Construction of TTT Profiles for the Cure of Unsaturated Polyester- Felt Composites used in CIPP

[Mohammad Razmara, Hossein Saidpour]

Abstract—*This paper aims to provide a comprehensive tool for evaluating the curing process of felt reinforced polyester resin composites used in the Cured In Place Pipe (CIPP) renovation techniques. During in-situ construction and renovation of pipelines, working time and temperature are important to precisely control the CIPP process. In this study the amount of catalyst used was varied in the range of 2-4%. The viscoelastic properties of the formulations were then investigated with the aid of Dynamic Mechanical Analyser (DMA) in the penetration mode. The results gave a full analysis of the curing process by providing measurements of different parameters including working time, gelation, vitrification and glass transition temperature of the resin-felt composite system. To clarify the thermal properties of the resin system a comprehensive profile of time temperature transformation (TTT) has been constructed for the different amount of catalyst used. The main purpose of the TTT profile was to develop a decision making tool to assist the CIPP designers in selecting the most suitable resin cure state.*

Keywords—*Polyester, cure, vitrification, DMA, CIPP, TTT Working time*

I. Introduction

It is essential to achieve optimum cure for any composite materials including those used in the renovation of broken pipes. The CIPP process has been successfully employed to rehabilitate deteriorated pipelines. It uses a special polyester impregnated felt material as a liner to cover and protect the broken pipe from inside.

Therefore it is of paramount importance to optimize the curing parameters of the polyester resin. Mixing catalyst with unsaturated polyester resin begins a chemical reaction that transforms the combined liquid ingredients to a solid. The catalyst used works as a free radical initiator rather than as a catalyst in the usual sense meant by chemists. It is not a true catalyst as it is consumed in the reaction [1].

Due to multi step nature of the polyester curing, optimisation of industrial processing requires an insight as to how each step is affected by time and temperature. As it cures, the resin passes from the liquid state (open time), through a gel state or gelation, before it reaches a solid state or vitrification and glass transition stage, Figure 1 [2]. Increasing attention is being given to mapping and modelling the transformation and
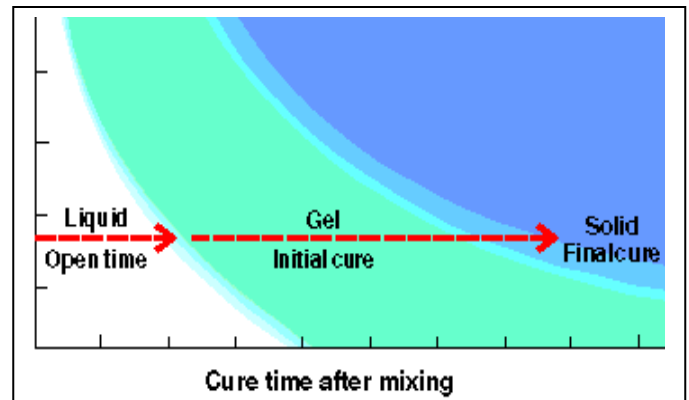

Figure 1. *Schematic process of resin cure, showing stages from a liquid state, through a gel, to a solid state (Vitrification). (Reproduced from [2])*

process characteristics of the curing process [3]. One of the mechanisms for understanding the chemical kinetics of a resin system is the experimental determination of its TTT profile, a similar concept to that used in metallurgical systems [4]. The curing kinetics and the different transformations that take place during curing of all formulations can be summarised in a TTT diagram [5].

It is possible, using reaction models and practical experimentation, to derive a TTT cure profile for a particular system, to optimise production and material properties by exploiting gelation and/or vitrification during material cure. These graphs are useful in the prediction of resin behaviour in the production environment [6]. They also provide valuable insight into the need for proper control of temperature in the curing process [7].

