Polymer Testing 31 (2012) 904–908

Contents lists available at SciVerse ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Test method

Investigation of the crosslinking behaviour of ethylene vinyl acetate (EVA) for solar cell encapsulation by rheology and ultrasound

W. Stark [a,*], M. Jaunich [a], W. Bohmeyer [b], K. Lange [b]

[a] BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, D-12205 Berlin, Germany[1]
[b] SLT Sensor- und Lasertechnik, Schulstr. 15, D-15366 Neuenhagen, Germany[2]

ARTICLE INFO

Article history:
Received 21 May 2012
Accepted 6 July 2012

Keywords:
Ethylene vinyl acetate
EVA
Crosslinking
Ultrasound
Rheology
Curemeter
DSC

ABSTRACT

EVA is a widely used material for the encapsulation of photovoltaic modules. It melts at elevated temperatures, and seals the module before it is crosslinked at temperatures above 130 °C by a peroxide-initiated crosslinking reaction. EVA has good optical properties necessary for application in solar modules. For process optimization and quality management, a method for the quick and reliable characterization of EVA crosslinking behaviour is of great value. Here, the practicability of ultrasound for online crosslinking monitoring is demonstrated. A sound velocity increase of about 8 m/s during the crosslinking reaction is found. The ultrasound results are compared with rheometer measurements performed with a curemeter typically used for the investigation of rubber crosslinking.

1. Introduction

Ethylene vinyl acetate (EVA) plays an important role in photovoltaic module manufacturing. It is used to encapsulate solar cells in a lamination process. During the lamination process, EVA is crosslinked by an incorporated curing agent, typically peroxide [1,2]. The degree of crosslinking, which is an important parameter for the long-term stability of the photovoltaic module, can be identified, e.g. by determining the gel content [3]. Therefore, the standardized extraction method with xylene is often applied [4]. Soxhlet extraction is carried out for 8 h in boiling xylene (a mixture of isomers) at about 140 °C. An antioxidant is added to the xylene. After the boiling procedure, the sample is dried and then stored for 3 h in a compartment dryer at 140 °C. The gel content is calculated as the percentage ratio of the final weight to the initial weight. This rather laborious and time-consuming method is ineffective for a production process, where quick decisions in quality management are necessary.

In the interest of finding methods to control the crosslinking process that are easier to handle, differential scanning calorimetry (DSC), curemeter and sound wave propagation experiments were carried out. The main task was to check whether the ultrasonic method is suitable for monitoring the crosslinking process of EVA.

A standard method for analysing chemical reactions such as crosslinking reactions is differential scanning calorimetry [5]. This method determines the temperature difference of a crucible with the sample in comparison to a thermally inert reference crucible in a temperature chamber under linear heating or isothermal conditions. Through the temperature difference, the occurrence of physical changes (glass transition, melting, and crystallization) and chemical processes (reaction) within the sample can be detected.

A special rheometer, the curemeter, is often used to record the progress of the crosslinking reaction in rubber [6–8].

Ultrasound wave propagation is also influenced by the mechanical properties of the material. The change of storage modulus during crosslinking can be observed as

* Corresponding author. Tel.: +49 30 8104 1614; fax: +49 30 8104 3328.
E-mail address: wolfgang.stark@bam.de (W. Stark).
[1] http://www.bam.de/en/index.htm.
[2] http://www.pyrosensor.de/index-engl.html. slt@pyrosensor.de.

0142-9418/$ – see front matter © 2012 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.polymertesting.2012.07.004

a change in sound velocity. Small ultrasound sensors can be integrated into a mould without any difficulty. Hence, ultrasound process monitoring has found widespread application for monitoring crosslinking reactions of thermosetting resins [9–14] and rubber vulcanisation [15–17].

2. Experimental

2.1. Sample material

Commercially available SOLAR EVA® RC02B (curing type: fast) from Mitsui Chemicals Fabro, Japan [18] was used. The material was delivered as foil 0.64 mm thick.

2.2. Thermal analysis by differential scanning calorimetry (DSC)

For DSC, a measuring instrument 204 F1 Phoenix®, Netzsch, Germany, was used. Standard crucibles with a manually perforated lid were deployed. A circular sample was punched out from the EVA foil. The measurement procedure consisted of three parts. First, the sample was heated from room temperature to 200 °C. This temperature was determined after a preliminary test run because it was high enough to allow the crosslinking reaction to take place. After this, the sample was cooled to room temperature and then heated again to 200 °C. The heating and cooling rates were 10 K/min.

