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MATCHING CURE CHARACTERISTICS OF AUTOMOTIVE RUBBER COMPOUND AND POLYURETHANE COATING[*]

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Abstract

The present investigation focuses on matching cure characteristics of EPDM rubber compound and polyurethane (PU) coating using temperature modulated and pressure differential scanning calorimetry (TMDSC, PDSC).

TMDSC provides a detailed and better understanding of the curing process of model rubber system as well as complex automotive rubber compounds. The low level of unsaturation present in EPDM, results in the small heat of vulcanization (2–5 J g^{-1}), which is difficult to accurately measure using conventional differential scanning calorimetry (DSC). Thus, curing of highly filled EPDM compound was investigated using TMDSC.

The kinetics of PU curing was monitored using pressure DSC (PDSC), and heat of curing was determined as 4.2 J g^{-1} at 10°C min^{-1} heating rate. It is found that complex automotive compounds and the PU coating are curing simultaneously.

Keywords: curing, EPDM rubber compound, polyurethane coating (PU), pressure differential scanning calorimetry (PDSC), temperature modulated differential scanning calorimetry (TMDSC)

Introduction

Automotive seal component is based on EPDM rubber due to its excellent heat and ozone resistance. However, EPDM exhibits high friction in contact with other substrate (glass) during application. To reduce the friction between the rubber surface and the glass, a primer and PU coating are successively applied during production onto the rubber surface followed by curing in a hot air oven. In order to promote adhesion between the rubber compound and the PU coating, it is important that the cure characteristics of both, the rubber compound and the polyurethane coating, closely

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match each other [1]. This work is focused on the cure behaviour of the rubber and coating using advanced thermoanalytical techniques.

The energy release associated with curing is important and meaningful to determine. Differential scanning calorimetry (DSC) is the instrumental technique to determine not only the energy associated with curing but also the reaction kinetics. DSC allows one to evaluate the heat of curing reaction [2]. However, the limitation of conventional DSC for detecting weak thermal events is due to varying degree of baseline drift. Also, in conventional DSC, the heat of reaction overshadows the evolution of heat capacity. The low level of unsaturation present in EPDM, together with the above-mentioned limitation of conventional DSC, makes it difficult to detect any heat flow event during its curing. Temperature modulated differential scanning calorimetry (TMDSC), a recent extension of DSC [3–7], has several advantages over DSC. In TMDSC, the heat capacity [8–11] signal can be directly measured therefore it is possible to get additional information during curing. Thus, it is this extension of DSC, which allows the total heat flow to be separated into two components and gives insight to complex thermal events such as vulcanisation. In this work curing of highly filled EPDM compound was investigated using TMDSC. The experimental conditions were established using model EPDM gum systems and comparing their heats of vulcanisation with the literature values.

During vulcanisation, the heat evolution from a rubber compound, as measured by TMDSC, is the arithmetic sum of the heats of many reactions (either endothermic or exothermic) but only one of which is crosslinking. In order to determine the heat of the vulcanisation reaction by TMDSC, it is assumed that the measured heat flow is proportional to the reaction rate, therefore, the enthalpy after integration is equal to the heat evolved only due to vulcanisation (crosslinking) reaction.

Similarly, the excellent performance of PU coating results primarily from the formation of cross-links during cure. Variation in the performance of the coating is often due to improper curing. While a number of factors such as the reactivity and stoichiometry of the reactants can influence the extent of the crosslinking reaction; the cure time, combined with temperature, finally controls the transformation of viscous liquid to an elastic gel. Reaction rate, kinetics of cure and state of cure are, therefore, key aspects of understanding and controlling the coating performance [12]. Pressure DSC (PDSC) applies to those systems, where solvent emission causes problems in the measurement and analysis. PDSC was used to monitor the cure behaviour of two-component PU coating.

Once a better understanding of the cure characteristics of the rubber and the coating was obtained, their co-curing was performed on the ground of those data.

Experimental

Materials: model system and EPDM rubber compound

Model systems were prepared by mixing ethylene propylene diene monomer (EPDM, JSR EP 103AF) with dicumyl peroxide (DCP, supplied by Aldrich Chemical Company) in different proportions (1–5 phr) in an open two roll mill. Compounding of the complex automotive rubber compound was carried out in an open two-roll mill according to the procedure described elsewhere [13] and identification of samples is shown in Table 1. These samples were used immediately after preparation, for curing studies in this study.

