_g for the same coating, clouds our understanding of the T_g values' correlation with material properties. It is imperative to understand when, how, and why coatings perform as they do from varying application methods, differing cure profiles, and a wide array of environmental conditions. Surprisingly, the general literature considers T_g to be a single number without considering the importance of the T_g range and differences that vary with changes in formulation, application, cure and crosslinking, and environmental parameters. In this paper, the term *in-service* T_g is defined as the T_g measured under the specific conditions at that moment in time.

Figure 1 simplistically presents the range of T_gs from one prepolymer, a single crosslinker, and a blend of two solvents in combination with three levels of water during the service life. The graphs show the dramatic differences between the low and high T_g values. The bottom right graph reveals that the combined effect of residual solvent and ambient moisture result in a *in-service* T_g ranging from 55 to 107 °C with identical raw material mass balances. The T_g differences are even more dramatic when faster evaporating solvents and ambient cure profiles are used in combination, whereby the cure and solvent evaporation result in vitrification limiting chemical conversion and potentially trapping higher concentrations of solvents.

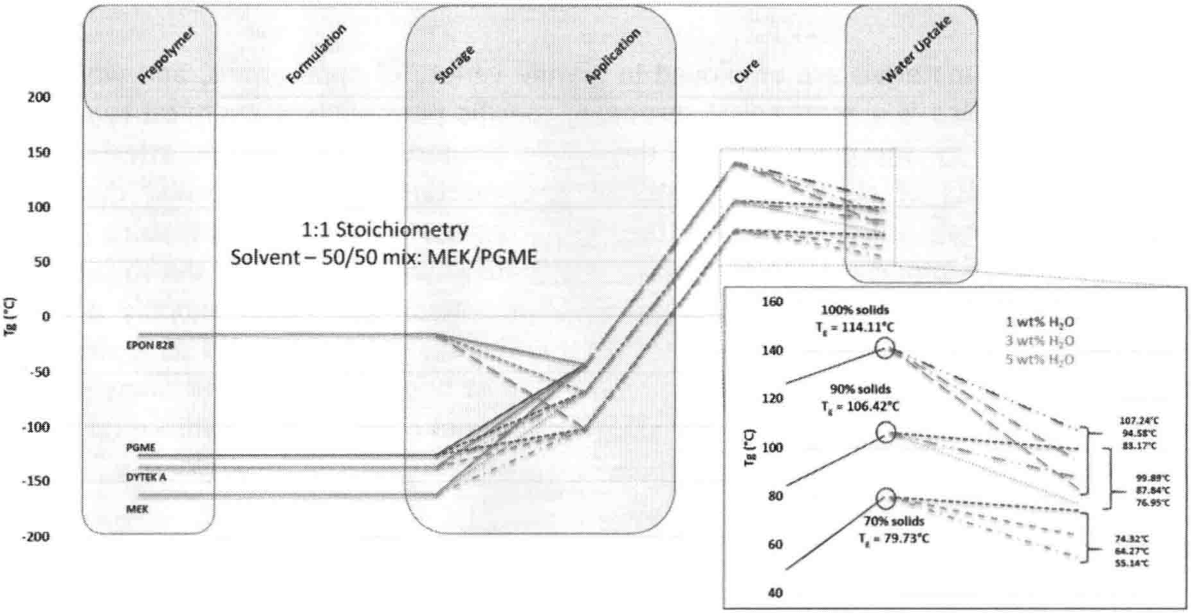

Figure 1. Overview of the life of a surface coating relative to the material's T_g during each period, raw materials, formulation and storage, application, cure, and utilization.

What Materials Exhibit a T_g?

A variety of materials and T_g ranges are shown in Table 1. In general, glassy materials are generated by cooling a wide variety of materials at sufficiently high rates to solidify or freeze them into an amorphous glassy state, often cooled from the melt state. Either the cooling rate or the materials' organizational structure (often both rate and structure) limit the combined materials' ability to crystallize, yet solidification occurs.[1] When focused on coatings, we also need to consider the polymer's interactions with pigments, additives, plasticizers, residual solvents, the substrate, and the influence of environmental conditions.