2.3. Rheology

A curemeter as typically used in rubber industry was employed for the rheological measurements. The curemeter measures the torque necessary to deform a sample by a definite angle. The crosslinking process causes the torque to increase in a characteristic way. A curemeter is characterized by high precision and good sensitivity, and the method is standardized in ISO 6502. The instrument used was the MDR 3000 Professional, by MonTech Werkstoffprüfmaschinen GmbH, Germany.

A diagram of the measuring die is represented in Fig. 1. In addition to the general cone-cone geometry typical for rheometers, the die of a curemeter has a special shape that incorporates grooves in the measuring plates to guarantee good connection between the sample and the plates to prevent errors by sliding effects. The lower plate is stationary, while the upper oscillates at a small angle (typically 0.5°) at a frequency of 1.67 Hz. The torque and the phase shift between the torque and oscillation angle are recorded continuously. From these data, the complex torque is calculated which can be split into the in-phase part – the storage torque S′ – and the part shifted 90° out of phase – the loss torque S′. The physical meaning is that S′ represents the elastic part and S″ the viscous part, leading to an energy transfer from mechanical to thermal energy through internal friction [19].

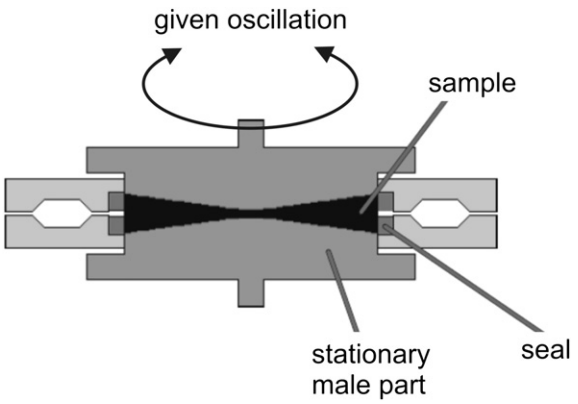

Fig. 1. Functional diagram of the die of a curemeter.

For all curemeter experiments, a combination of four films stacked one above the other was used to fill the die. The four films were punched by the MonTech rheometer volume cutter R-VS 3000. The measurements were performed under isothermal conditions at 140 °C, a value typical for the industrial solar module production process.

2.4. Process monitoring with ultrasound sensors in the mould

The ultrasound method is based on the emission and detection of a short longitudinal mechanical wave with a frequency in the range of a few MHz. Longitudinal ultrasonic waves are used as they can travel as well in liquids as in solids. Therefore, they can be used more universally in crosslinking monitoring [13,20]. This is especially important for EVA, which melts in the heating period before the crosslinking process starts.

For low damping α and short wavelength λ, this means that when the condition

$$\alpha \cdot \lambda << 1$$

holds, the sound velocity of a longitudinal wave v_s^{long} and the damping of this wave α^{long} are connected with the longitudinal storage modulus L′ and the longitudinal loss modulus L″ as follows [13,20]:

$$L' = \left(v_s^{long}\right)^2 \cdot \rho \quad and \quad L'' = 2\left(v_s^{long}\right)^3 \cdot \rho \cdot \alpha^{long}/\omega \tag{1}$$

where ρ is the density and ω the angular frequency.

L′ and L″ can be summarized as the complex longitudinal modulus L*:

$$L^* = L' + iL'' \tag{2}$$

The longitudinal wave modulus is connected with the compression modulus K* and the shear modulus G*.

$$L^* = K^* + \frac{4}{3}G^* \tag{3}$$

As a consequence of the crosslinking process, the compression and the shear modulus rise [21,22].

Small ultrasound sensors were used for sound wave excitation and reception. These can simply be incorporated into a mould. The sensors work with piezoelectric ceramics which are stable at high temperatures. A schematic view of the measuring unit incorporated into a moulding press is given in Fig. 2.

The sensors (3 and 4) are placed in the temperature controlled upper and lower parts of the mould (1 and 2) of a press arrangement. The sensors used can withstand temperatures up to 180 °C. The movable rack (5) is actuated by a pneumatic cylinder. A thickness measuring gauge (6) is added.

The ultrasound measuring equipment, called US-plus®, consisting of two sensors and a measuring unit, was developed by SLT Sensor- und Lasertechnik [23]. The measuring electronics allows the excitation frequency to be changed in order to stimulate the sensor over a wide range. The frequency range is limited mainly by the transducer type. The two sensors are identical. One is used as an emitter, the other as a receiver.

