# THERMAL ANALYSIS OF THERMOPLASTIC ELASTOMERS BASED ON RECYCLED POLYETHYLENES AND GROUND TYRE RUBBER[*]

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Thermal stability and phase structure of thermoplastic elastomers (TPEs) based on post-consumer materials such as recycled low- or high-density polyethylene and ground tyre rubber (GTR) were investigated by using TG, DSC and DMTA analysis. Preliminary reclamation of GTR leads to enhancement of compatibility between polyethylene matrix and dispersed GTR particles.

*Keywords: compatibility, ground tyre rubber, reclamation, thermoplastic elastomer*

## Introduction

Thermal analysis methods play an important role for characterization of structure-properties relationships in individual polymers and polymer blends. Several techniques are widely applied for the investigation of phase structure, thermal [1–3], and mechanical [4, 5] properties of polymer blends. Thermoplastic elastomers (TPEs), including polyolefin/rubber TPEs, are widely used in different fields of industry. In order to develop high performance TPEs from a combination of polymer wastes the problem of compatibility of the components should be solved.

In the present work three thermal analysis techniques, thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and dynamic mechanical-thermal analysis (DMTA) were used for phase structure characterization of polyethylene/rubber TPEs based on post-consumer components.

## Experimental

As polyolefins the recycled high-density polyethylene (HDPE$^R$) from post-consumer bottle transportation crates collected in Kiev (Roksana Ltd., Kiev, Ukraine) and the recycled low-density polyethylene (LDPE$^R$) from post-consumer greenhouse films were used. EPDM rubber (Buna$^®$ EP G 6470 of Bayer AG, Leverkusen, Germany), with 71 mass% of ethylene and 4.5 mass% of 5-ethylidene-2-norbornene contents, was used as a polymer compatibilizer. Ground tyre rubber (GTR) fraction with a particle size of 0.4 to 0.7 mm was kindly provided by Scanrub AS (Viborg, Denmark). A

specific reactive plasticizer (bitumen, $M_w$~14000, $M_n$~6500, content of sulfur around 3.4–3.6 mass%) was used for preliminary thermal-mechanical-chemical reclamation of GTR. GTR reclamation (reclaimed GTR is coded by GTR$^R$) by bitumen was carried out by preheating of GTR/bitumen blend (1/1 by mass) at 170°C for 4 h in oven [6]. Mastication of composition was carried out in the kneading chamber of a Brabender plasticorder (model PL 2000) at 160°C and 80 rpm. HDPE$^R$ or LDPE$^R$ was melted first for 2 min, then EPDM was added and melted for 2 min, and finally the GTR or GTR$^R$ blend was added and masticated with other components for further ~10 min. The composition of basic HDPE$^R$(LDPE$^R$)/EPDM blends was 40/35 (part by mass), whereas the composition of HDPE$^R$(LDPE$^R$)/EPDM/GTR and HDPE$^R$(LDPE$^R$)/EPDM/GTR$^R$ TPEs was 40/35/25 (mass%).

Thermogravimetry analyis was performed using the Q-1500D Derivatograph system developed by Paulik–Paulik–Erdey (MOM, Hungary)]. TG traces were registered in the temperature range from 25 to 660°C, at a heating rate of 10°C min$^{-1}$ in air, at evacuation of the volatile products. The mass of the samples was 50 mg.

DSC was carried out using PerkinElmer thermal analyzer Pyris 6 DSC. The scans were taken in the temperature range from –100 to 200°C with a programmed heating rate of 20°C min$^{-1}$. The melting temperature ($T_m$), corresponding to the maximum in fusion endotherm, was determined. Heat of fusion ($\Delta H_m$) was calculated from the area under the endothermic peak and the degree of crystallinity ($X_c$) was calculated accepting a melting enthalpy value, $\Delta H_m$=293 J g$^{-1}$, for the 100% crystalline polyethylene (PE).

