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The effect of cross-linking on the thermal properties of LDPE/wax blends

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Abstract

Thermal properties of cross-linked and uncross-linked low-density polyethylene (LDPE)/Fischer–Tropsch wax blends were investigated in this paper. For cross-linked blends, the gel content was determined. It was observed that the gel content increases with an increase in DCP concentration. The degree of crystallinity decreased with an increase in DCP concentration. The wax and LDPE were not mutually miscible at higher wax concentrations in the crystalline phase, as well as in the melt. The thermal stability of the blends decreased with an increase in wax content, and no direct correlation between thermal stability and cross-link density was observed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LDPE/wax blends; Cross-linking; Thermal analysis; DSC; TGA

1. Introduction

Low-density polyethylene (LDPE) has good mechanical properties and is often used in industry. It is a partially (40–60%) crystalline solid, melting at about 115°C, with a density in the range 0.91–0.94 g cm^{-3} [1]. It has high impact strength, low brittleness temperature, flexibility, film transparency, and outstanding electrical properties [2]. The physical properties of LDPE are functions of three independent structure variables: molecular weight, short chain branching and long chain branching. As molecular weight increases, so do tensile strength, tear strength, softening temperature and resistance to environmental stress cracking [2,3].

Paraffin waxes (Fischer–Tropsch synthesis) are white, translucent, tasteless and odourless solids consisting of a mixture of solid hydrocarbons of high molecular weight [4]. They are soluble in benzene, ligroin, warm alcohol, chloroform and carbon disulphide, but insoluble in warm water and acids. Their density is approximately 0.880–0.915 g cm^{-3}, melting point 47–65°C, and flash point 198°C. Common properties are water repellency, smooth texture, low toxicity, and freedom from objectionable odour and colour [5].

Cross-linking is a broadly used method for the modification of polymer properties. This process involves the formation of tri-dimensional structures, gels, causing substantial changes in material properties [6]. Different procedures may be used for the initiation of polyolefin cross-linking. One of them is based on macroradical formation via thermal decomposition of organic peroxides [7–9]. A detailed description of the various initiation procedures has been given in a comprehensive review by Lazar et al. [10]. The influence of cross-linking on the physical

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properties of waxes was also investigated, but a large amount of peroxide was needed [11,12].

In this paper, we shall discuss some effects of cross-linking on the thermal properties of LDPE/wax blends, such as melting temperature, crystallisation temperature, specific melting enthalpy, and thermal stability of cross-linked and uncross-linked LDPE/wax blends, and their dependence on the concentration of the cross-linking agent (dicumyl peroxide) and the wax content.

2. Experimental

A hard, brittle straight hydrocarbon-chain paraffin wax (Schumann-Sasol, South Africa, melting point 90°C, carbon distribution C28–C120, average molar mass 0.785 kg mol^{-1}, density 940 kg m^{-3}), LDPE (Sasol Polymers, South Africa, melting point 111–115°C, density 910–940 kg m^{-3}, MFI 20 g/10 min) and dicumyl peroxide (Sigma Aldrich) were used.

Blends were prepared by thorough mechanical mixing of the different components, after which the samples were pressed at 180°C for 10 min in a hot melt press. Gel contents were determined by a 12-h xylene extraction of 0.2 g samples wrapped in fine stainless steel mesh. Xylene was changed every 3 h.

DSC analyses were carried out in a PerkinElmer DSC7 thermal analyser in nitrogen atmosphere. The samples were heated from 25 to 140°C at 10°C min^{-1}, cooled to 25°C at the same rate, and reheated and cooled under the same conditions. Thermal properties, like melting and crystallisation temperatures and enthalpies were determined from the second scan.

TGA analyses were carried out in a PerkinElmer TGA7 thermogravimetric analyser in nitrogen atmosphere. The samples were heated from 25 to 600°C at 10°C min^{-1}.

