

# NEW TESTING CAPABILITIES FOR CROSSLINKED PE

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## ABSTRACT

Since the discovery of Sioplas® technology in the late sixties by Dow Corning, vinylsilane crosslinked polyethylene (PEX-b) pipes processing has been progressively well established and derived into various alternatives around the same theme, e.g., Monosil®, Visico®, or Spherisil®. All these routes are calling for the reaction of a vinyl-functional monomer with polyethylene in presence of free radical initiator. Independently from the processes used for modifying the high density polyethylene (HDPE), the goal in PEX-b pipes fabrication is to obtain a silylalkoxy modified HDPE that can then be extruded into pipes of various dimensions. For both compounds producers and pipes manufacturers, it is important to assess the rate of crosslinking with a high degree of precision and as rapidly as possible in order to verify the conformity of the material against pipe industry standard, i.e., meeting the 65-75% gel content requirement according to either ISO10147 or ASTM D2765 method.

Using Alpha Technologies/Dynisco VTM® (Viscosity Transition Modulus) rheometer, a method for determining rapidly the gel content and for monitoring the kinetics of crosslinking in PEX-b specimens was developed. Information on crosslinking density were obtained within 10 minutes versus ~12 hours using the standard methods. On one hand, plots of elastic shear modulus ( $G'$ ) against percentage strain applied to melted PEX-b compounds were recorded on a series of specimens prepared with different vinylsilane concentrations, before and after a standard curing step. Good correlation between  $G'$  values and the gel contents measured upon xylene extraction were observed. On the other hand, for a given concentration of vinylsilane, monitoring the increase of  $G'$  as a function of the time the PEX-b specimens were curing underwater was shown to be an extremely effective means of determining the rate of crosslinking of the material. By repeating the curing kinetics at different temperatures, the energy of activation of the crosslinking reaction was calculated. Further optimization of the method was also carried out in order to monitor the crosslinking process of PEX-b compounds within the chamber of the VTM® rheometer. This latter result demonstrated that crosslinking kinetics permitted to determine gel content in PEX-b material within approximately 1 hour starting from the vinyl-silane-grafted HDPE pellets.

The methods developed in this study are much faster, safer, more reliable and significantly more economically viable than the standard gel content measurements based upon extraction in refluxing xylene. The conclusions of the correlation between the two measurements, i.e., elastic shear modulus and gel content, are presented and discussed within the light of the plastic pipe industry needs to continuously improve material properties (R&D perspective) and/or their product quality (Quality Control perspective).

## INTRODUCTION

The characterization of vinylsilane crosslinked polyethylene (PEX-b) made according to either Sioplas® [1, 2], Monosil® [3], Visico® [4, 5], or Spherisil® [6] processes is a very important aspect for optimizing material properties for applications in, e.g. plastic piping systems. The principle consists of (i) grafting vinyltrimethoxysilane (VTM) to high density polyethylene (HDPE) during a reactive extrusion process in a twin screw extruder in the presence of peroxide and anti-oxidant, followed by (ii) adding the appropriate catalyst masterbatch containing the curing catalyst and any other additives (pigment, anti-oxidant, etc...) in a single screw pipe extrusion line. Pipes are then cured for several hours up to days underwater at 95°C conditions in order sufficiently high degree of crosslinking occurs in the material. The reason why Sioplas® process has become quite popular over the last three decades is due to the good balance between investment cost (low) and production rate (high). Depending on the choice of the polyethylene density and its molecular structure, properties of silane crosslinked material can be controlled to a certain extent [7]. One of the properties that pipes fabricators are looking for is the gel content, a very important characteristic of the material that reflects its degree of crosslinking, and that determines its mechanical properties (e.g., flexibility, resistance to hydrostatic pressure and resistance to fast and slow crack growth) as well as their stability up to temperature of ~130°C. However, the actual method used for the determination of degree of crosslinking established by either ISO [8] or ASTM [9], consists in gravimetric measurements of the gel content, or insoluble fraction, produced in crosslinked ethylene plastics after extraction in the appropriate solvent (xylene or decahydronaphthalene). A minimum of eight hours extraction in xylene under reflux (~140°C) is required, which is time consuming, expensive as well as susceptible to cause safety and health issues (~250ml xylene is used for one data point). It is important that gel ratio reach values in the range 65-75% in order the material will have optimal flexibility as well as mechanical, chemical and heat resistance.

