MODIFICATION OF THERMOPLASTIC MATERIALS BY ELECTRON BEAM RADIATION

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1. ABSTRACT

Heat shrinkable tapes are used for corrosion protection of pipelines and electron beam radiation is used to achieve cross-linking. In developing new tapes it is mandatory that the new materials respond well to the e beam radiation. Cross-linking improves adhesion strength, shear performance, heat distortion and chemical resistance. In the present study copolymer of ethylene and vinyl acetate, ethyl acrylate, butyl acrylate, methyl acrylate, ethyl acrylate, butyl acrylate maleated version, and maleated Linear Low Density Polyethylene were exposed to electron beam irradiation using a 3 MEV Electron Beam Accelerator with varying doses between 4 and 16 Mrads. After the samples were irradiated the following properties were evaluated: tensile stress and elongation at break, hot modulus, gel content, shear modulus and loss tangent, thermal properties and peel adhesion. It was found that all functionalized polyethylenes did cross-link in the e-beam treatment and that the adhesive properties were not affected or did improve.

2. INTRODUCTION

Tapes for corrosion protection of pipelines make use of e beam radiation technology to achieve cross-linking. A tape is irradiated and cross-linked at room temperature. Then it is heated above the melting point and stretched out. Finally it is allowed to cool and crystallize in the stretched state, thereby fixing the elongated dimension. Once the tape is heated again, the crystallites melt and the tape can shrink back to the relaxed state. This is very similar to shrink wrap used in packaging.

An illustration of such technology is depicted in figure 1 shown in the next page. The tape is wrapped around a pipe, and after heat has been applied, it shrinks and wraps the pipe tightly. The backing of these heat shrinkable tapes is made of polyolefin which are cross-linked as described above. The adhesive in this application is a heat activated hot melt. It softens and wets out easily at the higher temperatures, but is very hard at ambient temperatures and so creates high bond strength to the pipe surface.
Ionization radiation has been found to be widely applicable in modifying the structure and properties of polymers, and it can be used to tailor the performance of either bulk materials or surfaces. More than sixty years of research in polymer radiation chemistry has led to numerous applications of commercial and economic importance. Polymers that cross link maintain their shape and useful properties at elevated temperatures—i.e., they do not flow. Generally, they have better creep, strength, resistance to impact, stress cracking, and chemical resistance. On the other hand, cross-linking can decrease wetting properties and tack.

Some of the advantages of radiation cross-linking compared to the conventional chemical cross-linking are cost, speed and the ability to cross-link preformed parts at or near room temperature, absence or reduced amounts of chemical ingredients for environmental or toxicological reasons.

Several applications, either well established or of exceptional promise for future commercial use are cited by Clough et al. publication. Examples are

- Cross-linking of polymeric foams of automotive cushions, heat insulation, buoyancy products for marine use, and sporting goods.
- Wire and cable insulation and automotive tires
- Irradiation in the processing of polymer blends to improve compatibility
- Electron beam curing of compounds; use in surface coating, printing & packaging
- Heat shrinkable products (Shrink wrap)
- Polymer chain scission; i.e. PTFE conversion into micro powders to be used as additive in inks and coatings
Surface modification and grafting; altering surface of materials, such as films, fibers, powders and molded objects, in order to enhance properties as printability, wet ability, and adhesion with other materials or with biological components.

3. OBJECTIVE

In this report some basic concepts associated to cross-linking by ionization radiation are listed which are applicable to those individuals that engage in technologies dealing with ionization radiation. In addition, a study is presented for several functionalized polyethylene samples in terms of their radiation response, when exposed to electron beam irradiation using a Dynamitron Lineal Accelerator of 3 MeV, in a dose range from 4 to 16 Mrads (40 to 160 kGy). These materials are used to develop heat activated hot melt adhesive formulations which are used to manufacture heat shrinkable tapes. The purpose of this investigation is to establish if the materials cross-link in the e beam treatment and if there are any impacts on the adhesive properties.

