Novel Technique to Improve High-Velocity Cold Compaction
Processing of Polymer Powders and Polymer-Based Nanocomposite
High Performance Components

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AKADEMISK AVHANDLING

To the most beautiful....

My Kurdistan
ABSTRACT

Compaction of polymer powders and polymer-based nanocomposites by uniaxial high-velocity cold compaction (HVC), by high-energy ball milling (HEBM) and using a novel technique, relaxation assists, was investigated with a focus on the process parameters, the compactibility characteristics, surface morphology and friction. The basic phenomena associated with HVC are explained and the general energy principle is introduced to explain the pull-out phenomenon, springback gradient, delay time, relative time of the pressure wave, and stick-slip phenomenon during the compaction process. Experimental results for different compaction profiles, different particle size distributions and different milling system for polymer-based nanocomposite are presented, showing the effect of varying the process parameters on the compacted material; the compactibility in the compacted bed, the uniformity of the compacted surface, the pull-out phenomenon, the springback gradient, the stick-slip phenomenon and the homogeneity of the dispersions of nanoparticles in the polymer powders in the solid state. It was found that the high-velocity compaction process is an interruption process and that the opposite velocity and pressure loss during the compaction process have a major influence on the quality of the compacted material. The relaxation assist device is a novel technique that has been successfully developed to improve the compaction process. The relaxation assists are parts of the piston and they are regarded as projectile supports. They are constructed of the same material as the piston, and the diameters are the same but the lengths are different. The relaxation assist device leads to an improvement in the compaction of powders, polymer powders and polymer-based nanocomposites by giving a more homogeneous opposite velocity and a better locking of the powder bed in the compacted form during the compaction process with less change in dimensions in the case of both homogeneous and heterogeneous materials. If the movement of the particles is restricted the powder bed attains a higher density and the total elastic springback is minimized. In addition, there is a more homogeneous dispersion of nanoparticles in the case of a heterogeneous material. A much better transfer of the pressure through the powder bed and a smaller loss of pressure lead to a more homogenous stick-slip of the particles and a higher sliding coefficient due to the overall friction during the compaction process.

Keywords:

polymer powders; nanocomposites; high-velocity compaction; high-energy ball milling; relaxation assist; compactibility; morphology; particle size distribution; pull-out; springback gradient; delay time; stick-slip phenomenon; dispersions; opposite velocity; sliding coefficient; heterogeneous materials

Nyckelord:
Kallkompaktering, polymera pulver, nanokompositer, enaxlig höghastighetskompaktering, högenergi kulmalning, relaxationsstöd, kompatibilitet, ytmorfologi, partikelstorleksfördelning, utdragning, återfjädringsgradient, fördörjningstid, fast- och glidningsfenomen, dispersion, motsatt hastighet, glidkoefficient
LIST OF PAPERS

This thesis is based on the following papers:

I. ‘Development of a High-Velocity Compaction process for polymer powders’
   Bruska Azhdar, Bengt Stenberg, Leif Kari, Polymer Testing, 2005; 24(7): 909-919

II. ‘Determination of springback gradient in the die on compacted polymer powders during high-velocity compaction’
    Bruska Azhdar, Bengt Stenberg, Leif Kari, Polymer Testing, 2006; 25(1): 114-123

III. ‘Determination of dynamic and sliding friction, and observation of stick-slip phenomenon on compacted polymer powders during high-velocity compaction’
     Bruska Azhdar, Bengt Stenberg, Leif Kari, Accepted for publication in Polymer Testing, 2006.

IV. ‘Polymer-nanofiller prepared by high-energy ball milling and high velocity cold compaction’
    Bruska Azhdar, Bengt Stenberg, Leif Kari, Submitted to Polymer Composites, 2006.

My contribution to the appended papers:

Paper I: Performed 100% of the experimental work, 100% of the data analysis and writing.

Paper II: Performed 100% of the experimental work, 100% of the data analysis and writing.

Paper III: Performed 100% of the experimental work, 100% of the data analysis and writing.