A TTT profile for an unmodified epoxy casting system was provided by Gillham [8]. A typical TTT profile for a thermoset resin is shown in Figure 2. The terminology used in characterising TTT profiles is listed in Table 1. Ming et al. in their research have determined the same characteristic cure parameters such as initial glass transition temperature Tg_0, gelation glass transition temperature $gelTg$, and infinite glass transition temperature Tg_∞ to draw a TTT profile [9]. The rate of resin cure is dependent on the processing temperature i.e. the higher the resin temperature before cure, the faster the curing rate. The total processing temperature of resin consists of the ambient temperature plus the exothermic heat generated during its cure. Exothermic heat is produced by the chemical reaction that ultimately cures the resin.
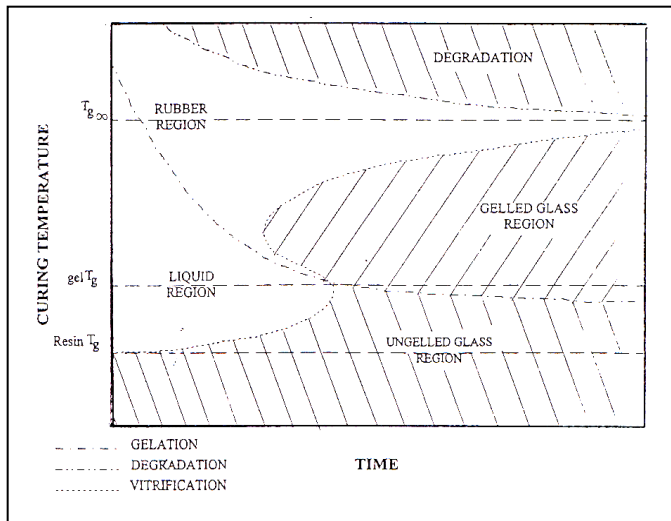
Figure 2. *A typical isothermal TTT profile for a thermoset resin*

However, if the same quantity is spread onto a thin layer, exothermic heat is dissipated, and the resin cure time is determined by the ambient temperature. The sequence of events that the reacting resin system undergoes depends on the cure temperature (T_{cure}). The thinner the layer of curing resin, the less it is affected by exothermic heat, and the slower it cures. Thus, when Tcure is above the ultimate glass transition temperature (Tg∞) of the cured material, the system will only gel. Gelation in condensation systems typically occurs between 50% and 80% conversion (degree of cure α= 0.5 – 0.8) [10].

Table 1. *Glossary of Characteristic Cure Parameters*

α	chemical conversion, degree of cure
α_{gel}	α at the gel point
T_{gel}	Gel time or time to gelation,
T_{vit}	vitrification time
T_g	glass transition temperature, a material property
T_{g0}	Resin T_g or for uncured thermoset with degree of conversion $\alpha = 0$, T_g of unreacted resin, ungelled glass region, max storage temperature
gelT_g	Tg for thermoset with degree of conversion αgel , The point at which Tgel = T_{vit}
$T_g\infty$	Tg for fully cured thermoset with conversion degree of $\alpha = 1$

If T_{cure} is below Tg∞ but above the glass transition temperature of the material at the gel point (gelTg), the system will first gel and then vitrify. Finally, when T_{cure} is below gelTg, the system will first vitrify and then undergo gelation if sufficient time is allowed. In many systems, the mobility in the vitrified state is too low to permit further reactions, in which case only vitrification occurs [11]. However, some studies

have reported results that do not agree with this typified conclusion [7].

There are different methods of measuring thermoset resin gelation, vitrification times and curing or post-curing control using DMA [12]. Enns and Gillham used the first peak in the mechanical damping curves, tan δ corresponding to points of inflection in the rigidity curves, E' to measure molecular gelation time and temperature [13]. Ramis et al., also determined Gelation point on the basis of maximum value of the loss tangent (tan δ) [14].

A second method, which is more commonly used, is the use of crossover point on the storage and loss moduli, where the tan δ = 1 [15]. However some materials do not have a crossover point [16].

A third method, which can verify the gel time, is the time that tan δ curves at various frequencies crossing each other, becoming temperature dependent [17]. Sandolo et al., in their studies indicated the gelation as the time when a crossover of tan δ curves were recorded at various frequencies [18]. This method is more preferred because it simply shows the intensity of tan δ at one reference point for all frequencies (results of this method with scanning frequency of 1 and 5 Hz can be seen in Figure 3), and consequently more consistent results can be obtained [19].

For vitrification measurement no generally accepted criterion has been defined [11, 20]. Van Assche in his dynamic rheometry observed the vitrification by the final increase in storage modulus, which occurs close to 80% conversion [21]. Also in some other studies, the vitrification has been identified as the peak value in loss modulus. Bilyen et al. used the Gillham's definition to determine the vitrification as the tan δ peak, which is usually correlated with the maximum value of the storage modulus during an isothermal testing [16].

