Detecting onset of chain scission and crosslinking of \(\gamma\)-ray irradiated elastomer surfaces using frictional force microscopy

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Abstract

We report here that atomic force microscopy (AFM) in frictional force mode can be used to detect the onset of chain scission and crosslinking in polymeric and macromolecular samples upon irradiation. A systematic investigation to detect chain scission and crosslinking of two elastomers, (1) ethylene-propylene-diene monomer rubber and (2) fluorocarbon rubber, upon \(\gamma\)-ray irradiation has been carried out using frictional force microscopy (FFM). From the AFM results we observed that both the elastomers show a systematic smoothening of its surfaces, as the \(\gamma\)-ray dose rate increases. However, the frictional property studied using FFM of the sample surfaces show an initial increase and then a decrease as a function of dose rate. This behaviour of increase in its frictional property has been attributed to the onset of chain scission, and the subsequent decrease in friction has been attributed to the onset of crosslinking of the polymer chains. The evaluated qualitative and semi-quantitative changes observed in the overall frictional property as a function of the \(\gamma\)-ray dose rate for the two elastomers are presented in this paper.

1. Introduction

Crosslinking of polymer chains improves the physical properties of rubber [1, 2]. Crosslinking is the key to the elastic, or ‘rubbery’, nature of any elastomer. On crosslinking, the glass transition temperature \(T_g\) [3,4], elasticity [5,6] and tensile strength [5–7] of the rubber increase and its elongation [5,6,8], wear and friction decrease [9]. These properties warrant safety and reliability of the rubber. Crosslinking is the process of forming a three-dimensional network structure from a linear polymer by a chemical or a physical method. The crosslinking in rubber can be achieved by (1) conventional thermal curing using chemical reagents (first-generation technology), and (2) physically inducing crosslinking by high-energy radiation (second-generation technology). The second method is gaining importance because of certain advantages. Radiation generates radicals and ions in the medium without any use of additional chemical catalysts and hence the electrical property of the rubber can be almost preserved and can be carried out at controlled temperature. Radiation induced crosslinking is a physically induced chemical reaction which is easier and preferable for continuous curing of the rubber. Crosslinking reaction pathways and mechanisms are still not completely understood and whether the reaction occurs mainly via radical or an ionic pathway or both is still one of the fundamental issues. But it is believed that upon irradiation by...
high energy radiation such as x-ray, proton, electron, neutron or γ-ray, high local concentrations of free radicals are formed in the rubber molecules.

Radiation causes chain scission of the polymer causing production of excited macromolecular radicals. They polymerise, combine or crosslink only beyond a certain critical concentration of free radical generation. The physical property of the irradiated rubber is determined by the competition between the rate of chain scission and crosslinking i.e. on the ratio of crosslinking to chain scission. Numerous studies related to the modification of the physical properties of polymers upon high energy radiation have been carried out [10–19]. In this paper we report a systematic study on the evolution of the local frictional property of elastomers upon γ-ray irradiation. The local frictional property has been studied using atomic force microscopy (AFM) in a frictional force mode (frictional force microscopy–FFM). To our knowledge no study to detect the onset of chain scission and crosslinking on elastomers upon γ-ray irradiation using FFM has been reported so far. We would like to show in the present study that FFM can be used to detect the competition between chain scission and crosslinking of the polymer upon high energy irradiation.

2. Experimental

Two sets of samples (1) ethylene-propylene-diene monomer rubber (EPDM) with the chemical formula [-CH2-CH2-CH2-CH(CH3)-]n and (2) fluorocarbon rubber (terpolymer of vinylidenefluoride, hexafluoropropylene and tetrafluoroethylene, FKM) with the chemical formula [-CH2CF2-CF2-CF(CF3)-CF2CF2]-n, with four samples for each set have been investigated to study the evolution of frictional properties upon γ-ray irradiation. The virgin samples were prepared by moulding and were then irradiated with γ-rays at room temperature and under ambient conditions for different dose rates but maintaining the total dosage as 103 Gy. Three different dose rates of 14 Gy h−1, 61.3 Gy h−1 and 110 Gy h−1 were selected for the present study. Three samples from both the sets were irradiated with these dose rates.

