Phenomenological description of the mechanisms of deformation and degradation of polypropylene particles during mechanochemical modification in the solid phase

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This work considers the mechanism of deformation and degradation of polypropylene (PP) particles during solid phase mechanochemical modification in an extruder. Electron microscopy was used to investigate the morphological changes to particles of different dimensions (4 hierarchical levels), their internal structure and surface during increases in the duration and intensity of their exposure to mechanochemical impacts in an extruder. We provided a detailed description of the morphology of the original PP in references (refs. 1–3). Table 1 contains information on the structure of the particles of the original PP.

The mechanochemical processes result from contacts between solid particles, between a solid particle and a working body, on the surface, in the 'toe' of a moving crack and on encounters with defects in the material during plastic deformation. The relaxation of mechanical energy takes place via various channels (ref. 7):
1. Its conversion into heat
2. The plastic deformation of the material
3. Cracking and the formation of a new surface.

<table>
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<th>Table 1 Morphology of PP particles</th>
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<td>Indicator</td>
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<tr>
<td>Type of object</td>
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In the case of particles with different dimensions and shapes, the nature of the load distribution is more complex and obviously the mechanical energy relaxation processes are complex. It is known (ref. 8) that in zones of local plastic deformation of the material, the temperature may increase by tens of degrees and the compression of the polymer increases the temperature of the relaxation transitions also by tens of degrees, 0.1–0.2 K MPa (ref. 9). In plastic deformation zones and on the juvenile surface, grafting of the monomer to the polymer may take place. Increasing the temperature in these zones encourages the grafting process and the relaxation of accumulated stresses.

Therefore, we set ourselves the task of using electron microscopy to investigate how altering the duration (7–70 minutes) and intensity (13–26 J/g·s) of the processing affects the mechanism of deformation and degradation during the modification of polypropylene in different areas of the particles:

1. In each of the four structural levels of the particles (see Table 1)
2. On the surface of the particles
3. In the internal 'dense' and 'loose' parts of the 4th level particles.

We compared the results obtained with the degree of the grafting of the monomer (ref. 4) to the polymer and the changes to the specific surface of the material.

The subject of the investigation and the modification conditions are described by us in another article (ref. 1). The method of investigation is also described there. The method of mechanochemical modification is given in (refs. 4–6).

RESULTS

1. Exposure time 7 minutes, intensity J = 13 g·s

With short exposure times, the processes of deformation and degradation are the same in both polypropylene (PP) without modifying additives and PP with any type of modifier (MK, MA, NaMt). For example, 1st-3rd level particles are subject to plastic deformation and degradation (Table 1). During this, fibres, strips, twisted and flattened particles form (Figs. 1 and 2). Particles of this type cover the surface of 4th level particles. The deformation process, the orientation of material with the fracture of individual fibres, affect all the fine (3rd level) particles (Fig. 2). The diameter of the particles is ~30 µm. Fibres, pores within the particles and a series of individual flattened 2nd level particles are observed.

The most important process that occurs with 3rd level particles is the opening up of cracks in particles (see Fig. 3). This is clearly shown in Fig. 3a and 3c, where, in addition to a spherical particle with an opening crack, we can see fibres, strips and also deformed 'dendrites' from the 3rd level (Fig. 3a, 3b and 3c). Fig. 3d, with a greater magnification, shows the places where the cracks opened up in the spherical particle in Fig. 3c. We can see deformed 1st and 2nd level particles providing a bond between two particles, which are probably the deformed surface layer of the dense, originally perfectly, spherical particle.

Another important process which occurs in 3rd level particles is the disintegration of the surface of the particles subject to the maximum level of disintegration (Fig. 4a and 4c). The width of the cracks is 0.2 µm. On the surface of the 3rd level particles, we can see a smoothed surface, pore formation and the formation of streaks in the pores (Fig. 5). The dimensions of the pores reach 3 µm.

At the same time, there is an agglomeration of the dendrite-like 3rd level particles. Particles of this type are shown in Fig. 4a and 4b. Dendrite-like particles may agglomerate to form a spherical particle (Fig. 6a). The dendrite structure is retained in the particle structure, see Fig. 6b (compare with Fig. 4b).
Spherical 4th level particles (after the extraction of the non-reacted monomer) retain their shape and dimensions (refs. 1, 2, 6). Particles retaining their dimensions and shape during the modification of PP with different monomers (MA, MK, NaMt) account for the majority (95%) in each batch of material.

