Specific Heats of Rubber Compounds

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ABSTRACT: The specific heats of rubber compounds are very important not only for the thermodynamic calculations in various rubber processings; mixing, extrusion, calendering, and vulcanization, etc., but also for the service life of the final products under repeated stressing conditions. In this study, the specific heats of various compounding ingredients and their compounds for tires were determined using a differential scanning calorimeter (DSC) in the temperature range from 45 to 95°C. The determined specific heats, C_p, were compared with the previous published results for natural rubber (NR), styrene–butadiene rubber (SBR), polybutadiene rubber (BR), and isoprene–isobutyl rubber (IIR). The effects of carbon black loading and vulcanization on the specific heats were investigated. The measured specific heats of the compounds were compared with the calculated values based on the fractional summation of the specific heat of each compounding ingredient. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1513–1522, 1999

Key words: specific heat; rubber compound; carbon black; vulcanization

INTRODUCTION

The specific heat is defined as the heat capacity per unit mass, where the heat capacity is the amount of heat needed to increase the temperature of different bodies by a given number of degrees.[1] The specific heats of rubber compositions is an important factor for thermal calculations in various thermal processes, such as mixing, extrusion, calendering, and vulcanization, as well as for predicting the temperature increase of rubber vulcanizates which affects the service life

of the products under repeated stressing conditions, such as tires and belts. For this reason, a number of investigations have been made of the measurement of the specific heats for rubbery materials[2–14] and various molten polymers.[15,16]

Bekkedahl and Matheson[2] determined the specific heats at temperatures sufficiently low to permit an accurate extrapolation to absolute zero in order to use the values for obtaining the free energy of the formation of rubber based on the third law of thermodynamics. Bekkedahl[3] showed how the specific heat data could be used for studying and predicting the polymerization reactions. Bekkedahl and Scott[4] measured the specific heats of synthetic rubber which is not crystallizable from 15 to 340 K. Ichimura[5] calculated the spe-

cific heat at a constant volume from that at constant pressure, which is measured experimentally.

On the other hand, Ornstein et al.,[6] Boissonnas,[7] and Mayor[8] studied the specific heats of strained rubber vulcanizates. They found somewhat conflicting results. Ornstein et al. found a strong dependence of strains, that is, the specific heat diminishes to about two-thirds of its original value when the extension is increased from 0 to 100%, and then it increases again with further extension. On the other hand, Boissonnas found consistency in the specific heats for a vulcanized rubber, while for unvulcanized rubber, it increased very slightly with elongation. Mayor also found a similar result to that of Boissonnas for unvulcanized rubber and vulcanized noncrystallizable rubber.

Recently, Kar and Bhowmick[14] suggested a model equation of heat generation of filled rubber vulcanizates in terms of specific heats together with various factors affecting the heat generation. The equation was successfully verified using a set of natural rubber (NR) and styrene–butadiene copolymer (SBR) vulcanizates.

However, little data have been published for the specific heat values of various compounding ingredients for typical tires. Also, little attention has been given to the effects of the type and loading of carbon black and the vulcanization on specific heats.

In this study, the specific heats of the various raw materials for rubber compounds were determined over the temperature from 45 to 95°C. Some measurements were also made for the rubber compounds to examine whether the specific heats could be obtained by fractional summation of each specific heat value of the components. The effects of both the carbon black type and loading and the vulcanization on the specific heats were also reported.

EXPERIMENTAL

Raw Material Samples

The typical grades of raw materials for the tire rubber compounds were selected in the specific heat measurements. The basic features of the selected raw materials are summarized in Table I. Four different types of rubbers and carbon blacks were selected to determine any differences in the specific heats according to their own physical characteristics. The selected rubbers were NR, SBR, 1,4-*cis*-polybutadiene (BR), and bromobutyl–isoprene–isobutyl rubber (BIIR), and those of carbon blacks were N-220, N-326, N-330, and N-660. The remaining materials were aromatic oil as a processing aid, Dyphene-8318 as a tackifier, ZnO and stearic acid (SA) as cure activators, Manobond and HMMM as bonding agents, TMQ and 6PPD as antidegradants, and MBS and 80% Crystex as cure systems. The SA, TMQ, 6PPD, and MBS were reported to have a melting point (or softening point) in the temperature range of specific heat measurement (45–95°C).

