

# Variations in Specific Heat and Microstructure in Natural Rubber Filled with Different Fillers as Studied by Differential Scanning Calorimetry

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Received December 24, 2013; Revised March 18, 2014; Accepted March 20, 2014

**Abstract** The variation of specific heat ( $C_p$ ) of natural rubber (NR) is studied by Differential Scanning Calorimetry (DSC). The NR samples are filled with different fillers (nanoclay,  $TiO_2$ , and nanosilica) at different concentrations. The DSC measurements are done in  $N_2$  atmosphere with constant pressure of 0.3 bar to prevent any oxidation of the samples. The temperature has been varied up to  $210^\circ C$  from  $-40^\circ C$  at a constant heating rate of  $10^\circ C/min$  throughout the experiment and Proteus analysis software is used to study the variation of specific heat ( $C_p$ ) as function of both temperature and filler concentrations. The investigation shows that the  $C_p$  values increase with the increase of filler concentrations. Due to nanometer range diameter, these fillers fill up some of the free volume holes of NR sample. The fillers also make cross-link with NR chains causing an increase the molecular weight of NR as well as the  $C_p$  values. Thus the fillers act as active fillers for NR sample.

**Keywords:** differential scanning calorimetry, natural rubber, fillers, specific heat, free volume

**Cite This Article:** Arunava Mandal, Sandip Pan, Subrata Mukherjee, Achintya K. Saha, Sabu Thomas, Asmita Sengupta, and Asmita Sengupta, "Variations in Specific Heat and Microstructure in Natural Rubber Filled with Different Fillers as Studied by Differential Scanning Calorimetry." *Journal of Polymer and Biopolymer Physics Chemistry*, vol. 2, no. 1 (2014): 25-28. doi: 10.12691/jpbpc-2-1-4.

## 1. Introduction

In recent years in polymer research, a key problem is to relate the atomic scale free volume to the thermal and mechanical properties of polymer [1]. These free volumes appear, in the amorphous region of the polymers due to their structural disorder, in form of many irregularly shaped cavities or holes of atomic and molecular dimension. The presence of free volume decreases the density of the polymer and effect remarkably on the mechanical and thermal properties. Free volume is affected by irradiation of ion beams, aging and by addition of various fillers [2-7].

Raw natural rubber (NR) undergoes curing process for it to be useful for any practical and industrial purpose. It is therefore compounded by mixing with variety of materials such as sulfur, zinc oxide, stearic acid etc. and then cure in a process called vulcanization [8]. During this process, NR forms cross links with sulfur improving its quality and usefulness [9]. Rubber is a class of polymeric materials, which is expected to show rubber elasticity when in use. Natural rubber is in use for its versatility as an elastomeric material. Polymeric materials such as natural rubber (NR), containing filler particles of nanometer size have excellent physical, mechanical, and thermal properties compared to their conventional micro composite counterparts

[10,11,12]. The main aim of the addition of fillers into natural rubber is to improve the properties and to cheapen the material for use in material science and industry. Among many types of filler carbon black is the most important filler due to its high ability to improve the quality of NR. But it has a serious drawback. It originates from petroleum and makes the NR black due to pollution. Several groups have studied NR and its blend compounds with different methods such as viscosity measurements, differential scanning calorimetry, dynamic mechanical spectroscopy, positron annihilation spectroscopy etc. [5,13,14,15,16,17]. The microstructure of free volume of NR filled with  $TiO_2$ , Nanosilica(NS), Nanoclay(NC) have been studied by positron annihilation spectroscopy [5]. In this paper an attempt is made to study microstructure and thermal properties NR filled with  $TiO_2$ , NS, NC at different concentrations by Differential Scanning Calorimetry (DSC). DSC measures the change in thermal properties and microstructures of any sample as a function of temperature.

The heat capacity of a substance can be defined as the amount of heat required to change its temperature by unity. A more useful quantity is the specific heat capacity, which is the heat capacity per unit molecular weight of the substance. The heat capacity of a polymer can be classified into two categories: one is for the "solid" state of the polymer, may be denoted as  $C_{ps}$  and the other one is for the "liquid" state of the polymer, may be denoted as

$C_{pl}$ . The behavior of the heat capacities of polymer samples with temperature may be attributed to the localized motion of its molecular segments i.e. it may not be bothered about the presence or the absence of any periodic molecular arrangements [18,19]. Therefore it can be concluded that the values of  $C_{ps}$  for both the amorphous and the crystalline states are closely the same.