Table 1. T_g Ranges for a Variety of Classes

Material	T_g Range (°C)	Specific Example
Polymers[2]	-173 – ~ 500	Poly(2-hydroxyethyl acrylate) (syndiotactic) (377 °C)
Plasticizers (Coalescing aids)[3]	-127 – -67	Propylene glycol methyl ether (-125 °C)
Water[4]	-136	
Solvents[5-9]	-196 – -84	
Ionic solvents[10]	159 – 409	1-alkyl imidazolium (174 - 211 °C)
Proteins[11-17]	146 – 256	Lysozyme (179 °C)
Amino acids[12]	232 – 931	Methionine (362 °C)
Sugars[18-21]	65 – 286	Sucrose (76 °C)
Silicate glasses[22-26]	423 – 1100	Pyrex (565 °C)
Phosphate glasses[26-32]	542 – 763	$Li_3Fe_2P_3O_{12}$ (724 °C)
Fluoride glasses[33-36]	262 – 332	53% ZrF_4, 20% BaF_2, 4% LaF_3, 3% AlF_3, 20% NaF (262 °C)
Amorphous metals[37, 38]	151 – 403	$Mg_{80}Ni_{10}Nd_{10}$ (181 °C)

The scientific literature is replete with examples where scientists have combined evaporation rates, solvent retention, hydroplasticization, and other environmental factors to estimate, quantify, and understand the momentary and/or practical *in-service* T_g between selection and use. The practical *in-service* T_g prediction and rate of T_g change and viscosity is invaluable for prediction of material state, rate of state change, and ultimate physical states for morphology, film formation, and polymer/surface coating performance. For example, 10% trapped residual solvent results in lesser hardness, higher impact resistance, and better flexibility, but only on a temporary basis. Early laboratory results are often misleading and performance under extended service considerations are required to understand material properties as a function of time.

What is a T_g?

In simple terms, the T_g is the temperature at which amorphous, non-crystalline, polymer morphological domains shift between glassy and rubbery physical states. Polymers are classified into physical states based upon the relative difference between the T_g and the application/use temperature (T); these states are glassy ($T < T_g$), leathery ($T \approx T_g$), or rubbery ($T > T_g$).[39] Macroscopically, the physical changes that occur at the T_g are similar for all materials. Upon heating beyond the T_g, initiation of flow occurs, along with increased tack and loss of modulus or softening.[39,40] Atomic and bond nature, number, size, and density each result in differences in material responses to thermal and mechanical forces based upon the summation of intra- and inter-molecular forces.

Amorphous polymers most often respond to the addition of thermal energy by enabling increased amounts of rotational and translational motions. With sufficient thermal energy, the polymeric material begins to experience chain slipping, uncoiling, and varying degrees of morphological change which leads to successive entanglements.[41] Thermally, crossing of the T_g often implies overcoming the energy barrier of the combined secondary, tertiary, or quaternary affinities and bonds. Such morphological changes occur without affecting the covalent bonds.[42] A common T_g definition for polymers can thus be constructed as the onset of segmental motion.[43] Below the temperature where segmental motion is possible, smaller motions, e.g., side chain rotations, are observed that translate into differences for resistance to deformation and yet, absence of bulk flow.

The chemical building blocks of a polymer, i.e., backbone, side chains, and chain to chain interactions and how all the chemistry is connected plays a distinctively important role in determining which chain motions are possible at what temperature. Increased interchain interactions result in higher T_gs. There are several approaches to describing and understanding the T_g, and the directly relevant are described in brief below.

The Free Volume T_g Theory

At the atomic level, a material's volume is the average sum of three components: 1) the space atoms physically take up, 2) interstitial volume between atoms associated with bonds or atomic packing, and finally, 3) voids or free volume (Figure 2). The atomic volume (van der Waals volume) is independent of temperature. The other occupied volume (the interstitial volume) component increases slightly with temperature due to larger oscillations between atoms. The free volume is nonlinearly affected by temperature. The void/free volume tends to be constant below the T_g but increases with temperature above T_g.[44]