4. POLYMERS TRANSFORMATION BY ELECTRON BEAM RADIATION

4.1 Describing the electron beam process
- It is a high energy interaction; the energies involved are much greater than the electron binding energy of any electron to a nucleus.
- It differs from (UV) irradiation in which the energy carried per particle (photon) is lower than the ionization energy of an atom or molecule.
- Covalent bonds are broken and formed when polymers are electron beamed; some polymers can degrade, others can cross-link more predominantly.

4.2 Can we tell if polymers will cross link or degrade?
- When the monomer unit of the polymer contains at least one α-hydrogen, cross-linking will take place. Example, see below (-CH2-CR1H- or -CH2-CH2 -), for example polystyrene, polypropylene, polyethylene.
- Polymers with two side chains attached to a single backbone carbon (-CH2-CR1R2-), i.e. those containing quaternary C atoms in the main chain will degrade such as polyacrylonitnire, polyvinyl butyral, cellulose, etc.
- Polymers of CX2-CX2 type (where X is a halogen type), i.e. poly(tetrafluoroethylene), degradation is the predominant process.

4.3 Cross linking of the polymers

The mechanism involves the cleavage of a C-H bond on one polymer chain to form a hydrogen atom, followed by the abstraction of second hydrogen from a neighboring chain. The two atoms form the H₂ molecule. Then the two adjacent polymeric radicals combine to form a cross-link leading to branching chains until, a three dimensional polymer network is formed. In contrast, scission is the breaking of a C-C bond in the
main chain. Cross-linking increases the average molecular weight, whereas scission reduces it.

It is difficult to predict the result for a polymer macrostructure after radiation, but one can measure the secondary species generated on irradiation using known analytical techniques such as, swelling, tensile testing, dynamic mechanical and thermal analysis, etc.

4.4 Units to express the absorbed dose

The International System unit of absorbed dose is the Gray (Gy), which is equal to the energy imparted by ionization radiation to a mass of matter corresponding to 1 joule per kilogram. The unit of radiation dose is a special unit, the rad, which is equal to the energy absorption of 0.01 joule per kilogram that is 0.01 kGy. For conversion purposes 1Mrad= to $10^4$ Gy= 10kGy

5. EVALUATIONS OF SAMPLES FOR EXPOSURE TO IONIZATION RADIATION

To conduct this study, several functionalized polyethylene materials were selected based on their possible performance response to ionization irradiation and their selection as potential ingredients to be used to develop heat activated hot melt adhesives.

In addition, we chose materials whose viscosities were relatively high enough to respond to radiation cross-linking. Some authors have studied previously Polyethylene (low density and high density), maleated Polyethylene, Polyethylene with Ethyl, Butyl, and Methyl Acrylates, and Vinyl Acetate copolymers.

The following table show the samples selected for evaluation and its properties
### Table 1: Typical Properties for Functionalized Polyolefin