A minute study on the variation of the specific heat of the natural rubber (NR) samples with both the fillers concentration and temperature are done in this paper.

## 2. Experimental

### 2.1. Samples

Natural rubber used for the study was procured from the Rubber Research Institute of India, Kottayam. The molecular weight of NR obtained by light scattering is  $M_n = 2.68 \times 10^5$  g/mol,  $M_w = 8.38 \times 10^5$  g/mol. All other ingredients used were of commercial grade and were kindly supplied by LANXESS.

NR samples are filled with  $TiO_2$  (10 phr, 20 phr, 30 phr, 40 phr), Nanosilica (5 phr, 10 phr, 20 phr) and Nanoclay (2 phr, 5 phr, 10 phr) for the measurements. The filler titanium dioxide,  $TiO_2$  (KEMOX RC 800 PG), was kindly supplied by Kerala Minerals and Metals Limited (KMML) Kollam, India. The surface modified nanosilica (AEROSIL R 8200) and nanoclay are obtained from Degussa, Germany. The characteristics of the fillers are given in Table 1, Table 2 and Table 3 respectively.

**Table 1. Characteristics of nanosilica (NS)**

Properties	Values
Specific Surface Area(BET)	$160 \pm 25 m^2/g$
Average Particle Diameter	12 -13 nm
Carbon Content	2.0 - 4.0 wt. %
Moisture	$\leq 0.5$ wt. %
pH	$\geq 5.0$
$SiO_2$ Content	$> 99.8$ wt. %

**Table 2. Characteristics of titanium dioxide ( $TiO_2$ )**

Properties	Values
Density	$0.90 gm/cm^2$
Oil Absorption	17 gm/100gm pigment
Average particle Diameter	190 nm
Specific Gravity	4.1
pH	6.0 – 8.0

**Table 3. Characteristics of Nanoclay (NC)**

Properties	Values
Organic Modifier	$\begin{array}{c} CH_3 \\   \\ CH_2 - N - HT \\   \\ HT \end{array}$ (HT~ 65% C18; ~30% C16; ~5% C14)
Modifier Concentration	125 meq /100 g clay
Density	1.66 g /cc
d001	31.5 Å

**Table 4. Formation of mixes**

Ingredients	Recipe, Per
Rubber	100.0
Zinc Oxide	5.0
Stearic acid	1.5
TMQ	1.0
CBS	0.6
Sulphur	2.5
Filler	Variable

TMQ: 2,2,4- trimethyl-1,2-dihydroquinoline, polymerised  
CBS: N-Cyclohexyl-2-benzothiazyl-sulphenamide

### 2.2. Preparation of Samples

Formulation of composite mixes is shown in Table 4. Compounding was performed in an open two-roll mixing mill (laboratory size). NR was first masticated on the two-roll mill for about two to three minutes followed by addition of the ingredients. Curing properties were analysed using an Oscillating disc rheometer (Monsanto R-100) at a temperature of  $150^\circ C$ . The composites were cured at their respective cure times in a hydraulic press under a pressure of about 120 bar at  $150^\circ C$ .

### 2.3. Differential Scanning Calorimetry

The Differential Scanning Calorimetry (DSC) measurements carried out by employing 2000 F3 model of DSC with intra-cooler 70 versions that is capable of lowering the temperature up to  $-70^\circ C$  and enhancing the temperature up to  $600^\circ C$ . The experiment is performed in  $N_2$  atmosphere with constant pressure of 0.3 bar to prevent any oxidation of the samples. The temperature has been varied up to  $210^\circ C$  from  $-40^\circ C$  at a constant heating rate of  $10^\circ C /min$  throughout the experiment. The heat difference between the two pans (reference and sample pan respectively) upon heating is determined with respect to the temperature enhancement. Proteus analysis software is used to study the variation of specific heat ( $C_p$ ) with temperature.