Alternative approaches were also envisaged and compared to the gel content method, e.g., FTIR [10, 11] and differential scanning calorimetry (DSC) [12]. To a certain extent both approaches were shown capable for determining the degree of crosslinking in silane-crosslinked thermoplastic materials, bringing forwards the benefits in terms of reduced labor intensity and improved health, safety and environmental friendliness. However, although these studies were bringing valuable information on the mechanisms of crosslinking in PEX-b, none of these approaches were pursued to such a degree that would have permitted to envisage them for use in quality control of PEX-b pipes fabrication. On one hand, the DSC measurements [12] were not very sensitive in the region 60-80% gel content. On the other hand, although the FTIR approach indicated a greater sensitivity in the high gel content range [11], the IR absorption index for the crosslinks, Si-O-Si, was continuing to increase without a simultaneous increase in gel content [10]. Motivated by the needs to simplify and accelerate product development in R&D lab as well as to provide a reliable method for quality control in production, this paper describes the result of the work carried out in collaboration between the Dow Corning Surface and Interface Solutions Center (SISC) and Alpha Technologies/Dynisco, focused at establishing the correlation between rheology measurements using a VTM® (Viscosity Transition Modulus) rheometer and the value of gel content obtained by the classical method used so far.

## EXPERIMENTAL

A series of PEX-b specimens were prepared using the formulations displayed in Table 1. Raw materials were used as received. Compounding was carried out in a Brabender Plastograph®350S mixer equipped with roller blades. Rotation speed was 100rpm, and initial temperature of the chamber was 200°C. Torque and temperature of the melt were monitored for controlling the reactive extrusion process of the ingredients. Total mixing time was 8 minutes, with a sequence of addition of the various ingredients in the mixer as follow, i.e.,

1. Loading the HDPE pellets, mixing for 2 minutes;
2. Loading the silane and the peroxide pre-adsorbed on the first 2/3 of porous HDPE pellets, mixing for 2 minutes;
3. Loading the antioxidants pre-adsorbed on the last 1/3 of porous HDPE pellets and the tin catalyst masterbatch, mixing for 4 minutes;
4. Dropping batch and casting into 2 to 4 mm thickness plates on Agila®PE30 press at 200°C for 5 minutes before cooling down to ambient temperature for 2 minutes.

The molded plates were then stored in a desiccator at 23°C and 20% relative humidity conditions before further testing was carried out.

**Table 1: PEX-b formulations, varying the quantity of vinyltrimethoxysilane and peroxide proportionally**

Run#	1	2	3	4	5	6
Ingredients	Part	Part	Part	Part	Part	Part
HDPE Basel Lupolen® 5031LQ 449K	87	87	87	87	87	87
Tris-(2,4-di-tert-butylphenyl)phosphite antioxidant, Ciba Irgafos®168	0.11	0.11	0.11	0.11	0.11	0.11
Tetrakis [methylene-3-(3, 5-di-tert-butyl-4-hydroxyphenyl-propionate)] methane antioxidant, Ciba Irganox®1010	0.05	0.05	0.05	0.05	0.05	0.05
Porous HDPE, Membrana Accurel® XP200	8.0	8.0	8.0	8.0	8.0	8.0
2,5-dimethyl-2,5-di-(tert-butylperoxy)- hexane peroxide (DHBP), Arkema Luperox®101	0.18	0.12	0.10	0.06	0.03	0
<b>Vinyltrimethoxysilane (VTM) Dow Corning Z6300</b>	<b>3.00</b>	<b>2.00</b>	<b>1.73</b>	<b>1.00</b>	<b>0.50</b>	<b>0</b>
	<b>Weight%</b> <b>2.90%</b>	<b>1.96%</b>	<b>1.70%</b>	<b>0.99%</b>	<b>0.50%</b>	
Tin catalyst masterbatch (0.7% DOTDL mixed in HDPE)	5.0	5.0	5.0	5.0	5.0	5.0

The HDPE polymer was Lupolen® 5031LQ 449K from Basel, with an MFR of 4.0g/10min (2.16kg/190°C) and a density of 0.955g/cm<sup>3</sup>. All raw materials indicated in Table 1 were used as received from the suppliers.

