Freezing point depression · Swollen networks · Rubber · Exfolliated nanocomposites

A novel experimental approach based on the freezing point depression of a solvent in the swollen gel has been developed to characterize the structure of the network on unfilled rubber and the formation of exfoliated nanocomposites. The freezing point depends on the conditions required for the formation of crystalline nuclei, which are limited by the elastomeric network restrictions as well as limitations in polymer chain movement. Thus, it can be the key to relate the microscopic parameters with the macroscopic properties of rubber compounds.

Lösungsmittelschmelzpunktdepression als neue Methode zur Eigenschaftsbewertung von Kautschukcompounds

Schmelzpunktdepression · gequollene Netzwerke · Kautschuk · exfoliierte Nanocomposite

Die Schmelzpunktdepression des Lösungsmittels in gequollenen Netzwerken wird als experimentelle Methode zur Beurteilung der Struktur von Kautschuknetzwerken und exfoliierten Nanocompositen vorgeschlagen.
Der Schmelzpunkt hängt ab von den Bedingungen unter denen Kristallisationskeime gebildet werden. Kettenbewegungen wie auch die Netzwerkstruktur behindern die Keimbildung und das Kristallitwachstum. Daher können mikroskopische Netzwerkparameter mit makroskopischen Eigenschaften der Compounds in beziehung gesetzt werden.

Solvent Freezing Point Depression as a New Tool to Evaluate Rubber Compound Properties[1]

Freezing point depression of a solvent in a crosslinked rubber is expected because of the lowering of the chemical potential of solvent molecules in polymer solution. However, the experimental results show a deeper depression than expected.

This "anomalous" freezing point depression has been studied by many authors, and several theories have been developed to explain it [1–5]. McGill, et al. [3] proposed a nucleation theory for freezing point depression of a solvent imbibed in a crosslinked elastomer network. The three-dimensional mesh of network chains subdivides the bulk solvent, creating temporary fluctuating restrictions on the amount of solvent available for the formation of a nucleus. The more heavily crosslinked the gel, the smaller are the solvent pockets in which nucleation can occur, and consequently, the larger is the freezing point depression. However, McGill, et al. theory is based, and it is only applicable to four functionality crosslink networks. Therefore, the goal of this work is to modify this theory to generalize it and be able to apply to any crosslink functionality. Hence, the freezing point depression has been used to study two of the mains topics in rubber science and technology, such as the network structure and the filler-rubber interactions.

Background

McGill, et al. theory [3] proposed an idealized model in which a three-dimensional mesh of polymer chains subdivides the imbibed solvent into cubic solvent pockets of length *x*. Only in larger cages (*nx*) the nucleation process occurs most readily. The value of n depends on segmental chain movements of polymer molecules. In addition, n is related to the cage size $n = n'x$, where n' is a constant. Finally a linear relationship between freezing point temperature (*T*) and the volume fraction of rubber (V_r) for a uniform network was found [6]:

$$T = T_0 + \frac{4\gamma T_0}{3n'\Delta H}\cdot V_r \qquad (1)$$

Where the y intercept value is the freezing point of the pure swelling solvent, and the slope is a combination of constants, being γ the strain energy per interfacial area, and ΔH the enthalpy of the freezing process. Therefore, for a given V_r there may exist only one uniformly crosslinked network that presents the maximum freezing point depression.

McGill et al. theory is based in a traditional four functional crosslink network ($\phi = 4$) and does not consider the possibility of formation of intensely crosslinked areas that act effectively as a crosslink with a higher functionality, namely cluster. But, it is well know that the network structure is not defined by the amount of crosslink and their spatial distribution, but also by the type of the network. Therefore, to generalize this theory for arbitrary crosslink functionality and realize a complete study of the network structure it was taken account that polymer chain movement not only depends on the density of the crosslinks but also on its functionality. It was expected that the increment in crosslink functionality causes restrictions in polymer chains movement, being narrower the size distribution of cages where nucleation process must occur. So we propose a new expression of *n* [8]:

$$n = n''x\,\frac{2}{(\phi - 2)} \qquad (2)$$

Therefore a new linear relationship is predicted for a uniform crosslinking with an arbitrary functionality:

$$T = T_0 + \frac{2\gamma T_0(\phi - 2)}{3n''\Delta H}\cdot V_r \qquad (3)$$

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Results and discussion

Swollen natural rubber (NR) networks were studied by measuring the freezing point depression of cyclohexane. Two curing agents, such as benzene-1,3 disulfonylazide (BSA) and dicumyl peroxide (DPC) were used at several proportions to obtain compounds with different crosslink density. BSA compounds were vulcanised at 105 °C to ensure that azides react to olefinic double bond of NR according to a cycle-addition mechanism, forming a four-functionality crosslink. Vulcanisation temperature of DCP compounds was varied from 140 °C to 180 °C to study variations in network structure. Determination of freezing point temperature was carried out using samples swollen in cyclohexane for 3 days and cooling it at 5 °C min^{-1} in a Mettler Toledo differential scanning calorimeter (DSC 822^e). Representation of freezing point temperature versus Vr is shown in *Fig. 1*.

Both, NR-BSA and NR-DCP compounds vulcanised at 105 °C and 180 °C, respectively, show the linear behaviour predicted for a homogeneous crosslinked network. Differences in the slope are a fact that cannot be explained by McGill theory, but the ϕ parameter introduced in (3) allows related it to changes in the crosslink functionality. When both slopes are compared, assuming four functionality in NR-BSA crosslink, it can be concluded that functionality of NR cured with DCP at 180 °C is approximately equal to 5 (equal percentage of crosslinks with a functionality of 4 and 6).

DCP compounds vulcanised at lower temperatures (from 140 to 170 °C) showed an intermediate behaviour with a non linear relationship, attributed to a heterogeneous network. Samples cured at low temperatures (140–150 °C) and low proportion of peroxide (1–2 phr) show freezing points similar to the samples vulcanised with BSA. Therefore, it can be expected that these samples are formed principally by four functionality crosslinks.

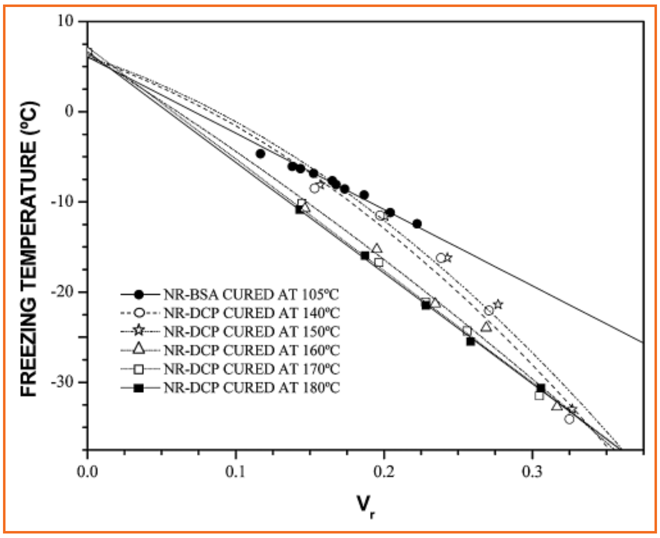

Fig. 1. Cyclohexane freezing point versus volume fraction of rubber (V_r) in swollen NR vulcanizated with BSA and DCP [8]

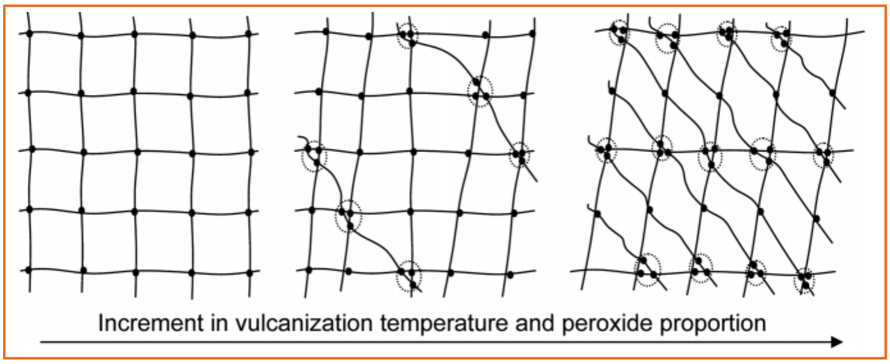

Fig. 2. Theoretical network models proposed to explain experimental freezing point depression results in NR-DCP compounds

However, when vulcanisation temperature or peroxide proportion are increased, the behaviour is displaced toward the samples vulcanised with peroxide at 180 °C. Therefore, it can be concluded that clusters with an overall functionality of 6 appear progressively in the matrix with the vulcanisation temperature or peroxide proportion. This process is illustrated in *Fig. 2*.