## 3. Results and Discussion

DSC measures the specific heat ( $C_p$ ) of any sample by following a very simple and straight forward theory. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes

$$\left(\frac{dq}{dt}\right)_p = \frac{dH}{dt}$$

In DSC measurement the specific heat ( $C_p$ ) of the sample can be determined by comparing it to that of a known sample. In our experiment we have considered sapphire as the standard known sample. The heat that flows into the sample is directly proportional to the specific heat. The heat flow into the sample is given by,

$$\frac{dH}{dt} = m \times C_p \times \frac{dT}{dt}$$

Where  $dH/dt$  is the heat flow rate measured in calories/seconds,  $m$  is the mass of the sample measured in grams,  $C_p$  is the specific heat measured in Calories/gram/ $^\circ K$ ,  $dT/dt$  is the rate of change of temperature in  $^\circ K$ /second.

This equation is used in order to derive the final equation which determines the specific heat of the sample given by,

$$\frac{C_p}{C_p'} = \frac{m' y}{m y'}$$

Where  $C_p'$  and  $m'$  are the specific heat and mass of the standard,  $y$  and  $y'$  are the ordinate deflections due to the sample and standard respectively measured in centimeters

Heat capacity is one of the most important thermal parameter because its macroscopic behavior can be linked with the microstructure of a substance and hence can be treated as an entity capable of illuminating the physical endeavor of atoms or molecules within a substance to maneuver themselves upon heating [18,19,20].

Figure 1 Shows the variation of specific heat with both temperature and nanoclay (NC) filler concentrations. Two important observations may be come out from Figure 1. Firstly it is found that specific heat ( $C_p$ ) of all samples, irrespective of filler concentrations, increase with temperature from a certain temperature  $-30^\circ\text{C}$  to near about  $200^\circ\text{C}$ . Beyond  $200^\circ\text{C}$   $C_p$  values shows a sharp decrease due to the onset melting process. The specific heat values also increase below  $-30^\circ\text{C}$ . Secondly  $C_p$  values show a remarkable increase with the nanoclay filler concentration. These two interesting phenomenon can be explained in the light of structural change of NR due to both temperature change and addition of increasing filler concentrations.

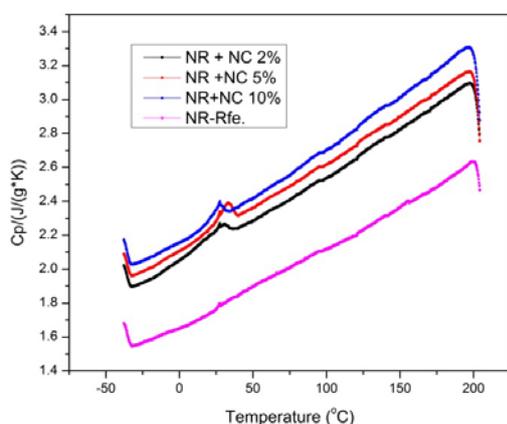


Figure 1. Variation of specific heat ( $C_p$ ) of Nanoclay (NC) filled Natural Rubber (NR) samples with temperature and filler concentrations (phr)

The  $C_p$  variation of  $\text{TiO}_2$  filled NR at different concentrations including the reference sample with both temperature and filler concentrations are shown in Figure 2. The variation of  $C_p$  values with temperature follows the same pattern as Figure 1. The  $C_p$  values increase with  $\text{TiO}_2$  filler concentration remarkably up to 20 phr. Above 20 phr  $C_p$  values are almost same below temperature  $75^\circ\text{C}$  and begin to increase with filler concentrations above  $75^\circ\text{C}$ .