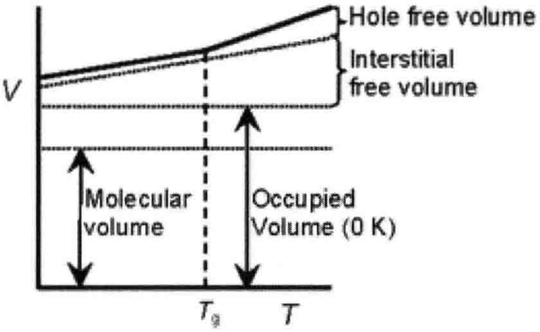

Figure 2. Specific volume representation of volume components.[45]

The free volume amount is nearly identical in each polymer at its respective T_g.[46] Most polymeric materials, regardless of composition, have similar thermal and mechanical characteristics at the T_g, e.g., almost all polymers have a viscosity of approximately 10^{21} Poise at T_g.[2] The free volume theory states that a consistent value of 2.5% free volume is required to achieve segmental motion. The T_g of a given polymer is determined to be the amount of energy required to expand the free volume beyond 2.5%. Differing environmental influences, e.g., metal or ceramic complex or affinity, result in higher levels of polymer organization as is the case with substrates or pigment surfaces and the most closely associated polymeric materials. The T_g is not adequately explained purely on the basis of thermodynamic transitions. Differences in the heating/cooling rate shift the resulting values of T_g. The T_g is dependent on the rate of temperature change which is indicative of a kinetic component to the glass transition.[47]

The Kinetic Theory of T_g

At a given temperature, each polymer possesses a specific equilibrium conformation and a characteristic amount of time is required for the side chains and backbone molecular motions.[48] Lower temperatures increase the time required for each constituent to move and relax. Each polymer passes through a temperature upon cooling where the polymer molecular motion dramatically decreases, resulting in deviations from the equilibrium state, i.e., the glassy state.[49] When a polymer is cooled below its apparent thermal T_g at any cooling rate and then held isothermally for an extended period of time, sub-T_g relaxation occurs, resulting in a conformation closer to the equilibrium liquid (Figure 3).[47]

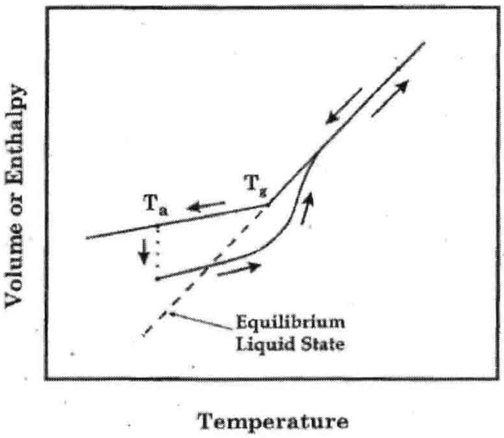

Figure 3. Cycle of aging: 1) cool below T_g, 2) densification, 3) reheat, 4) enthalpic recovery. Illustration based on conclusions made by Scherer.[50]

How is T_g Measured?

Numerous methods are used to measure T_g, a few of which are summarized in Table 2. The dominant methods employed in surface coatings are differential scanning calorimetry and dynamic mechanical analysis, and are expanded upon for our discussion.

Table 2. Techniques and Methodologies for Determining the T_g of Polymeric Materials

Technique	Vertical Abscissa	How T_g is Determined
Differential scanning calorimetry	Heat flow/C_p	Step in C_p/ heat flow
		Peak differential heat flow
Modulated DSC	Heat Flow	Mid-point reversible flow
		Peak differential reversible flow
Dynamic mechanical analysis	tan δ	Peak tan δ
	Storage modulus	Peak differential storage modulus
Thermomechanical analysis	Deformation	Change in CTE
Dielectric spectroscopy	Dissipation factor	Peak dissipation factor
Fluid confinement dilatometry	Specific volume	Change in V_{sp} slope

Differential Scanning Calorimetry (DSC)

DSC is the most common analytical technique for measuring polymer thermal transitions and is based on the differential in thermal transitions between a sample and a reference material. In particular, DSC measures any thermal transition and is primarily used to quantify the primary and secondary thermal transitions of polymers, liquid coatings, and/or the cure process, and/or finished and cured films.[51,52] Two common methods are used to determine the T_g from a DSC curve: a) differential curve peak (e.g., evaporation or cure), or b) the midpoint between extrapolated heat flow rubber and glass baselines as shown in Figure 4 (shifting specific heat values, endotherm is up for Figure 4).[51,52] The first time a sample is analyzed, the results are representative of a material's prior historical state and yet, material changes often occur during that evaluation. The first and later thermal analysis often differs for the same sample, whereby most of the thermal history is erased by heating above T_g. Prior environmental exposure can result in thermal behavior shifts as well, e.g., humidity, trapped solvents, physical aging, and annealing.[51,52] The T_g measurement is also sensitive to differing heating and cooling rates: the most common heating rate is 10 °C/min, while 5 and 20 °C /min are also used (but less frequently) in DSC analysis.[51] Slower heating rates provide narrower T_g regions, but lower signal intensities.