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Functional group</th>
<th>ID</th>
<th>Functional group</th>
<th>% Co monomer</th>
<th>Melt Index (MI) g/10 min</th>
<th>Melt Temp. °C</th>
<th>Vicat Temp. °C</th>
<th>Xc %</th>
<th>Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-15</td>
<td>EVA</td>
<td>18</td>
<td>EVA</td>
<td>8.0</td>
<td>86</td>
<td>61</td>
<td>9.5</td>
<td>0.941</td>
<td></td>
</tr>
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<td>M-9</td>
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<td>18</td>
<td>EVA</td>
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<td>64</td>
<td>10.7</td>
<td>0.941</td>
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<tr>
<td>M-10</td>
<td></td>
<td>18</td>
<td>EVA</td>
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<td>89</td>
<td>68</td>
<td>12.3</td>
<td>0.941</td>
<td></td>
</tr>
<tr>
<td>M-18</td>
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<td>25</td>
<td>EVA</td>
<td>2.0</td>
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<td>5.6</td>
<td>0.948</td>
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<td>M-14</td>
<td>EVA-Acid</td>
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<td>EVA</td>
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<td>NA</td>
<td>4.2</td>
<td>0.952</td>
<td></td>
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<td>20</td>
<td>EMA</td>
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<td>80</td>
<td>48</td>
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</tr>
<tr>
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<td>29</td>
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<td>&lt;40</td>
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<td>18</td>
<td>EMA</td>
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<td>87</td>
<td>55</td>
<td>10.3</td>
<td>0.940</td>
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</tr>
<tr>
<td>M-20</td>
<td></td>
<td>23 – 26</td>
<td>EMA</td>
<td>3.0</td>
<td>68</td>
<td>36</td>
<td>3.8</td>
<td>0.940</td>
<td></td>
</tr>
<tr>
<td>M-7</td>
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<td>17</td>
<td>EBA</td>
<td>3.5 - 4.5</td>
<td>91</td>
<td>60</td>
<td>13.3</td>
<td>0.930</td>
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</tr>
<tr>
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<td>17</td>
<td>EBA</td>
<td>7.0</td>
<td>92</td>
<td>58</td>
<td>13.7</td>
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<tr>
<td>M-27</td>
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<td>30</td>
<td>EBA</td>
<td>2.0</td>
<td>78</td>
<td>45</td>
<td>2.7</td>
<td>0.930</td>
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<td>M-11</td>
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<td>17</td>
<td>EBA</td>
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<td>0.926</td>
<td></td>
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<td>M-12</td>
<td>EBA-AA</td>
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<td>EBA</td>
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<td></td>
<td></td>
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<td>EEA-MAH</td>
<td>3</td>
<td>EEA</td>
<td>95</td>
<td>65</td>
<td>13.7</td>
<td>NA</td>
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<td>M-17</td>
<td></td>
<td>2.0</td>
<td>MAH</td>
<td>97</td>
<td>NA</td>
<td>27.4</td>
<td>0.927</td>
<td></td>
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<tr>
<td>M-23</td>
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<td>5.0</td>
<td>EBA</td>
<td>107</td>
<td>80</td>
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<td>0.940</td>
<td></td>
<td></td>
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<tr>
<td>M-13</td>
<td>EBA-MAH</td>
<td>9.0</td>
<td>EBA</td>
<td>102</td>
<td>78</td>
<td>25.0</td>
<td>0.940</td>
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<td>9.5</td>
<td>NA</td>
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<tr>
<td>M-4</td>
<td>EEA</td>
<td>15</td>
<td>EEA</td>
<td>98.9</td>
<td>67.2</td>
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<tr>
<td>M-6</td>
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<td>18.5</td>
<td>EEA</td>
<td>97.8</td>
<td>56.1</td>
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<td>M-1</td>
<td></td>
<td>4.0</td>
<td>MAH</td>
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<td>83</td>
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<td>M-22</td>
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<td>2.0</td>
<td>MAH</td>
<td>120</td>
<td>87</td>
<td>29.7</td>
<td>0.914</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-2</td>
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<td>8.0</td>
<td>MAH</td>
<td>NA</td>
<td>80</td>
<td>36.2</td>
<td>0.921</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-3</td>
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<td>6.0</td>
<td>MAH</td>
<td>NA</td>
<td>102</td>
<td>64.4</td>
<td>0.943</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-16</td>
<td></td>
<td>2.2</td>
<td>MAH</td>
<td>124</td>
<td>74</td>
<td>32.8</td>
<td>0.910</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NA: Not Available, VA= Vinyl Acetate, BA= butyl acrylate, AA= acrylic acid, EA= ethyl acrylate, MAH= maleic anhydride

### 6. SAMPLE PREPARATIONS AND TESTING TO ASSESS CROSS LINKING RESPONSE

Plaques of 60 ± 5 mil were molded between two Teflon sheets using a hydraulic press at max. 40 K lb/in² and 150 to 180 °C; followed by cooling using a second hydraulic press. Time and pressure were varied depending on the type of materials. For the hot press the temperatures used varied between 150 and 180°C, based on the type of material; dwell time was set at 3 min. and the pressure varied between 20K and 30K lb/in². The second press was set at 10±2 °C, with a dwell time of 2 min at 10 K lb/in².