To corroborate these results, the variation of glass transition temperature (T_g) as a function of the peroxide percentage has been evaluated. It is observed that T_g value increased with the temperature at low Vr, but this difference is practically negligible at high Vr as can be seen in *Fig. 3*.

It can be attributed to the fact that samples vulcanised at 170 °C have higher functionality, so movements of chains are more limited. At higher DCP content, network is formed in the same proportion by crosslinks with a functionality of 4 and 6 (overall), independently of the vulcanisation temperature. This fact is the cause of the variations in mechanical properties shown in *Table 1*.

On the other hand, following the tube model theory of elasticity [9–10], it is

Tab. 1. Mechanical properties of DCP compounds vulcanised at 150 and 170 °C

	DCP 1 phr		DCP 2 phr		DCP 3 phr		DCP 4 phr		DCP 6 phr	
	150	170	150	170	150	170	150	170	150	170
Modulus 100 %	0.53	1.02	0.80	1.62	1.14	2.33	1.31	–		–
Modulus 300 %	1.03	2.25	1.76	4.22	–	–	–	–	–	–
Modulus 500 %	1.71	4.19	3.05	–	–	–	–	–	–	–
Tensile strength (MPa)	12.1	5.51	14.2	7.13	4.40	3.22	1.78	1.23	0.95	0.96
Elongation at break %	900	600	850	430	300	145	140	75	40	45

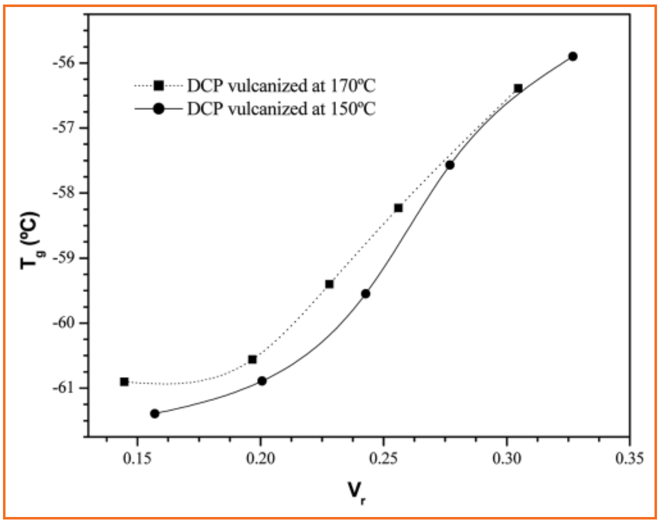

Fig. 3. Variation of Tg with the DCP content in the samples vulcanised at 150 °C and 170 °C. (Ref 8)

well known that there is a uniaxial stress-strain relation, which consists of two contributions:

$$\sigma_M = G_c + G_e f \quad (4)$$

Where σ_M is the Mooney stress, f is a function of the macroscopic strain ratio (λ), and G_c and G_e are the elastic modulus that corresponds to the crosslink and entanglement constraints, respectively. G_c depends of the number of crosslinks (N_j) and their functionality (ϕ_j), as well as the absolute temperature and the Boltzmann's constant:

$$G_c = kT \sum_{j=1}^{n} \left(\frac{\phi_j - 2}{2} \right) N_j \quad (5)$$

Therefore, it is possible to calculate the G_c value of a compound when the number of crosslinks is known, assuming a functionality equal to 4. Then, these values can be measured by a uniaxial stress-strain experiment, and to assume that differences are caused by crosslinks with different functionality. The variations between the values of G_c calculated theoretically and measured experimentally in samples with a DCP content of 1 phr are summarized in *Tab. 2*.

It was observed that differences between the G_c values calculated and measured are increased with the vulcanisation temperature. This fact confirms that the formation of high functionality crosslink is induced by the vulcanisation temperature. These clusters are the cause of the decrease in mechanical properties of the compounds.

On the other hand, freezing point temperature is caused by restriction of movement of polymer chains, so it can be used to characterize rubber-filler interactions. The improved properties of these compounds are only achieved when an exfoliated nanocomposite is formed. Polymer nanocomposites structure has been typically established by means X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. In this way three compounds were studied by freezing point depression (*Tab. 3*).