Paper IV: Performed 100% of the experimental work except for the milling, which was carried out at the materials science department, and the particle size characterization by laser, carried out at the Swedish Defence Research Agency (FOI).
    Performed 100% of the data analysis and writing.
### DEFINITIONS

**High-velocity compaction:** A high-velocity compaction (HVC) of powder materials is a dynamic process carried out with one or several strokes of a piston and the velocity is from about 1 m/s up to 100 m/s.

**Pre-compaction step:** This step is the primary step of the compaction process carried out in order to drive the air out from the compacted powder bed and to obtain a further densification of the powder.

**Post-compaction step:** This step is the secondary step of the compaction process carried out in order to increase densification and particle-to-particle bonding and possibly achieve an interlocking of particles.

**Compacting stage:** This stage is the stage when the material is compressed and the density of the material increases to a maximum value. The time to reach the maximum pressure is the compacting time.

**Decompacting stage:** After the maximum pressure has been reached and the piston starts to withdraw, the decompacting stage starts. The compressive stresses relax and the material expands due to the elastic energy stored in the material. The time to return from the maximum to the minimum pressure is the decompacting time.

**Total Work of Compaction:** The total energy transferred to the powder by the piston is the total work of compaction (TWC).

**Relaxation assists:** Parts of the piston which act as projectile supports. The pieces are constructed from the same material as the piston and the diameters are the same, but the lengths are different.

**Relative green density:** The ratio of the apparent density of the compacted powder to the theoretical density of the powder material.
**Sliding friction coefficient:** The coefficient of sliding friction is a ratio indicating the resistance (force) to relative sliding motion of the surfaces of two bodies (polymer powder and die wall) in contact.

**Stick-slip phenomenon:** An intermittently dynamic friction at very low stress, caused by the irregular nature of both the particle-particle and particle-wall frictional forces.

**High-energy ball milling:** A mechanical milling and mechanical alloying of powders by ball milling with a transfer of energy during collision between the starting materials and the elements of the milling media.
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$</td>
<td>Surface area of particle ($m^2$)</td>
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<tr>
<td>$d$</td>
<td>The diameter of the compacted powder bed (m)</td>
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<tr>
<td>$D$</td>
<td>Relative green density</td>
</tr>
<tr>
<td>$d_{eq}$</td>
<td>Equivalent particle diameter (m)</td>
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<tr>
<td>$E_k$</td>
<td>Kinetic energy (J)</td>
</tr>
<tr>
<td>$F$</td>
<td>Hydraulic force (N)</td>
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<tr>
<td>$h$</td>
<td>The height of the compacted powder bed (m)</td>
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<tr>
<td>$h/d$</td>
<td>Geometrical factor</td>
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<tr>
<td>$M$</td>
<td>Mass (kg)</td>
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<tr>
<td>$n$</td>
<td>Number of particles</td>
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<tr>
<td>$s$</td>
<td>Distance (m)</td>
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<tr>
<td>$T_g$</td>
<td>Glass transition temperature ($^\circ$C)</td>
</tr>
<tr>
<td>$V$</td>
<td>Velocity (m/s)</td>
</tr>
<tr>
<td>$V_B$</td>
<td>Opposite velocity (m/s)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Delay time (s)</td>
</tr>
<tr>
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</tr>
<tr>
<td>$P_t$</td>
<td>Transmitted pressure (N m$^{-2}$)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Coefficient of friction</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Angle of pressure (rad)</td>
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<td>$\eta$</td>
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1 INTRODUCTION

The powder processing technology, which is very well established for metals and ceramics, is being used for the processing of some speciality polymers such as polytetrafluoroethylene (PTFE) and ultra high molecular weight polyethylene (UHMWPE) since these polymers are not melt processible by conventional techniques because of their high melt viscosities [1-4]. Furthermore, for polymer-based composites, it is difficult using conventional melt compounding techniques to mix high concentrations of filler materials such as metal powder with polymers [5, 6]. The most significant powder processing techniques at room temperature and/or elevated temperature are: static pressing, dynamic pressing, hot and cold isostatic pressing (H & CIP) and the conventional powder metallurgy technique (P/M). The most common method involves pressing the polymeric powder with single-ended pressing in a rigid metal die [1, 7]. This technique appears to offer many interesting possibilities for conventional materials in specialized applications where conventional methods cannot be used. For example, since the technique does not require the polymer to flow on a macroscopic scale, heating is not needed as in a conventional melt flow process. This eliminates the need for thermal stabilizers, lubricating agents and other process aids, and the low process temperatures reduce the risk of degradation and improve the potential for scrap recovery. The high-velocity technique is more energy-efficient and permits shorter cycle times than conventional processing, since the relatively slow heating and cooling stages are eliminated [5].