3. Results and discussion

The gel content measurements are summarised in Table 1. In this table, samples are marked as follows: the *X*/*Y*/*Z* numbers in the sample column indicates the mass percentage ratios of LDPE/wax/DCP in the blends.

An increase in cross-link density with an increase in DCP content is observed. This is associated with an increase in the gel content. The gel content in the blends decreases with an increase in wax content, because wax needs a higher concentration of DCP for cross-linking [11,12]. Since the DCP concentration is too low for the cross-linking of the wax, it is more probable that only the LDPE portion is cross-linked.

Table 1
Gel content (g) values of cross-linked blends and values (g_o) related to the LDPE phase

X/*Y*/*Z*	g (%)	g_o (%)
99/0/1	77.3	78.1
89/10/1	73.1	82.1
79/20/1	71.5	90.5
69/30/1	68.2	98.8
59/40/1	63.1	106.9
98/0/2	82.4	84.1
88/10/2	79.5	90.3
78/20/2	77.3	99.1
68/30/2	75.6	111.2
58/40/2	72.9	125.7

It is interesting to compare the gel content values related to the LDPE phase (g_o), which are calculated from Eq. (1):

$$g_o = \frac{g}{w_{PE}} \tag{1}$$

where g is the gel content in the blends, and w_{PE} the mass percent of LDPE in the blends.

In the case of 40% wax (1% DCP), as well as 30 and 40% wax (2% DCP) the gel content related to the LDPE phase is found to be higher than 100%. This means that the gel content consists of all the LDPE, as well as some wax. Since previous works [11–13] showed that cross-linked wax does not create an infinite space network structure for small concentrations of DCP, it is probable that the wax is grafted onto the LDPE chains.

We can also calculate how much wax is included in the final gel. Let us define $g_w = m_{w,g}/m_w$, where $m_{w,g}$ is the mass of wax in the gel, and m_w the mass of the wax in the blend. If g is the gel content of the blends and g_{PE} the gel content after cross-linking of pure LDPE in the presence of the same concentration of DCP, Eq. (2) can be derived for g_w [14]:

$$g_w = \frac{g - g_{PE}(1 - m_w)}{m_w} \tag{2}$$

This equation is used to calculate the wax content in the final gel. If the concentration of DCP is 1%, then for a mass percent of wax $w_{\mathrm{w}} = 40\%$, $g_{\mathrm{w}} = 41.8\%$. For 2% of DCP and a mass percent of wax $w_{\mathrm{w}} = 30\%$, $g_{\mathrm{w}} = 59.7\%$. For the same concentration of DCP and a mass percent of wax $w_{\mathrm{w}} = 40\%$, $g_{\mathrm{w}} = 58.7\%$. Since both 1 and 2% DCP is too little for the cross-linking of wax, as we have discussed above, this supports the explanation that some portion of the wax is grafted onto the LDPE chains, and is included in the final gel.

The results obtained from DSC analysis are summarised in Table 2. $\Delta H_{\mathrm{m}}{}^{\mathrm{add}}$ was calculated according to the following equation (3):

$$\Delta H_{\mathrm{m}}{}^{\mathrm{add}} = \Delta H_{\mathrm{m,PE}} w_{\mathrm{PE}} + \Delta H_{\mathrm{m,w}} w_{\mathrm{w}} \tag{3}$$

where $\Delta H_{\mathrm{m,PE}}$ is the specific melting enthalpy of pure LDPE, w_{PE} the mass percent of LDPE in the blends, $\Delta H_{\mathrm{m,w}}$ the specific melting enthalpy of pure wax and w_{w} the mass percent of wax in the blends. We can see that, for uncross-linked blends, the experimental data of specific melting enthalpy are in good agreement with the additive rule, as can be expected. On the other hand, ΔH_{m} values of cross-linked blends have strong deviations from the additive rule. This indicates that cross-linking reduces the polyolefin crystallinity (degree of crystallinity is associated with specific melting enthalpy).

