

**UN/ECE INTERNATIONAL CO-OPERATIVE PROGRAMME
ON EFFECTS ON MATERIALS,
INCLUDING HISTORIC AND CULTURAL MONUMENTS**

**EVALUATION OF DECAY TO
POLYMER SAMPLES
AFTER 4 YEARS OF EXPOSURE (Draft)**

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1 Introduction

The degradation of polymer materials in the atmosphere is affected by several environmental parameters. Among the most important is UV-radiation, temperature, rain, oxygen, ozone, sulfur dioxide, nitrogen oxides, organic pollutants and dust. So far, the influence of UV-radiation, oxygen and ozone have been studied extensively, but the knowledge of the effect of other factors such as sulfur dioxide, nitrogen oxides is insufficient. However, studies of the influence of these factors are complicated, since they may act in many both qualitative and quantitative combinations.

This study is part of an extensive field exposure program within the United Nations Economic Commission for Europe (UN ECE) which was started in September 1987 and involves 39 exposure sites in 12 European countries together with the United States and Canada. The aim of the programme is to perform a quantitative evaluation of the effect of sulfur pollutants in combination with NO_x and other pollutants as well as climatic parameters on the atmospheric corrosion of important materials. This is achieved by measuring gaseous pollutants, precipitation and climate parameters at or nearby each test site and by evaluating the corrosion effects on the materials at each test site. A Task Force is organizing the program with Sweden as lead country and the Swedish Corrosion Institute serving as the Main research centre. Subcentres in different countries have been appointed, each responsible for their own group of materials, including structural metals, stone materials, paint coatings, electric contact materials, glass materials, and polymer materials.

An extension of the UN ECE ICP Materials including polymer materials was decided at the 9th Task Force meeting in June 1993, and the exposure of the polymer materials started on selected test sites during the autumn 1993. Two widely used materials with different expected degradation mechanism have been selected for the exposure. A homochain polymer; low density polyethylene, which degrades according to a radical chain reaction. The degradation process is supposed to be affected by pollutants, such as SO_2 , NO_2 and O_3 . Polyamide which have heteroatom chain is sensitive to hydrolytic degradation in acid environments, but UV-light is also important in the degradation of polyamide, since the absorption of light by the polyamide initiates radical oxidation reactions in the polymer.

This report gives a summary of the results obtained after the withdrawal after 2 years of exposure on the measurements of the degradation of polyethylene and polyamide, together with a statistical evaluation of the data. The final evaluation will be performed after the last, 4-year, withdrawal, which will take place in the fall of 1997.

2 Experimental

2.1 Test sites

The exposure of polymeric materials is undertaken at a sub-set of the 39 sites in the original exposure program. 21 test sites in 11 countries were selected. With numbers referring to the original program, the test sites selected were 2, 3, 5, 6, 7, 8, 10, 12, 13, 14, 15, 19, 21, 23, 24, 25, 26, 28, 34, 37, and 39. One of the main criteria for selecting the sub-set was the availability of O_3 measurements. A closer description of the test sites has been presented in a separate report [1].

2.2 Climatic measurements

Environmental data are continuously measured at or nearby each test site. This includes the climatic parameters temperature, relative humidity, time of wetness, and time of sunshine, the gaseous pollutants SO₂, NO₂, and O₃, and the characteristics of precipitation total amount, conductivity and concentration of selected ions (H⁺, SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, Ca²⁺, Mg²⁺, and K⁺). All climatic measurements are reported to and compiled by the Norwegian Institute for Air Research, which also controls the quality of the data. The climatic data have been presented in a separate report [2]. Recently, sunshine radiation (290 nm - 2900 nm) have been compiled based on the sunshine hours and the location of the test sites (longitude and latitude).

2.3 Exposure conditions

Specimens for measurement of mechanical properties were mounted 10 on a frame and specimens for IR spectroscopy were placed in three 50x50 mm² frames of ABS polymer used for projection of slides, supported on a larger frame. Samples were exposed in sheltered (S) and open (O) position and the exposure started in the fall of 1993. Samples were withdrawn after 0.5, 1, and 2 years of exposure. One additional set of samples is planned to be withdrawn after 4 years of exposure.

2.4 Materials and sample preparation

Non-pigmented low density polyethylene, [-CH₂-], (LDPE) with a low content of stabilizer and unpigmented and unstabilized polyamide, polyamide 6, [-CH₂-CH₂-CH₂-CH₂-CH₂-CO-NH-], (PA) were used in the exposure. Specimens for measurement of mechanical properties were prepared by stamping from 2 mm thick discs. Specimens for IR spectroscopy were prepared from 0.2 mm thick foils.

2.5 Measurements of mechanical properties

Mechanical properties of polyethylene and polyamide were determined with the aid of an Instron 5566 testing machine, on 7 parallel specimens, using a crosshead speed of 50 mm/min. The remaining 3 specimens are saved for future use. Figure 1 show typical tensile stress vs. strain curves for non-exposed PA and PE samples. Four measures of the mechanical properties have been calculated for each stress-strain curve: Young modulus (MO), Energy to break point (EN), Tensile strength (BT) and Elongation (BE). The modulus is the initial slope of the curve expressed in MPa and the energy is the total area under the curve expressed in J. The tensile strength and elongation the coordinates of the break point.

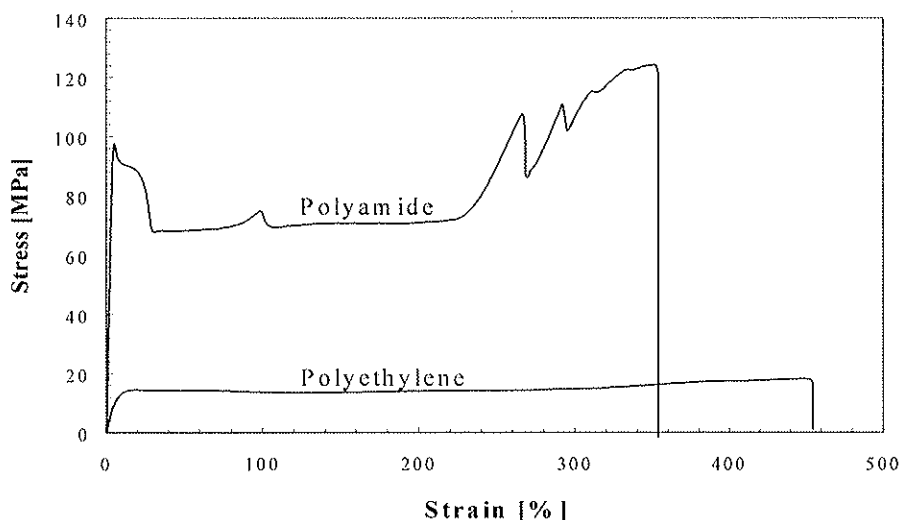


Figure 1 Typical stress-strain curves for unexposed polyamide and polyethylene samples.

2.6 IR-spectroscopy

The infrared spectra of the polyethylene foils after 1 year of exposure were obtained on a BIORAD FTS-60A spectrometer, collecting 64 scans for each sample at a resolution of 2 cm^{-1} . The IR absorbance spectra were evaluated by subtraction of the spectra for exposed samples with the spectra of unexposed samples. The subtraction factor was adjusted until the combination band at 2020 cm^{-1} was canceled in the subtracted spectra. The polyethylene films showed total absorbance in the CH stretching region ($2600\text{-}3100\text{ cm}^{-1}$), CH_2 deformation region ($1430\text{-}1490\text{ cm}^{-1}$), and the CH_2 rocking region ($710\text{-}740\text{ cm}^{-1}$). Consequently, no spectral information is obtained in these regions of the spectra.