Table 1 Compounding formulation of vulcanising systems

Identification/phr	*EV S_{1c}	EV S_{2c}	**SEV S_{3c}	EV S_{4c}
S	1.55	0.8	2.2	1.5
Accelerators (Total)	2.83	3.2	2.0	2.6
Vulkacit DM	0.97	–	0.4	–
MBT	0.58	0.8	0.4	1.2
TMTD	0.66	0.8	0.4	1.2
Butazate	0.40	–	0.4	–
ZDC	0.22	0.8	0.4	0.2
Tellurac	–	0.8	–	–

*EV–efficient system, **SEV–semi-efficient system
Vulkacit DM – dibenzothiazyl disulfide, MBT – 2-mercaptobenzothiazole,
TMTD – tetramethylthiuram disulfide, Butazate – zinc di *n*-butyldithiocarbamate,
ZDC – zinc diethyldithiocarbamate, Tellurac – tellurium diethyldithiocarbamate

A two-pack polyurethane coating was formed from a stoichiometric mixture of diol and diisocyanate. The synthesis of coating was reported elsewhere [14].

Analytical techniques, calibration and experimental procedure

TMDSC was conducted using DSC 2920 from TA Instruments to analyze the cure behaviour of rubber systems. Helium was used as the purging gas (100 mL min^{-1}). This range of flow rate of helium is found to be the most suitable to be used for accurate and reproducible measurements. Previous work carried out by Cser *et al.* [15] also shows that with the flow rate of helium up to 80 mL min^{-1}, the value of the cell constant changes rapidly. From values higher than 80 mL min^{-1} type of the dependency is smaller. Cell constant and temperature were calibrated using indium. The heat capacity constant was calibrated with sapphire under non-isothermal conditions using the same pans (hermetic aluminum pans) and the same experimental conditions (three different heating rates). The value obtained is in the range 0.84–1.03.

The sample mass used was kept between 6–10 mg. Non-isothermal experiments with modulation amplitude of ±0.5°C and period of 80 s were performed under three different heating ramp conditions from room temperature to 325°C. Period of 80 s used in non-isothermal conditions enables the curing reaction to be monitored under heat only conditions. The exotherm peak areas in J g^{-1} were used to measure the heat of vulcanisation.

The TMDSC experimental parameters for the complex EPDM compound were determined from the model systems such as EPDM/DCP. Established experimental parameters for model system were used for complex EPDM compound.

The curing study of PU coating was conducted using DSC 2920, TA Instruments, with PDSC attachment. A weighed amount of sample prepared in a hermetic pan covered by a lid with a laser-drilled hole was heated at a constant rate in nitrogen atmosphere at a pressure 500 psi. The measurements were carried out under nitrogen flow (50 mL min^{-1}) from room temperature to 325°C at different heating rates (10–30°C min^{-1}). The exotherm peak area in J g^{-1} was used to measure the heat of curing (ΔH) [16].

All the experiments were performed in triplicate and the average result was reported, with an error of 5%.

Results and discussion

Model system

Figure 1 shows TMDSC result of non-isothermal curing (4°C min^{-1}) of EPDM with 5 phr of DCP. In contrast to DSC, it shows additional two different signals due to non-reversing and reversing heat flows. From the figure it is obvious that the heat of curing appears in the non-reversing signal and the kinetic nature of the reactions is proven by the nature of the reversing heat flow. In the curing region, the change of the reversing heat flow is approximately 10% due to change in the heat capacity. This indicates that no other thermal event is occurring at the same time. A second heating run under similar condition was performed, when no exothermic event was observed at all, to check the completion of the curing reaction. Thus, in the present study, the non-reversing signal will be considered for studying the cure behaviour of model system and the complex automotive rubber compound.