It is known that even a small number of cross-links reduce the crystallinity of LDPE provided that the cross-linking is performed above the melting temperature of the polymer crystallites. The changes in crystallinity of LDPE brought about by cross-linking are reflected in the melting temperature [15,16], heat capacity and heat conductivity of the polymer [17,18].

A decrease in $T_{\mathrm{o,m}}$, T_{m} with an increase in DCP concentration is observed (Table 2). This is a consequence of the reduction of lamellar thickness of crystallites. In our case, this decrease is very small.

Figs. 1 and 2 show DSC heating and cooling curves in nitrogen atmosphere for pure wax, pure LDPE, and different concentration ratios of LDPE/wax in the blends. Figs. 3 and 4 show the DSC heating and cooling curves of LDPE/wax/DCP blends. For illustration, only the DSC curves of the blends cross-linked in the presence of 1% DCP are displayed.

The DSC heating curves of all the samples show a main endothermic peak at about 102°C and the presence of wax does not influence its position. The DSC heating curve of 100% wax shows three endothermic peaks. The main peak is at 78.2°C. The other two

Table 2
The parameters obtained from DSC measurements of uncross-linked and cross-linked blends in nitrogen atmosphere (m: melting, c: cooling, o: onset, p: peak, $\Delta H_{\mathrm{m}}{}^{\mathrm{add}}$: additive rule, given by Eq. (3))

X/Y/Z	$T_{\mathrm{o,m}}$ (°C)	$T_{\mathrm{p,m}} = T_{\mathrm{m}}$ (°C)	ΔH_{m} (J g^{-1})	$T_{\mathrm{o,c}} = T_{\mathrm{c}}$ (°C)	$T_{\mathrm{p,c}}$ (°C)	ΔH_{c} (J g^{-1})	$\Delta H_{\mathrm{m}}{}^{\mathrm{add}}$ (J g^{-1})
Wax	60.2	78.2[a]	210.4	96.5	93.3[b]	−227.9	210.4
LDPE	94.0	102.5	83.5	87.8	86.1	−100.4	83.5
90/10/0	95.6	102.6	94.8	87.8	87.5	−110.9	96.2
80/20/0	95.3	102.5	102.4	88.9	84.4	−109.7	108.9
70/30/0	94.9	102.7	120.3	89.5	83.1	−128.0	121.6
60/40/0	94.8	103.1	127.3	89.6	82.2	−118.6	134.3
99/0/1	89.1	99.5	77.7	85.7	85.4	−95.6	82.7
89/10/1	94.5	101.2	92.7	89.1	83.6	−109.9	96.2
79/20/1	94.2	102.5	107.8	91.4	83.0	−111.5	108.0
69/30/1	93.8	102.2	119.8	91.9	82.6	−110.3	120.7
59/40/1	93.1	101.7	120.5	88.8	82.3	−112.4	133.4
98/0/2	86.4	97.4	76.5	83.2	80.1	−84.2	81.8
88/10/2	93.5	102.4	90.8	86.4	83.1	−93.9	94.5
78/20/2	93.1	101.1	107.4	91.6	82.4	−101.5	107.2
68/30/2	92.5	102.0	110.1	89.6	81.6	−102.3	119.9
58/40/2	90.3	101.3	118.3	90.8	81.0	−112.4	132.6

[a] The DSC heating curve of pure wax shows three endothermic peaks. This one is the main peak.

[b] The DSC cooling curve of pure wax shows two exothermic peaks. This one is the main peak.