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The viscoelastic behaviour of the resulting TPEs was investigated using a DMTA device (Eplexor 150N of Gabo Qualimeter, Ahlden, Germany). Rectangular sheets having dimensions $30{\times}50{\times}0.8$ $mm^3$ were subjected to oscillating tensile loading. The testing temperature was varied in the range from $-100$ to $150^\circ C$ at heating rate of $3^\circ C$ $min^{-1}$ and a frequency of 10 Hz.

## Results and discussion

The thermal stability of $LDPE^R/EPDM/GTR$ and $LDPE^R/EPDM/GTR^R$, as well as of $HDPE^R/EPDM/GTR$ and $HDPE^R/EPDM/GTR^R$ TPEs, has been studied by TG in the temperature region from 25 to $850^\circ C$ and compared to that of the reference blends $LDPE^R/EPDM$ and $HDPE^R/EPDM$, respectively. The results obtained are presented in Figs 1 and 2. One can conclude that introduction of GTR into the basic $LDPE^R/EPDM$ or $HDPE^R/EPDM$ blends is not accompanied by significant changes in their thermal stability at temperatures lower than approximately the temperature of $250$–$300^\circ C$. It was established that the $LDPE^R/EPDM/GTR^R$ and $HDPE^R/EPDM/GTR^R$ TPEs are thermally stable (i.e. no mass loss observed) up to $\sim 210$ and $\sim 270^\circ C$ with maximal rate of decomposition at the temperatures of 427 and $455^\circ C$, respectively.

Representative results of DSC studies are presented in Fig. 3 and in Table 1. These results indicate some depression of the melting temperature $(T_m)$ values for the $HDPE^R$ components in the $HDPE^R/EPDM/GTR$ and $HDPE^R/EPDM/GTR^R$ TPEs $(T_m{=}127.5$ and $127.6^\circ C$, respectively), as compared to the individual $HDPE^R$ $(T_m{=}131.5^\circ C)$ and to the reference $HDPE^R/EPDM$ TPE $(T_m{=}128.0^\circ C)$. It is known that the depression of $T_m$ of polymers in the blends is caused by the formation of less-perfect crystallites or crystallites having a smaller size [7]. Irrespective of which mechanism is at work, the decrease in $T_m$ is always indicative of improved blend compatibility.

For the $HDPE^R$-matrix a significant shift of the onset of $T_m$ towards higher temperatures and narrowing of
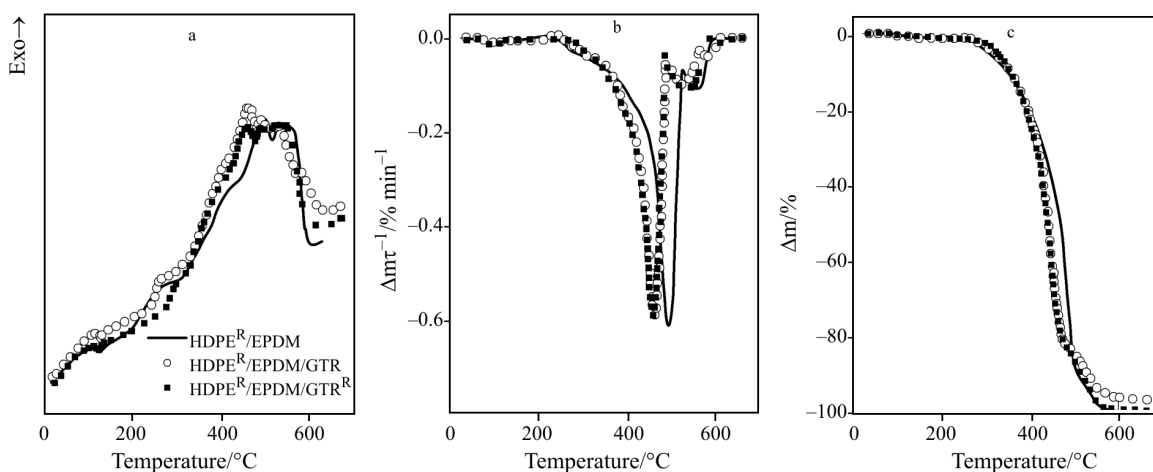