Common problems during powder compacting are a low green density and an inhomogeneous density distribution in the compacted powder bed (compacted material). During the cold forming of polymer and polymer-based composites, the most important parameter is pressure, and the disadvantage of the technique is the loss of pressure at the bottom of the die as result of friction between the powder particles and the container wall [8]. In addition to this pressure loss, there are four main phenomena that can affect the high-velocity compaction process negatively: pull-out, springback, delamination and capping, all of which are due to a breakdown in the product during and/or after the decomapping stage. In the pull-out phenomenon, the top surface of the product becomes uneven, while in springback the dimensions of the product change. In capping, the top or cap of the product breaks off, and in the case of delamination the sample splits into a number of layers. These problems can be due to an initially non-uniform distribution of the powder within the die or to an excessive compaction speed.
Earlier studies have revealed that friction between the powder particles and the die wall is the major factor leading to structural variations within the compacted materials. Other investigations have revealed that the pressure transmission through the powder is important for the success and efficiency of the process. Crawford [9] has reviewed the different aspects of solid-state compaction of polymeric powders, and has discussed the effects of the various process parameters such as compaction pressure, compaction rate, and dwell time. Crawford and Sprevak [10] studied the cold compaction of polymeric powders and found that, with a cylindrical die and the geometrical factor \( h/d = 2 \), where \( h \) is the height and \( d \) is the diameter of the compacted powder bed, and using single-ended compaction, the pressure loss at the bottom of the die was 91% of the applied pressure at the top. They tried to reduce the pressure loss by using a tapered die to reduce the cross-sectional area, but the reduction was not as large as expected. The influence of various parameters such as the velocity of the cylindrical rod, the rod diameter and length, the granular particle size and the compaction pressure (by studying drag and compression force) in granular materials under high pressure was investigated by Zhou et al. [11], and they reported that the pressure loss at the bottom of the cylinder when \( h/d = 1.18 \) was about 61% of the applied pressure. In investigations of the dynamic compaction of biomaterial powders, Trécant-Viana et al. [12] showed that peripheral cracks, uneven surfaces and inhomogeneous densification are characteristic of this technique, regardless of the static primary compaction (pre-compacting) step used before the dynamic secondary compaction (post-compacting) step. Canta and Frunza [13] studied the powder metallurgy technique (P/M) during cold die compaction by using the container movement, and they reported that the effect of their new proposed technique (compaction using container movement) on the density was similar to that of bilateral pressing. During the decompacting stage or an ejection of an object from a die, some degree of residual stress appears in the form of springback. Limit responses are related to cracking, delamination and capping. Dimensional tolerance problems caused by large-scale, time-dependent springback limit the size of the objects which can be compacted [14].

Several studies on springback and the dimensional changes in a compacted product, such as the effect of particle size, wall friction, glass transition temperature, and elastic recovery have been reported [15-20]. It is widely known that objects which have been compacted by high pressure, cold compaction, and high-velocity compaction are non-uniform and contain both density and stress gradients [5, 8, 12, 21]. Most investigations have assumed that the compacted materials have a uniform density and a dimensional homogeneity in the die and they have focused only on the gross axial changes after the compacting process.

The cold compaction of a polymer powder is a complex process involving many parameters, such as friction between particles, friction between particles and the die wall, pressure, compaction rate and geometrical factors. Friction between the powder particles and the die wall during the process is the major factor leading to structural variations within the compacted material during the pre-compaction step. This primary step in the compaction process drives air out of the compacted powder bed and leads to a densification of the powder. The secondary step, the post-compaction step, increases the densification and particle-to-particle bonding and possibly achieves an interlocking of particles. The compacting stage is
defined as the stage during which the material is compressed and the density of the material increases to a maximum value, and the decompacting stage is defined as the stage during which the compressive stresses are relaxed and the material expands due to the elastic energy stored in the material, leading to an inhomogeneous density distribution in the compacted powder bed, pull-out, springback, capping and delamination, all of which are due to breakdown in the product.