The Arrhenius equation expresses that as temperature increases, the rate of reaction enhances exponentially as a function of temperature. This effectively means that the rate of reaction doubles for every 10 ^{o}C rise in temperature [7]. The aim of this study is to describe a tool to assist the engineer in achieving optimum thermo-mechanical properties for the liner materials used in the "cured-in-place pipe" technology.

II. Experimental

A. *Material*

The polyester used was Gadress 4000 and the felt material used to reinforce the polyester was Gadliner. This is a non-woven low stiffness felt tube, coated with a plastic PVC film and the polyester resin used was high performance isophthalic unsaturated polyester resin, both resin and the felt were supplied by Gadmon Industries. Dibenzoyl peroxide was used as a catalyst, supplied by Reichhold UK Ltd. The aim of using
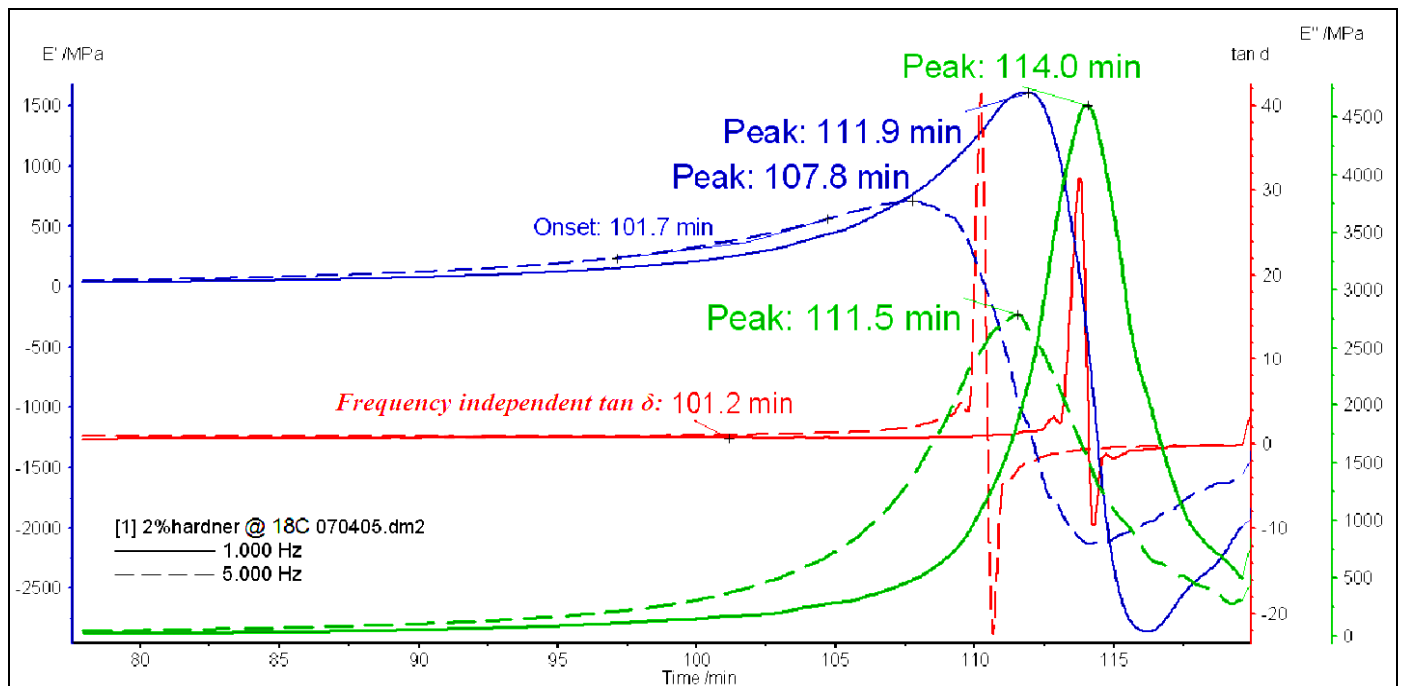
Figure 3. *An isothermal curing of UPE/F with 2% catalyst at 20°C*

impregnated Gadliner sample was to mimic the real performance of the material for CIPP application under the stipulated environment.