Rheology measurements were carried out on a VTM® (Viscosity Transition Modulus) rheometer with parallel plate dies from Alpha Technologies/Dynisco. Inspired by prior work described in the literature [13], kinetics of crosslinking of PEX-b specimens were

carried out on 3.1g circular (34mm diameter) specimens of 4mm thickness analyzed above their melting point, at temperatures of 180-230°C. Elastic shear modulus ( $G'$ ), storage shear modulus ( $G''$ ) and Tangent  $\delta$  were recorded upon strain sweep, e.g., 1%, 3%, 5%, 10% and 12% single strain amplitude (SSA) at constant oscillating angular frequency (3.14rad/s or 20rad/s).

Gel contents were measured upon 8 hours refluxing in xylene according to the well established and industry standardized method [8, 9].

For each particular step of our study, PEX-b specimens were prepared, crosslinked and tested slightly differently, i.e.,

1. For establishing the correlation between rheology and gel content measurements the PEX-b specimens described in Table 1 were tested on 4mm thickness molded plates before and after curing underwater at 95°C for 24 hours.  $G'$ @5% strain values were recorded at constant oscillating angular frequency of 20rad/s on specimens melted at 190°C, and plotted against the corresponding gel content values.
2. For studying the crosslinking kinetics underwater as a function of temperature, PEX-b specimens were prepared with 1.9% Dow Corning Z6300 (VTM) silane and 0.11% Luperox®101 peroxide according to the mixing procedure described above. However, no tin catalyst was added during the second step of the mixing process. PEX-b specimens were then molded into 2mm thickness plates and cured underwater at 30°C, 55°C and 95°C in the presence of 1% acetic acid dissolved in the water bath.  $G'$ @12% strain values were recorded at constant oscillating angular frequency of 3.14rad/s on specimens melted at 180°C.
3. For studying the crosslinking kinetics in the VTM® rheometer, PEX-b specimens were prepared according to the mixing procedure described above using 1.7% VTM silane in presence of 0.10% Luperox®101 peroxide. 95w% of pellets of this latter VTM silane grafted HDPE were then mixed with 5w% of pellets of the tin catalyst masterbatch, and molded into a 4mm thickness and 34mm diameter disks using the LMM, Laboratory Mixer Moulder, from Dynisco. The grafted PE and the catalyst materbatch were mixed for 5 minutes at 190°C before injecting in the 80°C mould. Crosslinking was then carried out in the chamber of the VTM® rheometer in presence of 35mg magnesium sulfate heptahydrate,  $MgSO_4 \cdot 7H_2O$  (Epsom salt) [14].  $G'$ @5% strain values were recorded at constant oscillating angular frequency of 20rad/s on specimens melted at 190°C.

## RESULTS AND DISCUSSIONS

In order to assess the benefits of using the VTM® rheometer for determining the degree of crosslinking in PEX-b material, the following steps were carried out. In a first step, a correlation was established between the elastic shear modulus ( $G'$ ) and the traditional gel content measurements on PEX-b specimens made with different concentrations of VTM silane as described in Table 1. In a second step, the elastic shear modulus measurements were carried out on PEX-b specimens that were cured at specific time intervals from the start to 24 hours underwater at different temperatures between 30-95°C. In a third step,

PEX-b specimens were allowed to cure in the chamber of the VTM® rheometer at different melt temperatures between 190-230°C, which enabled a rapid determination of the kinetics as well as the calculation of the energy of activation of the crosslinking reaction in PEX-b material.

### 1. Gel Content versus Elastic Shear Modulus ( $G'$ ) Correlation

For all PEX-b specimens prepared according to formulations of Table 1, the elastic shear modulus ( $G'$ ) measured on a 190°C melted sample remains constant in a range of single strain amplitude from 1 to 10%. In order to quantify the effect of increasing the VTM silane concentration used for grafting the HDPE, the elastic shear modulus at 5% strain ( $G'@5\%$  strain) were recorded on PEX-b specimens before and after a curing step underwater at 95°C for 24 hours. Results for both series of measurements are displayed in Figure 1.