The friction types encountered during the different steps are quite different. During the pre-compaction and post-compaction steps with low energy and low velocity during the compacting stage, the powder is not compacted and the rate of densification is great. At this point, the density of the powder is referred to as the tap density [22]. During this step, the mechanisms of both particle-particle and particle-wall friction are primarily stick-slip, due to the ability of the particles to move, rotate and slide past each other before any permanent deformation takes place. The friction between the powder particles and the die wall during the high-energy and high-velocity compacting stage is not of the same character as that during the decompacting stage. During the compacting stage, friction is a combination of both sliding and rolling friction due to particle contact with the wall combined with densification. During this stage, sliding between particles and elastic compression at the contact points leads to a further densification of the powder [23], the pressure increases and, finally, the material around the contact points is subject to plastic deformation and flows. At this point, the density of the material is referred to as the green density. During the decompacting stage, the friction is in a steady state due to the relative stable surface after permanent deformation takes place, but the compacted powder bed contains density gradients which depend on the characteristics of the powder material and on the compacting conditions.

It is difficult to measure the friction during cold high-velocity compaction of a polymer powder under single-ended pressing in a rigid metal die, since the characteristics of the powder change during the process and the process is not continuous, but rather includes several interruptions that are likely to have a great influence on the compacted material. These changes from an elastic to a plastic deformation lead to different types of friction. Powder particles have different sliding distances (when the pressure increases between the particles and rotations and slip between the particles become limited) depending on their position. During the compacting stage, the sliding distance is greatest for the particles at the top of the die and smallest for the particle at the bottom. Friction problems have been studied for many years, particularly for metal powders [13, 24-28]. More recently, studies have included pharmaceutical powders [15, 20, 29, 30] and ceramic powders [16, 31-34]. Many studies have sought to express the distribution of the pressure forces in a die as a function of related properties and relationships during the compaction [9, 35-44]. The most interesting formula for arbitrary samples of constant cross-section for single-ended pressing of cylindrical samples is given by Ballhausen [45].

There is an increasing interest in the modelling of powder compaction [46-54] but this requires correct input data. The frictional forces during the compaction process are a combination of friction during reorganization of the powder and friction during elastic and plastic deformation of the particles. An alternative approach to the problem is to use an
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Experimental model technique which permits direct measurement of the sliding coefficient between the particles and the die wall after the reorganisation stage under controlled conditions.

Compacting of polymer nanocomposite materials, organic polymers and inorganic nanoparticles, is a relatively new and unique area in materials science, and these represent an important group of engineering materials that have a wide range of applications. These materials offer cost effectiveness and rapid fabrication, and they combine the advantageous properties of metals and plastics, the interface between the inorganic nanoparticles and the polymer matrix [55]. A strong interfacial interaction between the inorganic nanoparticles and the polymer matrix can give rise to unique properties such as thermal stability [56], magnetism [57], non-linear optics [58], superconductivity [59], and a dynamic mechanical behaviour [60, 61]. In the past decade, a spate of research activities on polymer nanocomposites has shown great promise for high-performance composite polymer materials with low density and high mechanical strength and stiffness using nanoscale reinforcement [62]. Several methods have been used to produce polymer nanocomposites, such as sol-gel reaction [63], intercalative polymerization [64], and polymerization via melt processing [65], depending on the nature of the nanoparticles and on the manner of synthesizing the polymeric matrices. These composites are dispersed, usually by conventional methods of polymer processing; in the melt [66], for example, by casting [67-70], injection moulding [71-73] or extrusion [74-78]. It is however extremely difficult to disperse the nanoparticles homogeneously in the polymer matrix because of the easy agglomeration of nanoparticles and the high viscosity of the polymer. On the other hand, the production of blends by solution processing often generates environmental concerns regarding solvent removal and disposal. The blending polymers in the solid state by e.g. mechanical milling (MM) or mechanical alloying (MA) of polymers by ball milling [79, 80] is thus an attractive alternative since many of the problems presently encountered could then be avoided altogether [81]. High-energy ball milling (HEBM) [82, 83], a low-cost technique for the manufacture of polymer/metal composite powders [84, 85], is followed by high velocity cold compaction [86, 87].