Mohammad Razmara
University of East London
UK

Hossein Saidpour
Birmingham City University
UK

B. *Sample preparation*

The cylindrical felt samples of 6 mm diameter and 3 mm in length were cut, impregnated by the resin and then placed onto the pan of DMA 242C (Netzsch GmbH) in penetration mode. The different amount of catalyst used in the formulation included 2% w/w, 3% w/w and 4 % w/w (by weight).

During DMA testing each resin formulation was subjected to three different isothermal temperatures including 10°C, 20°C and 30°C and frequency scanning of 1 and 5 Hz.

III. **Results and discussion**

The results of DMA test are shown in Figure 4, which indicate an isothermal curing control of composite with 2 % w/w catalyst at 20 ^{o}C. After 101.2 min on tan δ curve, frequencies became temperature dependent (the method used by Vlassopoulos). This point was correlated with the onset of T_{gel} (101.7 min) on E´ curve.

As it can be observed by increasing the frequency from 1 to 5 Hz, T_{gel} was decreased by about 3.7%. Thus there was 2.2% reduction in T_{vit} on E" peak. Also according to the Menard method, the crossover point of the storage and loss moduli can be used as a T_{gel} approval, where the tan δ ≈ 1, which is the ratio of E″/E [15]. Therefore, tan δ value of 0.999 is assumed to correspond with the T_{gel} on E' peak. T_{vit} can be obtained from E″ peak at 111.5 and 114 mins for 1 and 5 Hz frequency scanning respectively.

Recent experimental and theoretical results have shown that in the context of a TTT cure profile for thermosetting; the isothermal cure temperature versus the time to vitrification is an S-shaped curve [22]. Therefore, above 35°C and below 10°C the S-Shaped curve can be extrapolated. Using all the above attained information, TTT profile of 2% system has been formed which can be seen in Figure 4. It can be seen that any increase in the isothermal curing temperature from 10 to 20 ^{o}C results in a sudden decrease in T_{gel} and T_{vit} values, T_{gel} decreases from 250 to 125 mins, showing a 50% reduction in T_{gel}. Also T_{vit} demonstrates a reduction of 54% from 350 to 160 mins. This indicates that the rate of reaction doubles for
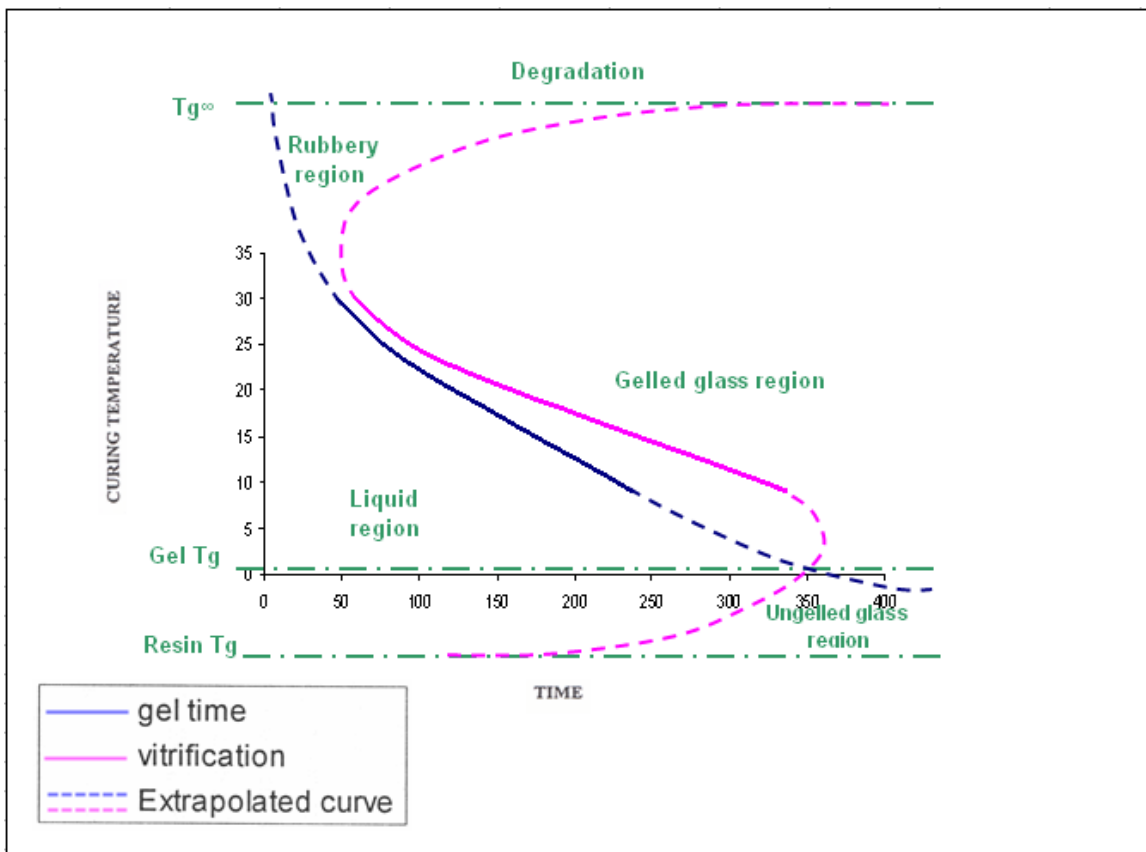
127