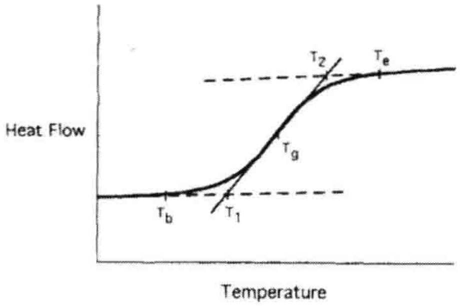

Figure 4. Methods of determining the T_g via DSC: peak derivative (left) and midpoint methods (right). Endotherm up on Y axis.

Dynamic Mechanical Analysis (DMA)

The term DMA covers many forms of mechanical analysis during thermal or frequency specific characterization. Albeit distinctly different from calorimetric measurements, the "mechanical" T_g methods of characterization are similar in concept.[51-53] The experimental parameters can be modified to obtain bending, compression, or torsional behavior; environmental chamber attachments are also available, e.g., humidity, immersion. The complex modulus is comprised of the storage modulus (real component) and the loss modulus (imaginary component); the ratio of the loss modulus to the storage modulus is also a well-defined parameter, termed tan δ.[51-53] The T_g in this type of analysis is known as the α transition (mechanical T_g) and can be defined as the tan δ maximum or the storage modulus peak derivative. Subtle or very minute material transitions are often detected and quantified by DMA, e.g. small differences in T_g or modality and ratios of T_g to distinguish between degrees of conversion, multimodal morphological domains, or it can even simultaneously detect cure and solvent evaporation.[51]

A Review of Polymers, Coatings, and Their Related T_gs

Modulus Relative to T_g

Polymeric materials are often simplistically described as glassy, leathery, or rubbery. There does not seem to be formal limits for these material types, thus for general purposes, materials exhibiting room temperature moduli of ≈ 0.5-2 GPa are considered leathery. Rubbery materials range from < 0.001-0.5 GPa, and glassy materials typically possess modulus values between 1.5-> 100 GPa. Figure 5 represents a wide range of material types to illustrate high to low Young's modulus values measured at standard temperature and pressure (STP) conditions.[2, 54, 55]

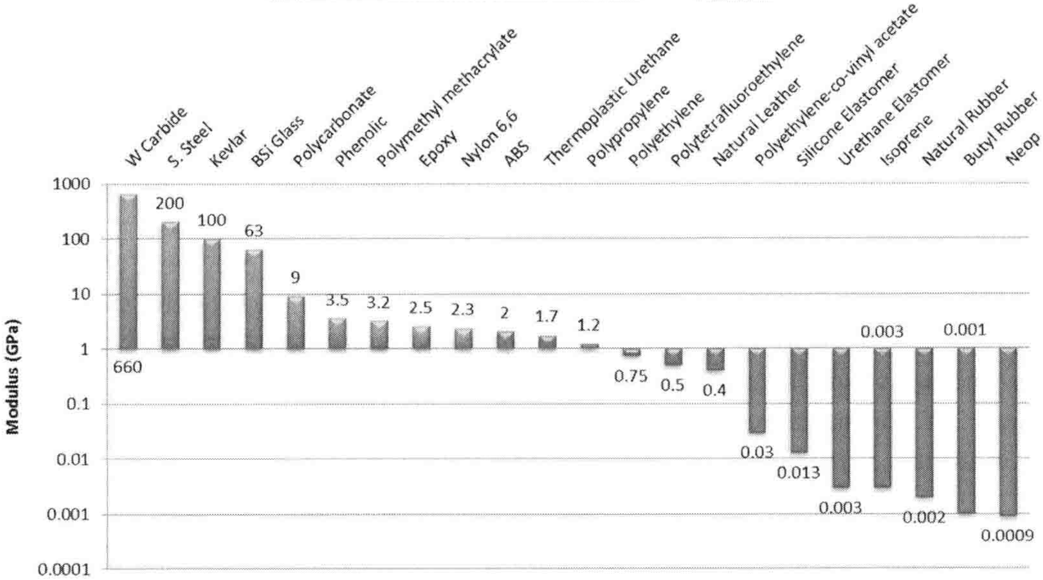

Figure 5. Young's modulus of various polymers and reference materials.[54-57]