The fundamental mechanisms that control polymer compaction and sintering are not well understood, and this makes it difficult to choose appropriate process parameters [88]. The present study has been performed to clarify the effects of the compacting conditions on the properties of the compacted products. An understanding of the influence of compaction process conditions, design and/or initial parameters of the compacting machine and parameters such as pressure, pressure transmission through the powder, pressure loss, compaction rate and geometrical factors on a large-scale should make it possible to improve the compaction process by controlling and reducing the frictional forces. The radial force measurement systems in use effectively integrate over the whole powder bed interfacial area, but a point-to-point examination of the frictional conditions using strain gauges positioned at various intervals, while the velocity, sliding distance and ratio of axial to radial force under a normal force are kept constant is possible [89, 90]. The sliding coefficient and wall friction data can be obtained in a separate test using an experimental model technique, but this is impractical in a high-energy, high-velocity compaction.
Attempts have also been made to explore the efficacy of preparing composite powder of nickel-ferrite, NiFe$_2$O$_4$, nanopowders and ultrafine poly (methyl methacrylate), PMMA, by co-milling the mixture of PMMA and NiFe$_2$O$_4$ in the solid state by low-temperature mechanical alloying, and producing a polymer nanocomposite (PMMA/NiFe$_2$O$_4$) using high-velocity cold compaction. PMMA was chosen because it has favourable physical properties: exceptional transparency, easy thermoforming, great machinability, and resistance to ageing. PMMA is used in many engineering constructions, for example in aviation, the nuclear process industry, machinery equipment, sanitary equipment, windscreens, impact protection, etc.

To improve the compaction process, a novel relaxation assist device has been successfully developed. The relaxation assists are parts of the piston and they are regarded as projectile supports. They are constructed of the same material as the piston, and the diameters are the same but the lengths are different. The relaxation assist device leads to an improvement in the compaction of powders, polymer powders and polymer-based nanocomposites, by giving a more homogeneous opposite velocity and a better locking of the powder bed in the compacted form with less change in dimensions in the case of both homogeneous and heterogeneous materials. By reducing the movement of the particles, the powder bed attains a higher density and the total elastic springback is minimized. Accordingly, a much better transfer of the pressure through the powder bed and a smaller loss of pressure lead to a more homogeneous stick-slip of the particles and a higher sliding coefficient due to the overall friction during the compaction process.

1.1 PURPOSE OF THE STUDY

The powder processing technology and conventional powder metallurgical (P/M) process for cold (room temperature) and high-pressure compaction, which is well established for metals and ceramics, has been extended to certain specialty polymers that are difficult to process in the melt [1, 4, 6, 13, 36, 91]. The disadvantages of the technique are the loss of pressure at the bottom of the die as result of friction between the powder particles and the container wall such as sliding friction and stick-slip phenomenon.

The fundamental mechanisms that control polymer compaction are not well understood; therefore this study has been performed to clarify the effects on the properties of compacted products polymers and polymer-based nanocomposites of the compacting conditions such as delamination, springback, pull-out, and capping. The effects of compaction pressure, energy and velocity on compaction characteristics have been studied and efforts have been made to improve the compaction process.
1.2 THEORETICAL BACKGROUND

In general, when a particulate material is placed in a rigid die at room temperature and is subjected to pressure, a number of distinct stages can be identified in the process as the material is transformed from a loosely packed powder to a closely packed (possibly solid) material. When the powder is first poured into the die, its density is the bulk density of the powder. This bulk density is a function of particle size and shape and it appears to have no influence on the material’s compactibility [9, 92]. When the compaction piston moves down onto the powder, the particles are reorganised in three stages: particle rearrangement, elastic deformation at contact points and plastic deformation at contact points. In the particle rearrangement stage, the particles, which have been held up lightly by friction and bridges within the powder, move to lower positions at a low pressure until further piston movement is not possible without particle deformation. At this point, the density of the powder is known as the tap density [22]. During the next stage, sliding between particles and elastic compression at the contact points leads to a further densification of the powder. Under low stresses, the solid behaves essentially as an elastic body, i.e. it reverts to its original state on removal of the stress [23]. During the final stage, the downward movement of the compaction piston continues, the pressure increases and finally the material around the contact points is subject to plastic deformation and flows as shown in Fig. 1.