IR-ATR spectra of selected samples of the polyamide foil were obtained using a Perkin-Elmer 1760 spectrometer equipped with a Spectra-Tech micro-ATR accessory. The foils were washed with deionized water and methanol before they were mounted on the KRS-5 crystal in ATR-accessory because of particles present on the foils after exposure. The spectra were obtained by adding 125 scans at a resolution of 4 cm^{-1} .

3 Results after 2 years of exposure and Discussion

3.1 Mechanical Properties

Table 1 show the mechanical properties of PA (table 1a) and PE (table 1b) after 0.5, 1, and 2 years of exposure. Each value of the mechanical properties MO, EN, BT, and BE, is expressed relative to the corresponding value of unexposed PA or PE. For example, look at Table 1a, open exposure (O), energy to break point (EN) and site 2 (Kasperske Hory). The values (0.278, 0.069, and 0.003) show a drastic decrease of energy with time of exposure and the value after 2 years of exposure is only 0.3% of the initial, i.e., $0.003 \times 54.97 = 0.16\text{ J}$. Each value in table 1 is based on measurements from 7 samples. When calculating the measure of location a 75 % trimmed mean was used, since the variability in raw material occasionally resulted in extreme values. If we rank the values in increasing order $[v_1, \dots, v_7]$ this means that the measure of

location is $(v_3+v_4+v_5)/3$. For a limited number of exposures only 6 samples were available, in which case $(v_3+v_4)/2$ was used instead to produce values in table 1. The average standard deviation for the triplicates is approximately 0.06, for samples with relatively unaffected mechanical properties such as elongation for the sheltered polyethylene samples.

Figure 2 shows an overview of table 1. The minimum and maximum values for the set of test sites are shown as a function of exposure time for each combination of the materials properties (MO, EN, BT, and BE) with materials/exposure conditions (PAO, PAS, PEO, and PES).

For the materials properties, EN and BE show similar characteristics. The reason is that BT is fairly constant over time, *i.e.*, the area under the stress-strain curve (EN) is directly proportional to the length of the integration interval (BE).

BE seems to be the parameter that is most affected by the exposure time, except for PES. The variation between sites for PES that is indicated in figure 2 can not be explained by the uncertainty in the measurement of degradation. PE is more resistant than PA and sheltered samples are more resistant to corrosion attack than open samples. The influence of UV-radiation on the degradation of polymers is well documented and it's absence is a probable cause for the fact that samples in sheltered positions are relatively unaffected after 2 years of exposure. For PES, MO or BT seems to be a better indicator of the degradation since these samples need longer exposure times to give elongation decreases.

Table 1a Mechanical properties of polyamide. All values are expressed as a fraction of values for an unexposed sample

Open exposure												
Site	MO Young modulus [2624 MPa]			EN Energy to break point [54.97 J]			BT Tensile strength [125.8 MPa]			BE Elongation [362.4 %]		
	0.5y	1y	2y	0.5y	1y	2y	0.5y	1y	2y	0.5y	1y	2y
2	0.419	0.431	0.537	0.278	0.069	0.003	0.473	0.398	0.305	0.415	0.094	0.012
3	0.393	0.379	0.510	0.172	0.061	0.038	0.447	0.377	0.404	0.268	0.091	0.055
5	0.409	0.350	0.481	0.477	0.095	0.054	0.637	0.335	0.420	0.654	0.140	0.073
6	0.358	0.361	0.486	0.320	0.079	0.007	0.488	0.351	0.353	0.492	0.117	0.017
7	0.398	0.405	0.457	0.261	0.066	0.004	0.465	0.383	0.305	0.402	0.092	0.014
8	0.475	0.406	0.504	0.279	0.072	0.035	0.491	0.383	0.424	0.412	0.099	0.054
10	0.460	0.418	0.457	0.291	0.066	0.038	0.476	0.383	0.398	0.415	0.095	0.059
12	0.491	0.418	0.467	0.239	0.066	0.046	0.472	0.385	0.415	0.342	0.093	0.063
13	0.322	0.356	0.430	0.201	0.074	0.036	0.431	0.359	0.389	0.331	0.110	0.057
14	0.306	0.349	0.430	0.204	0.076	0.005	0.404	0.350	0.302	0.355	0.115	0.015
15	0.353	0.366	0.419	0.266	0.080	0.036	0.459	0.285	0.380	0.422	0.125	0.058
19	0.403	0.370	0.459	0.242	0.077	0.049	0.460	0.360	0.410	0.373	0.111	0.070
21	0.433	0.392	0.494	0.282	0.083	0.050	0.479	0.362	0.417	0.408	0.119	0.068
23	0.417	0.339	0.505	0.405	0.085	0.003	0.555	0.343	0.278	0.580	0.127	0.011
24	0.573	0.517	0.475	0.135	0.077	0.048	0.490	0.422	0.398	0.180	0.096	0.068
25	0.569	0.459	0.497	0.298	0.089	0.050	0.506	0.388	0.421	0.401	0.117	0.068
26	0.539	0.503	0.514	0.328	0.052	0.002	0.497	0.412	0.262	0.445	0.068	0.011
28	0.411	0.475	0.510	0.125	0.077	0.013	0.435	0.505	0.401	0.204	0.119	0.026
34	0.448	0.385	0.506	0.307	0.076	0.043	0.486	0.361	0.422	0.437	0.111	0.059
37	0.278	0.405	0.481	0.125	0.067	0.003	0.389	0.382	0.291	0.236	0.095	0.012
39	-	-	0.470	-	-	0.004	-	-	0.322	-	-	0.014

Sheltered exposure												
Site	MO Young modulus [2624 MPa]			EN Energy to break point [54.97 J]			BT Tensile strength [125.8 MPa]			BE Elongation [362.4 %]		
	0.5y	1y	2y	0.5y	1y	2y	0.5y	1y	2y	0.5y	1y	2y
2	0.439	0.421	0.535	0.548	0.314	0.123	0.703	0.346	0.336	0.723	0.434	0.152
3	0.395	0.392	0.518	0.676	0.399	0.121	0.759	0.362	0.327	0.871	0.567	0.148
5	0.414	0.343	0.481	0.765	0.442	0.137	0.773	0.385	0.335	0.917	0.628	0.173
6	0.384	0.356	0.465	0.689	0.342	0.102	0.752	0.343	0.292	0.885	0.491	0.128
7	0.390	0.412	0.439	0.561	0.367	0.098	0.688	0.355	0.261	0.754	0.510	0.126
8	0.488	0.421	0.446	0.897	0.423	0.242	0.891	0.372	0.321	1.002	0.576	0.357
10	0.466	0.410	0.448	0.742	0.397	0.113	0.801	0.357	0.319	0.909	0.564	0.149
12	0.496	0.426	0.462	0.584	0.299	0.127	0.731	0.345	0.329	0.757	0.419	0.164
13	0.330	0.365	0.452	0.615	0.164	0.110	0.706	0.330	0.238	0.827	0.235	0.142
14	0.301	0.335	0.417	0.535	0.281	0.105	0.658	0.333	0.322	0.759	0.428	0.142
15	0.356	0.345	0.410	0.575	0.322	0.127	0.675	0.335	0.323	0.811	0.478	0.173
19	0.399	0.360	0.458	0.742	0.455	0.233	0.794	0.409	0.303	0.921	0.639	0.309
21	0.471	0.407	0.451	0.818	0.374	0.124	0.849	0.356	0.333	0.965	0.511	0.157
23	0.418	0.364	0.441	0.493	0.336	0.118	0.658	0.343	0.334	0.677	0.480	0.149
24	0.588	0.506	0.436	0.625	0.342	0.115	0.757	0.364	0.329	0.774	0.454	0.149
25	0.645	0.524	0.476	0.668	0.377	0.164	0.778	0.213	0.338	0.817	0.499	0.209
26	0.569	0.488	0.441	0.673	0.321	0.288	0.798	0.355	0.343	0.818	0.443	0.390
28	0.409	0.525	0.453	0.507	0.119	0.093	0.664	0.486	0.365	0.693	0.168	0.119
34	0.479	0.367	0.473	0.549	0.305	0.115	0.704	0.333	0.268	0.711	0.454	0.143
37	0.293	0.396	0.478	0.454	0.201	0.003	0.587	0.336	0.285	0.717	0.288	0.012
39	-	-	0.523	-	-	0.002	-	-	0.251	-	-	0.010

