

The effect of radiation on the thermal expansion of kaolin nano filled -XLPE materials.

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Abstract

Nano kaoline as a reinforcement agent in the concentration of 5% was added to different polyolefine materials. Said materials were crosslinked via chemical and Gamma radiation. The expansion coefficient (CLTE) using a linear thermal expansion technique for the cross linked LDPE and HDPE and Polypropylene Random Copolymer (PPRC) in the temperature range of 30 to 220°C was investigated. Prior to radiation the different sample were chemically crosslinked using silane and peroxide crosslinking agent. From the compounded resin; sheet and pipes were produced. Samples were cut and then subjected to gamma radiation at different radiation doses. The thermo elastic properties of mentioned samples, in particular the linear thermal expansion (α) at constant stress and the change in the length with temperature, were studied. It was found that α decreases with the increasing degree of grosslinking for polyethylene simillar to elastomer net works; whereby PPRC behaves like ordinary polymer. The thermo elastic inversion was also considered and the experimental observations were easily rationalized. Finally, the results were explained in the light of the change in the polymer micro structure and its change due to the effect of γ ray radiation

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has been determined in the temperature range of 30 to 220°C * Corresponding author (E-mail: arobaidi@yahoo.de)

1 Introduction:

Cross linked polyolefin's (XLPE) pipes and toys are intensively used in today's application and to replace metals in different industrial and engineering applications, especially in pipe heating systems and under floor heating. When heat is added to most materials, the average amplitude of the atoms vibrating within the material, increases its length or volume. This, in turn, increases the separation between the atoms causing the material to expand [1]. If the material does not go through a phase change, the expansion can be easily related to temperature change. The linear thermal expansion coefficient (α) describes the relative change in length of a material per degree of temperature change [2]. As shown in the following equation, α is the ratio of change in length (ΔL) to the total starting length (L_0) and change in temperature (ΔT).

$$\alpha = \Delta L / L_0 * \Delta T$$

ΔL Change in length of sample,

L_0 Original length of sample,

ΔT Temperature change during test

The information about radiation effects on the thermal properties of polymeric materials is of special interest as:

- 1) The temperature regime of technical structural units operated in the radiation fields is determined in many respects by the values of the material thermal constants and the rate of their degradation
- 2) The temperature and dose dependencies of heat conductivity and, especially, heat capacity characterize the polymer structure.

Polyethylene of high and low density, are materials with well-known partly-crystalline structure. When subjected to chemical peroxides or to radiation they do crosslinked [3].

The various physical polymer properties such as linear thermal expansion; thermal and electrical conductivities are extremely useful in understanding material behavior under specific applications. Crosslinked high density polyethylene (XHDPE) and cross linked Polypropylene (PPRC) materials are widely used for under floor heating systems. Such systems are expected to serve for 35-50 years [4]. The primary reason for cross-linking polyolefin's is to raise the thermal stability of the material under load. This substantially improves environmental stress crack resistance and resistance to slow crack growth. Considering expansion caused by heating and shrinkage of the material and the creep behavior of such systems will deteriorate the microstructure and influence the material used. Studies of the effect of irradiation on the thermal expansion on XLPE are scanty [5]. In view of this an attempt was made to study the effect of degree of cross linking and the

irradiation intensity on the XLPE thermo-elastic behavior. Most materials elongate when subjected to heat, and stressed as a result of that, exhibit a limited elastic region. Elasticity is the case where the material regains its original dimensions if the stress is removed. As the resulting strain is related to the extent of movements of atoms from their equilibrium conditions, substances such as crystalline solids and amorphous regions have elastic limits rarely exceeding 1% because atomic adjustments are localized [6-9]. The elastic properties of crosslinked materials however, are truly exceptional. XLPE and Elastomers are polymeric materials that can undergo large deformations without breaking owing to the ability of their constituent polymeric chains to rotate about the chain bonds.

The choice of stress, length (L), and temperature (T) as state variables are of prime importance to describe the equation of state. Rubberlike elasticity is described as an entropic effect, similar to the pressure of an ideal gas [6, 7]. It is shown, however, that XLPE is not behaving as an ideal elastomeric (because it verifies only approximately the generalized Joule's law), and this is related to the small but non-negligible energy changes in stretching [10-12].

2 Experimental details

2.1 Materials.

Test samples were cut from cross linked low density and high density PE and PPRC pipes and sheets that was produced commercially by Jordanian pipe manufacturer.