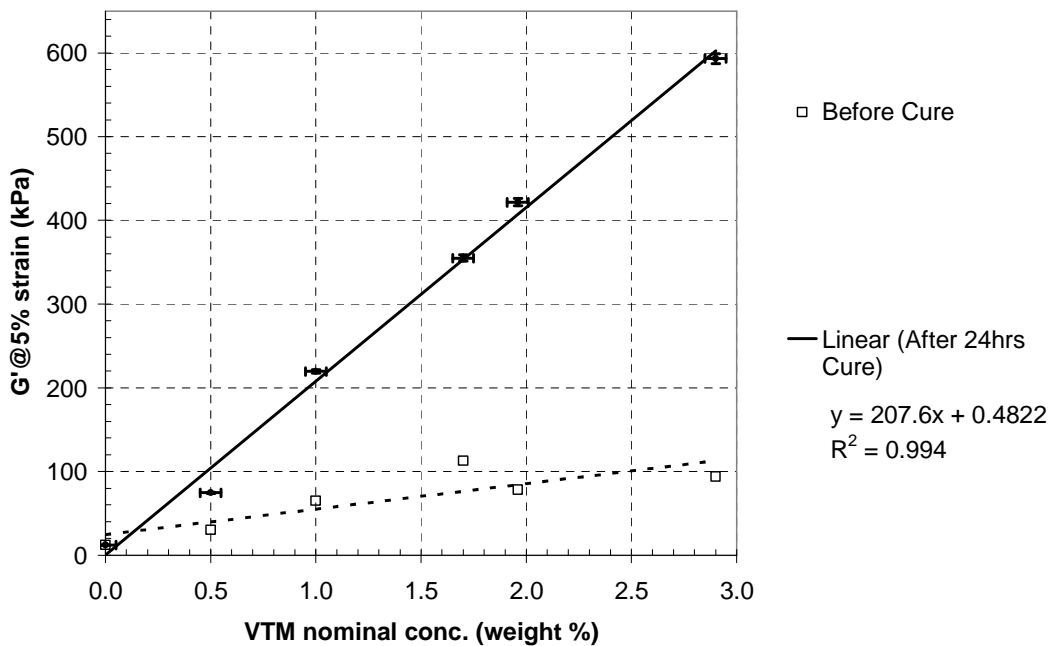
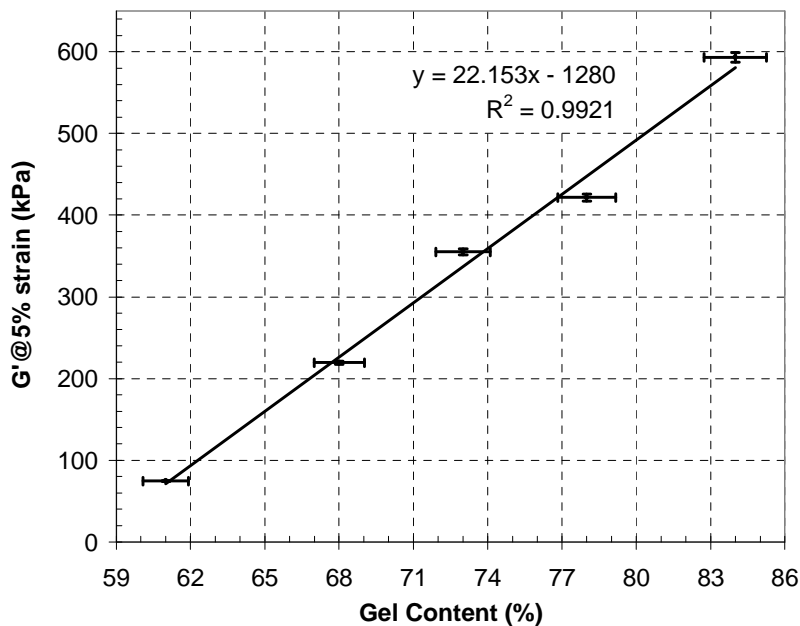


Figure 1: Plot of elastic shear modulus ( $G'$ ) at 5% strain (melt  $T=190^{\circ}\text{C}$ ) before and after curing underwater at  $95^{\circ}\text{C}$  for 24 hours of PEX-b specimens made with increasing amounts of VTM silane grafted to HDPE (see nominal concentrations of VTM silane and peroxide in Table 1).