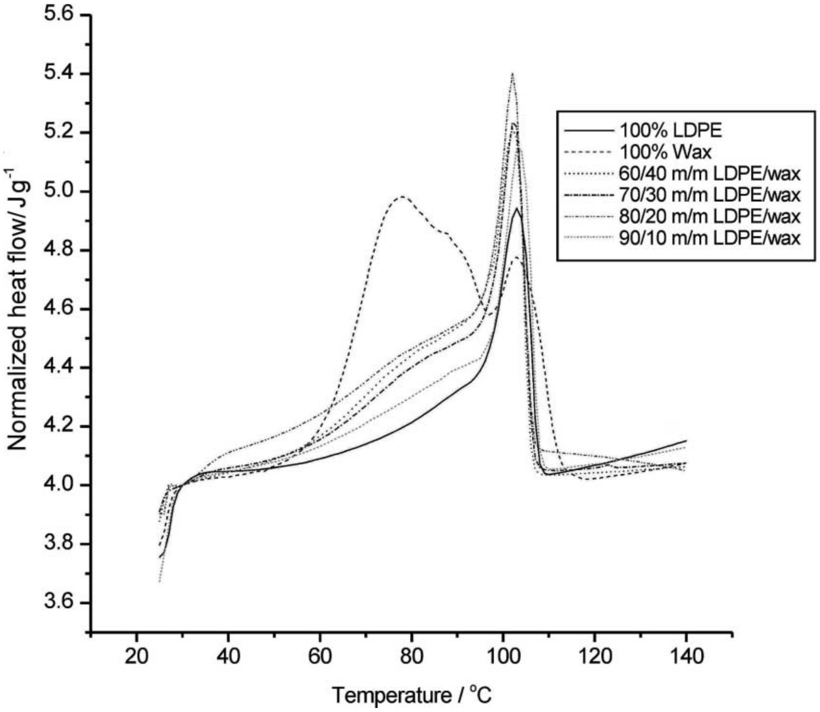

Fig. 1. DSC heating curve for LDPE, wax and uncross-linked blends.

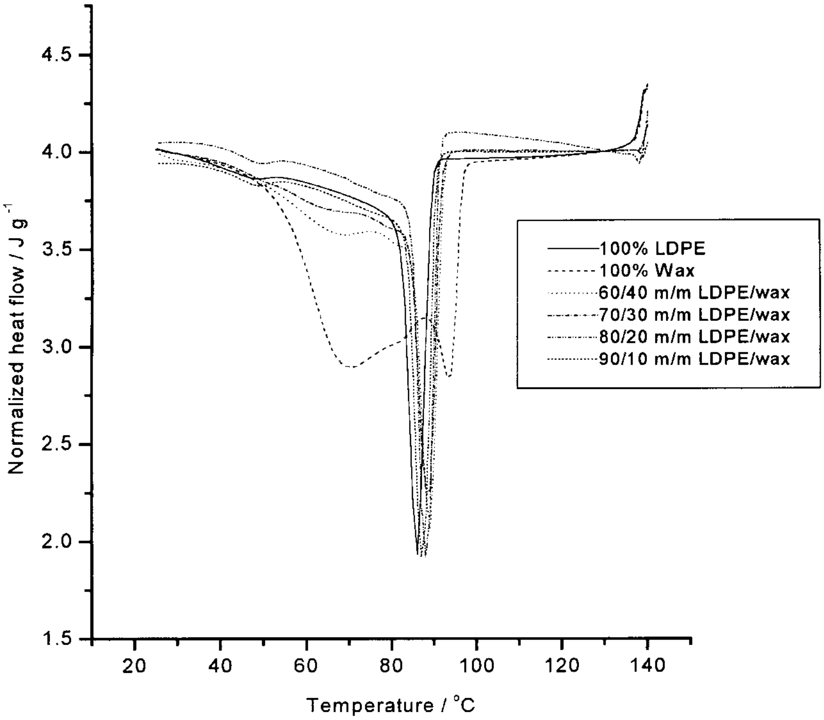

Fig. 2. DSC cooling curves for LDPE, wax and uncross-linked blends.