The excitation signal is applied to the emitter. The generated sound wave passes through the material in the mould and is then detected by the second sensor. The pulse travelling time together with the sample thickness is used to calculate the sound velocity. The change in signal amplitude provides the information to determine the sound attenuation. For our measurements, three excitation frequencies 4, 8.3 and 12.5 MHz were tested. The sound velocity and the attenuation were recorded automatically. The data acquisition rate was selected to one monitoring point per five seconds.

3. Results and discussion

3.1. DSC

The results of the first and second heating runs of the DSC measurement are shown in Fig. 3.

In the first run, two endothermic peaks are observed in the temperature range from 30 to 80 °C which are typically for crystal melting [24]. Starting from 125 °C, an exothermic peak appears that represents the heat release of the crosslinking reaction. The peak integral describes the progress of the reaction. The integral value is scaled to a range of values between 0 and 100% covering the area

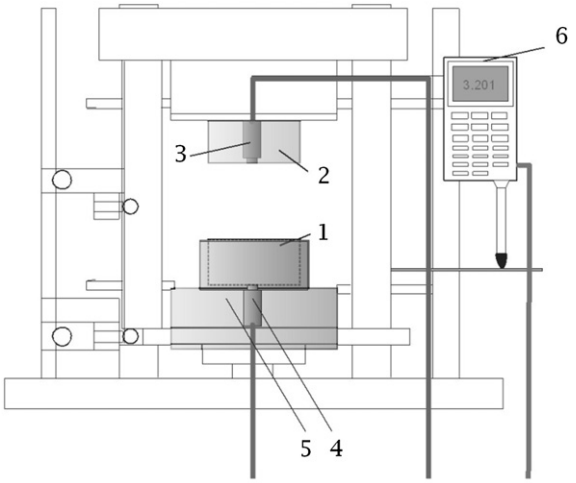

Fig. 2. Schematic view of the ultrasonic measuring unit incorporated into a moulding press: 1. and 2. Compression mould, with 3. and 4. incorporated ultrasonic sensors through transmission arrangement, 5. movable rack, 6. thickness dial gauge.

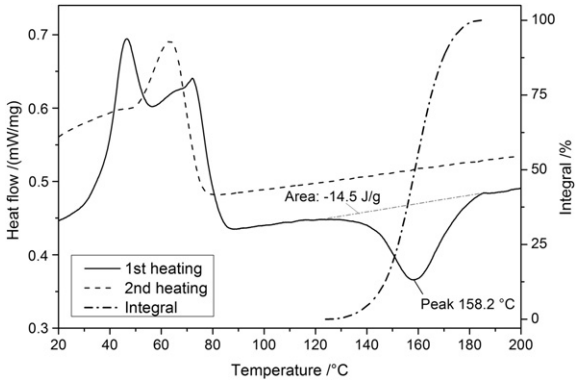

Fig. 3. DSC results for 1st and 2nd heating run, reaction integral for exothermic peak in 1st run is included, heating rate 10 K/min.

beneath the peak. In the second measurement, no indication of incomplete crosslinking is found, as the heat flow shows a straight line and no remaining exothermic peak. The DSC results are in good agreement with other published data [25,26].

For the isothermal crosslinking experiments with curemeter and ultrasound, a temperature of 140 °C was selected. According to the DSC results, this temperature is somewhat low for the crosslinking reaction, as only 5% of the crosslinking reaction took place here. However, considering the heating rate of 10 K/min for the DSC measurement and the lack of reaction time, it is expected that 140 °C will be sufficient for crosslinking if the sample is kept at that temperature for an appropriate time. In industrial module fabrication 140 °C is also a typical processing temperature.

3.2. Curemeter

The result of a typical curemeter measurement is given in Fig. 4. The storage torque and the loss torque show three typical sections. The drop in the first 30 s is caused by the quick heating to 140 °C and melting of the material. After that, the loss torque S″ increases rather quickly to a value of 0.6 dNm after 600 s, but the storage torque S′ shows only a very slight increase for the first 250 s, and then starts to increase substantially. This time is often called scorch time in the rubber industry, where it is associated with a 5% rise in the storage torque indicated by the standard ISO 6502. The growing polymer network increases the stiffness of the material drastically and, therefore, the measured torque value S′ rises. The storage torque overall shows a typical S-shape, with an inflection point observed at about 600 s, after which the slope levels off. From about 1500 s, the storage torque values show a nearly linear increase with time. In the chosen measuring time (2 h), the reaction does not come to an end. In rubber curemeter measurements this behaviour is called marching modulus.

