Manufacturing, structure and properties of recycled polyethylene terephthalate /liquid crystal polymer/montmorillonite clay nanocomposites

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Abstract. Polyethylene terephthalate (PET)/liquid crystal polymer (LCP)/montmorillonite clay (MMT) compositions were obtained by melt mixing. Their mechanical, structural, rheological and thermal properties were investigated.

1. Introduction
Polyethylene terephthalate (PET) is widely used thermoplastic material. As a consequence large amount of PET waste is generated every year. Biggest source of recycled PET (RPET) are soft drink and alcoholic beverage bottles. In last decades the technology of post-consumer PET recycling has increased to very high level. Now it is possible to use RPET not only for fiber or cheap product production, but also for manufacturing of new beverage bottles and high class engineering materials [1, 2].

Liquid crystal polymer (LCP) is an intermediate state between solid crystal and isotropic fluid. This group of polymers is recognizable by their rigid rod-like molecules [3]. LCP improves mechanical properties of matrix material, besides LCP makes easier processing, because of shear-thinning effect [4]. Furthermore, in extrusion or injection molding LCP easily orient in the flow direction. It gives reinforcement effect on matrix. LCP dispersed in an isotropic thermoplastic matrix, can exist in the shape of spheres, fibrils or lamellae [3].

Nano scale montmorillonite clay (MMT) is also often used for reinforcing of polymers because of its anisometric plate-like particle shape. Due to that MMT improves also thermal stability and barrier properties [3]. There are many investigations about nano clay impact on thermoplastic polymers [5]. Simultaneous effect of both of these modifiers on polymers is scarcely investigated. In this study impact of MMT and LCP on RPET structure and properties is investigated.

2. Experimental

2.1. Materials
As matrix material RPET, obtained from post-consumer beverage bottles, is used. As modifier MMT clay from Laviosa Chimica Mineraria S.P.A. (Italy) is used. Liquid crystal polymer is synthesized from p-acetoxybenzoic acid and polyethylene terephthalate.
2.2. Preparation of RPET/LCP/MMT compositions

RPET has melt mixed with MMT (1 to 5 wt. %) and LCP (5 wt. %) by using twin screw extruder, which have five heating zones (Thermo PRISM TSE 16 TC). Temperatures along the barrel length have been set in this way: 245 °C (feeding zone), 255, 260, 270 °C, 275°C (head zone). Screw rotating speed has been 80 rpm. Prepared compositions are listed in Table 1.

| Composition | RPET (wt. %) | LCP (wt. %) | MMT (wt. %) |
|------------|-------------|-------------|-------------|
| 1          | 98          | 2           | -           |
| 2          | 95          | 5           | -           |
| 3          | 90          | 10          | -           |
| 4          | 94          | 5           | 1           |
| 5          | 93          | 5           | 2           |
| 6          | 90          | 5           | 5           |

2.3. Preparation of specimens

Specimens for tensile tests have been produced by using injection moulding machine Mini Jector, Model 55. Temperatures have been set 250-290-300 °C from hopper to die.

2.4. Measurement of physical properties

Mechanical properties have been investigated by using universal material testing machine Zwick Roell BDO-FB020TN at constant speed of the upper cross-head - 50 millimeters per minute. Rheological properties have been estimated by determination of melt flow rate by using ИИРТ – АМ device at temperature of 265 °C and load of 2, 16 kg.

Calorimetric characteristics have been investigated by using Mettler Toledo DSC 1 differential scanning calorimeter. DSC curves have been recorded in three steps: first – heating from 25 to 300 °C; second – cooling from 300 to 25 °C; third – repeated heating from 25 to 300 °C. Heating or cooling rate has been 10 °C / minute. The data for analysis have been taken from the third run.

Density has been determined by using hydrostatic weighing method. Sartorius YDK 01 density measurement kit mounted on Sartorius KB BA 100 electronic balance has been used. Measurements have been made at 25°C temperature. Ethyl alcohol has been used as liquid media.

3. Results and discussion

3.1. Mechanical properties

Firstly it is necessary to find most appropriate RPET/LCP composition for modification with MMT. As base composition for modification with MMT, RPET blend with 5 wt. % of LCP has been chosen. This decision is based on the data from composition tensile test. Mechanical properties of various RPET/LCP blends are show in figure 1. Yield stress and stress at break (figure 1a) of the investigated RPET blends show maximum values at LCP content of 5 wt. %. Increase of Young’s modulus at this LCP weight content also is relatively larger than at higher modifier concentrations (figure 1b). It is interesting to note, that up to 5 wt. % of LCP, strain at break values of the blends also increases.

The effect of MMT on the tensile properties of the RPET/5%LCP based nanocomposites is shown in Figure 1c. As shown, by rising MMT content considerable increase of Young’s modulus is observed. The reason for the modulus increase most probably is reinforcement of the composite because of the orientation of the platelike clay particles in the direction of the applied load. Contrary to Young’s modulus, strain values of RPET/5%LCP/MMT composites considerably decrease along with raising MMT content. It is, however, well know that adding inorganic filler (in our case MMT clay) system strain values decreases [5].
3.2. Structural properties

The influence of LCP and MMT on the RPET density is illustrated in figure 2a for RPET/LCP and figure 2b for RPET/5%LCP/MMT composites.