As VTM silane concentration increased from 0.5 to 3% a progressively larger increase of  $G'@5\%$  strain was observed for the PEX-b specimen series that were cured against uncured series. For the cured series, one can notice the extreme sensitivity of  $G'$  measured on the melt at  $190^{\circ}\text{C}$  to variation in crosslinking density in PEX-b material, and the outstandingly accurate linear correlation with VTM silane nominal concentration ( $R^2=0.994$ ). A similar analysis made on the viscous component of the shear modulus,  $G''$ , and Tangent  $\delta$  showed that both were less sensitive and therefore less susceptible to detect changes in the properties of PEX-b material. More interestingly, the values of

$G'$ @5% strain were then plotted against the percentage gel content measured upon xylene extraction method [8] on the series of cured specimens. The resulting correlation is shown in Figure 2. Again, a quite good correlation coefficient ( $R^2=0.992$ ) was obtained. In order to assess the precision of these results, the  $G'$  measurements were repeated six times on each PEX-b specimens. As indicated by the error bars on  $G'$  values in Figure 1 and Figure 2, excellent accuracy was obtained. The 95% confidence interval on elastic shear modulus was indeed calculated to approximately 2% of the mean value. Measurements of gel content were confirmed being accurate within a 95% confidence interval of minimum 3% of the mean gel content value in the best case.

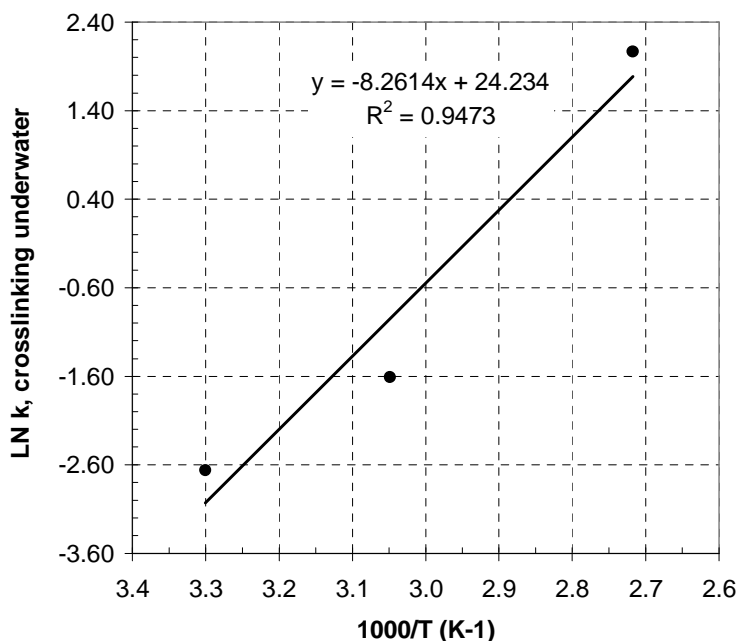


**Figure 2: Correlation between elastic shear modulus ( $G'$ @5% strain) and gel content measured on VTM silane grafted HDPE after 24 hours curing underwater at 95°C.**

The sensitivity of  $G'$  to small changes of gel contents of PEX-b specimens in the range between 60-85% (Figure 2) was therefore remarkable and extremely promising towards the development of a simplified, faster, safer and more reliable method for determining the degree of crosslinking in PEX-b material in comparison with the classical gel content method used so far. One can therefore already conclude that elastic shear modulus measurements are quite reliable for determining the degree of crosslinking in VTM silane grafted polyethylene, with the outstanding benefit that each data point takes approximately 5 minutes against approximately 12 hours using the gel content extraction method. On a quality control standpoint, this will enable PEX-b pipes manufacturers to dramatically improve their productivity by, e.g., decreasing cost of quality assurance testing, improving responsiveness to out of specification material and reducing wastes of toxic solvent.