3.3. Ultrasound

A typical result of the ultrasound measurement at 140 °C is given in Fig. 5.

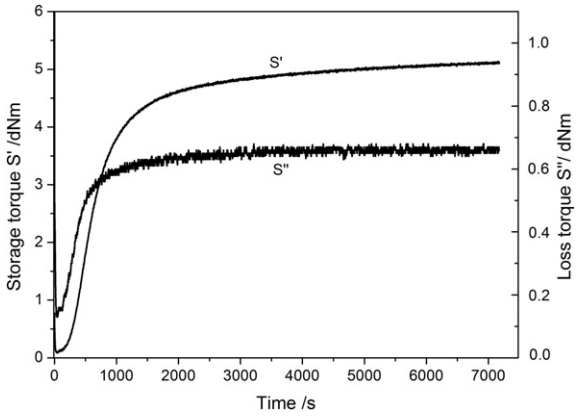

Fig. 4. Storage (S′) and loss torque (S″) over time, mould temperature 140 °C.

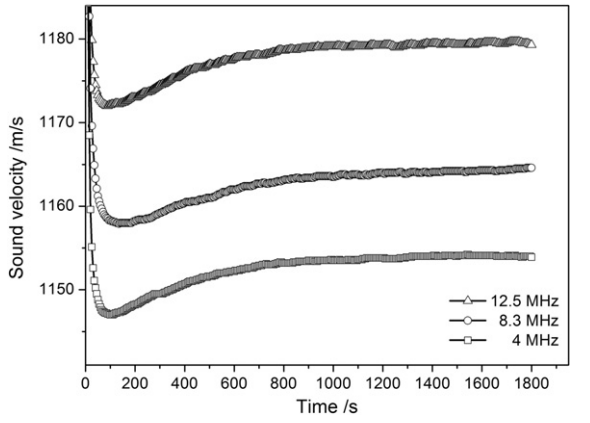

Fig. 6. Sound velocity over time at the crosslinking process, using the parameter ultrasonic frequency, mould temperature 140 °C.

As in curemeter results, three regions are seen in measured ultrasonic variables. In the first region, the sound velocity drops due to the softening and finally melting of the material caused by the temperature increase when it comes in contact with the heated mould. After about 150 s, the second region starts where the sound velocity begins to rise. The rise becomes steeper, runs through an inflection point and then levels off again, showing a typical S-shaped curve. After about 900 s, the third region starts where the sound velocity passes over into a region with a smaller rise.

The sound attenuation shows similarities to the sound velocity. The minimum is reached later and the region of nearly constant or slightly rising values is reached earlier (at about 400 s) than for sound velocity.

Since the sound velocity is directly proportional to the square root of the modulus, and thus easier to interpret, it is the preferred value to assess for process monitoring.

The influence of excitation frequency on sound velocity during crosslinking was additionally investigated to find out whether a particular range is preferred. A typical result is shown in Fig. 6. The frequency has an influence on the absolute value but not on the typical curve shape. A higher frequency leads to a higher sound velocity. The absolute change in sound velocity does not depend on frequency. In the example shown, the change in sound velocity is (7 ± 0.5) m/s for all three frequencies, which is within the range of measuring accuracy. In practice, a lower frequency is an advantage because sonic attenuation is reduced with lower frequencies.

The ultrasound method was also tested for reproducibility. In Fig. 7 an example of 12 individual measurements is given. For better comparability, the minimum value of the sound velocity is subtracted and only the change is shown. The slope of all curves shows identical behaviour and, therefore, demonstrates the good reproducibility of the method. At the end of the measurement the differences are in the range of about 1 m/s.

To check whether curemeter and ultrasound measurements give the same information about the crosslinking process, the results of both methods are combined in Fig. 8. For better comparison, the height of the step is normalised to the difference between the minimum and maximum value.

The analogy between curemeter and sound velocity data is evident. Obviously, softening in curemeter measurement is finished in a shorter time. This may be due to better heat

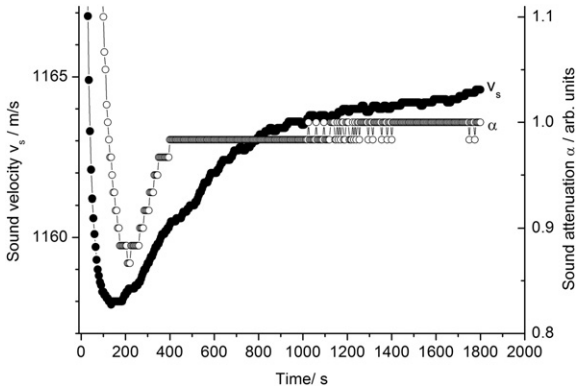

Fig. 5. Sound velocity and attenuation over time at the crosslinking process, mould temperature 140 °C.