Preparation of Rubber Compound Samples

To determine the effects of carbon black loading and vulcanization on the specific heat property, three different rubber compounds: unfilled and filled natural rubbers (UNR and FNR) and filled SBR (FSBR), were prepared by mixing the ingredients except the curatives in an internal mixer (Model 82BR, Farrel Co., USA) at about 120°C for 6 min. The cure agents were then added in a two-roll mill (Model M8422, Farrel Co.) at 100°C for 7 min. The mix recipes are given in Table II. N-220 was selected for the study of the black loading effect and its loading was varied up to 90 phr with an increment of 15 phr. N-330 and N-660 were used at a constant level of 75 phr in the study of the vulcanization effect. For a comparison of the specific heats before and after vulcanization, FSBR was vulcanized at 145°C for 50 min by a compression-molding technique so that the compound was completely cured.

Determination of Specific Heat, C_p

The specific heats were determined by a differential scanning calorimeter (Perkin–Elmer DSC-7, USA) equipped with DSC-7 kinetic software over a temperature range from 30 to 100°C at a heating rate of 10°C/min. The sample weight of each material was adjusted to 10 ± 0.5 mg. The rubbery samples including rubber compounds were cut into small pieces before the introduction into the DSC. N_2 gas was continuously purged into the sample chamber to prevent any possibility of oxidation. A blank run was made of the every measurement of the specimens for the determination of the enthalpy used in the calculation of the specific heat.

Table I   Characteristics of Raw Materials for Rubber Compounds Investigated

Ingredients	Type	Characteristics	Producer
Rubber	NR	Viscosity-stabilized natural rubber	Mardec, Malaysia
	SBR	Styrene–butadiene copolymer (23.5% styrene)	KKPC, South Korea
	BR	cis-1,4-Polybutadiene	KKPC, South Korea
	BIIR	Bromobutyl–isoprene–isobutyl rubber (2.1% bromine)	Exxon Chemical Co., USA
Carbon black	N-220	DBP^a/ρ_a^{b} = 116/345	LG Chemical Co., South Korea
	N-326	72/465	
	N-330	102/375	
	N-660	91/425	
Processing aid	Aromatic oil	Mixture of aromatic, paraffinic, and naphthalene (40/27/33 in weight percent)	Chonkwang Uwha, South Korea
Tackifier	Dyphene-8318	Octyl-phenol formaldehyde resin	PMC, USA
Cure activator	ZnO	Zinc oxide	Hanil Chemical Co, South Korea
	SA	CH_2—$(CH_2)_{16}$—COOH, $T_m{}^c$ = 59°C	LG Chemical Co., South Korea
Bonding agent	Manobond	Cobalt Boroacylate	Rhone Poulenc, UK
	HMMM	Hexamethoxymethylmelamine (65%) + Hisil-233 (35%)^d	CYTEC, USA
Antidegradant	TMQ	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline, $T_s{}^e$ = 88°C	Kumho–Monsanto Co., South Korea
	6PPD	N-(1,3-dimethylbutyl), N'-phenyl-p-phenylenediamine (6PPD), $T_m{}^c$ = 49°C	
Cure accelerator	MBS	N-Oxydiethylene-2-benzothiazole-sulfenamide, $T_m{}^c$ = 88°C	Flexsys, USA
Sulfur	80% Crystex	Insoluble sulfur (80%) + process oil (20%)	Flexsys, USA

^{a} DBP absorption value cm^3/100 g to represent the structure of carbon black (ASTM D2414).
^{b} Apparent density in kg/m^3 of carbon black.
^{c} Melting temperature.
^{d} Hisil-233 is a trade name of silica from PPG (USA).
^{e} Softening temperature.

RESULTS AND DISCUSSION

Specific Heats of Raw Materials

To determine the temperature dependence of the specific heat, all the specific heat data were fitted to the polynomial functions of temperature using the traditional least-square method. The obtained results are summarized in Table III. For most cases, except several types of raw materials having first-order transitions (melting or softening)

in the given temperature range, the specific heats, C_p, could be related to the temperature, T, by a simple equation as given by

$$C_p = a + bT + cT^2 \qquad (1)$$

where a, b, and c are constants.