PPRC raw material is manufactured by HYOSUNG-CORPORATION (MFR $\frac{1}{4}$ 2:5 dg/min at 230 °C, isotactic index = 98.5%). HDPE, LDPE raw material resin are manufactured by Borstar technology classified as an MRS 10.0 material (PE100). Silane produced by Dow chemical and commercial dicumyl peroxide ($[C_6H_5C(CH_3)_2O]_2$) were used to produce the Pipe. Samples were then cut and subjected to gamma radiation at different doses before testing as listed in table 1.

2.2 Cross-linked polyethylene (XLPE), is a thermoset material contains cross-linked network in its polymer structure. The degree of crosslinking represented by the cross linking density was determined before and after gamma radiation according to ASTM Standard F 876-93. Common degree of crosslinking in pipe heating systems, domestic water piping and insulation for high tension (high voltage) electrical cables is approximately between 67-70%. The samples were subjected to radiation as listed in table 1. The radiation dose applied led to different cross linking densities and at the same time has an unwanted effect in degrading the polymer chains. Gel Permeation Chromatography (GPC) analysis to determine changes in molecular weight and number is ongoing and will be reported later on.

Three sample of each material was subjected to radiation, at a varying dose and the degree of crosslinking was determined. The radiation source used is Co_{60} (cobalt 60), the process is carried out by exposing the samples to the source for a sufficient time to achieve the required dose.

	1 KGy	⇒	1h: 33min: 33s
Dose (KGy)	50		100
Exposing time (h:min)	66:40		133:33
Degree of cross linking XLPE %	78.6		80.2
Degree of cross linking PPRC %	22.2		23.1
Degree of cross linking HDPE %	74		77

Table 1. : Radiation dose and time selected to achieve a degree of cross linking similar to that one used in industrial Applications. Cross linking density is average of three tested samples.

The coefficient of linear thermal expansion (CLTE) of XLPE and polypropylene random copolymer (PPRC) has been determined by measuring the change in length of the specimen as a function of temperature as per ASTM E831. CLTE is measured using a dilatometer equipment manufactured by Linseis /Germany. The specimen of specific dimensions (50mm X 2mm X 2mm) was cut out from the central part of pipes. The specimens were held in an enclosure and are contacted by a probe leading to a displacement sensor. A small force of 1 to 100 mN is applied to the specimen to keep the probe in contact with the specimen. The enclosure is brought to a starting temperature. The temperature within the enclosure is increased at a rate of 5°C/min. The expansion of the specimen is measured by the displacement sensor over the temperature range up to 220 °C

3 Results.

The coefficient $\lambda_{\tau,v}$ at different temperatures is calculated and represented in Figure1 as a function of α_0 which represents the strain of crosslinked network related to its natural length at ambient temperature. $T_0 = 298.15$ K.

All curves in Figure 1 show a sign reversal of $\lambda_{\tau,v}$ when $\alpha_0 \approx 1.1$, which is in agreement with experimental observations as shown Figure 2. This means that the coefficient of linear expansion of XLPE becomes negative when $\alpha_0 > 1.1$, and therefore the XLPE band contracts when temperature increases and this agree with others [15, 16]. In contrast, the coefficient of linear expansion of XLPE is positive under very low stress ($\alpha_0 < 1.1$), and the usual (liquid like) increase in length with temperature is observed. This change is known in the literature as thermo elastic inversion.

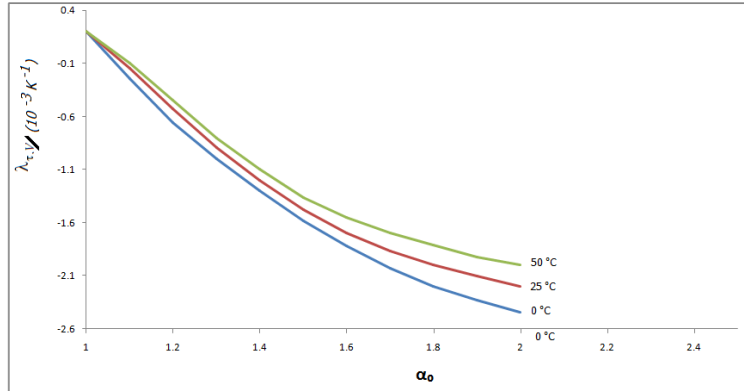


Figure1. Calculated coefficient of linear expansion of crosslinked network $\lambda_{\tau,V}$ as a function of strain $\alpha_0 = l/l_0(T_0)$ at temperatures 0, 25 and 50 °C

3.1 Radiation and CLTE

Gamma radiation was applied to achieve different cross linking densities; so that a relation of the thermal expansion coefficient to the degree of crosslinking could be determined. Figure 1-4 shows such dependency for crosslinked Polyethylene; XLPE and XHDPE and PPRC. Figure 22 indicates very clearly that the coefficient of the thermal expansion for low density XLPE decreases with increasing cross linking density. This behavior was observed for crosslinked rubber and polybutadiene. CLTE for crosslinked network and thermoset behaves similar as discussed above and could be described according to the State Variables and Equation of State. The change in CLTE in figure 2 and 3 could be compared to the Calculated coefficient of linear expansion of crosslinked network $\lambda_{\tau,V}$ as a function of strain $\alpha_0 = l/l_0(T_0)$.

