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# Estimation of dry rubber content in natural rubber latex by differential scanning calorimetry

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**Abstract** Differential Scanning Calorimetry (DSC) is employed to study the changes in enthalpy of natural rubber latex samples when heated under a controlled temperature program. It is found that the mass normalized areas of the DSC curves between room temperature and 170 °C for different latex samples are inversely proportional to the dry rubber content (DRC) of the samples, measured following the weighing and drying method. The changes in total enthalpy of the samples in this temperature range are interpreted as due to the variations in the quantity of water present in the samples. The measurements have been repeated by diluting selected samples with known quantities of water, and it is found that the normalized areas of the DSC curves are directly proportional to the amount of water added to the latex. The method can be used to estimate the DRC of natural rubber latex accurately. Its advantages and limitations are discussed.

**Keywords** Natural Rubber Latex · Dry rubber content · Differential scanning calorimetry (DSC) · Enthalpy change

## Introduction

Natural Rubber Latex (NRL) is a special form of cytoplasm containing a suspension of rubber and non-rubber particles and has dry rubber content (DRC) varying from about 20% to about 50% in an aqueous serum. In addition, it contains 2–4% different non-rubber substances such as lutoids, carbohydrates, proteins, lipids, and inorganic salts [1]. Fresh latex from the rubber tree is a thixotropic neutral milky fluid of density around 0.98 g cm$^{-3}$. DRC is defined as the mass in grams of rubber present in 100 g of latex [2]. DRC of *Hevea* latex is a very familiar term to all in the rubber industry. It is probably one of the few properties of latex first recognized and widely used for trade and processing ever since the commencement of commercial exploitation of *Hevea* trees [3] to draw rubber latex in the nineteenth century. The implications of DRC are very significant from a commercial point of view as rubber-based products, including automobile tyres, have grown into a multibillion dollar industry worldwide today.

Though the laboratory drying and weighing method, or the gravimetric method [4], is a fairly accurate and established technique for the estimation of the DRC of latex, it suffers from the disadvantage that the measurement is time consuming and labor intensive. Other techniques such as pulsed NMR [5], Capacitance (dielectric) measurement [6], Microwave attenuation [7], and many others have been attempted by different researchers to measure the DRC of latex accurately and quickly, but these techniques suffer from disadvantages such as being expensive, requiring skilled technical personnel for measurement, lacking reproducibility of measured values, etc. So the rubber industry has been looking for techniques to estimate the DRC of rubber latex with high accuracy and low cost. Moreover, the technique needs to be fast and easy to be used by non-technical personnel in the field.

Differential scanning calorimetry (DSC) is a well-known thermal analysis technique in which differences in heat flow into an experimental sample relative to a

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reference sample are measured as a function of sample temperature, while the two are subjected to the same controlled temperature program [8]. These measurements provide qualitative and quantitative information about the physical and chemical changes that involve endothermic as well as exothermic processes or changes in heat capacity of the experimental sample compared to the reference sample. DSC measurements are usually made over the temperature range from 30 to 1000 °C, with the sample atmosphere varied depending upon the nature of the changes in the sample [9]. The technique is very useful to investigate processes such as solid state phase reactions, phase transformations, inversions in single compounds, reaction kinetics, phenomena associated with polymerization, thermal oxidative degradation, solvent retention, curing or drying properties of products [10], etc. The DSC is a very widely used technique to study the properties of polymers, polymer composites, and all elastomers [10, 11].

In this study we have carried out a detailed investigation of the variations in the DSC curves with the DRC values of several natural rubber latex samples collected from different trees in a field. The enthalpy changes for each sample have been determined from the areas of the corresponding DSC curves in a predetermined temperature range and plotted against the DRC values determined by the standard laboratory weighing and drying method. The experiments have also been carried out on a few samples diluted with known quantities of water added to it, and the measured enthalpy changes have been evaluated and plotted against the volume of water added. All the results are presented and discussed.

## Principle of the method

According to the familiar Newton's law of heat flow, the rate of heat flow ($\mathrm{d}Q/\mathrm{d}t$) into or out of a body is directly proportional to the difference in temperature ($\Delta T$) between the body ($T_2$) and the surroundings ($T_1$). The heat flow also depends upon the nature of the surface of the body and the total area of the exposed surface. The rate of heat flow can be expressed as,

$$\mathrm{d}Q/\mathrm{d}t = k\Delta T \tag{1}$$

or

$$\Delta T = K\ \mathrm{d}Q/\mathrm{d}t = Kc_\mathrm{p}\beta \tag{2}$$

where $K$ is the calorimetric constant, $c_\mathrm{p}$ is the heat capacity, and $\beta$ is the rate of heating ($\mathrm{d}T/\mathrm{d}t$) of the body.