Figure 4. *TTT for 2% Catalyst,* polyester

every 10°C rise in temperature. The onset time of gelation at 25°C is 83 mins which can also be considered as liquid open time, working time or layup time. It can be observed that by raising the isothermal curing temperature to 30 ^{o}C, the values of T_{gel} and T_{vit} will reduce further by approximately 51%.

Hence the same approach has been used in constructing the TTT profiles for the 3% and 4% catalyst systems in temperature ranges of 10, 20 and 30 ^{o}C (Figures 5 and 6). It can be seen that the inclusion of any given catalyst amount leads to a distinctive temperature cure range. At any given temperature, each resin/catalyst combination will go through the same cure stages, but at different rates. The cure behaviour for the system with 2% catalyst (Figure 4) indicates that for any given reduction in the temperature, the gap between T_{gel} and T_{vit} will increase due to loss of energy and lower rate of reaction while for 3% catalyst content this is reversed (Figure 5). In Figure 5, at a temperature below the $_{gel}$Tg around 6-8°C there is no reaction; this is the safe storage temperature. It should be noted that in the 3% catalyst system, as vitrification occurs closer and closer to gelation, it becomes difficult to observe the gel point, hence it is not possible to define a rheological gel point below a cure temperature of 10°C. As it can be observed from Figure 5, due to the longer chemical reaction in the curing stage, above 32°C, the rubbery region begins to widen and therefore the time to vitrification increases.

Between 13 – 32 ^{o}C, intermediate cure temperature, i.e. the time between $T_{gel} - T_{vit}$ increases unexpectedly.

The rheological gel and vitrification times obtained for the 4% system are presented in Figure 6. As it can be seen, the gel time increases with decreasing cure temperature, whereas the vitrification time shows the same minimum characteristic (between 12 – 22 ^{o}C), i.e. intermediate cure temperatures [15]. Below 12 ^{o}C it is also evident that the rate of vitrification time extends over a large part of the cure. The results indicate that the composites with the catalyst content of 4% follow the same pattern as that of 2%. However in the case of 4% catalyst system the typical S-shape curve, which is expected to be seen in resin curing process with increasing temperature, takes place at a lower temperature and the gap between T_{gel} and T_{vit} is lifted above 23 ^{o}C. The profile of the samples cured at an intermediate temperature shows lower value of storage modulus, E' and loss modulus, E". The lowest value on E" peak was observed at 23 ^{o}C.