## 2. Kinetics of crosslinking underwater

The benefit of the correlation established between gel content and elastic shear modulus was then applied for studying the kinetics of crosslinking in PEX-b material. The kinetics of crosslinking was measured by using the value of  $G'$  @12% strain at specific time intervals from the start to 24 hours. The samples consisted of materials crosslinked underwater at 30°C, 55°C and 95°C in the presence of 1% acetic acid used as hydrolysis/condensation catalyst. As described in the experimental section, the VTM silane grafted HDPE was not containing tin catalyst for this part of the study. The crosslinking rate constants were determined from the initial slope of the  $G'$  @12% strain against time curves. Because of the quite limited degree of crosslinking developed in the material for temperatures of 30°C and 55°C, the determination of the rate constants for these two temperatures was not extremely accurate. However the best estimates were plotted against the reverse of the absolute temperature, and the resulting Arrhenius plot was reasonably good as illustrated in Figure 3 below.



**Figure 3: Arrhenius plot for kinetics of crosslinking underwater in presence of 1% acetic acid at 30°C, 55°C and 95°C for HDPE grafted with 1.9% VTM silane.**

The linear temperature dependence of the crosslinking reaction was clearly observed in Figure 3, and the energy of activation,  $E_a$ , was calculated to 68kJ/mole. Energy of activation for the same crosslinking reaction for VTM silane grafted low density polyethylene, catalyzed by dibutyl tin dilaurate catalyst was determined from gel content measurements, and calculated to 65kJ/mole [15]. More recently, also determined from gel content measurements carried out after various degree of crosslinking of VTM silane grafted ethylene-propylene-copolymer, the energy of activation of the crosslinking reaction was calculated to 85kJ/mole without catalyst, and 64kJ/mole in presence of di-n-hexylamine for instance [16]. All these energies of activation are in the same order of

magnitude. The differences can easily be assigned to differences in the polymer resin and/or in the catalyst system used.

### 3. Kinetics of crosslinking in a VTM® Rheometer

In order to further optimize and accelerate the method, attempts were made to monitor the crosslinking reaction of VTM silane grafted HDPE in the chamber of the VTM® rheometer. Molded disks prepared as described in the experimental section were placed between the parallel plates dies of the VTM® rheometer in presence of 35mg of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (Epsom salt) and the elastic shear modulus recorded as a function of time. Repeating the experiment at three different temperatures, 190°C, 210°C and 230°C, using a new disk for each temperature, the kinetics curves displayed in Figure 4 were obtained. A quite sharp increase of the  $G'@5\%$  strain was observed on a time scale of approximately one hour. After 2.5 hours at 210°C for instance,  $G'@5\%$  strain was reaching a plateau value at 425kPa. The corresponding gel content measured using the xylene extraction method on the disk specimen recuperated after the measurement made at 210°C was 79%. On the other hand, a fourth disk was cured for 24 hours underwater at 95°C. Gel content and  $G'@5\%$  strain values were respectively 81% and 452kPa. The  $G'$  versus gel content correlation was therefore confirmed, which was extremely promising towards the possible implementation of the  $G'$  measurement for the on-line determination of gel content within ~1 hour after starting the production of the silane grafted compound.

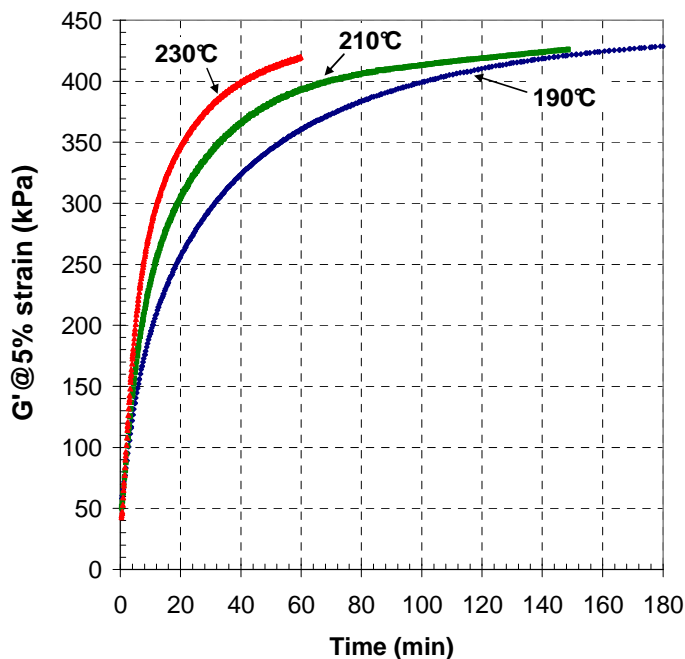


Figure 4: Crosslinking kinetics in the VTM® rheometer in presence of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  salt and tin catalyst masterbatch at  $T=190^\circ\text{C}$ ,  $210^\circ\text{C}$  and  $230^\circ\text{C}$  for HDPE grafted with 1.7% VTM silane.