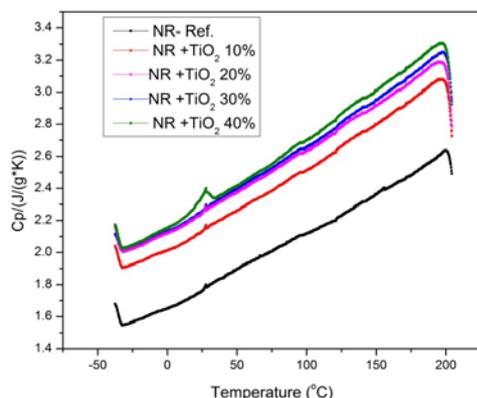


Figure 2. Variation of specific heat ( $C_p$ ) of Titanium Dioxide ( $\text{TiO}_2$ ) filled Natural Rubber (NR) samples with temperature and filler concentrations (phr)

Figure 3 shows the variation of specific heat of nanosilica filled rubber. The variations of  $C_p$  with temperature for this filler also follow same pattern as the previous two. But the variation of  $C_p$  values with nanosilica filler concentrations has some different interesting features than the previous two fillers. For nanosilica  $C_p$  values increase in a regular way with filler concentrations but rate of increase of  $C_p$  values with temperature are greater for 10 phr and 20 phr nanosilica than 5 phr and reference sample. Again the values of  $C_p$  of nanosilica filled natural rubber are highest among the above mention three types of fillers. Table 5. shows the values of highest and lowest value of  $C_p$  at different concentrations of filler and the reference sample.

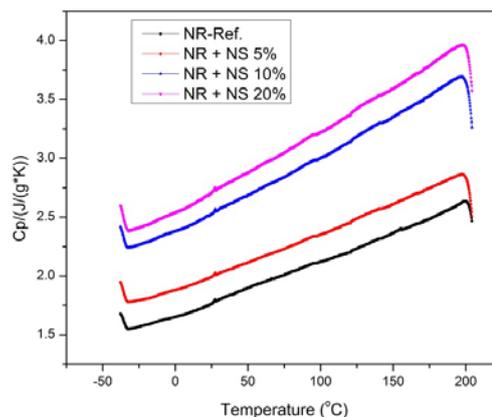


Figure 3. Variation of specific heat ( $C_p$ ) of Nanosilica (NS) filled Natural Rubber (NR) samples with temperature and filler concentrations (phr)

Table 5. Maximum and minimum values of  $C_p$  of NR samples with fillers including the reference one

Sample	Maximum value of $C_p$ (J/(g*K))	Minimum value of $C_p$ (J/(g*K))
NR-Reference	2.635	1.565
NR + NC 2%	3.097	1.898
NR + NC 5%	3.164	1.960
NR + NC 10%	3.306	2.035
NR + $\text{TiO}_2$ 10%	3.08	1.905
NR + $\text{TiO}_2$ 20%	3.252	2.013
NR + $\text{TiO}_2$ 30%	3.191	2.005
NR + $\text{TiO}_2$ 40%	3.275	2.095
NR + NS 5%	2.863	1.780
NR + NS 10%	3.693	2.239
NR + NS 20%	3.967	2.383

In our previous paper it is found that the size of free volume holes of NR sample decreases and the molecular weight increases upon addition of nanoclay,  $\text{TiO}_2$ , and nanosilica fillers. These fillers particles have diameter of nanometer order so they fill up the free volume holes of NR and well interact with NR chain, i.e. cross linking is established causing increase in molecular weight and decrease in amount of free volume of NR sample upon addition of these three fillers. As a result of this cross-linking between NR chain and filler particles  $C_p$  values should be increase with the increase of filler concentrations which is well observed. From Table 5. It is

also clear that the increase of  $C_p$  values highest upon addition of nanosilica. So the role of nanoclay, titanium dioxide and nanosilica as active fillers for NR is confirmed and well fitted to our previous results [5].

## 4. Conclusion

The variations of specific heat of natural rubber filled with different fillers are studied by DSC and the results have been correlated to the microstructure of free volume holes of rubber sample. It is observed that the  $C_p$  values increase as the filler concentrations increases for the above mentioned fillers. The variations of  $C_p$  clearly reflects that upon loading these three fillers particles, amount of free volume in the rubber sample reduces and molecular weight increases in terms of cross-linking. Hence the segmental motion of the molecules decreases and the  $C_p$  value becomes higher. So these fillers act as active fillers for natural rubber and among them nanosilica is the most active filler.

## Acknowledgement

The work is sponsored by SERC Division, D.S.T., Govt. of India, project No. SR/S2/CMP-57/2007.

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