Table 1b Mechanical properties of polyethylene. All values are expressed as a fraction of values for an unexposed sample

Open exposure

Site	MO Young modulus [267.9 MPa]			EN Energy to break point [11.72 J]			BT Tensile strength [18.13 MPa]			BE Elongation [448.4 %]		
	0.5y	1y	2y	0.5y	1y	2y	0.5y	1y	2y	0.5y	1y	2y
2	1.026	0.769	0.764	1.224	0.170	0.099	1.060	0.475	0.577	1.230	0.201	0.110
3	1.038	0.781	0.781	1.206	0.156	0.106	1.058	0.472	0.590	1.251	0.186	0.115
5	1.078	0.713	0.716	1.124	0.652	0.107	1.025	0.533	0.528	1.141	0.800	0.126
6	0.982	0.692	0.728	1.220	0.520	0.117	1.057	0.502	0.547	1.206	0.655	0.132
7	1.086	0.732	0.768	1.262	0.171	0.090	1.081	0.460	0.589	1.242	0.208	0.100
8	1.092	0.722	0.758	1.351	0.174	0.087	1.131	0.467	0.588	1.308	0.208	0.097
10	1.089	0.768	0.783	1.361	0.165	0.081	1.135	0.464	0.593	1.339	0.201	0.091
12	1.015	0.771	0.784	1.216	0.160	0.093	1.039	0.461	0.567	1.232	0.204	0.105
13	1.121	0.833	0.899	1.113	0.100	0.037	0.977	0.572	0.676	1.165	0.114	0.044
14	1.106	0.798	0.894	1.006	0.111	0.047	0.947	0.541	0.663	1.071	0.130	0.053
15	1.193	0.756	0.858	1.124	0.103	0.050	0.968	0.527	0.649	1.168	0.125	0.056
19	1.043	0.764	0.778	1.159	0.348	0.112	1.025	0.483	0.563	1.156	0.439	0.125
21	1.045	0.711	0.731	1.234	0.237	0.115	1.132	0.489	0.562	1.148	0.290	0.129
23	1.087	0.719	0.729	1.249	0.406	0.114	1.063	0.488	0.543	1.247	0.521	0.129
24	0.987	0.766	0.763	1.107	0.215	0.117	1.019	0.467	0.567	1.102	0.262	0.132
25	0.984	0.719	0.740	1.061	0.255	0.114	0.978	0.483	0.559	1.091	0.318	0.129
26	1.003	0.724	0.697	0.968	0.534	0.126	0.966	0.505	0.538	0.962	0.662	0.144
28	1.145	1.055	0.740	1.069	0.185	0.080	0.919	0.633	0.571	1.174	0.227	0.094
34	1.030	0.703	0.689	1.187	0.746	0.117	1.093	0.563	0.535	1.156	0.901	0.135
37	1.133	0.741	0.721	1.039	0.198	0.095	0.945	0.475	0.573	1.108	0.245	0.108
39	-	-	0.776	-	-	0.055	-	-	0.631	-	-	0.064

Sheltered exposure

Site	MO Young modulus [267.9 MPa]			EN Energy to break point [11.72 J]			BT Tensile strength [18.13 MPa]			BE Elongation [448.4 %]		
	0.5y	1y	2y	0.5y	1y	2y	0.5y	1y	2y	0.5y	1y	2y
2	1.064	0.630	0.574	1.276	1.057	1.247	1.113	0.743	0.807	1.218	1.158	1.301
3	1.095	0.617	0.589	1.380	1.200	1.226	1.128	0.766	0.771	1.331	1.327	1.342
5	0.933	0.695	0.600	1.175	1.181	1.317	1.088	0.764	0.797	1.120	1.248	1.424
6	0.948	0.632	0.637	1.366	1.194	1.321	1.135	0.770	0.783	1.278	1.306	1.405
7	1.053	0.582	0.618	1.282	1.249	1.007	1.093	0.791	0.699	1.248	1.362	1.140
8	1.047	0.648	0.593	1.249	1.289	1.266	1.093	0.803	0.790	1.205	1.372	1.349
10	1.063	0.612	0.645	1.145	1.237	1.188	1.084	0.775	0.719	1.140	1.408	1.355
12	1.060	0.687	0.666	1.100	1.150	1.183	0.994	0.709	0.704	1.124	1.317	1.376
13	0.985	0.661	0.613	1.263	0.988	1.257	1.077	0.702	0.775	1.260	1.132	1.371
14	1.018	0.619	0.595	1.351	1.139	1.167	1.147	0.768	0.764	1.258	1.216	1.233
15	1.004	0.636	0.593	1.259	1.100	1.121	1.088	0.743	0.750	1.160	1.256	1.171
19	1.091	0.648	0.609	1.231	1.077	1.157	1.053	0.695	0.719	1.229	1.298	1.278
21	1.044	0.658	0.600	1.244	1.052	1.135	1.114	0.698	0.744	1.163	1.169	1.238
23	1.058	0.637	0.594	1.222	0.907	1.142	1.054	0.671	0.733	1.198	1.071	1.256
24	0.973	0.619	0.600	0.886	1.214	1.077	0.924	0.774	0.714	0.927	1.339	1.225
25	0.930	0.698	0.609	1.191	1.196	1.136	1.038	0.779	0.743	1.182	1.316	1.266
26	1.011	0.698	0.597	1.151	1.176	1.121	1.024	0.764	0.732	1.150	1.283	1.244
28	1.035	1.008	0.591	1.323	1.184	1.157	1.110	1.038	0.739	1.293	1.297	1.288
34	1.027	0.642	0.595	1.198	1.121	1.113	1.113	0.755	0.713	1.132	1.223	1.229
37	1.087	0.722	0.628	1.164	1.146	0.911	1.072	0.794	0.701	1.155	1.183	0.972
39	-	-	0.614	-	-	1.284	-	-	0.791	-	-	1.388