**Fig. 1** Thermoanalytical curves for different $HDPE^R$-containing TPEs (indicated in the plot): a – DTA, b – DTG, c – TG
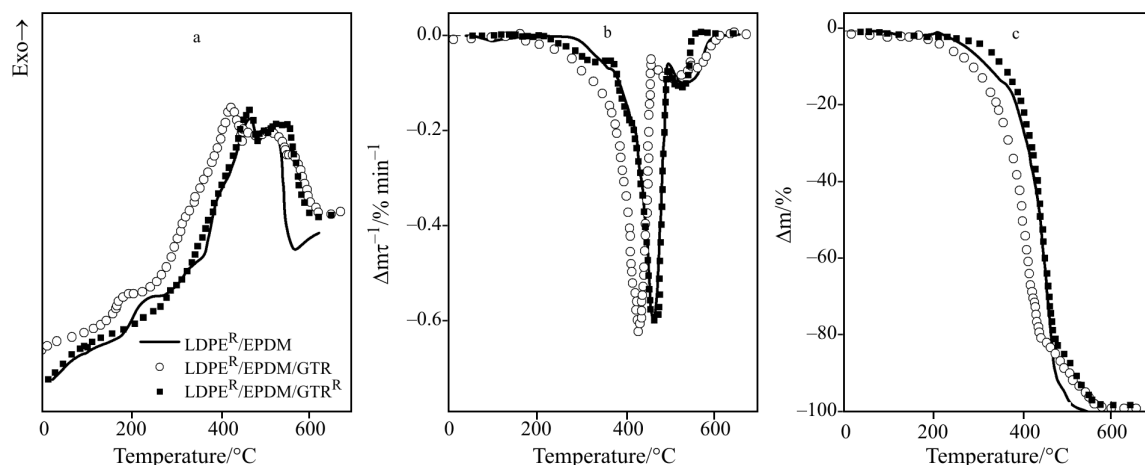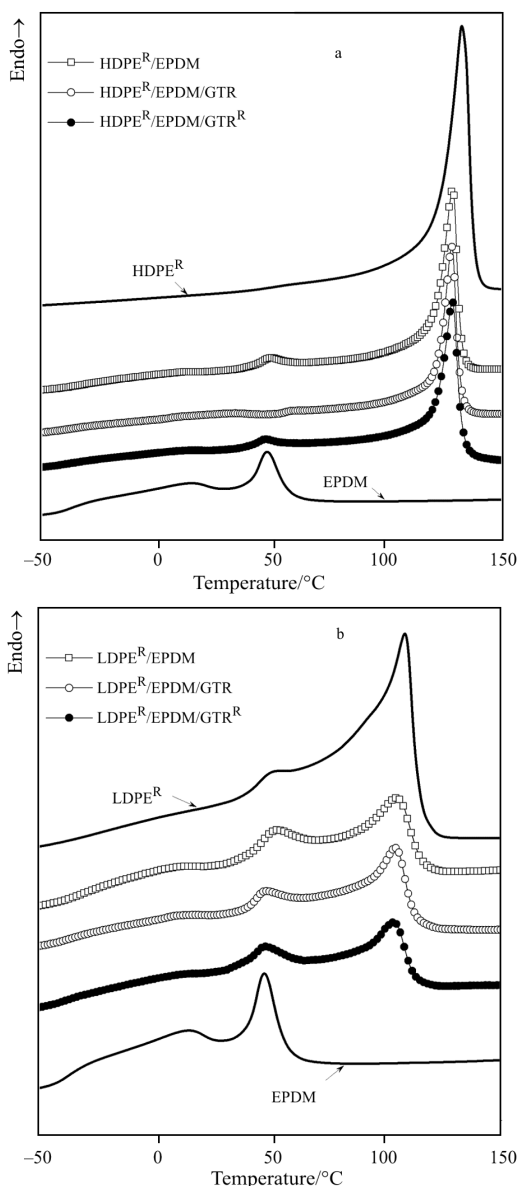