Samples were irradiated in air at room temperature using an Electron Beam Linear Accelerator, Model Dynamitron 300/400/1220 with 3.0 MeV. Three compression
molded plaques for each sample were irradiated in a dose range of 4, 8, 12 and 16 Mrads, some specific samples were irradiated at 20 Mrads since they did not respond to lower beam doses.

6.1 Testing procedures

6.1.1 Tensile Properties; dumbbells were made in reference to ISO 527 standard. An Instron 5565 model was used with an Extensometer, model 2603-080. A cross head speed was set at 4 in/min and samples evaluated at 23 ± 2 ºC to determine tensile stress and elongation at break. Five replicates were tested for each sample.

6.1.2 Hot Modulus; is the modulus of the material at elevated temperature and 100 % elongation; strips for the irradiated samples were prepared in reference to ISO 527 standard. An Instron 4465 with an Environmental Chamber capable of controlling temperatures within 2 ºC of accuracy was used. The cross head speed set was at 2 in/min and samples were elongated by 2 inches and the corresponding hot modulus measured at temperatures between 100 and 150ºC, temperature selected depended on the type of material. Five replicates were tested for each sample.

6.1.3 Gel content; only irradiated samples were tested for this property, the gel fraction was measured gravimetrically; samples were extracted in boiling decahydonaphthalene for 6 hours. After that, samples were dried in vacuum for 1 h @ 150ºC. The gel content was calculated from the weight of sample before and after extraction. These entire tests were made in duplicate for each sample.

6.1.4 DSC Studies; They were conducted using a DSC Q100 analyzer at a heating rate of 10 ºC/min in nitrogen with a ramp to 150ºC then cooling to 50ºC and back up again to 150ºC. A melt point was calculated from the second heating scan. The crystallinity ($X_c$) was calculated from the heat of fusion, which is the area of the melting peak, using the relation:

$$X_c = \Delta H_m / \Delta H_c \times 100$$

Where $\Delta H_m$ is the melt enthalpy of the sample and $\Delta H_c$ is the melting enthalpy of a perfectly crystalline PE (290 J/g).

6.1.5 Rheology; modulus and loss tangent were determined using a TA Instruments ARES apparatus in oscillatory shear mode. The rheological testing was performed at a temperature high enough where there was no influence of the glass transition, the rubber plateau, and the crystallinity. A temperature of 150 ºC was selected as the testing condition to run frequency sweeps. Modulus and loss tangent were found not to depend on frequency, as expected from cross linked materials. Data from 0.1 to 10 rad/s sweeps were collected and plotted for each group of materials and their different levels of dose exposure.
6.1.6 Peel adhesion Test;  
This test was performed in order to assess whether the level of cross linking given to those materials would drastically change its adhesive characteristics. To carry out this test, steel panel type 302 or 304 as prescribed in ASTM D1000 were used. The panels were cleaned with a surgical gauze and heptane to leave the surface free of dust and contamination. From compression molded plaques samples were collected to carry out the peel test. The non-irradiated and irradiated samples were placed onto the steel panels, bonded for 15 min. inside an oven, at temperatures oscillating from 180 to 200 ºC depending on the material selection, followed by a rolling step and a pressure application through the use of a preheated 10 Kg weight. After this step was completed, the plates together with the weights on top were allowed to condition at room temperature for 8 hours prior to the peel test. The peel test was done at an angle of 180º. An Instron model 5565 was used to conduct the test at 23 ± 2ºC with a cross head speed set to 4 in/min. Five replicates were tested for each sample.

7. RESULTS AND DISCUSSION

7.1 Tensile Stress and Elongation at Break

To demonstrate the cross link response of the polymers we plotted the tensile stress and elongation at break for Vinyl Acetate groups, samples M-9, M-10, M-15 and M-18, see figures 2(a) and 2(b).