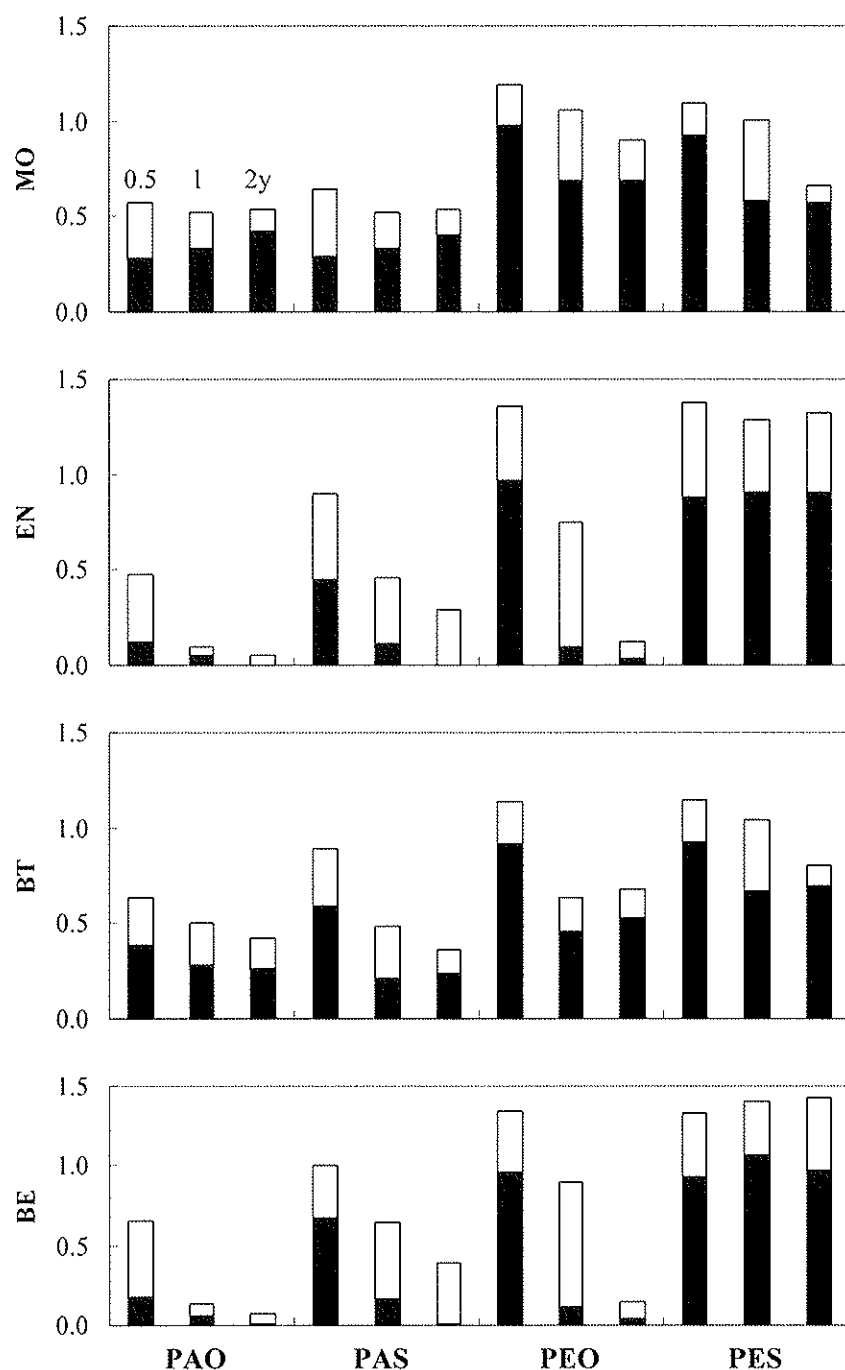


Figure 2 Minimum (filled bars) and maximum (unfilled bars) values from table 1 (all sites). MO-Young modulus, EN-Energy to break point, BT-Tensile strength, BE-elongation, PA-polyamide, PE-polyethylene, O-open, S-sheltered. All values are expressed relative to an unexposed sample. The time development 0.5-1-2 years of exposure are indicated by three consecutive bars (4x4 groups of time development triplets)

3.1.1 Analysis of time dependence

It was concluded that BE is the parameter that varies most with time, except for PES for which BT or MO changes more. Figure 3 shows, for samples exposed at two different test sites, the elongation vs. time of exposure for open polyethylene. For early exposure times, an increase in

elongation is observed. After the maxima, which occurs at different exposure times and elongation values, elongation decreases until all mechanical strength is lost. Polyethylene is a semicrystalline polymer, and its crystalline phase is considered virtually unaffected due to its relative impermeability to oxygen. An increase in elongation during early stages of exposure is usually attributed to the predominance of chain scission and an increase in crystallinity [3].

Can a life time be extracted from the time dependence presented in figure 3? It has become almost a rule to consider that the useful life of a material ends when it reaches 50% of its original mechanical properties [3]. This is in accordance with DECHEMA Corrosion Handbook [4] which states that a polymeric material is no longer resistant if the elongation is less than 50% or the tensile strength is less than 80%. It is thus possible to calculate a characteristic time (time to failure or service life time) from the time curves. This is illustrated in figure 3 and gives 0.59 years for site 14 and 1.52 years for site 34 (the extreme values for open polyethylene). The complete list of life times is given in table 2. For sheltered polyethylene the elongation is larger than 50% for all test sites even after 2 years of exposure (figure 2). For this material and exposure condition the time to failure was defined as the time when the tensile strength reached 80% of its original value.

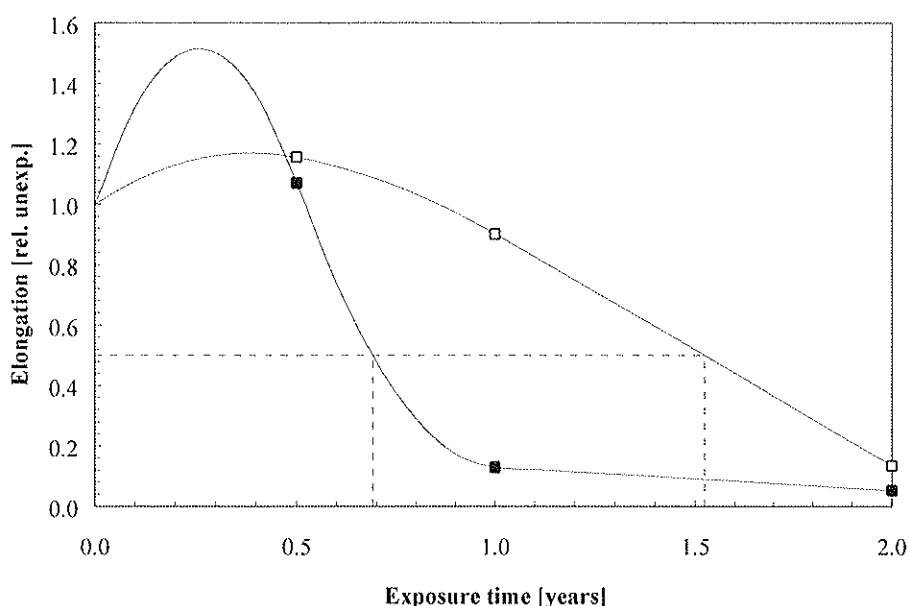


Figure 3 Elongation at break point vs. exposure time for open polyethylene exposed at site 14 (□) and site 34 (■). The points are fitted to quadratic (0-0.5 and 0.5-1.0 years) and linear (1.0-2.0 years) splines. The life times corresponds to the intersection of the curves with 50% reduction in elongation (0.69 and 1.52 years, respectively).

Table 2 Life times in years of open and sheltered polyamide and polyethylene. The times are estimated as the time when elongation at break point reaches 50% of its original (unexposed) value, except for sheltered polyethylene where time at 80% tensile strength was used for the life time estimation. Thus, absolute comparisons should not be made between the life times of sheltered polyethylene and the other life times. The estimations of the bold values are shown in figure 3.

Site	<i>Polyamide</i>		<i>Polyethylene</i>	
	open	sheltered	open	sheltered
2	0.43	0.83	0.74	0.79
3	0.27	1.16	0.73	0.85
5	0.58	1.28	1.45	0.82
6	0.49	0.98	1.30	0.85
7	0.42	1.03	0.74	0.94
8	0.43	1.35	0.75	1.25
10	0.43	1.16	0.75	0.87
12	0.35	0.81	0.74	0.72
13	0.33	0.67	0.70	0.73
14	0.35	0.83	0.69	0.86
15	0.43	0.94	0.70	0.80
19	0.38	1.42	0.89	0.73
21	0.42	1.03	0.76	0.75
23	0.55	0.94	1.05	0.70
24	0.21	0.88	0.74	0.82
25	0.41	1.00	0.77	0.87
26	0.46	0.82	1.31	0.82
28	0.21	0.60	0.74	1.80
34	0.45	0.87	1.52	0.83
37	0.24	0.68	0.74	0.95
39	-	-	-	-

3.2 IR-spectroscopy

The chemical changes in the PE foils during the degradation was measured by IR-transmission spectroscopy. Figure 4 show the IR-transmission spectra of a polyethylene sample exposed one year at site 24 (Stockholm South) as well as the spectra of the unexposed film, and the spectra obtained by subtraction of the spectrum of the exposed foil with the spectrum of the unexposed foil. The main spectral changes after exposure are the appearance of a strong band due to carbonyls at 1712 cm^{-1} , and the growth of peaks due to vinyl groups at 1640 , 909 and 990 cm^{-1} . The growth of vinyl groups shows that chain-terminating unsaturated groups have been formed, probably as the result of chain scission. The peak due to the vinylidene group at 887 cm^{-1} decreases after exposure, but there is a slight increase in the peak at 966 cm^{-1} , due to trans -CH=CH- groups within the chain. The carbonyl band is composed of several components, such as aldehyde, ketone, acid and peroxyacid. The peak present in the unexposed spectrum at 1740 cm^{-1} is probably due to a stabilizer and the broad band at 1180 cm^{-1} is due to carboxylic acid groups [5].