DSC measurement on a sample provides a curve showing the heat flow into or out of the sample, depending upon whether the processes involved is endothermic or exothermic, as a function of temperature or time. The DSC curve can be used to determine the enthalpies of transitions whenever the sample undergoes any transition or phase change driven by temperature changes. Heat energy is released in an exothermic process whereas energy is absorbed in an endothermic process driven by temperature changes. In a DSC thermogram a negative peak ($-\Delta H$) is indicative of an exothermic process whereas a positive peak ($+\Delta H$) indicates an endothermic process. The change in enthalpy of a system during a process can be written as [12],

$$\Delta H = H_\mathrm{Final} - H_\mathrm{Initial} \tag{3}$$

or

$$\Delta H = KA \tag{4}$$

where $\Delta H$ is the change in enthalpy during a process within a specified temperature range, $H_\mathrm{Initial}$ and $H_\mathrm{Final}$ are the enthalpies of the system at the initial and final temperatures, respectively, measured in joules, and $A$ is the area under reaction curve.

## Experimental method

In this study, we have used a Mettler Toledo Model DSC 822$^\mathrm{e}$ Differential Scanning Calorimeter to carry out thermal analysis on different sets of natural rubber latex samples. The temperature readings of the instrument have been calibrated following the guidelines of the manufacturer with the melting points of high-purity indium, lead, or tin as the reference temperature standards. Fresh natural rubber latex samples collected directly from different trees in a field are used in this study. Each latex sample of weight 10–15 mg, weighed with a Model MX5 Mettler Toledo microbalance, is placed in an aluminum pan after filtration. The sealed aluminum pan containing the sample is then loaded into the DSC instrument, with an identical empty pan used as the reference. The sample is heated from 30 to 170 °C at a heating rate of 10 °C min$^{-1}$ and then cooled back to 30 °C naturally under standard laboratory conditions. The heat flow curves for 15 different latex samples collected from 15 different trees have been recorded. The samples have been chosen in such a way that they have wide variations in their DRC values, as determined by the weighing and drying method. Further, heat flow curves for four different latex samples, each diluted with distilled water (in 5% increments) keeping the total volume of the sample at 1000 μL, have also been recorded. The normalized areas under each of the heat flow curves, recorded as described above, are determined using the system software of the DSC instrument.

The latex samples for all the experiments described in this study have been collected from the experimental field of the Rubber Research Institute of India, Kottayam, Kerala, India. Fresh latex samples from different trees (Clone: RRII 105, Year of planting: 1989–1993, Tapping system: D3), with wide variations in DRC, have been collected for experimentation. The latex samples have been filtered and 10–15 ml of each sample is collected in separate containers to determine their DRC values following the standard laboratory weighing and drying method and another 10–15 mg of each for DSC measurements, as outlined above.

## Results and discussion

Figure 1 shows a typical DSC curve of one latex sample during heating and cooling cycles. From such DSC curves for all the samples, the areas of the thermograms between 30 and 170 °C for all the samples have been determined and normalized for sample mass. Since the DSC curves for all the samples are similar to Fig. 1, the curves for other samples are not shown. Figure 2 shows the variation of mass normalized areas under the DSC thermogram with the corresponding DRC values for the samples. Figure 3 shows the variation of the mass normalized areas of the DSC thermograms plotted for one latex sample diluted with different known quantities of distilled water. Since the corresponding variations for other samples are similar to Fig. 3, others are not shown here.