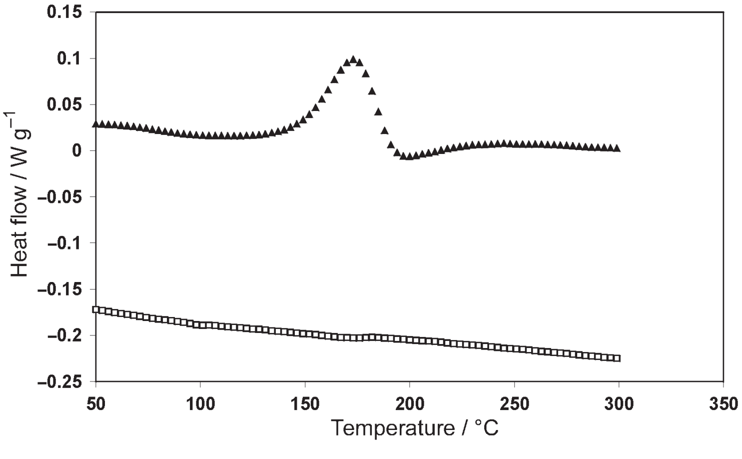

Fig. 1 Non-reversing (top) and reversing (bottom) heat flow signals for EPDM model system

As curing of rubber is an exothermic reaction, therefore, a great care was taken to determine the appropriate heat only amplitudes. This means that the modulated heating rate never becomes negative and the sample is always heated during vulcanisation. Though the early work by Asche *et al.* [17] assumed that the temperature modulation is small so that over the temperature interval of one modulation the response of the rate of kinetic processes to the temperature can be approximated as linear, the heat flow response can be written as

$$dQ/dt=C_p\,(\beta+A_T\,\omega\cos(\omega t))+f(t,T)+A_k\sin(\omega t) \qquad (1)$$

where Q in J (Joule) is the amount of heat transferred to the sample, $f(t,T)$ in W (Watt) is the average response of a kinetic process to the underlying temperature program and A_k in (W) is the amplitude of the kinetic response to the temperature modulation, ω is the modulation angular frequency ($2\pi f$) in s^{-1} and t is the time in s yet, it is important to establish the heat only conditions for all kinetic work. Later, the authors [18] claimed that the cure kinetics is affected neither by temperature modulation nor the period. Thus, heat only conditions are not necessary for correct and quantitative interpretation of results. However, in the present case all non-isothermal works were carried out under heat only conditions. In order that the sample follows the heating regime imposed on it, the following parameters (amplitude of modulation (A), heating rate (β) and period (P) of oscillation) should be adjusted according to the Eq. (2),

$$A=\beta(P/2\pi\ 60) \qquad (2)$$

Figure 2 shows the heat only conditions, for curing of EPDM with 5 phr DCP at 4°C min^{-1} with more than 4 modulations during curing.

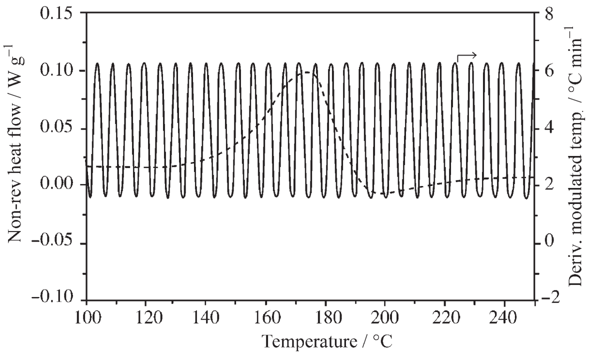

Fig. 2 Heating only conditions for curing of EPDM model system

The ability of the TMDSC to measure heat capacity during vulcanisation reaction is revealed in Fig. 3. At the initial stage of curing an increase (linear) in C_p is observed due to the onset of network formation and hence increase in molecular mass. As curing progresses the mobility of the system decreases, due to three-dimensional structure formation and hence limited degree of freedom in the system. The heat capacity remains more or less constant after the exothermic maximum, which implies