The spectra show the same qualitative features on all exposure sites and does not differ on the sheltered samples. The intensities of the peaks, however, differ considerable. Table 3 show the intensities of the carbonyl peak at 1712 cm^{-1} for the different exposure sites. It is also worth noting the large differences between the intensities for open and sheltered exposure.

The IR-ATR spectra of polyamide foils exposed open at site 3, 12 and 25 show, when compared to the unexposed foil, the presence a band in the region from 1730 to 1770 cm^{-1} . This band is due to various carbonyl structures, such as imides, ketones, aldehydes etc., formed during the exposure of the polyamide foils. The intensity of the carbonyl band relative to the intensity of the amide I band at 1640 cm^{-1} , is highest in the spectrum from site 3, followed by site 25 and 12. This is similar to the results obtained for the polyethylene samples were the degradation of the foils as measured by the carbonyl intensity at 1712 cm^{-1} , follow the same trend for these exposure sites.

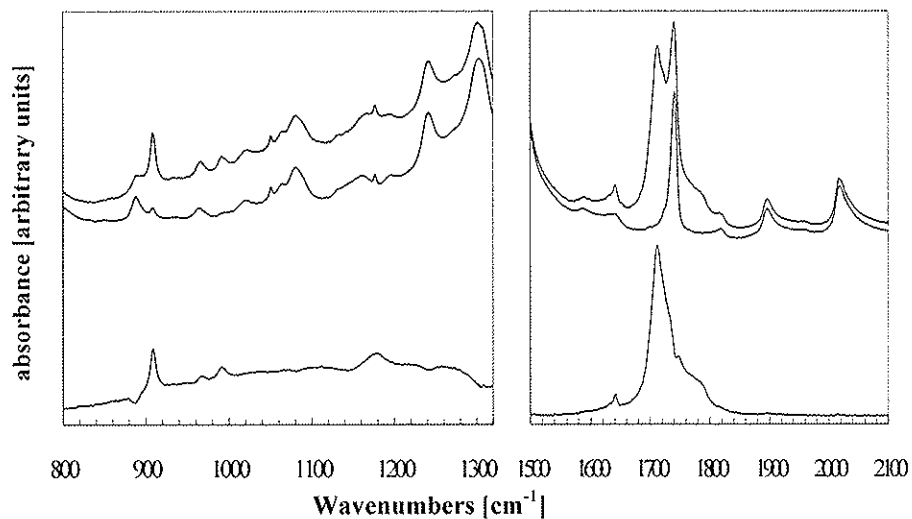


Figure 4 Infrared absorbance spectra of polyethylene (PE) foils after 1 year open exposure at site 24, Stockholm South (top spectrum), unexposed (middle spectrum) and difference (bottom spectrum). Two spectral regions of the same spectra are shown, 800-1300 cm^{-1} (left panel) and 1500-2100 cm^{-1} (right panel).

Table 3 Infrared absorption of polyethylene at 1712 cm^{-1} .

<i>No</i>	<i>open</i>	<i>sheltered</i>
2	0.389	0.012
3	0.490	0.008
5	0.169	0.005
6	0.239	0.008
7	0.405	0.010
8	0.471	0.018
10	0.482	0.010
12	0.302	0.006
13	1.063	0.148
14	0.746	0.019
15	0.826	0.051
19	0.381	0.007
21	0.365	0.012
23	0.224	0.007
24	0.301	0.049
25	0.353	0.016
26	0.286	0.008
28	0.287	0.048
34	0.236	0.016
37	0.246	0.026
39	-	-

3.3 Statistical analysis

3.3.1 Correlation table

Table 4 show Pearson correlation matrices for the mechanical properties. Energy (EN), tensile strength (BT), and elongation (BE) forms a clear group of similar measurements, distinct from modulus (MO). This trend is obvious after 0.5 and 2 years of exposure but not so obvious after 1 year of exposure. Another exception is open polyethylene after 2 years of exposure where MO/BT form a pair, negatively correlated to the EN/BE pair. This means that the strength increases as the elongation decreases, *i.e.*, the samples are hard and brittle and breaks easily. The formation of carbonyl and vinyl groups for open polyethylene as measured with IR is negatively correlated with elongation. Worth noting is also that the correlation is larger with the two-year mechanical data even though the IR-measurements were performed after 1 year of exposure.

Table 5 shows a Pearson correlation matrix for selected mechanical properties for polyethylene, IR measurements and environmental data. The environmental data that have been used are for the first year of exposure. Environmental data for site 28 is lacking for the entire exposure period which means that this site is not included in the statistical analysis that involves environmental data. The correlation coefficients are very similar to those obtained if data from the first half year exposure period or the entire two-year exposure period are used instead. Great care should be taken when interpreting these correlation coefficients. First, there is the effect of pure

Table 4 Pairwise Pearson correlation matrices for mechanical properties, and IR-measurements for open polyethylene. For mechanical properties, twelve separate 4x4 matrices are shown, each corresponding to a particular material, exposure condition, and exposure time. Coding: ++ ($R > 0.85$); + ($0.45 < R < 0.85$); - ($-0.85 < R < -0.45$); -- ($R < -0.85$)

		0.5 years				1 year				2 years			
		MO	EN	BT	BE	MO	EN	BT	BE	MO	EN	BT	BE
<i>open polyamide</i>	modulus (MO)	++				++		+	-	++			
	energy (EN)		++	++	++		++	-	++		++	++	++
	tensile strength (BT)			++	+		+	-	++		++	++	++
	elongation (BE)				++		-	++	-	++		++	++
<i>sheltered polyamide</i>	modulus (MO)	++			+	++				++			
	energy (EN)		++	++	++		++		++		++	+	++
	tensile strength (BT)		+	++	++			++			+	++	+
	elongation (BE)			++	+	++		++		++		++	++
<i>open polyethylene</i>	modulus (MO)	++				++		-	-	++	--	++	--
	energy (EN)		++	++	++		-	++		++	++	--	++
	tensile strength (BT)		++	++	+				++		++	--	++
	elongation (BE)		++	+	++		-	++		++	--	++	++
	IR-measurements	+				+	-		-	++	--	++	--
<i>sheltered polyethylene</i>	modulus (MO)	++				++				++			
	energy (EN)		++	++	++		++	++	++		++	+	++
	tensile strength (BT)		++	++	+		++	++	+		+	++	+
	elongation (BE)		++	+	++		++	+	++		++	+	++
	IR-measurements	+				+	-		-	++	--	++	--

Table 5 Pairwise Pearson correlation matrix for environmental data for the first year of exposure and selected mechanical properties (elongation at break, BE and modulus, MO) and IR-measurements. Coding: ++ ($R > 0.85$); + ($0.45 < R < 0.85$); - ($-0.85 < R < -0.45$); -- ($R < -0.85$).