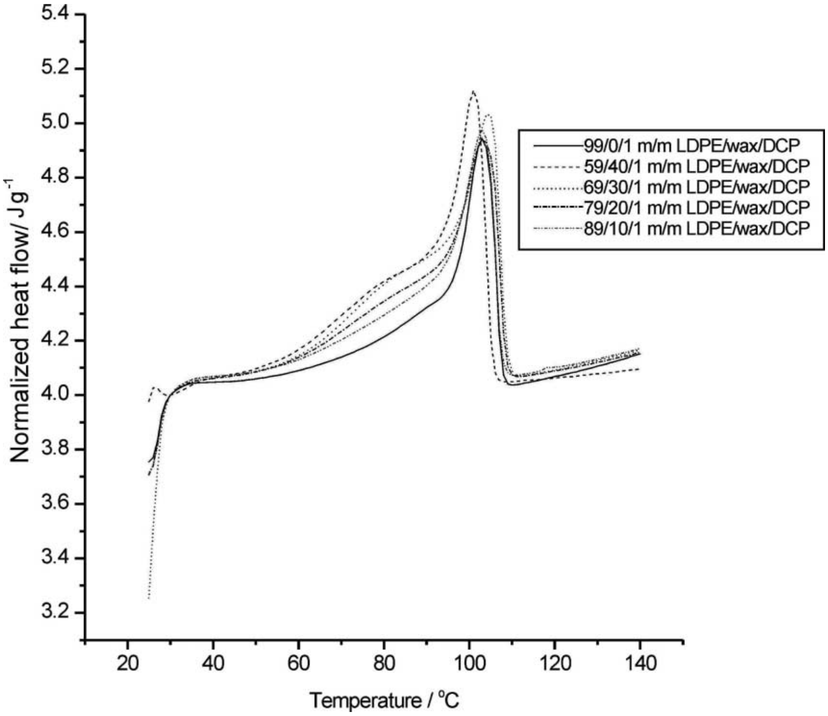

Fig. 3. DSC heating curves for cross-linked blends.

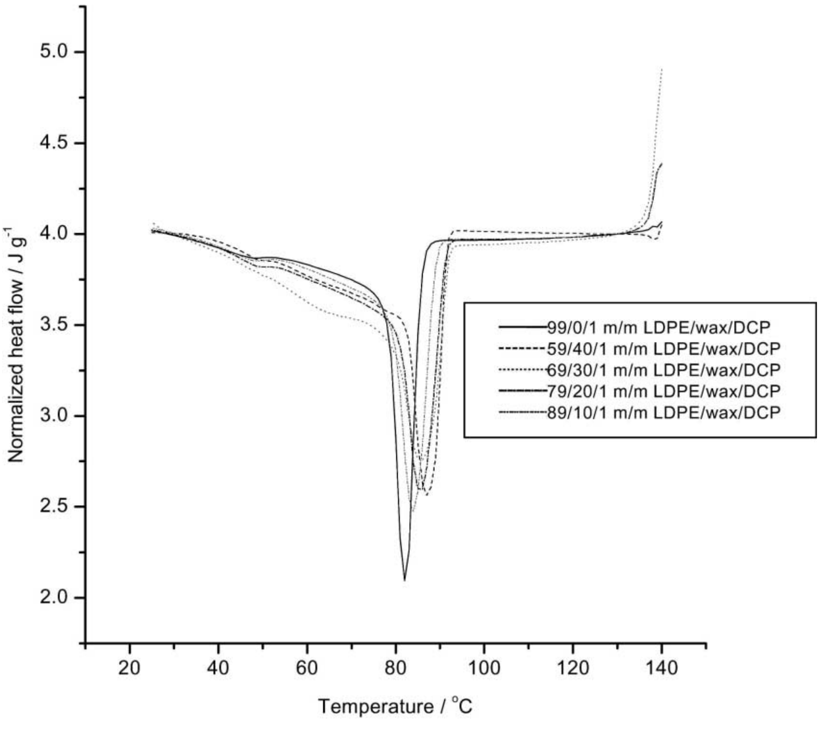

Fig. 4. DSC cooling curves for cross-linked blends.

peaks are at about 88 and 102°C, respectively (Fig. 1). For 10% of wax in the blends, only one endothermic peak is observed, despite the fact that pure wax has three endothermic peaks. One explanation is that LDPE and wax are miscible in the crystalline phase [19] in this concentration region. Another, maybe more probable explanation is that the wax and LDPE are not miscible, but display apparent homogeneity on a macroscopic level.