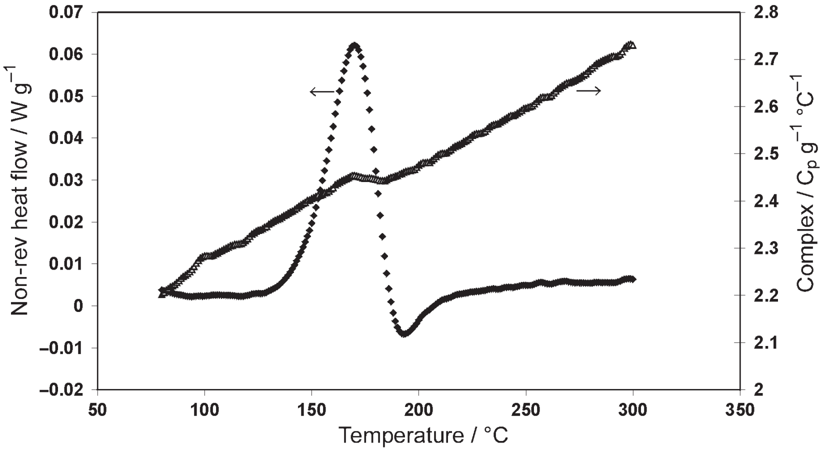

Fig. 3 Non-isothermal curing of EPDM model system with 5 phr DCP at 3°C min^{-1}

that, the heat capacity changes more during the first stage of curing (crosslinking) than during the final stage of curing. However, there is a steady increase in heat capacity during post-curing region.

Lissajous plots

Examination of the modulated heating rate profile or the Lissajous plot of modulated heat flow *vs*. modulated heating rate also provides an indication that reasonable conditions were used. Lissajous figures are obtained by plotting time-dependent heat flow *HF*(*t*) of TMDSC *vs*. change of sample temperature T_s (*t*), heating rate β (*t*) or dT_s/dt. The Lissajous figure is an ellipse plot with a certain slope. One full ellipse is produced by a single modulated cycle and many modulated cycles will result in the corresponding number of overlaid ellipses. A typical plot will be elliptical retrace as

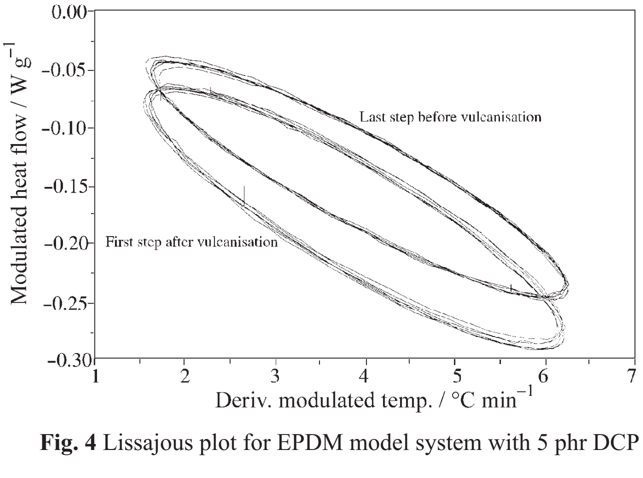

Fig. 4 Lissajous plot for EPDM model system with 5 phr DCP

far as C_p is constant over the modulation period and a steady state is maintained. A distortion in the ellipse shape and a change of its slope occur near to a transition. If the system is under control, the ellipse should retrace. A change in the slope corresponds to the change of heat capacity before and during curing.

In order to obtain additional information on the change of heat flow or heat capacity and approach to steady state, the Lissajous plot was made over the vulcanisation temperature range. The Lissajous plot of EPDM with 5 phr DCP is shown in Fig. 4. It shows very little change in heat capacity, which is normally obtained from the slope of the ellipse. Thus a slow approach to the steady state is observed from Fig. 4.

From non-isothermal TMDSC run, the rate of the reaction can be followed quantitatively in the non-reversible heat flow signal. The conversion is a function of time and temperature. Table 2 shows the enthalpy from non-reversing heat flow at different heating rates. It is noteworthy that there is a systematic trend between the observed enthalpy and the heating rate. The heats of vulcanisation of EPDM/DCP model systems at a particular heating rate and different DCP contents are presented in Table 2. At any particular heating rate, the onset of curing occurs at lower temperature with higher curative content. Values of experimentally obtained heat of vulcanisation were compared with the literature values [19]. Those values are in good agreement for model systems studied under non-isothermal conditions.