		Climate				Gases			Precipitation					Optional						
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Temperature	1	++	-	-	-	+										+		+	+	
Relative humidity	2	-	++	+				-	+											
Time of wetness	3		+	++												+	+		+	+
Sunshine hours	4				++						+									
Radiation	5					++		-	+											
SO ₂	6						++	+				+						+		
NO ₂	7						+	++										+	+	
O ₃	8								++				-					-	-	-
mm	9									++						+		+		
Conductivity	10										++	+								
H ⁺	11				+						+	++								
SO ₄ ²⁻	12						+	-					++	+				+		
NO ₃ ⁻	13												+	++				+	++	+
Cl ⁻	14				+					+					++			+	++	+
NH ₄ ⁺	15		+	+	-			-			-			+	++	+		+	+	
Na ⁺	16			+						+	-			+	++	++		++	+	
Ca ²⁺	17		+		-		+	+	-			+	+	+			++	+	+	
Mg ²⁺	18		+		+					+	-		++	++		+	++	+	++	+
K ⁺	19				+	-		+	-			-		+	+	+	+	+	++	
<i>open polyamide</i>	BE - 0.5																			
	BE - 1.0																			
	BE - 2.0				-							-								
	MO - 0.5					-														
	MO - 1.0																			
	MO - 2.0				+	-		+					+							
<i>sheltered polyamide</i>	BE - 0.5																		+	
	BE - 1.0																			
	BE - 2.0																			
	MO - 0.5					-														
	MO - 1.0																			
	MO - 2.0												+	+						
<i>open polyethylene</i>	BE - 0.5																	+	+	+
	BE - 1.0																			
	BE - 2.0																			
	MO - 0.5							+												
	MO - 1.0																	+	+	
	MO - 2.0																	+	+	
IR - 1.0																	++	+	+	
<i>sheltered polyethylene</i>	BE - 0.5																	+	+	+
	BE - 1.0																			
	BE - 2.0																			
	MO - 0.5					+												+	++	+
	MO - 1.0																			
	MO - 2.0																		+	+
IR - 1.0																	+	-		

chance. Approximately one out of twenty +/- signs are expected to be random effects (0.05 significance level). Second, the number of observations are not uniform in the table. Particularly, the optional ions in precipitation have many missing values and the actual number of sites used for calculation of a correlation coefficient is typically 50% of the total number of sites when these parameters are involved. Strong correlations are observed between the temperature and open polyethylene after 2 years of exposure, and between sheltered polyethylene and $\text{Na}^+/\text{Ca}^{2+}$ after 0.5 years of exposure.

The correlation between temperature and modulus for open polyethylene are positive and between temperature and elongation negative. As mentioned before, the IR measurements are positively correlated with the modulus. The strength of the IR-band is a measure of the oxidation of the sample. This means that the PE samples are more oxidized at higher temperatures, become more brittle and breaks more easily. Radiation and ozone concentration also correlates but the sign for ozone is wrong and seems to indicate that higher ozone concentration means less degradation! This is obviously not true but arises from the fact that ozone and temperature show a strong negative correlation which shields the ozone effect. The reason why temperature and ozone is correlated is not obvious and is not a general statement. It only seems to be true for the particular selection of test sites used for the polymer exposures. When using all test sites in the original programme, this correlation is not as high.

After this, open polyethylene, PEO, is the only material/exposure condition that is presented in the statistical analysis. Investigations of the other materials/exposure conditions have been performed but no results have been obtained. For open polyamide and sheltered polyethylene the reason for this depends on the time scale used for the measurements. Open polyamide was severely degraded on most sites already after 0.5 years of exposure whereas sheltered polyethylene is relatively unaffected on all sites even after 2 years of exposure. In view of this, it is not surprising that dose-response relations can not be obtained. It should be possible to obtain a relationship for sheltered polyamide, however, all attempts so far have failed.

3.3.2 Linear regression

From the previous sections it is indicated that the dominating factors for degradation of polymeric materials are temperature and exposure condition (sheltered/open), to a larger extent than pollutant concentrations. The material that has the largest correlation with temperature is open polyethylene. A linear regression for elongation and temperature after one and two years of exposure gives:

$$\begin{array}{ll} \text{BE}_{\text{PEO1}} = 0.67 - 0.037T_1 & R^2 = 0.49, n=19 \quad [1] \\ \text{BE}_{\text{PEO2}} = 0.16 - 0.006T_2 & R^2 = 0.76, n=20 \quad [2] \end{array}$$

The equation after 2 years of exposure is not greatly affected by the extra site (number 39). As a note, if 1-year temperature data is used for the estimation of BE_{PEO2} , R^2 drops to 0.74 and the coefficients are not changed significantly. After 0.5 years of exposure the elongation was independent of temperature and had an average value of 1.2 relative to an unexposed sample. Figure 5 shows the raw data for elongation and temperature on which the equations are based.

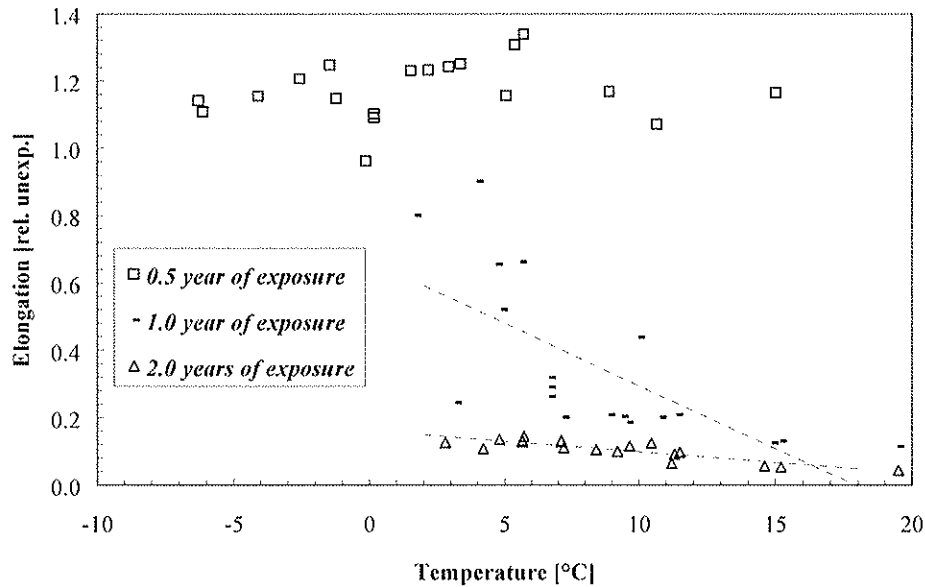


Figure 5 Elongation of open polyethylene after 0.5, 1, and 2 years of exposure, relative to an unexposed sample, vs. average temperature for the corresponding exposure periods. Dashed lines indicate equations 1 and 2.

Eq. 2 has an excellent fit but all polyethylene samples described by this equation are useless from a mechanical point of view since the elongation is lower than 16% of the original value. Therefore, eq. 1 is preferred as a dose-response relation. The reason why the equation after 2 years of exposure is so much higher explained variability is unclear. Having estimated the equations for elongation after 1 and 2 years of exposure, it seems relevant to compare with a similar equation for life times (table 2):

$$\tau_{PEO}(BE) = 1.22 - 0.038T_1 \quad R^2 = 0.38, n=19 \quad [3]$$

where the life time, τ , is measured in years. The constant 0.038 is measured in year/°C which means that the effect of temperature is a life time decrease of approximately 2 weeks/°C for open polyethylene. It should be stressed that the explained variability in eq. 3 is rather low and this is due to the fact that the real relationship between τ and T not is linear.

Recalling the correlation table 5, infrared spectroscopy (IR), was the variable that had the highest correlation with environmental variables. The life time variable and eq. 3 could so far be used as a practical damage function but for modeling degradation and searching for other important factors for the degradation besides temperature the infrared measurements seems better. Both temperature and sunshine radiation show a significant correlation with IR-measurements. Estimating equations for temperature only and the combination of temperature and radiation gives:

$$IR_{PEOI} = 0.00 + 0.050T_1 \quad R^2 = 0.90, n=16 \quad [4]$$

$$IR_{PEOI} = -0.12 + 0.045T_1 + 0.00005Rad_1 \quad R^2 = 0.91, n=16 \quad [5]$$

Where the radiation is measured in MJ/m² for the interval 290 nm - 2900 nm. These relations are illustrated in figure 6. The improvement when including radiation is minor but one should remember that a prerequisite for multiple linear regression is that the independent variables are uncorrelated. The correlation between temperature and radiation is as large as 0.69 and this can introduce systematic errors in the estimation of the coefficients. Techniques that handle this problem exists and will be presented in the next section.