**Fig. 2** Thermoanalytical curves for different $LDPE^R$-containing TPEs (indicated in the plot): a – DTA, b – DTG, c – TG

**Fig. 3** Typical DSC traces for individual components and for different TPEs (indicated in the plot): a – HDPE$^R$-containing TPEs, b – LDPE$^R$-containing TPEs

**Table 1** DSC characteristics for individual polyethylenes and TPEs produced on the basis of the polyethylenes

| Composition | $T_m$/°C | $\Delta H_m{}^a$/J g$^{-1}$ | $X_c{}^b$/% |
|---|---|---|---|
| HDPE$^R$ | 131.5 | 198.2 | 67.6 |
| HDPE$^R$/EPDM | 128.0 | 107.8 | 69.0 |
| HDPE$^R$/EPDM/GTR | 127.5 | 91.6 | 77.8 |
| HDPE$^R$/EPDM/GTR$^R$ | 127.6 | 88.8 | 75.7 |
| LDPE$^R$ | 108.3 | 95.6 | 32.6 |
| LDPE$^R$/EPDM | 104.8 | 35.2 | 22.5 |
| LDPE$^R$/EPDM/GTR | 104.2 | 28.9 | 24.5 |
| LDPE$^R$/EPDM/GTR$^R$ | 103.8 | 25.2 | 21.5 |

$^a$The heat of fusion $\Delta H_m$ value was taken per unit mass of the blend sample. $^b$The $X_c$ (crystallinity) value was calculated taking into account the mass fraction of PE in the blend.

improving components compatibility in the GTR$^R$-containing TPE. The same tendencies have been found also for the LDPE$^R$-containing TPEs (cf. Fig. 3b and Table 1). Indeed, we observe the depression of the $T_m$ values for the LDPE$^R$ components in the LDPE$^R$/EPDM/GTR and LDPE$^R$/EPDM/GTR$^R$ TPEs ($T_m$=104.2 and 103.4°C, respectively), as compared to the individual LDPE$^R$ ($T_m$=108.3°C) and to the reference LDPE$^R$/EPDM TPE ($T_m$=104.8°C). In addition, a decrease of the $X_c$ value of polyethylene component is observed for GTR$^R$-containing TPE, as compared to GTR-containing TPE. As discussed above, this fact can be explained by improving components compatibility in the LDPE$^R$/EPDM/GTR$^R$ TPE. This conclusion will be confirmed later by DMTA data and tensile measurements.

The viscoelastic properties of individual polymers, as well as of the HDPE$^R$- and LDPE$^R$-containing TPEs, have been investigated by DMTA and the results are presented in Figs 4 and 5, respectively. EPDM has one sharp relaxation peak at –10.5°C ($\alpha$-transition), corresponding to the $T_g$ of its amorphous phase. A slight increase in tan$\delta$ values around ~50°C can be attributed to the melting of residual polyethylene crystallites that is confirmed by the DSC data. HDPE$^R$ and LDPE$^R$ have broad relaxation peaks (cf. Fig. 4) at around –12 and –18°C, respectively (cf. Figs 4 and 5), assigned to the glass transition of their amorphous phases, which consist mainly of branched macromolecules [7, 8]. Note, that in HDPE$^R$ and LDPE$^R$ samples at temperatures higher than ~35°C vibration and rotational motions of –CH$_2$– groups in the crystalline phases start due to recrystallization of less perfect crystallites ($\alpha_c$-transition) [8]. Also this result is confirmed by the DSC data. For EPDM and both the HDPE$^R$ and the LDPE$^R$ samples the low temperature transition below –100°C ($\gamma$-transition) is observed due to the crankshaft mechanism of –CH$_2$–CH$_2$– polyethylene chain segments [9].