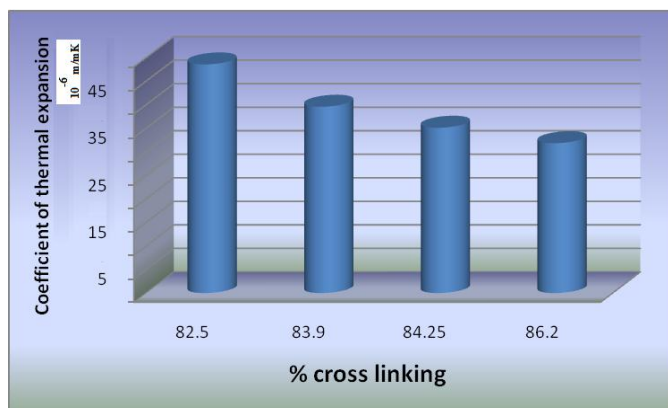


Figure 2: coefficient of the thermal expansion versus degree of cross linking for XLPE materials.

This is in line with our previous discussion and the elasticity theory of rubber network systems. The similarity between calculated curve in figure 1 and the experimental value in Figure 2 and 3 is obvious. This behavior was expected to some extent. PPRC and with its high crystalline content and low degree of cross linking compared to XLPE showed an different behavior.

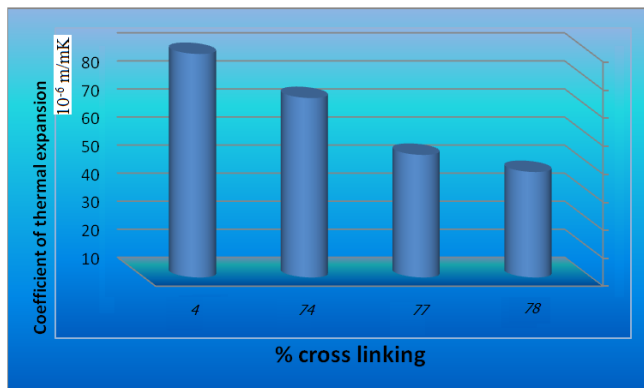


Figure 3: Thermal expansion Coefficient for HDPE vs. degree of crosslinking

Figure.4 shows the relation between radiation dose and thermal expansion coefficient for PPRC sample, where the thermal expansion coefficient showed a minor increase at low radiation dose (low degree of crosslinking 22%) at 50- KGy, followed by a decrease at 100KGy or a 23.1% degree of crosslinking. An increase at 26.2% degree of crosslinking was then measured. This incosency was related to degradation mechanism that took place at higher dose radiation. DSC scan could confirm this staetement. Changes in the position and shape of DSC peaks was observed for reference and the crosslinked samples. Typical DSC thermograms obtained during the first and second heating runs on the fresh and irradiated samples are displayed in Figures 5. at different temperatures. An endothermic peak, corresponding to the melting temperature of the crystalline part of the polymer, was observed. The main DSC peak is narrow and sharp, while radiated samples did not indicate any melting peak at approximately 130°C.

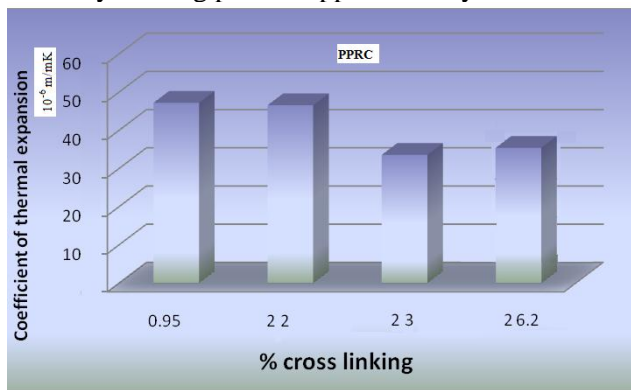


Figure 4: Coefficient linear thermal expansion of crosslinking in PPRC vs. degree of crosslinking

