Reinforcement of Natural Rubber with Organoclays

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Introduction

Organoclays are clays with organic interlayer ions. Most commonly used is montmorillonite, which consists of silicate sheets ~1nm thick and 30-500nm in diameter. The organic ions have the dual effects of making the clay's surface more hydrophobic and physically increasing the separation of the clay sheets. This enables the sheets to delaminate within a polymer. Polymer/clay nanocomposites were first developed by Toyota in 1993[1], and since then have been the subject of much interest[2].

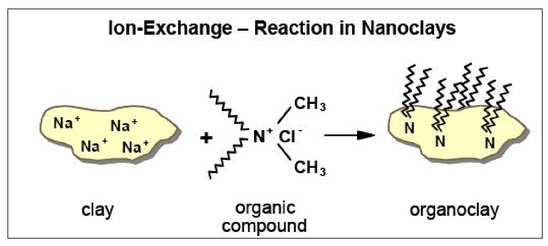


Figure 1: Production of Organoclays

The organoclay used in this work is Nanofil 8, (Süd-Chemie) with distearyldimethylammonium chloride [DSDMAC] as the modifying agent.

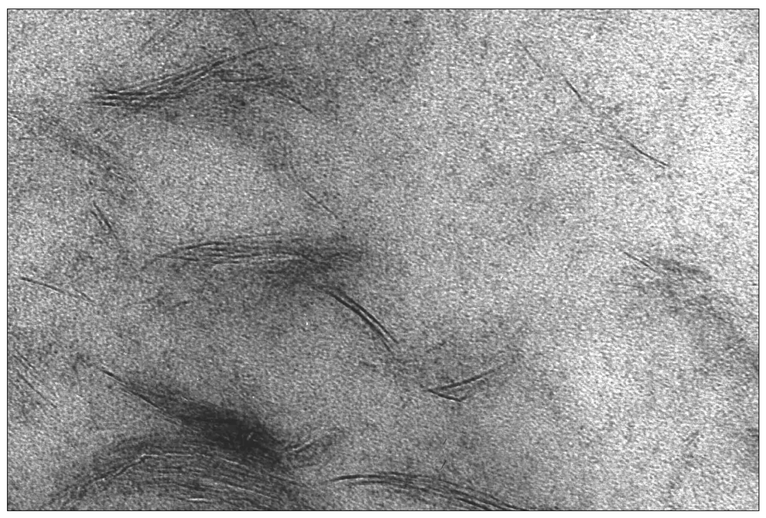
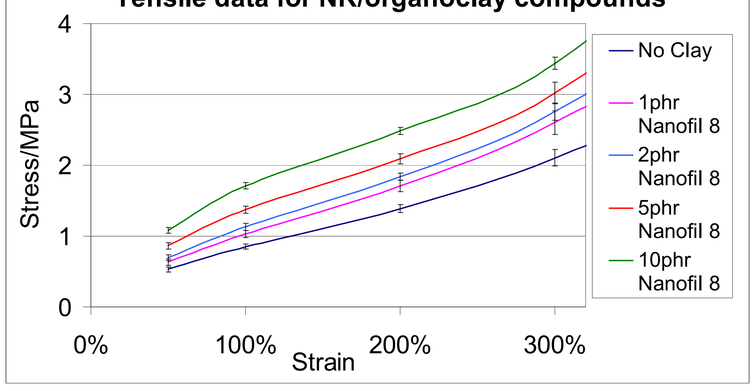