It is appreciated that the freezing point depression, ΔT, in the unmodified clay vulcanizates is lower than in unfilled compounds. This is probably because of the absence of compatibility between the unmodified filler and rubber, giving rise to the formation of phase-separated composites. When the vulcanizates contain fillers that do not form bound rubber will, on swelling, give rise to vacuoles around filler particles [11]. Therefore, the freezing point of the solvent in such vulcanizates should be higher than in the unfilled material, since freezing will be initiated in the vacuoles. However, it is appreciable the increase in freezing point depression in organoclay composites, which suggest a tighter network has been formed. Nevertheless, the inclusion of reinforcing fillers such as carbon black increases the Vr in the swollen vulcanizate but was accompanied by a slight decrease in the freezing-point depression. This increase has been explained by the fact that the uniform dispersion of nanometer layers into NR matrices gives rise to a strong filler-matrix interaction, which reduces chain mobility and therefore causes freezing point depression. Hence, in order to estimate the real effect of the organoclay, the freezing point depression measurements were evaluated at similar crosslinking density (see compounds denominated natural rubber 2 and NR/organoclay 2, in *Tab. 4*). It can be observed that even at the same crosslinking density, ΔT increases by adding organoclay. These results suggest that the organoclay not only increases the crosslinking density of the rubber but also restricts the size of solvent cages in which nucleation takes place, hindering the formation of solvent crystalline nucleus

Tab. 2. Network parameters of compounds with 1 phr of DCP at different temperatures

	Vulcanization Temperature			
	150	160	170	180
Crosslinks (crosslink/cm^3)*10^{-19}	3.01	2.96	2.86	2.36
G_c Theoretical (MPa)	0.1220	0.1198	0.1159	0.0956
G_c Experimental (MPa)	0.1200	0.1206	0.1212	0.1379
ϕ = 4 (%)	100	97.6	93.5	53.1
ϕ = 6 (%)	0	2.4	6.5	46.9
Tensile Strength (MPa)	12.10	6.52	5.51	5.16
Elongation at break (%)	900	625	583	575

Table 3. Crosslinking density and freezing point depression measurements

Compound	Vr	n, mol.cm^{-3}	ΔT, °C
Natural Rubber	0.1619	8.97*10^{-5}	15.6
NR/clay	0.1372	3.98*10^{-5}	14.2
NR/organoclay	0.2096	1.61*10^{-4}	17.7

Formulation of the compounds (phr units): Natural rubber, 100; Zinc oxide, 5; Stearic acid, 1; Sulphur, 2.5; Benzothiazyl disulfide (MBTS), 1; Phenyl beta naphtyl amine (PBN), 1 and filler (clay and organoclay), 10

Tab. 4. Freezing-point depression of two compounds				
Compound	MBTS[a)],phr	Organoclay[a)],phr	Vr	ΔT, °C
Natural Rubber 2	2	–	0.1952	15.7
NR/Organoclay 2	0.5	10	0.1903	16.2

[a)] The other components of the vulcanising system are the same as described in Table 3

within the swollen gel [12]. It can be concluded that the addition of the organoclays gives rise to strong filler-rubber interactions, which limits segmental movement of the polymer chains. This restricts the size of solvent cages that can form, thus decreasing the nucleus size and consequently depressing the freezing point at a given volume fraction of solvent.

Figure 4 shows the X-ray diffraction patterns of the clay and organoclay and their respective NR composites, confirming the previous results. NR/clay composite shows a slight decrease in the diffraction angle, attributed to the formation of a conventional composite at a microscopic scale. However, in the case of NR/organoclay nanocomposites, this diffraction disappeared because of the higher layer spacing resulting from insertion of the elastomer into the galleries of the organophilic saponite, this indicates that an exfoliate structured is formed. These results were confirmed by TEM images (*Fig. 5*).

Conclusions

Measurements of freezing-point depression of a solvent imbibed in rubber vulcanizates is a simple method to determine network structure in unfilled rubber compounds as well as rubber nanocomposite structures, which are two of the main research topics of rubber science and technology.

A novel linear relationship between freezing point temperature and volume fraction of rubber for a uniform network with an arbitrary functionality was established. In this work, it was proven that variation of dicumyl peroxide and/or temperature of vulcanisation changes network structure in NR compounds. Formation of clusters is the cause of the decrease in network elasticity, transforming it into a stiff network and bringing about catastrophic effects on the ultimate tensile strength. Thus, clusters could be seen as high crosslink areas that inhibit the correct stress distribution, accumulating higher stress areas where microcracks can be formed and enhance crack propagation.