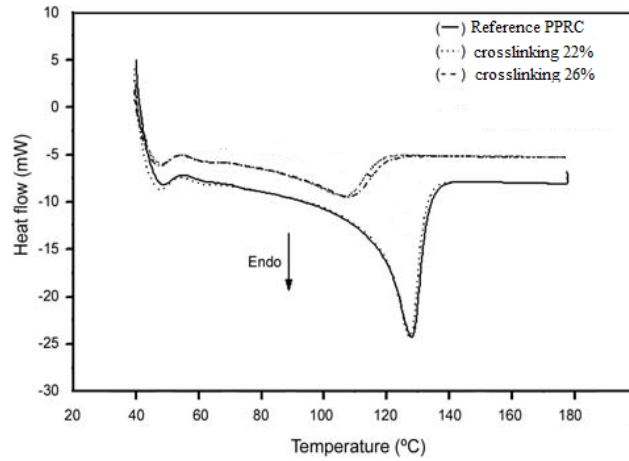


Figure 5: A typical measured DSC diagram for PPRC.

A typical measured linear thermal expansion curves are presented in figure 6 . The curves indicate the change in length versus temperature for the three different radiation doses. The plots shown were measured by linseis dilatometer instrument.

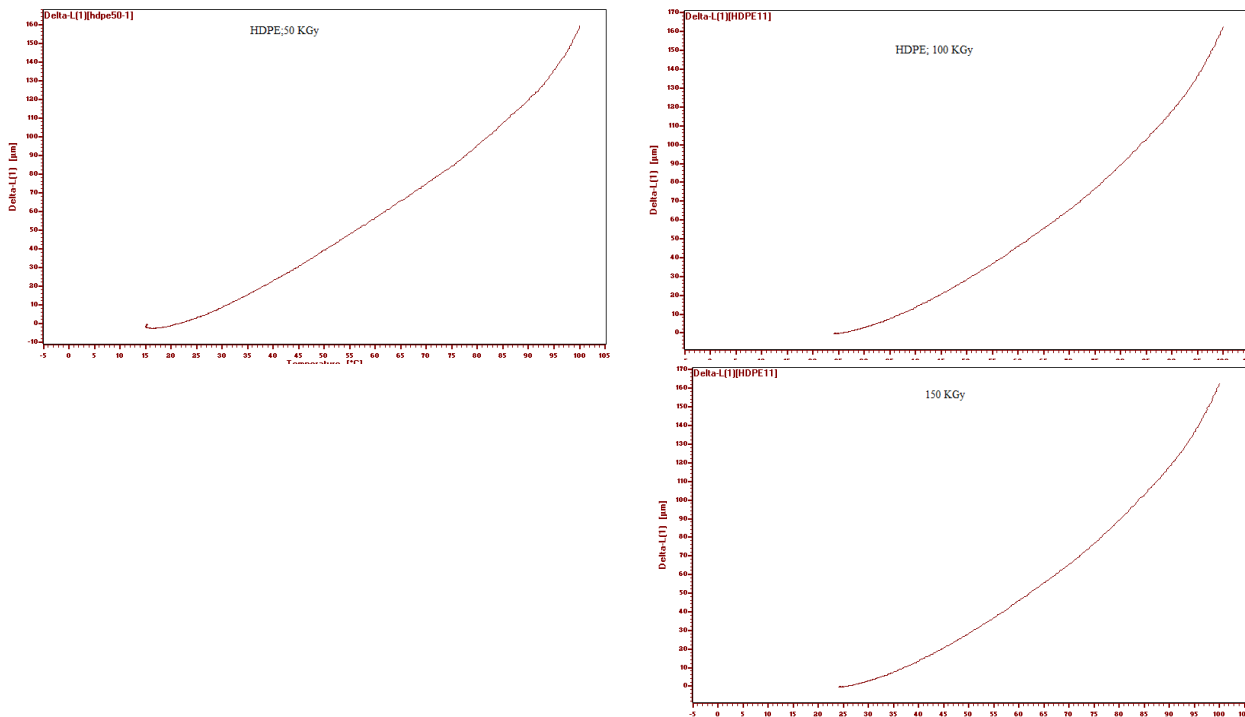


Fig. 6: The change in length for HDPE a) 50 KGy b) 100KGy c) 150 KGy

4 State Variables and Equation of State

A solid surface is said to be under uniform stress if there is force acting on the surface whose magnitude is proportional to the surface area. The force, as a vector quantity, may be oriented in any direction with respect to the surface. This statement is restricted to forces applied perpendicular to the surface.