We carried out the present investigation using a scanning probe microscope from NT-MDT, Russia [20]. The AFM and the FFM measurements were carried out in contact mode with the stiffness constant of the cantilever around ~0.1 N m−1 having a radius of curvature of the tip ~100 Å. The normal force applied for the topographic and frictional (torque) measurement was around ~25 nN. All measurements were done ex situ at room temperature and at ambient conditions. The scan size for all the samples were 30 μm × 30 μm.

3. Results and discussion

In the frictional force microscopic technique, one can measure simultaneously both the topography and the frictional property by recording the current signals 1ver proportional to normal bending of the cantilever (which carries the AFM tip) and 1tor which is proportional to torsional bending of the cantilever simultaneously. The current signals 1ver represent the topographical height distribution and the current signals 1tor represent the frictional component of the sample surface in that region [21–24]. This is described schematically in figure 1. In figure 2 we show schematically the data analysis scheme adopted in this investigation. The current signal 1tor due to the torsional bending of the cantilever during a line scan along the forward (left to right) and backward (right to left) directions is shown. Since the torsional angle (β) changes sign when moving in the opposite direction the current signal 1tor also changes sign. We have also shown in figure 2 a histogram of the torsional bending of the cantilever proportional to the current 1tor. We would like to mention that throughout our experiment on all the samples the position of the laser beam
on the cantilever was kept on the same spot and the scan
speeds were also maintained the same. This is very important
since we know that variation of the position of the laser beam
on the cantilever determines the amplitude of bending of the
cantilever and we have also observed that the speed of the
cantilever affects the measurement of its bending and frictional
property. This aspect of velocity dependent frictional property
is under progress with simpler sample surfaces.

In figure 3 we show the topographical AFM images of the
EPDM samples: (a) being that of the virgin sample and images
(b)–(d) being those of the samples with increasing dose rate.
The roughness values are tabulated in table 1. In figure 3
we can clearly see the topographical changes as a function of
irradiation dose rate. The virgin sample (figure 3(a)) shows
agglomeration of grains (grains are marked by circles and
agglomerates i.e., collections of grains are labelled as region
A, B and C). With the lowest dose rate, the agglomerates are
broken and the grain sizes are seen to increase (figure 3(b)).
For the next higher dose rate (figure 3(c)), the grain sizes are
smaller than in figure 3(b) but the grains start to agglomerate
and with the highest dose rate (figure 3(d)), the agglomerates
and the grain size do not change any further.

In figure 4 we show the topographical AFM images of the
FKM samples: (a) being that of the virgin sample and images
(b)–(d) are those of the samples with increasing dose rate.
From the AFM image we observe that the virgin FKM sample
(figure 4(a)) is smoother than the virgin EPDM (figure 3(a))
sample, as also indicated by the value of the rms roughness
tabulated in table 1. For the low irradiation rate (figure 4(b))
there seems to be not much change in the topography but the
rms roughness decreases (see table 1). For the next higher
dose rate (figure 4(c)) blisters (seen as small light spots in the
image) start appearing (seen in and around the region marked
by the circle). For the highest dose rate (figure 4(d)) the
blisters formed are similar and there is no marked change in
the topography with respect to figure 4(c). As will be seen
later from the FFM analysis, the FKM sample shows phase
separation and these blisters may be grains of the second phase.
The mounds, marked by arrows, are present in all the samples.
We would like to point out here that since the experiments
were performed on different samples and it is not an in situ
measurement, the variation in the rms roughness was found to
be ≤10%. The topographical images give only a qualitative
picture of the surface modifications upon any radiation. To

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**Table 1.** Roughness obtained from AFM images, average current signals corresponding to torsional bending of the cantilever at maximum N or shoulders for FKM sample obtained from figure 6(a) and b for phase I in EPDM and FKM samples and phase II for the FKM samples and Δμ/μ for each of the phases of EPDM and FKM samples.