From the kinetics plots of Figure 4, the rate of conversion to the plateau value were then plotted against time for each three temperatures according to DIN53529 method [17, 18].

For conversion rate between 20-80% best linear fits illustrated in Figure 5A were obtained for an order of reaction,  $n=1.67$ . The rate constant of the crosslinking reaction were given by the slope of each linear plots. The Arrhenius plot of Figure 5B was obtained, illustrating the outstanding linear dependence to temperature, and the energy of activation,  $E_a$ , calculated to 64kJ/mole. It was remarkable to notice that the values for the energy of activation obtained by curing PEX-b either underwater in presence of acetic acid or in presence of tin catalyst and hydrated salt in the VTM® rheometer were outstandingly similar. The difference being easily assigned to differences in sample preparation and/or catalyst used to accelerate the crosslinking reaction.

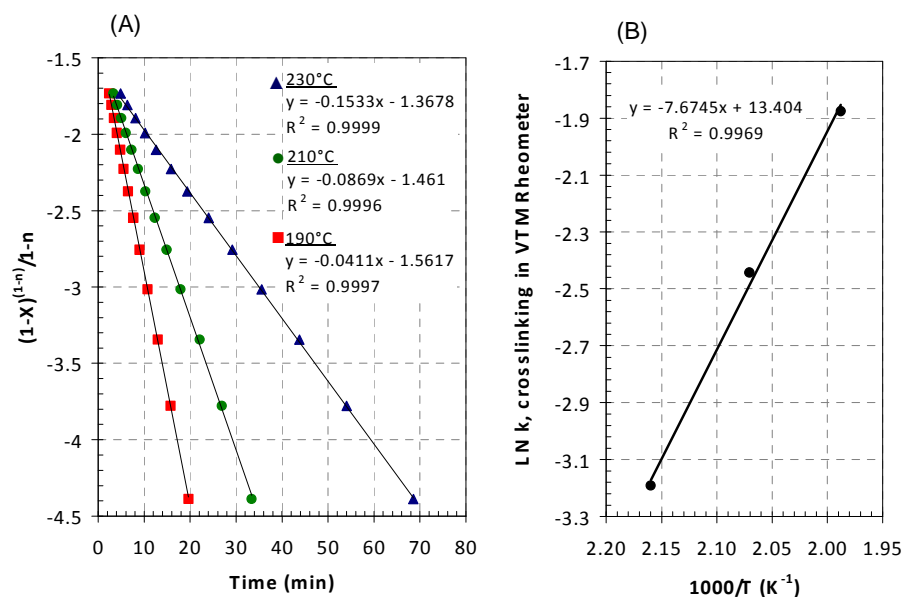


Figure 5: (A) Rate of conversion plots of crosslinking in the VTM® rheometer in presence of  $MgSO_4 \cdot 7H_2O$  salt and tin catalyst masterbatch at  $T=190^\circ C$  (triangles),  $210^\circ C$  (circles) and  $230^\circ C$  (squares) for HDPE grafted with 1.7% VTM silane. (B) Corresponding Arrhenius plot.

## CONCLUSIONS

For the first time, the present study demonstrated that elastic shear modulus ( $G'$ ) measurements on PEX-b compound melts using a VTM® rheometer are outstandingly reliable for determining the degree of crosslinking in VTM silane grafted polyethylene. A true correlation and an extremely high sensitivity with variation of gel content in the crosslinked material were shown. Additional benefits of the VTM® rheometer were demonstrated in terms of, e.g.,

- Time savings, i.e., each data point takes approximately 5 minutes against approximately 12 hours using classical ISO or ASTM method;
- Cost savings, i.e., reducing the total variable cost (manpower, raw materials, waste) as well as minimizing loss of productivity caused by the fabrication of out of specification PEX-b compound or pipe;

- iii) Environmental, health and safety impacts, i.e., suppressing the use of toxic and flammable solvent (xylene or decahydronaphthalene);
- iv) Opportunity of on-line gel content determination using VTM® rheometer equipment associated with automatic disk specimens loading and un-loading device.
- v) Possibility to carry out crosslinking kinetics at different temperatures in presence of hydrated salt within the chamber of VTM® rheometer with an outstanding accuracy, which permitted to confirm energy of activation of the crosslinking reaction at 64kJ/mole.