This corresponds with a smaller fraction of molecules participating in the reaction at 23 ^{o}C. The tan δ peak at 23 ^{o}C in Figure 7 indicates the reason for widening the gap between T_{gel} and T_{vit}. As the value in tan δ peak increases, the tendency of polymer changing from rubbery state into glassy state decreases. When tan δ reaches a maximum value during isothermal curing, viscosity tends to approach infinity.
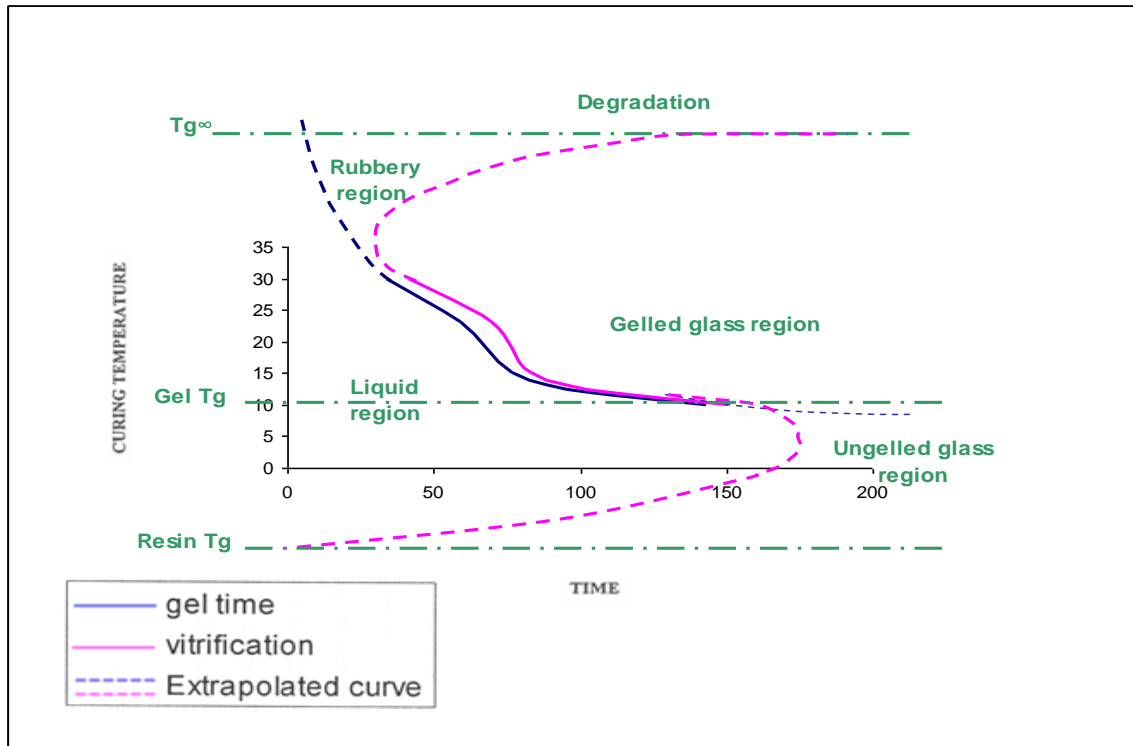
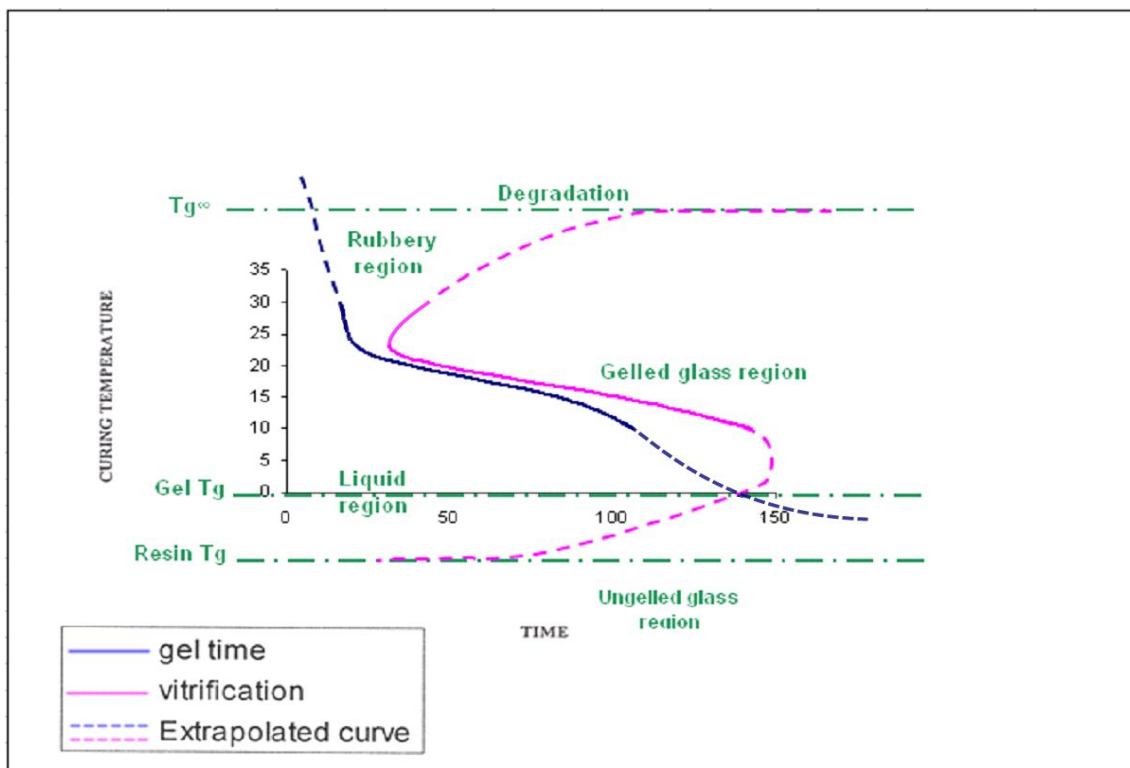Figure 5. *TTT for 3% Catalyst- polyester*