Table 2 Curing of the model systems under non-isothermal conditions

Elastomer	DCP/phr	Heating rate/ °C min^{-1}	ΔH/J g^{-1}		Peak temperature/°C			
			exp.	lit.*	exp.		lit.*	
					T_b	T_p	T_b	T_p
EPDM	1	3	9.5	12.5	131	172	154	198
		4	12.6		133	174		
		5	13.3		137	179		
	2	3	16.9	19.7	122	171	150	200
		4	19.4		126	175		
		5	20.5		128	177		
	5	3	38.1	47.3	105	170	140	198
		4	46.8		109	173		
		5	49.1		112	176		

Literature values [19] correspond to a heating rate of 20°C min^{-1}, T_b – onset temperature, T_p – peak temperature

The non-reversing heat flow signals *vs*. temperature, are presented in Fig. 5 for curing EPDM with 5 phr of DCP, using two different heating rates. From the figure, it is obvious that there is an increase in crosslink density as the reaction progresses and maximum peak temperature corresponds to maximum degree of conversion, which shifts to higher temperature with heating rates (3 and 4°C min^{-1}). Also, the ΔH value changes from 38.1 to 46.8 J g^{-1} (Table 2).

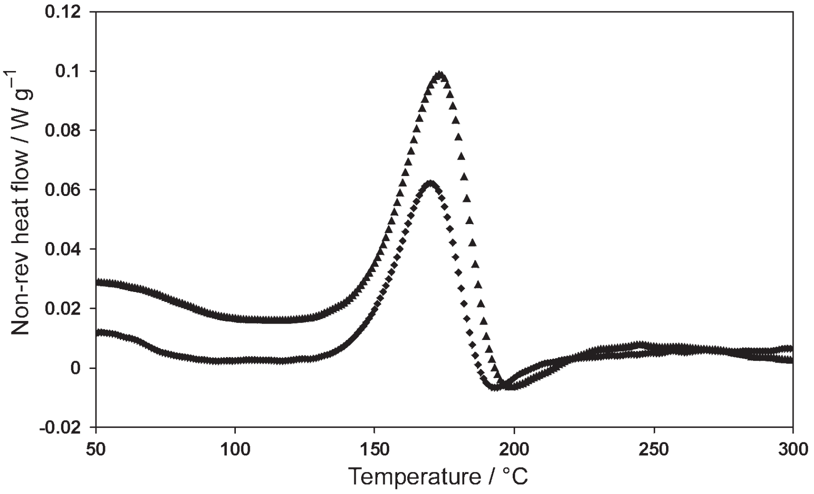

Fig. 5 Non-isothermal cure of EPDM model system with 5 phr DCP

Complex automotive rubber compound

The right parameters established for non-isothermal curing of model EPDM/DCP system under heating only condition have been used for curing of EPDM rubber compound under non-isothermal conditions. Curing of the complex automotive rubber compounds (S_{1c}, S_{2c}, S_{3c} and S_{4c}) were carried out at three different heating rates. The plot of non-reversing heat flow and derivative of modulated temperature *vs*. temperature, for samples S_{1c} is presented in Fig. 6.

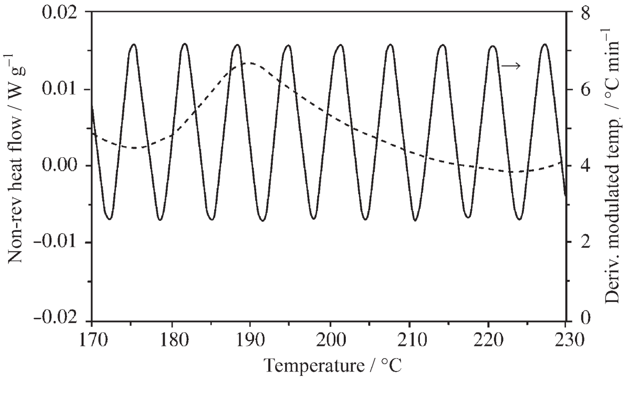

Fig. 6 Cure behaviour of S_{1c}

From the figure it is evident that sample S_{1c} is exposed under heat only conditions and modulated temperature program with more than 4 modulations within the transition. Table 3 shows non-isothermal cure enthalpy and peak temperatures for all systems studied.