It was reported[11,13] that the specific heat of an amorphous elastomer is a nearly linear function of temperature and the slope increases slightly

Table II   Compound Recipes

Ingredients	UNR	FNR	FSBR
NR	100	100	—
SBR	—	—	100
Carbon black	—	15–90[a]	75[b]
ZnO	10	10	3
SA	1	1	2
Aromatic oil	6	6	20
Manobond	0.7	0.7	—
Dyphene-8318	1	1	—
TMQ	1	1	2
6PPD	1	1	2
HMMM	3.7	3.7	—
80% Crystex	4.7	4.7	—
Sulfur	—	—	2.02
MBS	0.8	0.8	1.7

[a] Carbon black type: N-220, N-326, N-330, and N-660.
[b] Carbon black type: N-330 and N-660.

with increasing temperature over the temperature range above the glass transition temperature T_g. In an attempt to see any difference depending on the rubber type, the specific heat of four different rubbers, NR, SBR, BR, and BIIR, were plotted against the temperature. The results are given in Figure 1. The specific heats were found to

Figure 1   Specific heat, C_p, of four different rubbers as a function of temperature.

behave in a similar fashion within the temperature range investigated from previous observations.[11,13] Moreover, BIIR showed the highest specific heat, while BR showed the lowest value. The specific heats of SBR were found to be very slightly lower than that of NR, and they lay between those for BIIR and BR.

To examine the determination method of the specific heat used in this study in order to provide a representative value, the specific heats of the four selected rubbers at a constant temperature of 50°C are compared with those from previous

Table III   Specific Heat Equations of Various Raw Materials for Rubber Compounds Investigated

Materials	C_p (J g^{-1} °C^{-1})	Temperature Range (°C)
NR	$2.009 - 1.962 \times 10^{-3}\,T + 3.077 \times 10^{-5}\,T^2$	45–95
SBR	$1.994 - 1.105 \times 10^{-3}\,T + 1.786 \times 10^{-5}\,T^2$	45–95
BR	$1.901 - 0.643 \times 10^{-3}\,T + 1.655 \times 10^{-5}\,T^2$	45–95
BIIR	$2.298 - 8.037 \times 10^{-3}\,T + 7.291 \times 10^{-5}\,T^2$	45–95
N-220	$1.290 - 4.556 \times 10^{-3}\,T + 1.263 \times 10^{-5}\,T^2$	45–95
N-326	$0.827 + 0.519 \times 10^{-3}\,T + 0.300 \times 10^{-5}\,T^2$	45–95
N-330	$1.234 - 2.007 \times 10^{-3}\,T + 1.784 \times 10^{-5}\,T^2$	45–95
N-660	$0.824 + 2.351 \times 10^{-3}\,T - 1.469 \times 10^{-5}\,T^2$	45–95
Aromatic oil	$2.191 - 10.04 \times 10^{-3}\,T + 6.788 \times 10^{-5}\,T^2$	45–95
ZnO	$0.857 - 11.94 \times 10^{-3}\,T + 8.569 \times 10^{-5}\,T^2$	45–95
SA	$1.986 + 2.02 \times 10^{-3}\,T$	70–95
Manobond	$1.376 + 6.00 \times 10^{-3}\,T$	45–50 and 90–95
HMMM	$1.948 - 12.86 \times 10^{-3}\,T + 9.273 \times 10^{-5}\,T^2$	45–95
Dyphene-8318	$1.370 + 6.51 \times 10^{-3}\,T$	45 and 85–95
TMQ	$1.714 + 0.75 \times 10^{-3}\,T$	70–95
6PPD	$1.835 + 0.85 \times 10^{-3}\,T$	60–95
MBS	$0.994 + 5.34 \times 10^{-3}\,T$	45–70 and 90–95
80% Crystex	$1.762 - 21.89 \times 10^{-3}\,T + 14.35 \times 10^{-5}\,T^2$	45–95

Table IV   Comparison of Specific Heat, C_p, of Four Different Rubbers Determined in the Present Study at a Constant Temperature 50°C with Those from Previous Works

| Rubber Type | C_p (J g^{-1} °C^{-1}) at 50°C | | |
	Present Result	Reference	Remark
NR	1.988	2.003	Bekkedahl[3]
SBR[a]	1.983	1.971	Furukawa et al.[9]
Butadiene[b]	1.910	1.929	Dainton et al.[10]
Isobutyl	2.078[c]	2.058	Furukawa and Reilly[11]

[a] Bound styrene content: about 23%.
[b] High Cis-polybutadiene: above 95%.
[c] Brominated isobutyl rubber.

works[3,9–11] in Table IV. A fairly good agreement within the difference of no more than 1% was observed. Thus, the selected test method used in this study gives representative data for a specific heat.