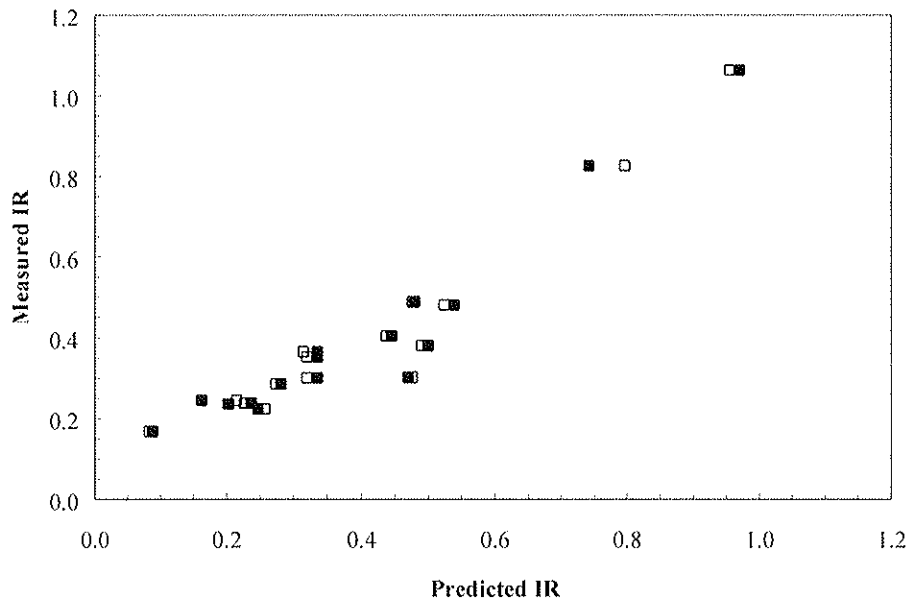


Figure 6 Measured vs. predicted values of IR-measurements for open polyethylene after 1 years of exposure the predicted values are calculated from eq. 4 (□) and 5 (■).

3.3.3 Principal component analysis (PCA)

Principal component analysis (PCA) is often used for finding the underlying dominant structure in data tables. In short, PCA corresponds to a mathematical decomposition of the original data table with the aim of extracting as much information as possible and store the result in a few principal components. In the ideal case you have data reduction without information reduction. The relation between the original data table and the principal components is calculated as scores, for the observations or sites, and loadings, for the variables [6].

Principal component analysis (PCA) is a projection technique. Suppose that 10 environmental parameters (Temperature, relative humidity, ..., SO_2 , NO_2 , ...) are available. To get an overview of this 10-dimensional space it is common to use another type of projection technique, namely to produce X-Y plots for pairwise selection of variables. In this case, it means that $10 \times 9 / 2 = 45$ plots needs to be investigated. It is difficult to get an overview of the data by looking at 45 plots and, consequently, it is common to limit the selection of plots. The risk is that relevant information is missed. PCA is a way to circumvent this problem by using the fact that most of the original variables are correlated. This means that the information can be represented in a space that has lower dimensionality than the original. Mostly, it is only necessary to have 2-4 components even if the original dimension is 10 or more. The components, *i.e.*, the axes of the lower dimension, are linear combinations of the original variables and all components are orthogonal. If two components are sufficient it means that one X-Y plot (component plot) is sufficient to see all the variability of the data, compared to the full set of 45! The drawback is that it can be difficult to assign a clear-cut meaning to the components.

Figure 7 shows the result from two different PCAs, one for environmental data (X-variables) and one for corrosion data (Y-variables). It is the scores and loadings mentioned above that are plotted for the first two components. The score plot is useful for an overview of the sites and identifying groups of sites and outliers. In the loadings plot, similar variables can be grouped together. In other words, correlated variables lie close to each other in the loadings plot. In the example presented in figure 7, environmental data from the both first and second year of

exposure (7th and 8th year in the original programme) has been included to improve the stability of the calculations. Generally, the difference between years is small except for hydrogen concentration in precipitation, conductivity of precipitation and sunshine hours. For the corrosion data, modulus and IR is strongly correlated since the second component not is significant. When two parameters is negatively correlated they are located on opposite sides from a reflection in origo, as is the case for IR and BE measurements. Worth noting is that directions in the score and loading plots are the same. This means that site 9 has high values of MO and IR, and a low BE-value, whereas the opposite is true for site 18.

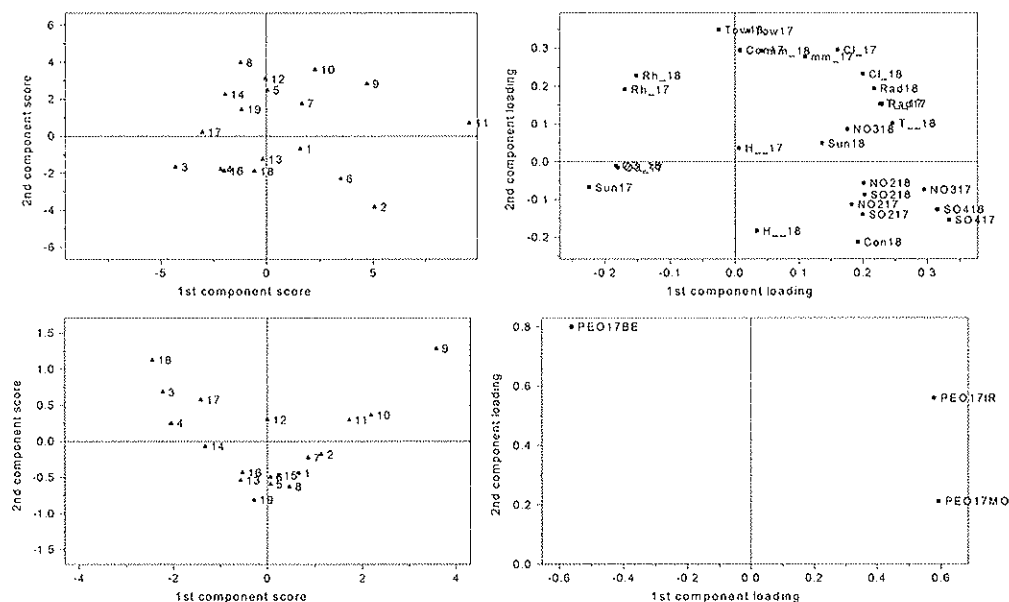


Figure 7 Results from principal component analysis (PCA), 2nd component vs. 1st component. Upper panel: PCA for environmental data; Lower panel: PCA for selected corrosion data (open polyethylene after 1 year of exposure); Left panel: scores for sites; Right panel: loadings for variables. The 2nd component for the PCA of corrosion data is not significant.

The information that can be extracted from PCA-plots is similar to that obtained from a correlation analysis. The advantage with PCA is that all sites are used and that outliers can be detected at a glance. A disadvantage is that correlations between X- and Y-variables can not be extracted. A way to solve this is to make a PCA for all variables together and look at X-variables that are close to Y-variables in the loading plot. A better way is to use projection on latent structures (PLS).