![Figure 2 (a) for tensile stress and 2(b) for elongation at break](image)

Tensile strength at break increased for all the EVA-EVA-Acid ter-polymer due to a formation of a network structure. Within M-9 (MI=2.5), M-10(MI=0.7) and M-15 (MI-8) samples, which have the same co-monomer content, M-10 sample, the one that had the lower melt index (higher viscosity), appeared to develop a greater beam response when moving from 4 to 16 Mrads, a similar trend would be observed on the hot and dynamical modulus. In the case of elongation at break, all samples showed a decrease within the
beam dose studied, indicating that cross linking had occurred. All materials under investigation showed a similar behavior.

7.2 Hot Modulus

To illustrate the polymer response to radiation using hot modulus as an indicator we selected again the vinyl acetate sample group, see figure 3(a).

Figure 3(a) hot modulus determination

All samples show a linear response to the hot modulus. Within the same co-monomer content samples, M-9, M-10 and M-15, sample M-10 which possesses the lower melt index, developed the largest hot modules, the same response was observed for the tensile stress at break previously discussed. Sample M-18 resulted in higher tensile stress at break without been irradiated when compared to all the Vinyl Acetate group samples. M-18 sample could be a polymer of interest if a high tensile stress material is needed for a special application. All the remaining samples of this investigation, presented a similar response to irradiation in terms of their hot modulus measurements.

For the EMA group sample a plot a hot modulus vs. beam dose where the co-monomer content was varied from 18 to 29% is reported, Figure 3(b)

Figure 3(b) hot modulus with various co-monomer content EMA samples

A linear correlation was observed within the EMA series, greater co-monomer samples showed the greatest cross link response, these samples have comparable viscosity (in terms of their reported MI)

7.3 Gel Content determination

Results for Vinyl Acetate sample groups, M-9, M-10, M-15 and M-18 are demonstrated below in Figure 4(a).
All samples developed greater gel content when moving from an adsorbed dose of 4 to 16 Mrads. The higher values of gel content at higher irradiation dose indicate a formation of a three-dimensional network structure. Evaluation of gel content for all other sample groups demonstrated similar behavior to that of the vinyl acetate groups.

7.4 Rheology

Rheological data can be used to measure as well the degree of cross-linking. The shear modulus, same as the tensile modulus discussed in 6.2, is directly related to the cross-link density. Cross-linking raises the modulus and increases the elasticity, i.e., decreases the tan delta. The rheological testing has to be performed at a temperature high enough where there is no influence of the glass transition, the rubber plateau, and the crystallinity.

Figure 5(a) shows a typical temperature sweep for the materials in this investigation. At ambient temperature and below the materials are very hard due to the crystallinity of the material. The glass transition is at very low temperatures and cannot easily be seen because of the crystallinity. The Polyethylene copolymers show a gradual softening and a broad melting range. In Figure 5, the melting range is from about 50 to 110 °C and shows two steps. Above the melting point, the properties are almost independent of temperature. This is where the cross-links dominate the rheological properties. These materials are well cross-linked as is seen from the loss tangent being well below 1.0. A temperature of 150 °C was chosen for the rheological characterization of all samples.
Figure 5b shows a plot of the modulus and the loss tangent as a function of beam dose for sample M-8.

For the Vinyl Acetate sample (M-8) the modulus increases and the value of tan delta decreases with radiation dose, indicating that cross-linking increases from 8 to 16 Mrads.

Figure 5(b)... Modulus, $G^*$, and tan delta, as a function of beam dose.