A similar plot of the specific heat versus temperature is given in Figure 2 for four different carbon blacks: N-220, N-326, N-330, and N-660. It was found that the specific heats ranged from generally 0.8 to 1.2 J g^{-1} °C^{-1}, which was considerably lower values than those of rubbers, 1.9 to 2.2 J g^{-1} °C^{-1}. The observed difference may be explained by the density difference; for instance, the specific gravity of carbon blacks is about twice higher than that of typical rubbers. Moreover, the temperature dependence was greatly diminished in the carbon blacks.

The specific heats were also affected by the type of carbon black, that is, the specific heat was in the decreasing order of N-330 > N-220 > N-660 > N-326. It should be noted here that the measurement of the specific heat was made for the carbon black alone without any deformation such as compression and shearing. Thus, the specific heat possibly depends on the shape characteristics, that is, porosity and free volume, of the carbon black, even though the effect of reinforcement in a rubber compound strongly depends on the particle size (thus, surface area) of the carbon black. To determine a possible explanation of the strange order of the carbon black, the specific heats of each carbon black were averaged over the temperature range investigated, and they are re-

plotted in Figure 3 as a function of both the apparent density and DBP absorption number (see Table I), which is a usual way of representing the carbon black structure. It was found that the specific heat shows a reciprocal relation with the apparent density, but it has a linear proportional relation with the DBP absorption number, although there are some deviations in the data. It seems that the degree of structure development affects the apparent density of the carbon blacks, which causes the change in the specific heats.

Figure 4 shows the temperature dependence of the specific heats for several ingredients (6-PPD, SA, and MBS), showing their first-order transitions (or softening) within the temperature range from 45 to 95°C. Three peaks were observed at about 50, 60, and 95°C, which are the corresponding melting (or softening) temperatures of 6-PPD, SA, and MBS, respectively. In the temperature range outside the melting region, the specific heat could be represented by eq. (1).

Specific Heats of Rubber Compounds

Effect of Carbon Black Loading

To determine the effect of carbon black loading on the specific heat in the rubber compound, a set of specific heat measurements was made as a function of temperature for the NR compound filled with N-220 carbon black. The carbon black loading was varied from 0 to 90 phr with an increment of 15 phr. The observed result is shown in Figure 5. The temperature dependence on the specific heat was similar to that from observations of raw rubbers, as discussed earlier. For instance, it generally in-

Figure 2 Specific heat, C_p, of four different carbon blacks as a function of temperature.

Figure 3   Specific heat, C_p, of carbon blacks (left) versus apparent density, and (right) versus DBP absorption.

creases with increasing temperature. On the other hand, the specific heat decreased with increasing the carbon black loading because of the carbon black characteristics of lower specific heat values. The difference in the specific heats between 75 and 90 phr of carbon black loading was smaller than those of carbon black loadings below 75 phr. This might come from the effect of dispersion, since the incorporation of 90 phr of N-220 into NR and SBR is somewhat difficult. About a 20% reduction of specific heat was observed against a loading level of 90 phr of N-220 carbon black.

To extend the loading effect and to establish a quantitative relation between the specific heat

Figure 4   Specific heat, C_p, of antioxidant (6-PPD), stearic acid (SA), and cure accelerator (MBS) as a function of temperature.