3.3.4 Projection on latent structures (PLS)

PLS is an abbreviation for both ‘projection on latent structures’ and ‘partial least squares’. Like PCA, it is a projection technique but it is also a regression technique, i.e., a technique for establishing a relation between Y and X, *i.e.*, a dose-response relation. The starting point for PLS is individual PCAs of the X- and Y-space separately, *i.e.*, the results presented in figure 7. Both projections are then changed slightly so that the correlation between the individual X- and Y-components are maximized. The more the projections are changed the less accurate is the description of the two spaces. Therefore, PLS is a compromise between the goal of describing X and Y, and the goal of correlating X and Y. These two extreme cases have already been presented and are called principal component analysis (PCA) and multiple linear regression (MLR), respectively. The name partial least squares for PLS should now be evident. MLR is a least squares technique, PLS is not, since it also needs to make a description of X- and Y-space. In short, PLS is a combination of PCA and MLR.

In the first model estimated by PLS the same variables were used as those presented in figure 7. The overall result is described in table 6, which shows the R^2 and Q^2 values. R^2 is the normal explained variability but Q^2 is a measure of the prediction ability of the model. It is calculated in the same manner as R^2 but instead of using one model several are used, with different subsets of the test sites. For each model the excluded sites is used for the calculation of Q^2 . Naturally, Q^2 is lower than R^2 but should be considered a better measure of the model since the point of establishing a model is to use it to predict the behavior at new test sites. The relation is also illustrated in figure 8. Part of the figure shows the individual sites and variables and is similar to figure 7, part shows the relative importance of the different environmental variables, for the final projection. Temperature, radiation and ozone seem to be important parameters. As explained before, the sign of ozone is wrong due to the correlation with temperature and successive components (3, 4, etc.) are not significant.

Table 6 Summary of PLS-model showing total and individual R^2 and Q^2 for open polyethylene parameters after 1 year of exposure (2 components).

	R^2	Q^2
modulus (MO)	0.86	0.64
elongation (BE)	0.51	0.35
infrared (IR)	0.84	0.77
Total	0.74	0.54

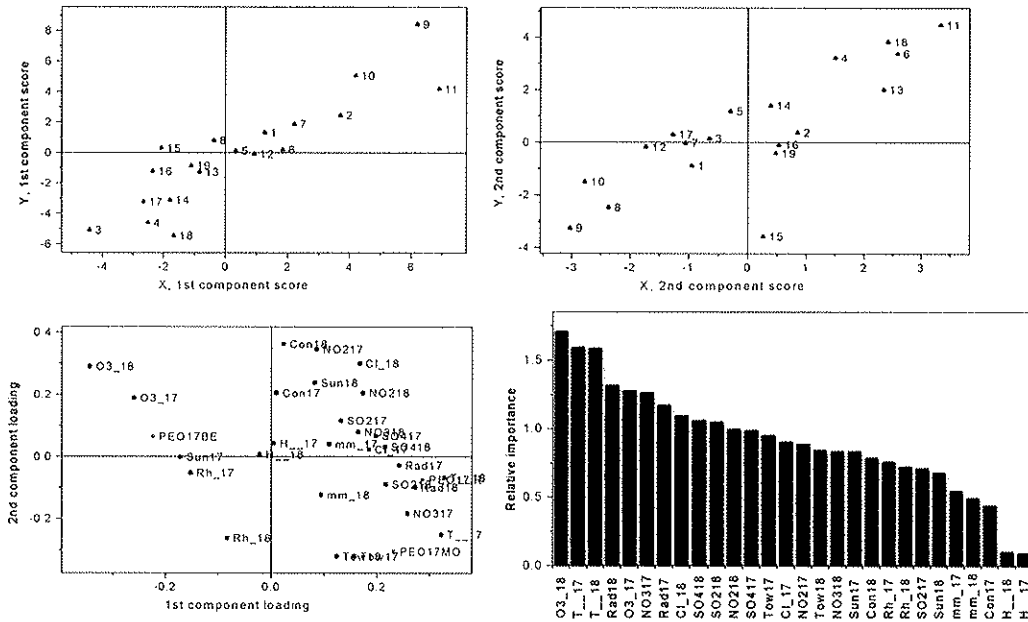


Figure 8 Results from projection on latent structures (PLS). Upper: Y vs. X scores for the 1st and 2nd components; Lower/left: Y and X loading for the 1st and 2nd components; Lower/right: relative importance of X-variables in projection.

The second model estimated with PLS is a comparison with eq. 5, which is repeated here, and resulted in eq. 6:

$$\begin{aligned}
 IR_{PEO_1} &= -0.12 + 0.045T_1 + 0.00005Rad_1 & R^2 &= 0.91, n=16 & [5] \\
 IR_{PEO_1} &= -0.38 + 0.030T_1 + 0.00017Rad_1 & R^2 &= 0.86, n=16 & [6]
 \end{aligned}$$

The Q^2 -value for eq. 6 is 0.78 and for eq. 5 the Q^2 -value has not been obtained. The data set was identical for the two estimations. Eq. 6 has a lower R^2 -value but that is expected since multiple linear regression is a least squares technique which maximizes R^2 for a particular equation and data set. Even so, eq. 6 should be used instead of eq. 5. The reason is that T_1 and Rad_1 is highly correlated and that uncorrelated variables is a prerequisite when using multiple linear regression. Worth noting is that MLR underestimates the effect of solar radiation in favor of temperature.

4 Sheltered polyethylene after 4 years of exposure

Site 37: 7 observations between 0.18 and 0.34 gives a mean of 0.25 ± 0.05 (95%)

Table 1b Elongation of sheltered polyethylene. All values are expressed as a fraction of values for an unexposed sample (448.4%).

Site	0.5y	1y	2y	4y
2	1.218	1.158	1.301	1.058
3	1.331	1.327	1.342	1.024
5	1.120	1.248	1.424	1.114
6	1.278	1.306	1.405	1.352
7	1.248	1.362	1.140	1.180
8	1.205	1.372	1.349	1.210
10	1.140	1.408	1.355	0.979
12	1.124	1.317	1.376	1.181
13	1.260	1.132	1.371	1.234
14	1.258	1.216	1.233	0.996
15	1.160	1.256	1.171	1.075
19	1.229	1.298	1.278	-
21	1.163	1.169	1.238	1.237
23	1.198	1.071	1.256	1.097
24	0.927	1.339	1.225	1.216
25	1.182	1.316	1.266	-
26	1.150	1.283	1.244	1.211
28	1.293	1.297	1.288	1.164
34	1.132	1.223	1.229	1.102
37	1.155	1.183	0.972	0.253
39	-	-	1.388	-

5 Conclusions

The present report is based on evaluation of mechanical properties of polyethylene samples and polyamide samples exposed 0.5, 1, and 2 years in open and sheltered positions and from measurements of IR spectra of polyethylene samples exposed for 1 year. The evaluation has resulted in the following conclusions:

- Elongation is the best measure of degradation of the four parameters investigated (modulus, energy, tensile strength, and elongation).
- Polyethylene is more resistant to attack than polyamide.
- The sheltered samples are more resistant to attack than the open.
- For shorter exposure times, elongation and strength are positively correlated but becomes, after a transition time, negatively correlated resulting in very hard samples that breaks easily.
- It is possible to estimate service life times from mechanical properties but this parameter is difficult to correlate to environmental properties.
- The exposure of polyethylene results in the formation of carbonyl and vinyl groups in the polymer and this formation is correlated to the degradation of the material.
- Polyethylene exposed in open position can be described by a dose-response relation with temperature and sunshine radiation. Temperature is the most important parameter and warmer temperatures relates to more degraded samples.
- The relative importance of sunshine radiation, compared to the effect of temperature, is underestimated by conventional linear regression.
- At almost all test sites, polyamide exposed in open position was severely degraded already after 0.5 years of exposure. Consequently, no dose-response relation was found.
- At all test sites, polyethylene exposed in sheltered position was relatively unaffected even after 2 years of exposure. Consequently, no dose-response relation was found.
- No dose-response relation was found for polyamide exposed in sheltered position.
- It has not been possible to quantify the effect of gaseous pollutants.

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7 References

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