In the extreme case of a fully plastic response, there is no recovery of the original shape. At this point, the density of the material is known as the green density. An early transition from elastic to plastic deformation is found in powders where the particle shape is irregular, since high stresses are created on small regions of contact between particles, and this means that the elastic limit is overcome under a relatively low compaction pressure [38]. Deformation processes that occur in the powder material under dynamic loading differ significantly from those that occur under static loading [3, 4, 36, 93, 94].

When the material is subjected to a dynamic load, the portion of the body that is exposed at the point of impact is stressed instantaneously while other portions may not yet have experienced the effect of the imposed load, since the effect requires time to propagate through the body (Fig. 2. caption-b).
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Fig. 1. Plastic deformations at contact points between particles on the bottom surface of compacted PA11 (20-30 µm) after pre-compaction at 60 J/g and post-compaction at 300 J/g.

Fig. 2. Pressure waveforms recorded by two strain gauges (upper and lower-strain gauge) (a) First reflecting waveform, compacting and decompacting stage, (b) delay between upper strain gauge and lower strain gauge.
This propagation occurs with a velocity which depends on the state and characteristics of the material. A high strain rate (compaction speed) is usually achieved by accelerating the impacting projectile via a hydraulic pump, a light gas gun or an explosive generator. In this investigation, a hydraulic power system was used to drive a piston [95]. The various parts of the compaction equipment are illustrated in Fig. 3.

Fig. 3. Diagram of the compaction testing cell equipment.
In engineering mechanics, the general energy principle may be stated as: The work done on a system is equal to the sum of the changes in kinetic energy and potential energy and the energy losses. The kinetic and potential energies are stored within the system and are recoverable. All other energy forms, such as friction, are considered to be losses. When friction is present, the work done depends on the path taken. Further experience of the physics of the problem suggests that other measurable changes may be taking place [96, 97]. In the first place, a local vibration and a change in temperature are expected. It is possible that a change such as melting of the material may take place. In mechanics, these latter changes generally represent a loss to the system, but such 'losses' may be regarded as 'gains' in the potential energy in the material [98, 99]. In addition to the bulk material properties of the powder, each powder particle is defined by its particle mass and velocity. The compaction process is defined by four additional system-state parameters: the kinetic energy $E_k$, the hydraulic force $F$, the mass $M$, and the velocity of the stroke $V$, and the opposite velocity during the decompacting stage, boundary velocity $V_B$ (Fig. 2. caption-a).

The total energy transferred by the piston, the Total Work of Compaction (TWC), and absorbed by the material powders may reflect the particle behaviour, e.g. the elasticity, viscoelastic flow, brittle fracture and breaking of bonds in the material [100-102]. This can be calculated directly as:

$$\text{TWC} = \int_{0}^{s_{\text{MAX}}} F \, ds,$$

(1)

where $F$ is the hydraulic force on the piston and $s$ the distance between the bottom surface of the hammer and the top surface of the piston.

The TWC is equal to the change in kinetic energy:

$$\int_{0}^{s_{\text{MAX}}} F \, ds = \frac{MV^2}{2},$$

(2)

where $F$ is the hydraulic force on the piston, $s$ is the distance between the bottom surface of the hammer and the top surface of the piston, $M$ is the mass of the hammer and $V$ is the velocity of the hammer at $s = s_{\text{MAX}}$. This kinetic energy is transferred to the compacted powder bed during the compaction stage [103].