| Sample          | Roughness (nm) | I_{av,avg} (nA) | Δμ/μ | Δμ/μ Ph I Phase II Ph I Phase II |
|-----------------|----------------|-----------------|------|-------------------------------|
| EPDM (virgin)   | 150            | 0.2             | —    | —                             |
| EPDM (14 Gy h⁻¹) | 110            | 1.05            | 4.3  | 4.3                           |
| EPDM (61.3 Gy h⁻¹) | 105            | 0.43            | 1.2  | 1.2                           |
| EPDM (110 Gy h⁻¹) | 100           | 0.47            | 1.3  | 1.3                           |
| FKM (virgin)    | 90             | 0.27            | 0.10 | 0.10                          |
| FKM (14 Gy h⁻¹) | 75             | 6.4             | 0.10 | 22.7                          |
| FKM (61.3 Gy h⁻¹) | 65             | 2.8             | 0.24 | 9.4                           |
| FKM (110 Gy h⁻¹) | 55             | 1.3             | 0.28 | 3.8                           |
detect the process occurring at the molecular level, we have carried out FFM measurements on these samples. In the following paragraphs we would like to address these questions:

(a) What happens to the frictional properties of these elastomers upon various γ-ray dose rates?
(b) Does the frictional property decrease with the decrease in the roughness due to irradiation?

In figure 5 we show a typical FFM image of the EPDM sample taken during both the forward (i.e. left to right scan directions). We observed contrast inversion when the scanning direction is reversed, as explained schematically in figure 2. The FFM images of the FKM samples showed similar contrast inversion. One can quantitatively obtain the overall change in the frictional property by plotting a histogram for both the scan directions as described schematically in figure 2. In figure 6((a) and (b)), we have plotted this histogram i.e. the number of points (\(N\)) versus torsional bending (proportional to \(I_{\text{tor}}\)) obtained from the FFM images for the EPDM samples and the FKM samples respectively. Both the sample sets show a maximum in the histogram for scans obtained in both the scan directions. The average value \(I_{\text{tor,avg}}\) is defined as

\[
I_{\text{tor,avg}} = \frac{I_{\text{tor,max}}(+) + |I_{\text{tor,max}}(-)|}{2},
\]

where \(I_{\text{tor,max}}(+)\) and \(I_{\text{tor,max}}(-)\) are the values of \(I_{\text{tor}}\) each corresponding to the maximum \(N\) for the forward and reverse scan directions respectively and are tabulated in table 1 for both the sets. We observe from figure 6(a) that the virgin EPDM sample shows a very low frictional coefficient compared with the irradiated samples since the maximum of the histogram has the lowest torsional bending (see curve (a)) for this sample. On irradiation with the lowest dose rate the maximum of the histogram shifts to higher torsional bending (\(I_{\text{tor}}\)), indicating an increase in the overall frictional coefficient (see curve (b)). On a further increase in the dose rate we observe that the maximum shifts back to lower value of \(I_{\text{tor}}\), indicating a decrease in the overall frictional coefficient of the sample (see curve (c)). With a still further increase in the dose rate the frictional coefficient approaches a stable value. Thus we observe that the overall frictional coefficient of the sample as a function of the dose rate initially increases and then decreases and stabilizes to a lower value with an increasing dose rate. For the FKM samples the histogram shown in figure 6(b) shows a similar behaviour. At a closer look we observe an additional interesting feature, i.e. a very sharp peak at very low values of torsional bending for the FKM samples (inset of figure 6(b)). Additionally, the broad maxima becomes a shoulder to the low value peak in the histogram as the dose rate increases. These shoulders are marked by arrows in figure 6(b). In table 1, we have tabulated the broad maxima and the shoulder values of \(I_{\text{tor,avg}}\) (phase I). The two maxima in the histogram signify the existence of two distinct phases, with two different frictional coefficients. The appearance of the sharp peak on irradiation at lower values of \(I_{\text{tor}} < 0.5\, \text{nA}\) (see table 1, phase II) arises due to the formation of another phase having lower frictional coefficient. With an increasing dose rate the height of the sharp peak increases, indicating that the formation of the second phase is caused by irradiation and the quantity of this phase increases with the
respectively. We obtain two main results: increase in the dose rate. By adopting the histogram scheme we obtain two main results:

(a) The overall frictional coefficient of the sample as a function of the dose rate initially increases and then decreases and stabilizes to a lower value with increasing dose rate.

(b) Two maxima were observed in the histogram for the FKM sample, indicating generation of two distinct phases having two different frictional coefficients, whereas the EPDM sample shows only one maximum. Below we discuss the result (2) first and then the result (1) for clarity.