the region of crystallite melting were observed for all TPEs studied compared to the individual HDPE$^R$ (cf. Fig. 3a). The first fact evidences of disappearance of smaller and less perfect crystallites, whereas the narrowing of the region of crystallite melting is a result of the decreasing dispersion of crystallite sizes. One can see (cf. Table 1) that GTR$^R$-containing TPEs are characterized by lower degree of crystallinity $X_c$ of polyethylene component, as compared to GTR-containing TPE. It can be supposed that this is a result of decreased microphase separation between amorphous and crystalline phases in the HDPE$^R$/EPDM/GTR$^R$ TPE (in comparison to GTR-containing one) due to destruction and involving of some crystallites into the amorphous phase during the mixing and vulcanization processes. This evidences of
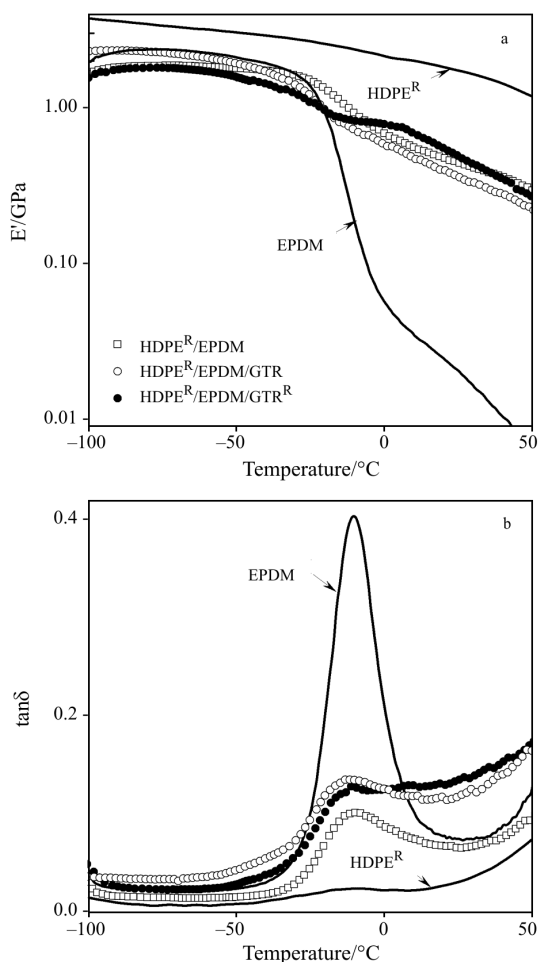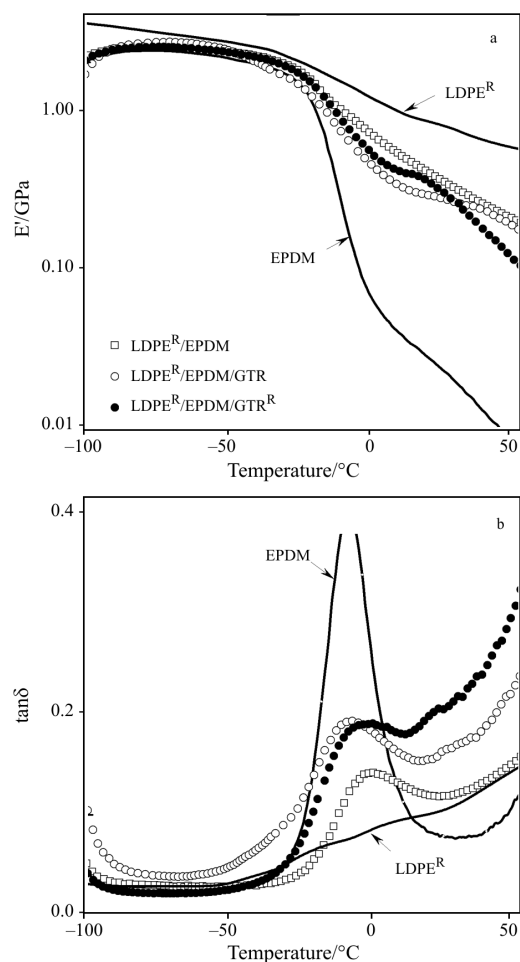
**Fig. 4** Temperature dependence of a – storage modulus ($E'$) and b – loss factor (tan$\delta$) for HDPE[R], EPDM and different HDPE[R]-containing TPEs produced (indicated in the plot)