During the process of the mechanochemical modification, the size of the monomer particles is reduced from 0.4 to 4 µm (see Fig. 5c [ref. 2]). The cracks on the surface of the 4th level particles (between the 3rd level particles) may expand to 10–20 µm (see Fig. 5c [ref. 1]) so that the monomer is able to penetrate into a crack, expand it, deform and disintegrate the partition in the internal ‘loose’ part of the particle with the formation of a juvenile surface. It is probable that a grafting process takes place on this surface. The disintegration of the partitions gives the monomer access to the internal ‘loose’ porous part of the polymer particle where grafting may take place at the same time as plastic deformation. Evidence of this is provided by the increase (up to 30%) of the specific surface of the modified PP (for all three monomers) compared to the original PP (ref. 2). Therefore, plastic deformation of the polymer and monomer takes place simultaneously on the surface of the PP particles, in the cracks and in the 4th level particles.
The tegular shape of the surface of 4th level particles and their internal structure (the presence of ‘dense’ external and ‘loose’ internal parts is retained in the majority of particles).

II. Duration of exposure 21 minutes, intensity \( J = 13 \text{ J/g·s} \) and \( J = 26 \text{ J/g·s} \)

Let us look at the mechanism of the deformation and degradation of PP particles with a duration of exposure of 21 minutes and an intensity of \( J = 13 \text{ J/g·s} \) and \( J = 26 \text{ J/g·s} \). The conditions investigated are characterised by all the processes described in the previous section (duration 7 minutes), but in addition, the greater part of the larger material fraction (200–315 \( \mu \text{m} \)) and individual particles in the fraction (400–630 \( \mu \text{m} \)), i.e. 4th level particles, are also subject to deformation and degradation.

The process of the deformation of the external ‘dense’ part of the 4th level particles is illustrated in Fig. 7 and the degradation of this part in Fig. 8. The external layer of particles measuring from 100 to 1500 \( \mu \text{m} \) is destroyed. For example, a 300 \( \mu \text{m} \) particle is shown in Fig. 8a and a 600 \( \mu \text{m} \) particle in Fig. 8b. We can see that this crack goes deep within the surface layer. Fig. 9 shows microphotographs of individual particles with cracks in their surface layer (Fig. 9a) and Fig. 9b, 9c and 9d the sequence of processes in the surface layer. Fig. 9b shows the area of the crack in which the external layer is greatly deformed. In individual areas of Fig. 9c, the material is destroyed to form 6 \( \mu \text{m} \) pores and next to this material with maximum plastic deformation (multiple ‘neck’ formation). Fig. 9d shows the part of the crack in which the ‘necks’ rupture to form a strip up to ~50 \( \mu \text{m} \) in length and ~10 \( \mu \text{m} \) in width. In the strip, we can see the ends of the ruptured ‘necks’. The microphotographs in Fig. 9b, 9c and 9d show different places in the same particle crack shown in Fig. 9a. They look like ‘motionless’ pictures of the sequential process of the deformation and degradation in the surface areas of the particle.

Fig. 6 Agglomeration of dendrite-like particles with a spherical particle (a). Structure of this particle at greater magnification (b)

Fig. 7 Deformation of the ‘dense’ external part of 4th level particles obtained with \( t = 21 \text{ minutes}, J = 26 \text{ J/g·s} \)
Figure 10a and 10c shows particles:
1. With a crack, which divides the particle into parts (Fig. 10a)
2. With a crack, which partially destroys the particle (Fig. 10c).

Figure 10b shows the place in the particle from Fig. 10a marked with an (*) at a greater magnification. We can see that 'dense' external part of the particle has undergone deformation (top of Fig. 10b).

This is ~10 µm thick. The 'loose' internal part of the part is greatly deformed. Fig. 10d shows the place of the crack in Fig. 10c (with the 'toe' of the moving crack) with a high degree of magnification. We can see that the internal 'loose' part of the 4-level particle is greatly deformed. The original globular particles and particles with a complex shape (Fig. 1 [ref. 1]) are deformed into thin, as it were flattened, open-work plates with different shape. An analysis of numerous particles of this type leads one to suggest that the internal part is deformed, but not the deformed 1st and 2nd level particles which have fallen into the crack.

