



**DUTCH-BELGIAN BEAMLINE  
AT ESRF**

**EUROPEAN  
SYNCHROTRON  
RADIATION FACILITY**




## **Experiment Report Form**

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

(next page)



	<b>Experiment title:</b> Relaxation behavior of thermoreversibly cross-linked rubbers based MAn-g-EPM	<b>Experiment number:</b> 26-02-413
<b>Beamline:</b> BM26B	<b>Date(s) of experiment:</b> From: 7-2-2008 To: 11-2-2008	<b>Date of report:</b> 5-3-2008
<b>Shifts:</b> 12	<b>Local contact(s):</b> Giuseppe Portale	
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## Report:

The main objective of this proposal was to relate microscopic structural changes in modified ethylene-propylene copolymers with grafted maleic anhydride units (MAn-g-EPM) and thermoreversibly cross-linked with different hydrogen bonding units to the processing characteristics via temperature-dependent and macroscopic stress relaxation experiments, but it was not possible to do most of the tensile experiments due to unstable beam conditions, so we restricted ourselves to temperature dependent measurements with long exposure times. Trial experiments with a special pressure cell were because of this also unsuccessful.

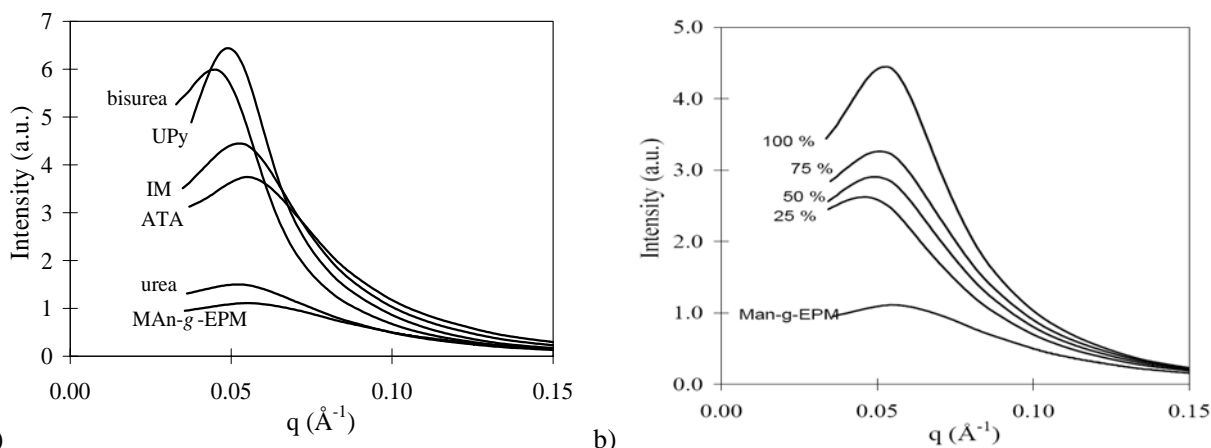
Maleated elastomers are of special interest, because of the high and versatile reactivity of the grafted maleic anhydride groups. The materials were converted into thermoreversible rubbers, i.e. thermoset properties at service temperature and processable at elevated temperatures, using hydrogen bonding. The strength of a single hydrogen bonding donor and acceptor pair is limited, but it is in principle relatively easy to improve the strength of hydrogen bonds by combining them in arrays of hydrogen bonding sites. Several different arrays have been successfully used in the preparation of reversible polymer networks, such as phenyl-urazole groups, imide-diaminopyridine arrays, ureido-pyrimidone groups, and bisurea groups. Recently, Chino et al. reported on thermoreversibly cross-linked rubbers obtained by the modification of maleated rubbers with 3-amino-1,2,4-triazole (ATA), for which the authors suggested a six-point hydrogen bonding structure. Leibler and co-workers developed imidazolidone groups, called UDETA, which are capable of forming double hydrogen bonding dimers, with a good thermal stability. We noticed in earlier work that microphase separation into polar MAn-rich aggregates occurs for MAn-g-EPM and all cross-linked materials, which act as physical cross-links. The cross-link density does not change upon modification, but the strength of the aggregates is significantly increased. One of the remaining questions was how the materials deform, both at room temperature, important for long-term properties, and at elevated temperatures, important for processing, and what is the importance of the number of aggregates and the relative strength of the aggregate, which can be controlled by the hydrogen bonding unit, during deformation.