The robustness of the correlation between elastic shear modulus and gel content measurements definitely answered the needs of the plastic pipe industry to continuously improve R&D lab capabilities for supporting new material development and/or for improving product quality control in the fabrication of crosslinked plastic parts.

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## REFERENCES

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1. H.G. Scott, *Crosslinking of a polyolefin with a silane*, US 3 646 155, 1972.
  2. H.G. Scott, J.F. Humphries, *Crosslinking of Polyethylene*, Rev. Plast. Mod., 1974, 28, 413.
  3. P. Swarbrick, W.J. Green, C. Maillefer, *Manufacture of extruded products*, US 4 117 195, 1978.
  4. B.A. Sultan, M. Palmlof, *Advances in crosslinking technology*, Plastics, Rubber and Composites Processing and Applications, 1994, 21, 65-73.
  5. B-A. Sultan, J. Oderkerk, J. Kenneth, J. Jungkvist, *Crosslinkable high pressure polyethylene composition, a process for the preparation thereof, a pipe and cable prepared thereof*, EP 1 512 711, 2003.
  6. W. Kempter, *Method and device for the preparation of a crosslinked extruded polymeric product*, US 5 744 553, 1994.
  7. W.K. Wong, D.C. Varrall, *Role of molecular structure on the silane crosslinking of polyethylene: the importance of resin molecular structure change during silane grafting*, Polymer, 1994, 35(25), 5447-5452.
  8. *Pipes and fittings made of crosslinked polyethylene (PE-X) — Estimation of the degree of crosslinking by determination of the gel content*, International Standard ISO 10147, Second edition 2004-11-15, 2004.
  9. *Standard Test Method for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics*, ASTM D2765, 2001.
  10. T. Hjertberg, M. Palmlof, B-A Sultan, *Chemical Reactions in Crosslinking of Copolymers of Ethylene and Vinyltrimethoxy Silane*, Journal of Applied Polymer Science, 1991, 42, 1185-1192.
  11. K. Sirisinha, S. Chimdist, *Comparison of techniques for determining crosslinking in silane-water crosslinked materials*, Polymer Testing, 2006, 25, 518-526.
  12. K. Hullihen, *Determining Gel Content of Polyethylene Using Differential Scanning Calorimeter*, Ind. Eng. Chem. Res., 2006, 45, 6095-6098.
  13. T. Marinovic, Z. Susteric, I. Dimitrievski, Z. Veksli, *Dynamic Vulcanization of PP/EPDM Blends, Effect of crosslinking degree on properties of TPV*, KGK Kautschuk Gummi Kunststoffe, 1997, 51, 189-193.
  14. T. Chen-chi Yu, *Process for making a thermoplastic vulcanisates*, US 0 128 907, 2006.

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15. A.K. Sen, B.M. Mukherjee, A.S. Bhattacharyya, P.P. De, A.K. Bhowmick, *Kinetics of Silane Grafting and Moisture Crosslinking of Polyethylene and Ethylene Propylene Rubber*, Journal of Applied Polymer Science, 1992, 44, 1153-1164.
  16. K. Adachi, T. Hirano, *Controllable Silane Water-Cross-Linking Kinetics and Curability of Ethylene-Propylene Copolymer by Amine Compounds*, Ind. Eng. Chem. Res. 2008, 47, 1812-1219.
  17. *Testing of rubber and elastomers; measurement of vulcanization characteristics (curometry); evaluation of cross-linking isotherms in terms of reaction kinetics*, DIN53529 – part 2, 1983.
  18. *Testing of rubbers; curemetry; types and applications of rotorless curemeters*, DIN53529 – part 3, 1983.