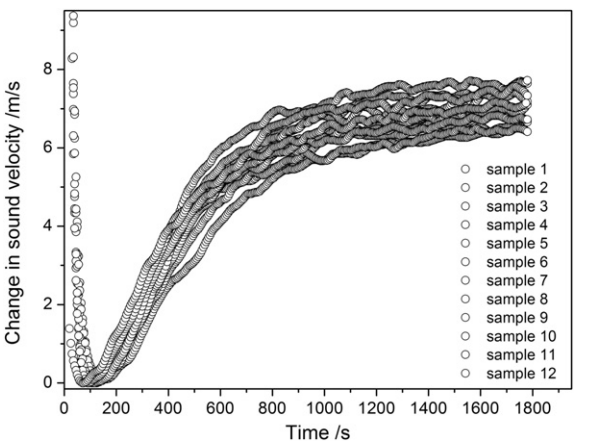

Fig. 7. Change in sound velocity over time at the crosslinking process – test of reproducibility, mould temperature 140 °C.

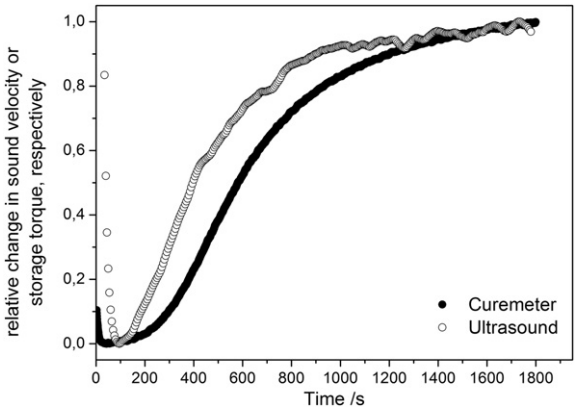

Fig. 8. Comparison of change in sound velocity and curemeter storage torque S′ over time at the crosslinking process, mould temperature 140 °C.

transfer from the mould to the material. However, a distinct increase appears earlier in the ultrasound measurement. The deviations at the beginning of the rise may come from the influence of the specifics of the measuring methods. The curemeter uses relatively large scale deformation of the sample and thus measures the overall stiffness of the sample, whereas the ultrasound wave exerts only minor deformation. Hence, it may detect crosslinking at an earlier state where a local network begins to rise. The curemeter mainly shows the formation of a macroscopic network, so that a distinct increase is expected when a gel structure is formed.

4. Summary

The crosslinking process of EVA can be well investigated by DSC. The reaction takes place in a temperature region from 130 to 180 °C. The crosslinking process was also traced by curemeter measurements and registration of the change in ultrasound wave propagation properties. The experiments were carried out at a constant temperature of 140 °C, which was in the typical range of the industrial sealing process.

The curemeter gives typical curves for a crosslinking material – at first the influence of material warming to mould temperature is seen, followed by a long-lasting crosslinking process. The results of the ultrasound method are very similar to the curemeter. The sound velocity and damping data clearly show the heating period after the mould closes and the subsequent crosslinking process. In the range from 4 MHz to 12.5 MHz the form of the crosslinking process is independent of the frequency. The reproducibility of the ultrasound experiments was rather good.

Therefore, it is shown that a curemeter, typically used for rubber like materials, gives valuable information about the crosslinking process in EVA. The drawback that the curemeter can only be used offline can be overcome by ultrasound online monitoring. It was shown that the US method delivers qualitatively the same information as the curemeter, with the advantage that it can be incorporated directly into the production process of e.g. photovoltaic modules.