Table 3 Curing of different crosslinking systems under ramping conditions

Sample	Heating rate/°C min^{-1}	ΔH/J g^{-1}	Peak temperature/°C
S_{1c}	3	3.72	184.7
	4	2.89	187.5
	5	2.59	189.7
S_{2c}	3	2.22	193.8
	4	3.78	200.2
	5	2.46	210.1
S_{3c}	3	4.82	188.3
	4	3.27	199.1
	5	3.96	205.9
S_{4c}	3	4.33	200.0
	4	3.43	202.4
	5	4.45	204.0

As the heating rate increases, the peak temperature shifts to a higher temperature. However, the cure enthalpy does not show any systematic change, it varies from 2.59 to 3.72 J g^{-1} for S_{1c}, from 2.22 to 3.78 J g^{-1} for S_{2c}, 3.27 to 4.82 J g^{-1} for S_{3c} and from 3.43 to 4.45 J g^{-1} for S_{4c}. The highest enthalpy is revealed in semi-efficient curing system S_{3c} due to the highest proportion of sulphur in this formulation. However, it must be mentioned that the exothermal changes observed contain contribution from all possible reactions such as formation of cross-links and their degradation (to some extent such as polysulfidic to di/mono sulfidic) in the material over the heating range.

For steady state and constant heat capacity, the phase-shifted, sinusoidal heat flow is a linear response to the temperature modulation, i.e. it has an identical frequency, ω, and the Lissajous figure takes on the shape of ellipse. As mentioned before, non-linearity between modulated heat flow and temperature leads to distortions

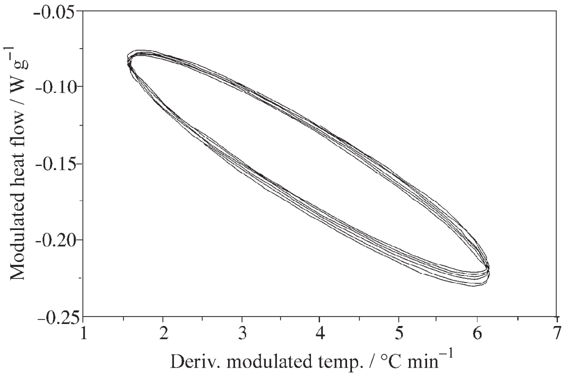

Fig. 7 Lissajous plot for S_{2c}

from the regular elliptic shape. The steady state achieved in the first step, after vulcanisation of the sample S_{2c} is shown in Fig. 7.

Matching cure characteristics of rubber and coating

The total enthalpy for four rubber compounds and PU coating from TMDSC and PDSC are listed in Table 4 at 5 and 10°C min^{-1} heating rates respectively. For all different complex automotive compounds, ΔH values are small and in the range of 2.2 to 4.8 J g^{-1}. The small value is ascribed to the low level of unsaturation present in EPDM [16]. From the table it is obvious that the total enthalpy ΔH and nominal peak temperature T_p of rubber compounds cured at 5°C min^{-1} heating rate, as well as ΔH and T_p of polyurethane coating cured at 10°C min^{-1}, are comparable indicating close matching of their cure behaviour. Compound S_{1c} shows the lowest T_p, whereas the cure temperatures of S_{2c} and polyurethane approach each other (although at different heating rates). Again, ΔH values of S_{3c}, S_{4c} and PU are closely matching (from 3.9 to 4.4 J g^{-1}). It must be emphasized that different experimental conditions in conventional and pressure DSC may lead to the differences in T_p and ΔH values. However, the close matching of their cure characteristics is expected to offer better adhesion at the interface of rubber and coating.

Table 4 MDSC/PDSC enthalpy data

Sample	Heating rate/°C min^{-1}	ΔH/J g^{-1}	Exotherm temp., T_p/°C
S_{1c}	5	2.59	189.7
S_{2c}	5	2.46	210.1
S_{3c}	5	3.96	205.9
S_{4c}	5	4.45	204.0
Polyurethane coating PU*	10	4.26	243.7

*For PU, the data is shown at 10°C min^{-1} because of more defined PDSC peak shape than at 5°C min^{-1}. At the same time the limitation of TMDSC is that it can not be run at 10°C min^{-1}

Conclusions

- TMDSC definitely has the potential to extract the amount and quality of information during curing of complex formulations.
- A good agreement is observed between the literature value of heat of vulcanisation (from conventional DSC) and TMDSC experimental data for curing EPDM with different proportions of DCP under non-isothermal conditions.
- More importantly, TMDSC is capable of detecting such weak thermal events in complex EPDM compound, which was not possible by conventional DSC.
- Comparison of the cure characteristics of complex automotive compounds, particularly S_{2c} and S_{4c}, with polyurethane coating shows that they are closely matching.

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