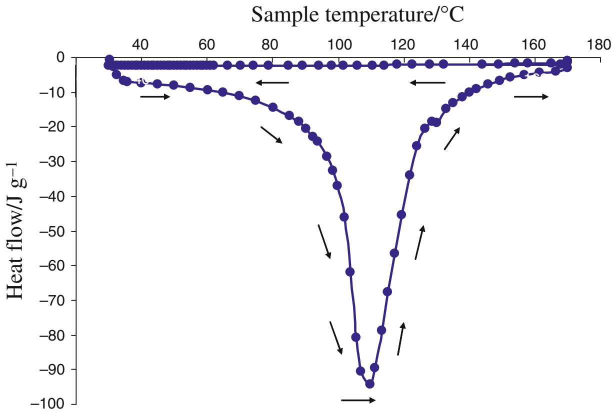

**Fig. 1** A typical DSC curve of one latex sample during heating and cooling cycles

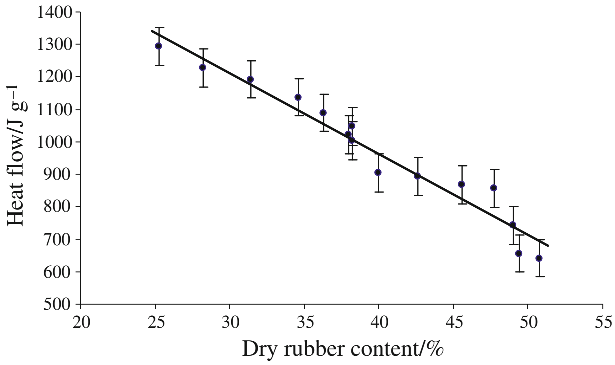

**Fig. 2** Variation of mass normalized DSC thermogram area (heat flow) with DRC of 12 different natural rubber latex samples

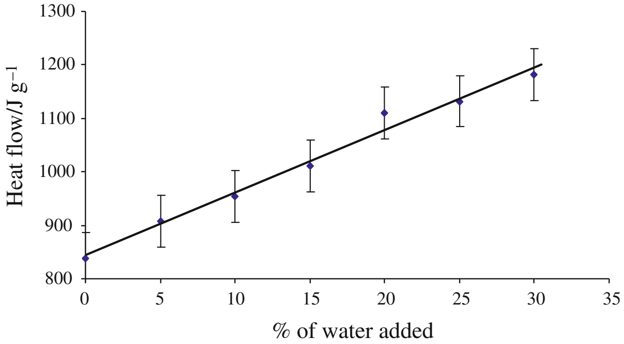

**Fig. 3** Variation of mass normalized DSC thermogram area (heat flow) with percentage of water added to one sample of latex

The normalized areas under DSC thermograms have good correlation with the DRC values of the samples. The mass normalized areas under the DSC curve exhibit a negative correlation with coefficient 0.97 with corresponding DRC values. Similarly, the mass normalized areas of the DSC curves for the sample diluted with water exhibit a positive correlation with coefficient 0.99 with the volume of water added. We have estimated that a maximum variation of ±5% can occur in the values of the mass normalized areas under the DSC curves of latex samples. Consequently this can cause an estimated error of ±0.5% in DRC values.

It can be noted from Fig. 2 that the mass normalized area of the DSC curve, or the heat flow into the sample, is inversely proportional to the DRC of latex, or as the rubber content in the sample increases the heat flow into the sample decreases. This can be explained in terms of the difference in heat capacity between rubber and water. Since water has a higher heat capacity than rubber, the heat flow into the sample decreases as the rubber content increases, or as water content decreases.

The result shown in Fig. 3 is in tune with the result shown in Fig. 2. The purpose of this study is to establish the relation, if any, between changes in enthalpy of the latex sample as water escapes from it with its DRC value and see whether it can be used as a technique to measure the DRC values of unknown samples. We could establish a good correlation between DRC values and the mass normalized areas, which are a measure of the change in enthalpy of the samples. By recording the mass normalized DSC curve for any unknown sample, its DRC can directly be read from Fig. 2.

Though we could establish a direct relation between the changes in enthalpy of the reaction between 30 and 170 °C with the DRC values, we have not been able to separate the effects of non-rubber constituents such as lutoids, carbohydrates, proteins, lipids, and inorganic salts involved in this reaction. Moreover, it has not been possible to study the effect of anticoagulants and adulterants in latex samples on their DSC curves.

## Conclusions

Thermal analysis of natural rubber latex following DSC technique has established a direct proportionality between normalized areas of the DSC curves or changes in enthalpy of transition between 30 and 170 °C with the DRC of natural rubber latex. It is found that the above transition is caused by loss of water from the sample, and it is an exothermic process with the sample absorbing heat from the surroundings. This result is in tune with the fact that a major constituent of natural rubber latex is water. It is seen that the DSC technique provides an accurate technique to determine the amount of heat absorbed by the sample during heating cycle and it is related inversely to the DRC values of the samples. Further, the results on the variation of the change in enthalpy of the sample diluted with water (Fig. 3) support the interpretation of the results on raw samples with different DRC values (Fig. 2).

We think that the information provided by the present investigations would be useful for quick quantification of dry rubber content in natural rubber latex and to design quality standards for products manufactured using natural rubber latex. In this study we have been able to show that differential scanning calorimetry is an accurate technique for the estimation of the DRC of rubber latex, though it does not overcome other limitations such as being expensive, requiring skilled personnel for measurement, and not being adaptable to use in the field.

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