reduction and the carbon black content, an additional measurement of the specific heat was made for four types of carbon blacks, N-220, N-330, N-326, and N-660, at temperatures of 45 and 90°C. The ratio of the specific heat of the filled rubber compounds to that of the unfilled one, $C_p(f)/C_p(u)$, is plotted in Figure 6 as a function of the volumetric fraction, ϕ, of the carbon black. Although some experimental errors were seen for the case of the lower temperature, 45°C, at the lower concentration regions of carbon black, a fairly good linear relation was observed between the specific heat ratio and the concentration of carbon black in the range of carbon black concentration from 0 to 30%. Based on the statistical regression, a linear line of the slope of about -0.7 could be drawn, with a regression coefficient, R^2, of about 0.9. Thus, for the given condition of the temperature range from 45°C to 90°C and the carbon black loading level up to 90 phr, the specific heat, $C_p(f)$, of carbon black-filled rubber compounds can be predicted from that of unfilled rubber compounds, $C_p(u)$, using a simple equation, which is similar in form to Einstein's one,[17] as given by

$$C_p(f) = C_p(u)(1 - k\phi) \qquad (2)$$

where k is a constant (0.7 in this study) and ϕ is the volume fraction of carbon black in the rubber compound.

Figure 5 Specific heat, C_p, of natural rubber compounds filled with various levels of carbon black, N-220, as a function of temperature.

Effect of Vulcanization

The vulcanization of a rubber compound causes a significant change in various physical properties. However, little knowledge on the vulcanization effect is known. To verify the vulcanization effect, the specific heats were measured for the fully cured SBR compounds filled with two types of carbon blacks: N-330 and N-660 (FSBR in Table II). The measured specific heats are plotted against the temperature in Figure 7. A considerable decrease in the specific heat was found due to the vulcanization, and the slope became lower. One possible reason for the reduction is that the density of a rubber compound increases by either the vulcanization itself or the applied pressure. A further study is necessary to separate each effect on the specific heat.

Calculation of Specific Heats of Rubber Compounds

It is of interest of whether the specific heat of rubber compounds can be obtained from those of

individual compounding ingredients with good accuracy, since the procedure of determination of the specific heats is a kind of time-consuming work and a very tedious job. It was suggested[18] that the specific heat of a rubber compound can usually be obtained by summation of each fractional specific heat of its component, as is given by

$$C_p = \sum_{i=1}^{n} C_{p,i} w_i \qquad (3)$$

where $C_{p,i}$ and w_i are the specific heat and weight fraction of the ith raw material in the compound, respectively.

To examine the above additive character, the specific heat of the rubber compound filled with N-660 carbon black was calculated using eq. (3), and it was compared with the values from real measurements. As can be seen in Figure 8, the highest loading compound, FNR-90, showed the closest agreement, and a slight discrepancy was

Figure 6 Ratio of specific heat of filled to unfilled rubber compounds, $C_p(f)/C_p(u)$, as a function of volumetric fraction, ϕ.

Figure 7 Specific heats of uncured and cured FSBR as a function of temperature.

Figure 8 Comparison between measured and calculated specific heats of FNR.

observed for the unfilled and lower reinforced NR compounds (UNR and FNR-45), suggesting that the additivity of specific heat is more effective in the rubber compounds with lower specific heats. The discrepancy for the FNR-45 seems to be come from the assumption that the interaction between the rubber and carbon black is neglected in the calculation. Moreover, somewhat higher values are observed in the measured specific heats at temperature ranges between 70 and 90°C. This might be come from the reaction of curatives in the temperature range. For instance, the specific heat variation due to melting is ignored in the calculation of the specific heat. This effect became negligible with increasing carbon black loading. Nevertheless, it could be concluded that the specific heat of a rubber compound can be predicted with reasonable accuracy by simply summing up each specific heat of the composing materials according to the weight fraction, only when a considerable carbon black is loaded. Thus, care should be given to the calculation of the specific heat based on the simple summation.

CONCLUSIONS

The specific heats increased with increasing the temperature in the temperature range between 45 and 95°C for most compounding ingredients for typical tires, except for several materials having any transitions in the temperature range investigated. The specific heats of carbon blacks were more than twice lower than those of rubbers, and they were in the decreasing order of N-330 > N-220 > N-660 > N-326.

The carbon black loading strongly affects the specific heats, that is, about a 20% reduction in the specific heats was found when 90 phr of carbon black was loaded. Moreover, a simple linear relation of slope of −0.7 was found between the ratio of specific heats of the rubber compounds and the volumetric concentrations. The effect of vulcanization on the specific heats was also significant. The calculated specific heats of rubber compounds based on the simple fractional summation of an individual one agreed reasonably with the measured values only when the rubber

compound is sufficiently filled with the carbon black.

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