As crystallinity influences both the T_g and modulus, it is important to differentiate between amorphous and semi-crystalline polymers. The degree of crystallinity may vary substantially between same composition samples depending upon formulation variables and thermal history.[2, 53] Figure 6 details modulus trends in purely amorphous samples of both thermosetting and thermoplastic polymers.

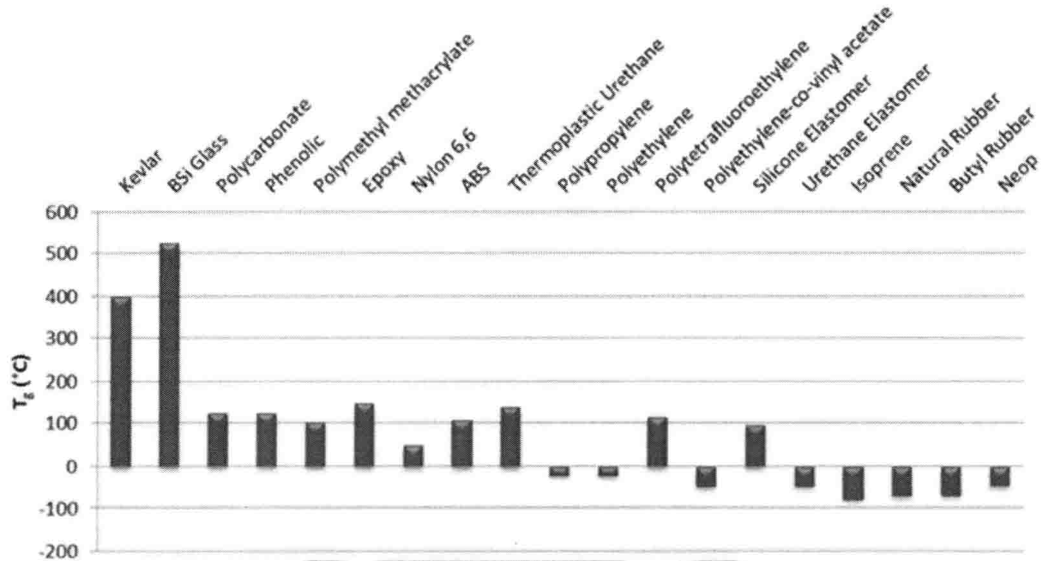

Figure 6. T_g of various polymers and reference materials described in Figure 5.[54-57]

Within a narrow set of building blocks, the typical thermoset polymer will concurrently exhibit high modulus and T_g. Each characteristic is driven by a complex set of parameters; however, in combination, these parameters shift together, e.g., restricted molecular mobility driven by higher density/quantify of crosslinks results in higher T_g. Thermoplastic polymer chains are capable of a wider range of movement in terms of flow or translational motion. Thermoplastic polymers comprised of highly rigid monomers exhibit very high T_g and moduli values but are still melt-processable. Highly rigid backbone structures, bulky side groups that restrict/hinder rotation around the primary chain, and intermolecular interactions all combine to increase T_g and modulus through molecular resistance to motion and flow.[2] As these molecular features or barriers to chain rotation and translation are reduced or eliminated, the T_g and modulus decrease. For example, linear aliphatic amorphous polymers are more likely to possess low T_gs and demonstrate rubbery modulus values.[55-57] Lightly crosslinked elastomer rubbers comprise of extremely low T_g building block polymers that are lightly crosslinked and exhibit low moduli values as chain flexibility increases and allows for less resistance to elastic deformation. A correlation exists between Young's modulus and T_g for many amorphous polymeric materials as replotted in Figures 7 and 8 below.