![Figure 1. Mechanical properties of RPET/LCP composites (a, b) and RPET/5%LCP/MMT nanocomposites (c): yield stress and stress at break (a), Young’s modulus and strain at break (b, c) as functions of modifier weight content.](image)

![Figure 2. Density of RPET/LCP (a) and RPET/LCP/MMT (b) composites as function of modifier content. With continuous line additive density values, which are calculated by using equation 3.1., are shown](image)

Experimental density values are determined by means of hydrostatic weighting. Theoretical density values are calculated by using equation 3.1.

$$\rho_{add} = \sum_{i=1}^{n} \rho_i \phi_i$$  \hspace{1cm} (3.1)

were $\rho_{add}$ – additive (theoretical) density, g/cm$^3$, $\rho_i$ – densities of the components, g/cm$^3$, $\phi_i$ – volumetric contents of the components in the composite.

It has been found, that the experimental density values are almost equal to the theoretical ones, especially in the case of RPET/LCP blends, for which deviations are below 1%. Indirectly this can testify about certain compatibility of the blend components, most probably due to the presence of ethylene terephthalate moieties in the LCP macromolecule.

The effect of LCP and MMT on the crystallinity degree ($\chi$) and glass transition temperature ($T_g$) of RPET have been investigated by means of differential scanning calorimetry (table 2). It is observed that $\chi$ increase by ca 50% along with addition of LCP to RPET. Addition of MMT to RPET/5%LCP blend also raises crystallinity of the system by approximately the same level. Increase of $\chi$ probably is the main reason why real density of the RPET/10%LCP blend is above the theoretically calculated. In the case of MMT containing RPET/5%LCP based nanocomposites this effect is hindered because of greater incompatibility of the polymeric constituents of the blend and MMT. Increased RPET $\chi$ values testify that both modifiers promote crystallization of RPET matrix, being another factor, which is responsible for increased stiffness and strength characteristics of the investigated compositions. There is also some increase of $T_g$ of RPET along with raising the content of either LCP or MMT. Rising of
T_g approves, that MMT, and most probably also LCP, reduce chain flexibility of RPET, thus stiffening the material. This is another reason why stiffness of the investigated compositions rises.

### Table 2. Crystallinity degree and glass transition temperature of the investigated compositions.

| Composition | Crystallinity degree χ (%) | Glass transition temperature T_g (°C) |
|-------------|----------------------------|-------------------------------------|
| RPET        | 21                         | 74                                  |
| RPET+2%LCP  | 24                         | 76                                  |
| RPET+5%LCP  | 24                         | 77                                  |
| RPET+10%LCP | 31                         | 81                                  |
| RPET+5%LCP+1%MMT | 30                    | 78                                  |
| RPET+5%LCP+2%MMT | 31                     | 79                                  |
| RPET+5%LCP+5%MMT | 33                      | 80                                  |

#### 3.3. Rheological properties

Rheological properties of the investigated compositions have been estimated by means of melt flow rate (MFR) measurements. It is well known that LCP in thermoplastic polymer compositions acts as a processing aid by decreasing viscosity and respectively increasing melt flow rate of the matrix polymer [3]. In figure 3a RPET melt flow rate dependence on LCP content is illustrated. As we can see only at LCP concentration 10 wt. % there is significant increase in MFR. In composites filled with MMT situation is quite unusual (figure 3b). Contrary to the widely accepted assumption that addition of inorganic filler increase viscosity (decrease MFR), in this case an opposite effect is observed. Similar situation is also referred by other authors [5]. It is thought that under shear stress MMT layers orient in the flow direction, thereby decreasing viscosity.

![Figure 3a](image1.png)  
![Figure 3b](image2.png)

**Figure 3.** Melt flow rate of RPET/LCP blends (a) and RPET/5%LCP/MMT nanocomposites (b) as functions of modifier weight contents.

#### 4. Conclusions

Increase of mechanical properties of RPET by modification with rigid-rod LCP and plate-like nanolevel MMT has been achieved. Positive effect of LCP and MMT nanoparticles on the crystallinity degree and glass transition temperature of RPET matrix is another reason for stiffness and strength increase. Addition of aforementioned modifiers eases also flowability of RPET, which is important for manufacturing of thin-wall items.

#### 5. Acknowledgements

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#### References

[1] Sheirs J 1998 *Polymer Recycling: Science, Technology & Applications*. John Wiley & Sons, 121-182
[2] Hannawi K, Kamali-Bernard S and Prince W 2010 *Waste Manage.* 30 2312-2320
[3] Lee M W, Hu X, Li L, Yue C Y, Tam K C and Cheong L 2003 *Comos. Sci. Technol.* 63 1921-1929
[4] Cidale M T, Fernandez M, Filipe S and Santamaria A 2012 *Polym. Test.* 31 290-296
[5] Pavlidou S, Papaspyrides C D. 2008 *Prog. Polym. Sci.* 33 1119-1198.