Figure 2: TEM micrograph of Nanofil 8 in NR

Tensile Properties

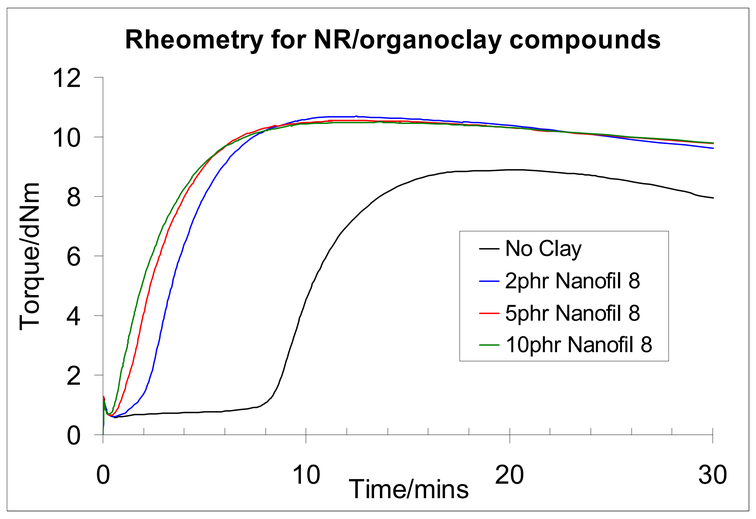
- Tensile stress/strain measurements were made for five NR/clay nanocomposites
- Organoclay loading level was between 0 and 10 parts per hundred parts of rubber (phr)
- Four separate series of these compounds were produced to estimate the variability



- 10phr produces a large increase in tensile modulus at all strains
- Even 1phr of Nanofil 8 provides a noticeable level of reinforcement
- As strain increases the relative contribution made by Nanofil 8 decreases

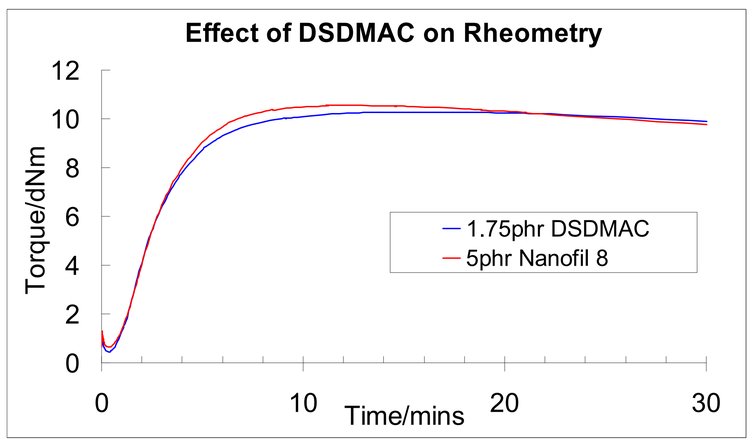
Scorch Problems and Control

- Rheometry was performed on four different NR/organoclay nanocomposites at 150°C.

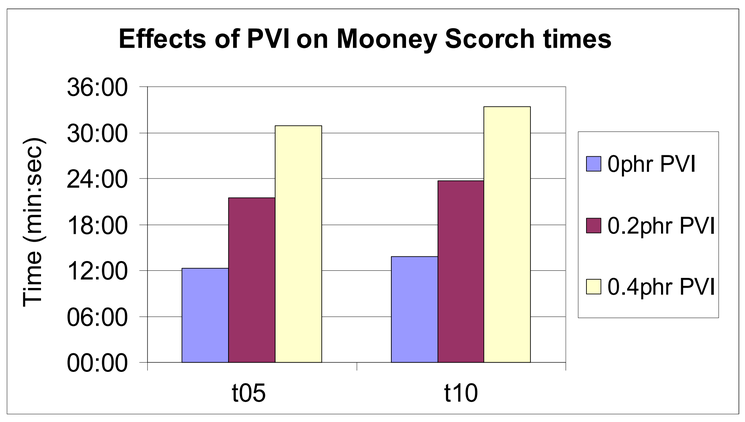


- Organoclay dramatically reduced the scorch period at the beginning of the cure
- Concomitant decrease in cure times observed

As unmodified clay has little effect on scorch, 1.75phr of DSDMAC (equivalent to the amount in 5phr of Nanofil 8) was added to an unfilled compound to determine if it was responsible for the scorch problems.