For 20%, but especially for 30 and 40% of wax, another small broad endothermic peak is observed in the temperature range 70–85°C, which corresponds to the main peak of pure wax. In this case, LDPE and wax are not mutually miscible. This behaviour is observed for both uncross-linked and cross-linked blends. In a previous investigation [14], it was found that linear LDPE/wax blends show only one endothermic peak in the concentration region from 0 to 40% of wax, both for uncross-linked and cross-linked blends.

The crystallisation temperature (T_c) of the uncross-linked blends does not depend on the wax content, but cross-linking does influence T_c. Since cross-links reduce crystallinity, and also play the role of defect centres, which impede the folding of macromolecular chains, and thus decrease the size of the lamellar crystals, T_c decreases with an increase in DCP concentration, as noted above for T_m (Figs. 2 and 4, Table 2). In our case, a very definite decrease in T_c is observed.

In Figs. 2 and 4, we can see three exothermic peaks. The first one at about 80–90°C is the most intense and corresponds to the crystallisation of LDPE. The second broad peak is at about 60–70°C and corresponds to the main peak of crystallisation of wax. This is observed for blends with a higher concentration of wax. It indicates that LDPE and wax are not miscible in the molten state, but since this peak is not very intense, it is possible that the components are partially miscible into each other. The third peak is at about 50°C. Since this peak is observed for pure LDPE, its intensity does not change with an increase in wax content. This peak was observed for pure LDPE, cross-linked and uncross-linked blends, and it is probable that its origin is in the LDPE structure. It is large for cross-linked blends (Fig. 4).

The thermal stability of cross-linked and uncross-linked blends was characterised in terms of temperatures of 10 and 20% mass loss. The results are summarised in Table 3. Our measurements show that:

Table 3
Temperatures of 10 and 20% mass loss of cross-linked and uncross-linked blends in nitrogen atmosphere

X/Y/Z	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)
LDPE	415.5	430.8
90/10/0	399.1	428.6
80/20/0	377.2	415.0
70/30/0	366.8	403.4
60/40/0	348.0	395.9
99/0/1	425.2	444.6
89/10/1	426.6	446.5
79/20/1	389.8	417.6
69/30/1	443.6	464.1
59/40/1	386.9	431.1
98/0/2	433.7	442.1
88/10/2	433.0	444.4
78/20/2	326.1	355.7
68/30/2	349.5	398.5
58/40/2	393.0	430.7
Wax	315.1	343.0

1. The thermal stability of the blends decreases with an increase in wax content. This is a logic consequence of the lower stability of the wax (Figs. 5 and 6, Table 3).
2. DCP content does not seem to have much influence on the thermal stability of LDPE or its blends.
3. Direct correlation between thermal stability and cross-link density (characterised in terms of the gel content) is not observed (Table 3).
4. No char yield was observed at temperatures higher than 500°C.

Cross-linking can initiate degradation due to the formation of weak points, defects in the structure and lower crystallinity (if cross-linking is initiated via peroxide decomposition). On the other hand, formation of more compact three-dimensional structures can improve thermal stability, since it is more stable against formation of gaseous products during heating. In our case, cross-linking not only creates a three-dimensional structure, but also decreases the degree of crystallinity, as discussed above. The consequence is that no direct correlation between cross-linking