7.5 DSC Study

We selected several group of samples (Vinyl Acetate and Ethylene Methyl Acrylate) to determine the changes in crystallinity and melt temperatures, results are presented

<table>
<thead>
<tr>
<th>Beam Dose (Mrad)</th>
<th>Sample ID</th>
<th>0</th>
<th>4</th>
<th>8</th>
<th>12</th>
<th>16</th>
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<tr>
<td></td>
<td>Beam dose</td>
<td>$T_m$ $\degree\text{C}$</td>
<td>$X_c$ %</td>
<td>$T_m$ $\degree\text{C}$</td>
<td>$X_c$ %</td>
<td>$T_m$ $\degree\text{C}$</td>
</tr>
<tr>
<td></td>
<td>M-9 (VA)</td>
<td>86</td>
<td>10.7</td>
<td>85.4</td>
<td>8.8</td>
<td>83.5</td>
</tr>
<tr>
<td></td>
<td>M-10 (VA)</td>
<td>88.8</td>
<td>12.3</td>
<td>86.5</td>
<td>11.6</td>
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<tr>
<td></td>
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<td>68.4</td>
<td>0.96</td>
<td>69.1</td>
<td>0.60</td>
<td>69.2</td>
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</table>

In general for all sample groups a decrease in melt temperature and crystallinity was observed while increasing the beam dose. A decrease in melt temperature can be related to a reduced crystal size whereas a reduced crystallization can be explained by a reduced amount of crystals. Some authors suggest that a confined crystallization can developed as a result of a radiation induced cross-linking when they studied the effect of electron beam irradiation on the cross-link density and crystalline structure of low and High Density Polyethylene.

A direct correlation was also notice in cross linking response vs. crystallinity, within the same group sample, i.e. vinyl acetate and EMA, with a similar viscosity among the
samples compared, those samples that are more amorphous (less crystalline) had more efficient cross link response vs. the most crystalline ones, for example, sample M-18 (X_c of 5.6%) had better cross link response vs. M-9 (X_c of 10.7%). A similar trend was noticed for EMA group samples M-26, M-20 and M-25; the greatest cross link response was observed for sample M-26 (X_c of 0.96%), followed M-20(X_c of 3.8%) and finally the least reactive to cross linking within the group and yet of a comparable viscosity was M-25(X_c of 10.3%).

7.6 Adhesion test

Results for those samples tested are described in Table 3 and Figure 6(a)

<table>
<thead>
<tr>
<th>Beam dose (Mrads)</th>
<th>Beam dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample ID / t-peel test (Lb/in)</td>
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</tr>
<tr>
<td>M-12 (EEA/Acrylic Acid)</td>
<td>&gt;33.9</td>
</tr>
<tr>
<td>M-6 (EEA)</td>
<td>&gt; 33.5</td>
</tr>
<tr>
<td>M-3 (LLDPE-MAH)</td>
<td>&gt; 61.7</td>
</tr>
<tr>
<td>M-9 (Vinyl acetate)</td>
<td>&gt; 30</td>
</tr>
</tbody>
</table>

Table 3; adhesion results

Figure 6(a) Peel plot in function of beam dose
All heat activated hot melt samples listed above which were cross-linked between 4 and 16 Mrads remained adhered to the steel panels; this is an indication that the copolymers wetting properties were not significantly altered after cross-linking.

All adhesive samples were tested as a single layer material, i.e. they were not backed up with a film and tested as unsupported. For this reason, tensile failure was seen during testing when the tensile stress of the adhesive film was too low. The samples either stretched or break occurred in a tensile failure. Figures 6(c) and 6(d) illustrate both failure mechanisms. Because of this, the adhesions to steel shown in table 3 are values for the tensile failure. The actual peel adhesion value is greater than those numbers. Samples M-6, M-9 and M-12 stretched out during peel testing and M-3 sample have broken in a tensile mode. M-3 (maleated LLPDE sample) was the strongest copolymer before and after irradiation in comparison to the other adhesive copolymers tested.

**Figure 6(b) Peel test set up for unsupported adhesives**
8. CONCLUSIONS

- Several Polyethylene copolymers with Vinyl Acetate, Ethyl Acrylate, Ethylene Butyl Acrylate, Ethylene Methyl Acrylate, Ethylene Ethyl Acrylate, and Ethylene Butyl Acrylate maleated versions, and maleated Linear Low Density Polyethylene have been irradiated between 4 and 16 Mrads. They all responded well to the e beam irradiation and cross-linking occurred in all of them.