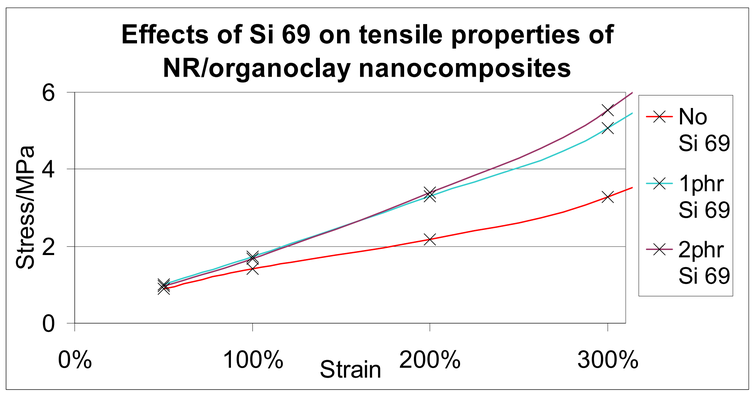
The rheometry shows that the DSDMAC has the same effect on the cure as the organoclay, and so is likely to be the cause of the problem. As the reduced scorch could be a major disadvantage for NR/clay nanocomposites, it was necessary to find a way to counteract it. The best method found of increasing scorch used N-(cyclohexylthio)phthalimide[3], a pre-vulcanisation inhibitor available as Santogard PVI.



Adding 0.4phr of Santogard PVI to a compound containing 5phr of Nanofil 8 increased the scorch at a given temperature by >150%, without affecting the physical properties of the cured compound.

Silane Coupling Agents

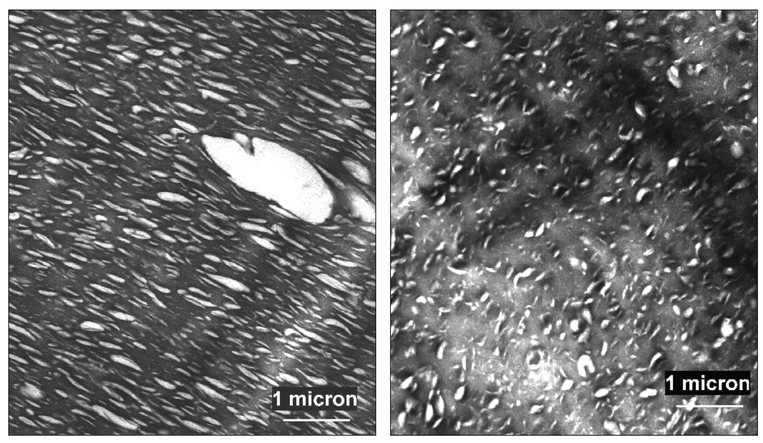
It had been reported[4,5] that silane coupling agents such as Si 69 increased reinforcement with organoclays. Tests with Si 69 and Nanofil 8 showed that the silane increased tensile modulus, particularly at strains >100% .



In addition, network visualisation microscopy was performed on these compounds. The basic process of network visualisation is:

- Swell a vulcanisate in styrene
- Polymerise the styrene
- Stain the rubber network
- Visualise using TEM.

The styrene preferentially enters the spaces between the clay sheets and the rubber network, leading to polystyrene voids surrounding the clay particles.



Figures 3 and 4: Network visualisation micrographs of nanocomposites containing 0phr and 2phr of Si 69 respectively

The voiding is reduced in the compound containing Si 69, demonstrating an increased amount of rubber-filler interaction. The alignment of the clay visible in Figure 3 is caused by milling and curing under pressure. This is lost in Figure 4 because the coupling to the rubber reduces the clay's freedom to move.

Conclusions

- Organoclays produce a significant increase in tensile modulus in Natural Rubber
- Organoclays produce a dramatic reduction in scorch times, caused by the DSDMAC used as the modifying agent
- Using a pre-vulcanisation inhibitor can counteract this scorch reduction
- Si 69 further increases tensile modulus by increasing rubber-filler interaction

References

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Acknowledgements

Thanks to those people at TARRC and at Queen Mary College who have provided assistance with this work. Thanks also go to Süd-Chemie, Degussa and Flexsys for supplying materials.