The force per unit area acting on a solid surface of arbitrary orientation can be evaluated from three (Cartesian) normal stress components τ_{xx} , τ_{yy} , and τ_{zz} ; the components have two sub-indexes because stress is a second-rank tensor [13].

The (intensive) thermodynamic state of an isotropic elastic solid is then determined by the stress components and the temperature. In particular, for small and moderate strains, the equation of state of an isotropic XLPE sample of length L at temperature T under stress τ (in Newton's) is

$$\tau = kT \left[\frac{L}{L_0} - \left(\frac{L_0}{L} \right)^2 \right] \quad (1)$$

at constant volume, where k is a constant that depends on the composition and geometry of the sample considered and L_0 is the original sample length in the absence of applied stress, which depends only on temperature. In deriving equation 1 it is assumed that the strain of the XLPE sample takes place at constant volume [8, 13]. However, it is sometimes preferable to keep the volume dependence in the stress–strain equations, especially for detailed comparison with the results of statistical theories.

4.1 Cross-linked network is Not an Ideal Elastomer

According to the first and second laws of thermodynamics, the deformation of an elastic system (at constant volume) involves changes in both internal energy and entropy which are related by

$$\left(\frac{\partial U}{\partial L} \right)_{T,V} = \tau + T \left(\frac{\partial S}{\partial L} \right)_{T,V} \quad (2)$$

The derivative $(\partial U/\partial L)_{T,V}$ vanishes for ideal elastic systems [13, 14] which, in the case of XLPE materials, means that the polymer chains can rotate freely and its internal energy U does not change with conformation similar to the case of an ideal gas, where the absence of molecular forces implies that its internal energy does not change with volume. The use of equation 1 and the Maxwell relation, $(\partial S/\partial L)_{T,V} = (\partial \tau/\partial T)_{L,V}$, yields

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = kT^2\lambda_0\left[\frac{L}{L_0} + 2\left(\frac{L_0}{L}\right)^2\right] \quad (3)$$

where

$$\lambda_0 = \frac{1}{L_0} \frac{dL_0}{dT} \quad (4)$$

λ_0 is the coefficient of linear expansion of XLPE under zero stress; dL_0 is considered to be a function of temperature only, which is valid at constant and low pressures. This value of this coefficient was determined to be $\lambda_0 = 2.2 \times 10^{-5} \text{ K}^{-1}$ and remains approximately constant with temperature up to 125 °C.

4.2 Thermoelastic Inversion

The behavior of XLPE in response to temperature changes is rather complex. Whereas most materials exhibit a positive coefficient of linear expansion, that of XLPE changes from positive to negative values with increasing strain. Making use of equation 1, the coefficient of linear expansion at constant tensile stress and volume takes the form.

$$\lambda_{\tau,V} \equiv \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_{\tau,V} = \lambda_0 - \frac{1}{T} \frac{[L/L_0(T)]^3 - 1}{[L/L_0(T)]^3 + 2} \quad (5)$$

The term λ_0 of equation 5 accounts for the normal liquid like thermal expansion and the second term describes the thermo elastic behavior of the entropic restoring force of the polymer Chains .

4 Discussion

A thermodynamic study of a crosslinked polyolefin's (LD-XLPE; HDPE and PPRC) at constant volume under uniaxial stress has been presented on the basis of its equation of state. The study is rather thorough and includes the most representative characteristics of rubberlike elasticity; the agreement between theoretical results and experimental observations for XLPE is remarkable.

Based on the result presented we can confirm that the:

1. Thermal expansion coefficient affected by structure change (cross linking) decreases for polyethylene with increasing radiation dose. No direct relation was observed in PRC.
- 2) For XLPE pipe application and under floor heating a shrink behavior should be considered rather than an expansion in the heating system,

3. Radiation could be destructive or instructive for cross linking according to type of materials and doses. X ray analysis should be applied to determine degradation mechanism

5 Conclusion:

The linear thermal expansion for different type of polymeric materials; XLPE; HDPE and Polypropylene random copolymer were measured. The mentioned materials were subjected to different gamma ray radiation to crosslink those materials at different radiation doses' to achieve different degrees of crosslinking densities. Thermal expansion generally decreases with increasing bond energy, which also has an effect on the hardness of solid thermoplastic polymers, so, harder materials are more likely to have lower thermal expansion. Gamma radiation also gets the interaction between polymer chains can be cut as linkage between them, leading to smaller molecules or degradation or may receive a link with each neighboring chains and so called networked cross linking

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