Figure 6. *TTT for 4% catalyst, Polyester*

Thus it shows lower polymeric stiffness which would be due to reducing the rate of polymer crosslinking [23]. It seems that chain stiffness and connectivity have a central role in linking the properties of the composites [24].

Increasing viscosity involves an increase in dissipated energy and therefore the loss modulus ($E"$) associates with the viscous portion. Therefore the highest peak in $E"$ curve can be taken as a starting point in vitrification. Therefore, the highest tan δ value in Figure 7 correlates to a delay in vitrification start up.

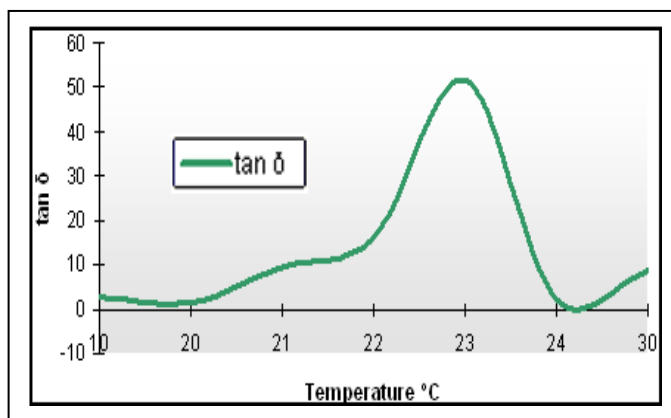Figure 7. *tan δ vs. T_{cure}*

IV. **Conclusion**

TTT Profile for the different composite systems at different temperatures containing 2%, 3% and 4% catalyst have been determined, considering different curing parameters including; liquid open time, gellation (Tgel) and vitrification time (Tvit).

- Gelation has been found to occur before vitrification at all cure temperatures where it could be observed above $_{gel}T_g$, which is the safe storage temperature.
- Rate of reaction effectively doubles for every 10 ^{o}C rise in temperature in agreement with Arrhenius equation.
- It is identified that by increasing the frequency, both T_{gel} and T_{vit} have been reduced extensively since the reactions need to take place in shorter time.
- At any given temperature, each resin/catalyst combination will go through the same cure stages, but at different rates.
- It has been established that 3% resin-catalyst system resulted in the optimum liquid open time and vitrification time for CIPP application. The safe storage temperature was found to be below the $_{gel}Tg$, around 6-8 ^{o}C.
- For intermediate cure temperatures i.e. 13 – 32 ^{o}C, the time range between $T_{gel} - T_{vit}$ increased significantly. For temperatures above 32 °C, due to the longer period of curing, the rubbery phase was found to be longer with increasing vitrification.

References

[1] M. Razmara & S.H. Saidpour, "Thermo-Mechanical Performance Of A Novel Composite Liner Used In Cured-In-Place Pipe Renovation Process", *Design, Advances in Computing & Technology*, *4th Annual Conference Proceeding*, ICGES Press, , pp 226-234, 2009.

[2] West System, "Epoxy Chemistry", *http://www.westsystem.com/ss/epoxy-chemistry/,* last accessed on 12/12/2012.