The observed features, i.e. double maxima, and the single maximum in the histogram can be explained as follows. The FKM sample is a copolymer consisting of three different types of monomers (1) Hexa fluoro propylene (CF$_2$=CF–CF$_3$) and (2) tetrafluoroethylene (CF$_2$=CF$_2$) having only a C-F bond and (3) vinylediene fluoride (CH$_2$=CF$_2$) having both C-H and C-F bonds. The FKM with two dissimilar bonds gets phase separated on irradiation giving rise to chemical or structural changes hence leading to two distinct phases having different distinct overall frictional coefficients. Further spectroscopic study is needed to identify the two phases. On the other hand, the EPDM sample is composed of ethylene (CH$_2$=CH$_2$) and propylene (CH$_3$=CH–CH$_3$) both having only C-H bonding and hence cannot show any phase separation. Thus, it shows only one component of the frictional coefficient on irradiation. This comparison shows that the analysis using histogram scheme reveals whether there exists different phases of materials with different frictional coefficients in the sample.

The other important result obtained from this investigation was that both the samples exhibit an overall increase in the frictional coefficient on lower dose rate and on further increase in the dose rate the frictional coefficient decreases. The change in the frictional coefficient ($\Delta \mu$) is proportional to the difference in the $I_{tor \text{ avg}}$ value for each of the irradiated samples and the value of $I_{tor \text{ avg}}$ of the virgin sample. Normalizing $\Delta \mu$ with the value of $I_{tor \text{ avg}}$ of the virgin sample, we obtain the normalized change in the overall frictional coefficient $\Delta \mu/\mu$ as

$$\Delta \mu/\mu = \frac{(I_{tor \text{ avg}})_{irr} - (I_{tor \text{ avg}})_{vir}}{(I_{tor \text{ avg}})_{vir}},$$

where the subscripts irr and vir represent the irradiated and virgin samples respectively. The calculated values of $\Delta \mu/\mu$ for both the sets are tabulated in table 1. We observe that the overall frictional coefficient ($\Delta \mu/\mu$) increases by more than 4 times for the EPDM sample and more than 20 times for the FKM sample for the $\gamma$-ray dose rate of 14 Gy h$^{-1}$ and on further increase in the dose rate, the normalized frictional coefficient decreases in both the samples. The second phase formed on irradiation for the FKM sample does not show much change in the overall frictional coefficient. The initial increase in the frictional coefficient observed in the case of both the samples upon $\gamma$-ray irradiation can be attributed to the formation of free radicals due to chain scission. Formation of free radicals
Detecting onset of chain scission and crosslinking of γ-ray irradiated elastomer surfaces

beyond a critical concentration leads to crosslinking among the macromolecular radicals at higher dose rates. The crosslinking of polymer chains due to the recombination of free radicals leads to the lowering of the frictional coefficient. The tip of the AFM adheres to these free radicals present on the sample surface, and with the onset of crosslinking the frictional coefficient decreases. Hence, one can conclude from the above experimental results that when the elastomers are exposed with higher dose rate then the probability of chain scission is larger and the macroradicals formed in close proximity promotes the crosslinking of the polymers. The low concentration of free radicals will not promote crosslinking. The local frictional property of these materials depends on the ratio of crosslinking to the chain scission. The frictional coefficient decreases with an increase in this ratio. Thus with FFM, one can detect the competitive behaviour between the chain scission and the crosslinking process.

4. Conclusion

The frictional force microscopy technique has been used to detect the onset of chain scission and crosslinking of γ-ray irradiated elastomer samples. In the present study we observe an initial increase in the frictional coefficient upon γ-ray irradiation with a low dose rate and the frictional coefficient decreases upon irradiation with a higher dose rate for both the EPDM and the FKM elastomer samples while maintaining the total dose constant. The increase in the frictional coefficient has been attributed to the formation of free radicals and the decrease in the frictional coefficient has been attributed to the onset of crosslinking. The crosslinking takes place beyond a certain critical concentration of free radicals produced. With the FFM technique we could distinguish the presence of coexisting phases with different frictional coefficients. We could infer from the reduction of the surface roughness upon γ-ray irradiation that the frictional property of the sample determined using FFM depends on the atomic and molecular interaction between the tip and the sample surface rather than on the asperities (roughness) of the sample surface. The radical formation and the crosslinking occur at the molecular level; thus FFM analysis can help in understanding these processes at the molecular level better than macroscopic tribological techniques.

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