References

[1] A. El Amrani, et al., Solar module fabrication, International Journal of Photoenergy (2007). Article Number: 27610.
[2] K. Agroui, et al., Thermal stability of slow and fast cure EVA encapsulant material for photovoltaic module manufacturing process, Solar Energy Materials and Solar Cells 90 (15) (2006) 2509–2514.
[3] H.A. Khonakdar, et al., Thermal and mechanical properties of uncrosslinked and chemically crosslinked polyethylene/ethylene vinyl acetate copolymer blends, Journal of Applied Polymer Science 103 (5) (2007) 3261–3270.
[4] Standard, EN 579 – Plastics Piping Systems; Crosslinked Polyethylene (PE-X) Pipes; Determination of Degreee of Crosslinking by Solvent Extraction (1993).
[5] G.W. Ehrenstein, G. Riedel, P. Trawiel, Thermal Analysis of Plastics Theory and Practice, Carl Hanser, 2004.
[6] R. Ding, A.I. Leonov, A kinetic model for sulfur accelerated vulcanization of a natural rubber compound, Journal of Applied Polymer Science 61 (3) (1996) 455–463.
[7] C.-P. Liu, J.-H. Lin, Kinetic study on cross-linking and blowing behavior of EVA/EPDM/CPE high elasticity material, Journal of Applied Polymer Science 106 (2) (2007) 897–908.
[8] ISO6502, Rubber – Guide to the Use of Curemeters; Publication date: 1999-12.
[9] J. Doring, et al., Ultrasound process control yields mechanical parameters of thermosetting plastics, Materialprufung 49 (5) (2007) 238–242.
[10] M. Rath, et al., Process monitoring of moulding compounds by ultrasonic measurements in a compression mould, Ndt & E International 33 (2) (2000) 123–130.
[11] I. Alig, et al., Continuous monitoring of quality parameters – inline monitoring in the extrusion process using ultrasonics, Kunststoffe-Plast Europe 90 (5) (2000) 96.
[12] I. Alig, D. Lellinger, G.P. Johari, Relaxation in thermosets 28. Ultrasonic studies of curing kinetics of ethylene diamine cured epoxide, Journal of Polymer Science Part B-Polymer Physics 30 (8) (1992) 791–799.
[13] R.E. Challis, et al., Following network formation in an epoxy/amine system by ultrasound, dielectric, and nuclear magnetic resonance measurements: a comparative study, Journal of Applied Polymer Science 88 (7) (2003) 1665–1675.
[14] I. Alig, et al., Polymerization and network formation of UV curable materials monitored by hyphenated real-time ultrasound reflectometry and near-infrared spectroscopy (RT US/NIRS), Progress in Organic Coatings 55 (2) (2006) 88–96.
[15] M. Jaunich, W. Stark, Influence of curing on properties of urea resin, Materials Testing-Materials and Components Technology and Application 51 (11–12) (2009) 828–834.
[16] M. Jaunich, W. Stark, Monitoring the vulcanization of rubber with ultrasound: influence of material thickness and temperature, Polymer Testing 28 (8) (2009) 901–906.
[17] M. Jaunich, W. Stark, B. Hoster, Monitoring the vulcanization of elastomers: comparison of curemeter and ultrasonic online control, Polymer Testing 28 (1) (2009) 84–88.
[18] Internet, SOLAR EVA http://eu.mitsuichem.com/service/fabricated_products/film/eva/.
[19] M.T. Shaw, W.J. MacKnight, Introduction to Polymer Viscoelasticity, third ed., John Wiley & Sons, Inc, Hoboken, New Jersey, 2005.
[20] R.J. Freemantle, R.E. Challis, Combined compression and shear wave ultrasonic measurements on curing adhesive, Measurement Science & Technology 9 (8) (1998) 1291–1302.
[21] I. Alig, et al., Monitoring of film formation, curing and ageing of coatings by an ultrasonic reflection method, Progress in Organic Coatings 58 (2–3) (2007) 200–208.
[22] D. Lellinger, S. Tadjbach, I. Alig, Determination of the elastic moduli of polymer films by a new ultrasonic reflection method, Macromolecular Symposia 184 (2002) 203–213.
[23] SLT, homepage. http://www.pyrosensor.de/index.html.
[24] W. Stark, M. Jaunich, Investigation of ethylene/vinyl acetate copolymer (EVA) by thermal analysis DSC and DMA, Polymer Testing 30 (2) (2011) 236–242.
[25] J.A. Reyes-Labarta, M.M. Olaya, A. Marcilla, DSC and TGA study of the transitions involved in the thermal treatment of binary mixtures of PE and EVA copolymer with a crosslinking agent, Polymer 47 (24) (2006) 8194–8202.
[26] J. Vogel, C. Heinze, Reactive processing of polyethylene and polyethylene-co-vinyl acetate, Angewandte Makromolekulare Chemie 207 (1993) 157–171.