On the other hand, measurement of the freezing point depression of a solvent in swollen gels provides a ready method of estimating polymer nanocomposite structure. As the freezing point depression is experimentally easy to determine, it can be used as a routine measurement. It is a suitable completion of the well-known methods of nanocomposites characterization, such as X-ray diffraction and transmission electron microscopy.

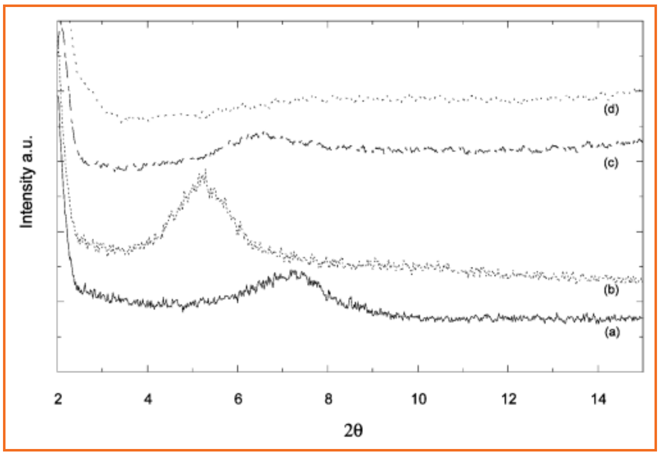

Fig. 4. XRD patterns of clay (a), organoclay (b), NR/clay composite (c) and NR/organoclay (d). (Ref 12)

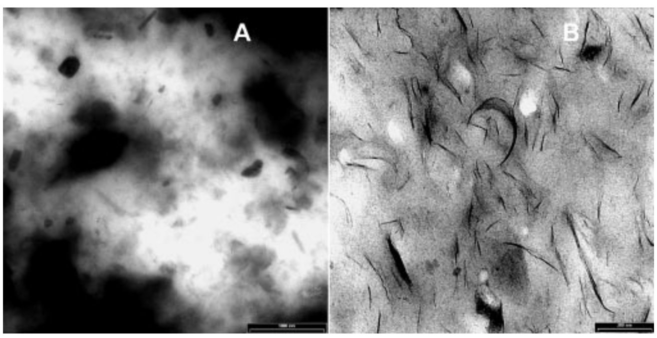

Fig. 5. TEM images of NR/clay composite (a) and NR/organoclay nanocomposite (b). (Ref 12)

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References

[1] W. Kuhn, E. Peterli, H. Majer, Rubber Chem. Technol. **33** (1960) 245.

[2] B. B. Boonstra, F. A. Heckman, G. L. Taylor, J. Appl. Polym. Sci. **12** (1968) 223.

[3] D. Honiball, M. G. Hudson, W. J. McGil, J. Polym. Sci. Part B: Polym. Phys. **26** (1988) 2413.

[4] H. Oikawa, K. Murakami, J. Macrmol. Sci. Phys. **B28** (1989) 187.

[5] C. L. Jackson, G. B. McKenna, Rubber Chem. Technol. **64(5)** (1991) 760.

[6] J. H. A. 12.Grobler, W. J. McGill, J. Polym. Sci. Part B: Polym. Phys. **31** (1993) 575.

[7] E. W. E. van Bevervoorde-Meilof, D. van Haeringen-Trifonova, G. J. Bancos, L. Does, A. Bantjes, J. W. M. Noordermeer, Kautsch. Gummi Kunstst. **7–8** (2000) 426.

[8] J. L. Valentín, A. Fernández-Torres, A. Marcos-Fernández, A. Rodríguez, L. González, Polymer. Submited.

[9] G. Heinrich, E. Straube, G. Helmis, Adv. Polym. Sci. **85** (1988) 33.

[10] T. A. Vilgis, G. Heinrich, Macromol. Theory Simul. **3** (1994) 271.

[11] G. Kraus, J. Appl. Polym. Sci. **7** (1963) 861.

[12] M. A. López-Manchado, J. L. Valentín, B. Herrero, M. Arroyo, Macromol. Rapid Commun. **25** (2004) 1309.