The 'nose' of the moving crack shown in Fig. 10c and 10d may be seen more clearly in another particle (Fig. 11).
These are the places where the grafting process may take place in the particle. We can see the 'nose' of the moving crack in the upper part of the particle (Fig. 11) and also very distinctly in the lower part. Cracks of this kind moving towards the centre of the particle may cause the particle to divide into parts and result in the fragmentation of the particle shown in Fig. 10a and 10b. The results of the investigations which are shown in Fig. 10 are grounds for suggesting that in Fig. 11b we can see the deformed internal part of the particle inside the 'nose' of the crack.

The deformation of the surface is reflected in the flattening of the tegular relief of the 4th level particles (Fig. 12).

Therefore, increasing the time to 21 minutes and the intensity to 26 J/g·s causes processes of plastic deformation and degradation to take place even in the 4th level particles: in their 'loose' internal part and on the surface of these particles. If the content of 4th level particles is 95% of all particles and the grafting processes are linked to the processes of plastic deformation and degradation (ref. 7), increasing the time to 21 minutes should lead to an increase in the content of carboxyl groups. As shown in (ref. 4), the grafting process reaches a maximum in virtually all fractions at precisely 21 minutes. The greatest number of grafted groups was observed (ref. 4) in the finest fraction (less than 200 µm). According to the results of electron microscopy, the fine fraction is less robust and is the first fraction to undergo deformation and degradation during modification as described by us in (refs. 1-2).

III. Exposure time 70 minutes, intensity 13 and 26 J/g·s

The main microphotographs of the material with an exposure time of 70 minutes in 'gentle' (J = 13 J/g·s) and 'harsh' (J = 26 J/g·s) PP modification conditions and their interpretation are given in article No. 4 in this journal (see Figs. 5-7). Here, we should stress that increasing the time from 7 to 70 minutes causes the deformation and degradation processes, which were determined in the experiments on the fine material fraction, to be frequently observed in the fraction with the largest particles of material (level 4).
The majority of the material in all fractions underwent deformation and degradation. For example, with 'harsh' conditions and a time of 70 minutes, in the PP with no modifier about 50% of the 4th level particles lose their shape: they become flatter, twisted and are destroyed in parts. The known processes of deformation and degradation in polymer mechanics are observed by us in individual particles obtained after synthesis.

Therefore, the investigations performed in the initial modification stage (t = 7 minutes, J = 13 J/g·s) found the following:

1. With a time of 7 minutes and an intensity of J = 13 J/g·s with modifier, the particles in levels 1–3 underwent plastic deformation and degradation. These particles covered the surface of the 4th level particles accounting for the majority of the material (95%).

2. We observed surface cracking and extensive degradation of the 3rd level particles with maximum deformation.

3. We observed pores and streaks on the surface of the 3rd level particles.

4. The dendrite-like 3rd level particles may agglomerate.

5. 4th level particles generally retain their shape, dimensions, surface appearance and the existence of a external 'dense' part and an internal 'loose' part, which leads us to suspect that the modification process takes place without the fusion of the polymer. However, the external and internal structures of the 4th level particles are destroyed under the action of the more solid monomer. Cracks open up in the external layer between the 3rd level spheres. The boundaries in the internal layer are deformed and destroyed, which confirms the increase (to 30%) in the specific surface.

6. Increasing the duration and intensity of modification causes the processes of plastic deformation to take place in the 4th level particles as well as resulting in an 5.5 times increase in the specific surface.

Therefore, the investigations performed enable us to determine how the intensity and duration of the modification affect the mechanism of the deformation and degradation of the material during its solid phase mechanochemical modification. This explains the nature of the change to the material in all four hierarchical particle structural levels after modification.

We established the results of the process of the deformation and degradation of the material in each of the 4 structural levels of the particles, on their surface and in the internal part of the particles. The process of the grafting of the monomer to the polymer takes place during their simultaneous plastic deformation in all 4 structural levels of the material and on the newly formed juvenile surface of the material. Therefore, knowledge of the mechanism of deformation and degradation in specific areas of the material enables us to produce a more complete representation of this complex modification process.

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