For all tensile experiments the Linkam tensile stage, recently purchased by DUBBLE, was used, while the standard Linkam furnace was used for the temperature dependent runs. Small tensile bars were prepared from compression molded films. All modifications were aimed at 100 % conversion of the anhydride groups. The octadecylamide-acid and the (bis)urea materials were obtained as follows. Typically, MAn-g-EPM was dissolved THF at 80 °C, after which the solution was cooled down to RT. The required amount of reactant was added to the solution, which was stirred for 1 h. The products were precipitated in acetone and dried for at least one day at 50 °C under vacuum. The (bis)urea materials were compression molded between Teflon in a Collin press at 150 °C, while the octadecylamide-acid was compression molded at 80 °C. The di-acid was obtained via hydrolysis of the anhydride groups during exposure of compression-molded films of MAn-g-EPM for several days at RT. The modification reactions with ATA and IM were performed in the melt on a Haake Rheomix OS internal mixer. The required amount of MAn-g-EPM was charged to the mixer at 150 °C and homogenized for 1 min. Next, the required amount of hydrogen bonding unit was added, followed by mixing for 5 min at 100 rpm. The products were compression molded for 20 min at 180 °C.

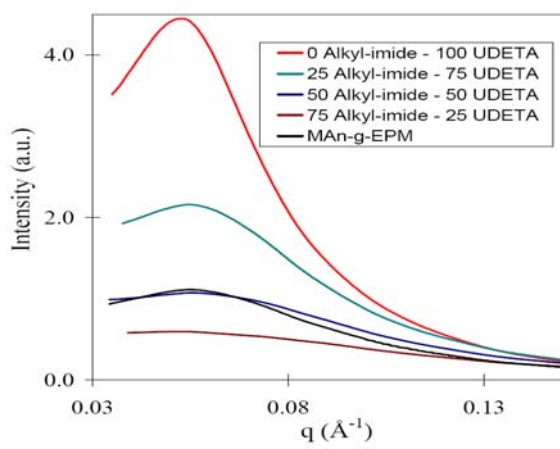
Figure 1a shows that broad scattering peaks are present for all hydrogen-bonded materials, which indicates that the microphase-separated aggregates persist after modification. The (large) increase in scattered intensity compared to

MAN-g-EPM indicates that the (polar) arrays mainly reside within the aggregates. For the materials with different hydrogen bonding arrays, the highest electron density differences and, concomitantly, scattering intensities are observed for the highly polar arrays and, to a lesser extent, for IM and ATA. The urea material obviously contains groups with lower polarity than the bisurea material, which explains its lower intensity. The peak intensities for the di-acid, octadecylamide-acid and  $\text{NH}_3$ -imide were only somewhat higher than for the MAN-g-EPM precursor (not shown here), since the respective functional groups are only slightly more electron dense than the anhydride groups, as discussed in the previous study. The position of the peak maximum shifts to lower  $q$ -values for the different arrays with the following order in peak position: bisurea < UPy < urea < IM < ATA < MAN-g-EPM, while the scattering peak becomes narrower as well. The introduction of the hydrogen bonding arrays results in stronger anchoring of the corresponding chain segments to the aggregates and, concomitantly, in a larger restricted mobility layer surrounding the aggregates, which explains the changes in the SAXS profiles. Consequently, the aforementioned order in peak position may be indicative of the relative strengths of the arrays, although care must be taken, since differences in the modification reactions also influence the aggregation process. The peak positions did not change significantly for the octadecylamide-acid, the  $\text{NH}_3$ -imide and the di-acid compared to MAN-g-EPM, because of their relatively weakness.

One of the parameters to control the aggregation was to partially convert the MAN-groups, as shown in Figure 1b, or block the anhydride groups by a reaction with mono-functional amines, the remainder of the anhydride groups is then cross-linked with the hydrogen binding unit. The effect of partial blocking of the unreacted MAN-groups after modification with UDETA is shown in Figure 2. This can even be strengthened by the addition of a so-called processing oil, which selective swells the apolar matrix. It is evident that the aggregation can be controlled. Especially the temperature-dependent measurements (not shown here) indicated that for the partially blocked systems, the aggregation can be suppressed at higher temperatures. This is very important for the processing of these materials.



**Figure 1.** SAXS profiles of a) MAN-g-EPM modified with different multiple hydrogen bonding arrays after compression molding at 175 °C and b) MAN-g-EPM modified with different levels of UDETA.



**Figure 2.** SAXS profiles of a) MAN-g-EPM modified different levels of UDETA and remaining MAN-groups reacted with alkyl-amine to form an imide and b) systems extended with processing oil.

## References

- Van der Mee, M.A.J. PhD-thesis Eindhoven University of Technology, 2007.
- Van der Mee, M.A.J., Goossens, J.G.P., van Duin, M. *Rubber Chemistry and Technology*, 81, 2008.
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