[3] L. Barral,"Characterisation of Thermosets", *Journal of Applied Polymer Science*, , Vol. 61, 1996.

[4] J.K. Gillham & S.L. Simon, "Thermosetting cure profiles: calculation and application", *Journal of Applied Science*, Vol.53, 1994

[5] D. Santiago, X. Fernández-Francos & X. Ramis, "Comparative curing kinetics and thermal–mechanical properties of DGEBA thermosets cured with a hyperbranched poly(ethyleneimine) and an aliphatic triamine", *Thermochimica Acta,* pp 9-21, Vol. 526, 2011.

[6] C.D. Wingard, "Crosslinking of an epoxy with a mixed amine as a function of stoichiometry, Final properties via Dynamic Mechanical Spectroscopy", *Journal of Applied Science*, Vol.41, 1990.

[7] M. Razmara, "Optimum pipeline renovation using CIPP techniques", *PhD thesis*, University of East London, 2008.

[8] J.K. Gillham, "Formation and properties of network polymer materials", *Polymer engineering and science*, Vol.19, 1979.

[9] Z. Ming, A. Xuefeng, T. Bangming & Y. Xiaosu, "TTT Diagram Used to Control Phase Structure of 2/4 Functional Epoxy Blends for Advanced Composites", *Chinese Journal of Aeronautics*, Issue 4, Pp 449-452, Vol. 22, 2009.

[10] Y. Huang, "Material Properties - Characterisation of LLDPE/nano-SiO2 composites by solid-state

dynamic mechanical spectroscopy", *Journal of Polymer Testing*, Vol. 23, 2004.

[11] J. Lange, "Understanding vitrification during cure of epoxy resins using dynamic scanning calorimetry and rheological techniques", *Polymer Engineering Science*, Vol. 41, 2000.

[12] H. Bayerl, W. Stark, H. Goering & U. Michel, "Online monitoring of thermoset post-curing by dynamic mechanical thermal analysis DMTA", *Polymer Testing*, pp 561﹣566, Vol. 28, 2009.

[13] J.B. Enns & J.K. Gillham, *Journal of Applied Polymer Science*, Vol. 28, Pp. 2567-2592, 1983.

[14] X. Ramis, A. Cadenato & J.M. Morancho, "Curing of a thermosetting powder coating by means of DMTA, TMA and DSC", Polymer, Vol. 44., Pp 2067–2079, 2003.

[15] K. P. Menard, *"Dynamic Mechanical Analysis, a practical introduction",* CRC press Ltd., ISBN: 0-8493-8688-8, 1999.

[16] B. Bilyen, D. Brostow & K.P. Menard, "Evaluation of the curing process in a fibre reinforced Epoxy composite by DSC and DMA", *ASTM STP 1402*, west Conshohocken, PA, 2001.

[17] D. Vlassopoulos, "Gelation Kinetics in Elastomer/Thermoset Polymer Blends", *Journal of Rheologica Acta*, , Vol.37., 1998.

[18] C. Sandolo, P. Matricardi, F. Alhaique & T. Coviello, "Effect of temperature and cross-linking density on rheology of chemical cross-linked guar gum at the gel point", *Food Hydrocolloids*, Pp 210–220,Vol. 23., 2009.

[19] B. Bilyen & K.P. Menard, "Material characterisation", *Proceedings of the 6th International Conference on Polymer Charactrisation*, Denton, TX, pp. 67, 1999

[20] J. Lange, R. Ekelöf & G.A. George "Indications of micro-vitrification during chainwise cross-linking polymerisation", *Polymer Engineering Science*, Vol.40, 1999.

[21] G. Van Assche, "Gelation and Vitrification and the auto acceleration of Gel effect during the cure", *27th annual conference of the North American Thermal Analysis Society*, Savannah, 1999.

[22] J.K. Gillham & M. Aronhime, "The transformation of liquid to amorphous solid", *Journal of coating technology*,Vol. 56, 1984.

[23] H. Dhakal, "The Manufacture and Properties of Natural Fibre/nanoclay Reinforced Unsaturated Polyester Composites", *PhD Thesis*, University of Portsmouth, 2006.

[24] A. Bartolotta, "DSC and DMA study of annealed cold-drawn PET: a three phase model interpretation", *Polymer*, Vol. 44, Pp 5771-5777, 2003.