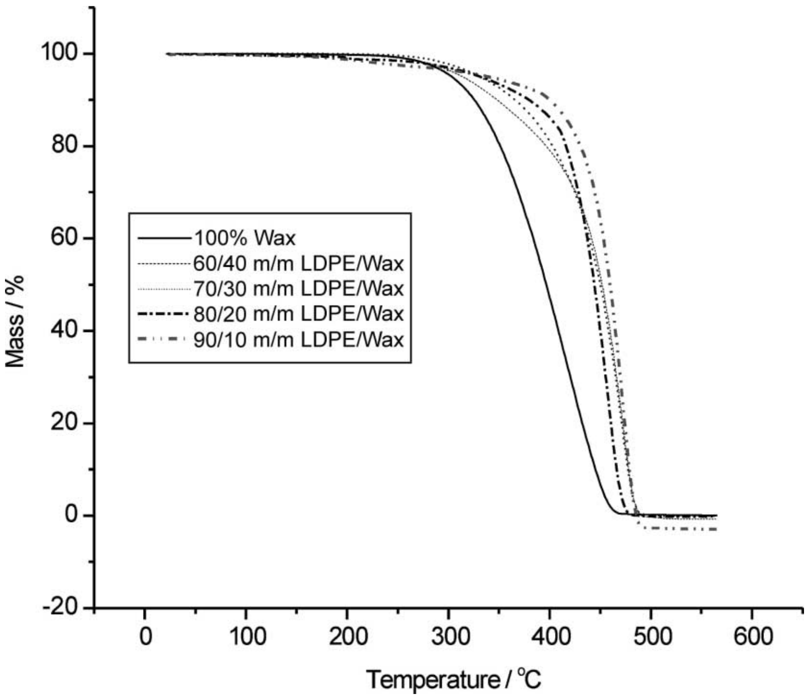

Fig. 5. TGA curves for uncross-linked samples.

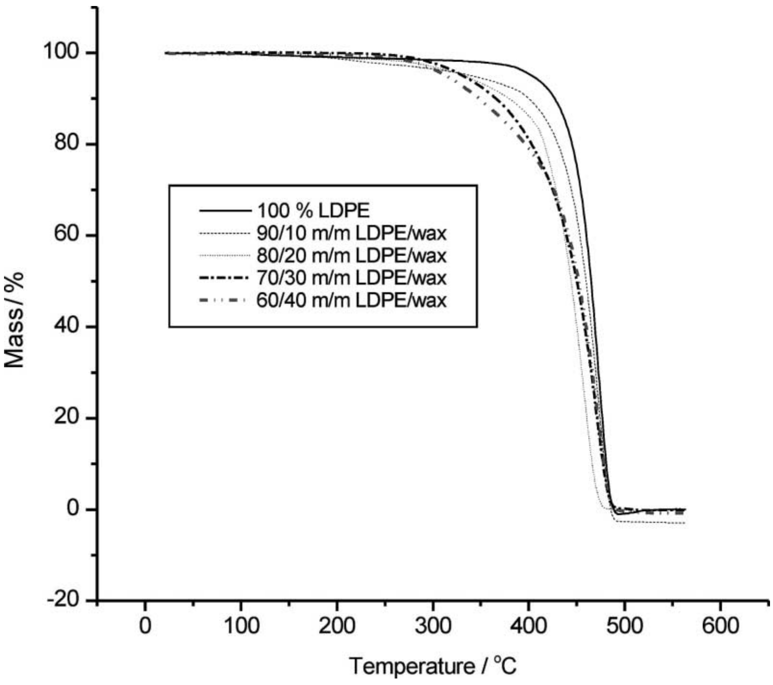

Fig. 6. TGA curves for cross-linked samples.

density (represented by gel content) and thermal stability is observed.

Generally, the correlation between cross-link density and thermal stability has been studied with contradictory results [20]. For example, it was shown [21] that the flammability of epoxy resins does not depend on cure conditions and therefore on cross-link density. In a separate investigation on another type of resin, it was found that the char yield increases and the flammability decreases with an increase in the cross-link density [22]. Char yield was also studied in modified thermoplastics [23]. Polyethylene was cross-linked with gamma-irradiation, and an increase in char yield was observed. A small improvement in the thermal stability of LLDPE, cross-linked with gamma-irradiation, was also observed [24].

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