- The amount of cross-linking achieved was not high enough to change the crystallinity or wetting capabilities markedly. All samples still performed well in adhesion tests and did not show a decrease of peel adhesion. The copolymer samples cross linked between 8 and 16 Mrads, M-3, M-6, M-9 and M-12 were tested for adhesion to steel panels using certain temperature and pressure conditions. None irradiated samples were also tested for adhesion. Both none and irradiated were tested as unsupported adhesives. All samples remained well adhered to steel, indicating that the level of irradiation did not significantly alter the copolymer wetting properties.

- Among the copolymers groups having the same co-monomer content, those ones with greater viscosity responded more efficiently to cross linking. As an example, from the vinyl acetate group with 18% content, samples M-10 (MI=0.7) has a hot modulus at 100ºC of 43.9 and 55.8 Lb/in² at 12 and 16 Mrads respectively, sample M-9, the next in viscosity (MI= 2.5), had a modulus of 29.2 and 39.7 Lbs/in², whereas sample M-15 (melt index of 8), had a hot modulus at 100ºC of 24.1 and 32.4 Lbs/in² at the same beam dose. A similar trend was observed for the Butyl and Ethyl Acrylate functionalized Polyethylenes. From the EBA group samples containing around 17% co-monomer, M-11 (MI=1.5) had a hot modulus at 120ºC of 13.7 and 19.2 Lb/in² at 12 and 16 Mrads respectively, sample M-7
(MI = 3.5) had a hot modulus at 120°C of 7.9 and 14.1 Lb/in², whereas sample M-8 (MI= to 7) had a hot modulus at 120°C of 4.9 and 8.1 Lb/in² at the 12 and 16 Mrads respectively.

- Another interesting observation was the response to cross linking within the same functional copolymer group but different co-monomer content. For example, in the EMA series which were comparable in terms of their reported MI (melt indexes), we observed that lowest co-monomer content sample, M-25(18% co-monomer) had 40% lower hot modulus at 100 ºC at either 12 or 16 Mrads, in comparison to the largest co-monomer sample (M-26 with 29% co-monomer), whereas sample M-20 (24% co-monomer content), the next higher in co-monomer content, had a 12% and 18% lower hot modulus at 100 ºC when tested at 12 and 16 Mrads respectively, this in comparison to M-26 samples. So, this would indicate that starting from a higher co-monomer content EMA sample, one could have a material which will develop a greater hot modulus at the tested temperature.

- Crystallinity vs. amorphous content also played a role on beam response, the more amorphous samples within each group, responded better to ionization radiation, meaning they develop a greater hot modulus, examples given for the EMA and Vinyl Acetates revealed those observations. Sample M-18 (Xc of 5.6%) had better cross response vs. M-9 (Xc of 10.7%). For EMA group samples M-26, M-20 and M-25; the greatest cross link response was observed for sample M-26 (Xc of 0.96%), followed M-20(Xc of 3.8%) and finally the least reactive to cross linking within the group and yet of a comparable viscosity was M-25(Xc of 10.3%).

- Maleated Linear Low Density samples were also found to respond to radiation between 4 and 16 Mrads. A very interesting area where LLDE-g-MAH could be used is as compatibilizer, in order to improve the miscibility of LLDPE-PP blends by mean of cross-linking through the not miscible LLDPE and PP phases.

9. ACKNOWLEDGMENTS

I would like to thank all my colleagues in the product development group at the various locations of the Engineered Materials Division of Berry Plastics, in particular to Amanda Safford for her assistance in the Rheology and DSC measurements, to Marisela Sosa and Joel Espinoza, for preparing samples for irradiation and testing on tensile properties, gel content, hot modulus and peel adhesion test, to Karitina Sosa for her collaboration on consolidating data and creating plots, to Mr. Abboud Mamish, V.P. of R&D, my manager, for encouraging to submit the paper and to Roland Horst and Svetlana Contrada, Research Managers, for their many helpful discussions that lead me to a better understanding of the hot melt heat activated adhesives.
10. LITERATURE CITATIONS

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