**Fig. 5** Temperature dependence of a – storage modulus ($E'$) and b – loss factor (tan$\delta$) for LDPE[R], EPDM and different LDPE[R]-containing TPEs produced (indicated in the plot)

It is worth to note that the shape of the storage modulus $E'(T)$ curves for all TPEs prepared is similar to that for the individual polyethylenes, i.e. the polymer blends obtained should possess thermoplasticity. It was established that introduction of GTR into the basic HDPE[R]/EPDM or LDPE[R]/EPDM blends resulted to essential changes of their viscoelastic properties. Indeed, a new relaxation transition (shoulder) around –40°C appears (cf. Figs 4b and 5b) that is characteristic for the rubber component of GTR [10]. An uptrend in the tan$\delta$=$f(T)$ curves and a downtrend in the $E'$=$f(T)$ curves at $T$>–50°C, as well as some lowering of the $T_g$ values of the mixed polyethylene/rubber amorphous phase, by 3 and 7°C, respectively, were observed for the HDPE[R]/EPDM/GTR TPE and LDPE[R]/EPDM/GTR TPEs, as compared to the GTR-free samples. All these changes suggest a significant increase of chain flexibility of the components of the GTR-containing samples due to disordering of the thermoplastic matrix by the dispersed cross-linked GTR particles caused by poor interphase adhesion between the components [11]. As a result the tensile characteristics of the GTR-containing samples are much lower compared to the corresponding GTR-free samples (cf. Table 2).

One can see that both GTR[R]-containing TPEs studied (viz. HDPE[R]- and LDPE[R]-based samples) are characterized by increased (by 3–6°C) $T_g$ values of the mixed polyethylene/rubber amorphous phase in comparison to the corresponding GTR-containing samples (cf. Figs 4b and 5b). Further, some uptrend of the $E'$=$f(T)$ curves (cf. Figs 4a and 5a) and some re-

**Table 2** Composition and tensile properties of TPEs produced

| Composition | Tensile strength/MPa | Elongation at break/% |
|---|---|---|
| HDPE[R]/EPDM | 13.0 | 840 |
| HDPE[R]/EDPM/GTR | 4.4 | 114 |
| HDPE[R]/EDPM/GTR[R] | 13.3 | 625 |
| LDPE[R]/EPDM | 9.3 | 634 |
| LDPE[R]/EPDM/GTR | 4.1 | 440 |
| LDPE[R]/EPDM/GTR[R] | 12.9 | 720 |

duction of the tanδ values in the glass transition region can be observed, as compared to the corresponding GTR-containing samples. Undoubtedly, such simultaneous changes of viscoelastic properties of the samples studied evidence a hampering of chain flexibility of the blend components in the amorphous phase. We consider that this is due to increase in the degree of crosslinking of the dispersed EPDM/GTR[R] rubber phase in the TPEs (compared to the corresponding GTR-based samples), i.e. bitumen induced reactivation (partial devulcanization) of GTR is accompanied further by (re)covulcanization of GTR[R] with EPDM during mastication of the composition in the Brabender plasticorder. Finally, GTR[R]-containing TPEs exhibit high values of tensile strength and ultimate elongation (cf. Table 2). Based on this fact, an improved interfacial adhesion between the dispersed GTR[R]/EPDM rubber phase and the plastic HDPE[R] or LDPE[R] matrix can be definitely quoted.

## Conclusions

The hypothesis of enhancement of compatibility between the components of the HDPE[R](LDPE[R])/EPDM/GTR[R] TPEs during the dynamic vulcanization process has been confirmed on the basis of the results of DSC and DMTA investigations. Importantly, the TPEs studied possess high thermal stability.

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