At a low strain rate (low-velocity compaction), the particles follow the common cyclic limit conditions in the horizontal plane ($x$ and $y$-directions). Under these conditions, there is more opportunity for the particles to move, rotate and slide past each other [20]. In this case, the motion often becomes intermittent. This instability is caused by the irregular nature of both the particle-particle and particle-wall frictional forces, developed at very low stress, so that the system alternately sticks and slips forward (the stick-slip mechanism). At a high strain rate (high-velocity compaction), the motion in the $z$-direction is more energetic. Under this
condition, there is less opportunity for the particles to move, rotate and slide past each other. In this case, the frictional force is basically independent of contact speed and the system usually slides smoothly (sliding mechanism) \[104, 105\]. The bottom wall reflects the particles, the powder bed, to begin the decompacting stage with the inverse velocity, the boundary velocity \( V_B \). The piston ultimately returns toward its original position and the particles, the powder bed, follow it. The movable top wall of the mould takes over in this case. However the top wall of the mould moves faster than the compacted powder bed, due to the elastic response of the compacted material. A large elastic response and non-homogeneous particle velocities can, however, lead to delamination, springback, capping, and pull-out problems.

Many studies have sought to express the distribution of the pressure forces in a die as a function of related properties and relationships during the compaction \[9, 15, 34-44, 106-108\]. The most interesting formula for arbitrary samples of constant cross-section for single-ended pressing of cylindrical samples is given by Ballhausen \[45\]:

\[
\frac{P_a}{P_t} = \eta \tan \frac{S H}{4F}
\]

where \( P_a \) is the applied pressure, \( P_t \) the transmitted pressure, \( \mu \) the coefficient of friction, \( \Phi \) the angle of the pressure transmission from the top to the wall of the die, \( F \) the cross-section area, \( S \) the cross-section perimeter and \( H \) the height of the powder bed at the point of examination.

The magnitudes of \( P_a \), \( P_t \), \( S \), \( H \) and \( F \) can easily be measured. In order to determine the coefficient of friction \( \mu \), it is necessary to correctly estimate the angle \( \Phi \). As yet, no reliable method has been proposed for the determination of \( \Phi \) and consequently, an accurate friction coefficient \( \mu \) cannot be obtained.

For practical purposes, a similar approach is used by Gasiorek [109-114] in the Ballhausen-Gasiorek model [115]. The modified Ballhausen–Gasiorek equation is a more practical and general expression for a uniaxial single-sided pressing process

\[
\frac{P_t}{P_a} = \eta \frac{S H}{4F} \quad \text{or} \quad \eta = \left( \frac{P_t}{P_a} \right)^{\frac{4F}{S H}}
\]

The coefficient of sliding friction \( \eta \) characterizes the efficiency to transfer the compaction force through the polymer powder. This ratio is simply defined as the resistance (force) to the relative sliding motion of the surfaces of two bodies (polymer powder and die wall) in contact. This relation makes it possible to predict the sliding friction coefficient for any particular cross-sectional area of the powder bed, provided \( P_t \) and \( P_a \) are known.
2 EXPERIMENTAL

2.1 MATERIALS

Polyamide-11 powders (Rilsan® Polyamide-11, ARKEMA A/S) were used as received. The powders had been sieved prior to delivery to produce grades with different particle sizes. Nickel iron oxide (NiFe$_2$O$_4$) nanopowders (20-30 nm) as shown in Fig. 4 were obtained from Nanostructured & Amorphous Materials, Inc., USA and were used as received.

![Image of Nickel iron oxide nanopowders](image.png)

**Fig. 4.** Nickel iron oxide (NiFe$_2$O$_4$) nanopowders, from Nanostructured & Amorphous Materials, Inc., USA.
Polymethylmethacrylate (PMMA) powders were obtained from ALTUGLAS® BS, ARKEMA A/S. The PMMA powders were roughly ground in liquid nitrogen using an ultracentrifugal mill ZM 100 and sieved using Analytical sieve shakers AS 200 (Retsch GmbH, Germany) to produce grades with different particle sizes. The particle size distributions of Polyamide-11 and PMMA were measured by studying particles imaged on micrographs. The areas of approximately 500 particles were measured using imageJ 1.33u (National Institutes of Health, NIH, USA). The measurements were processed and the equivalent particle diameter $d_{eq,i}$ for particle $i$ was calculated according to

$$d_{eq,i} = \sqrt{\frac{4A_i}{\pi}}, \quad (5)$$

and the arithmetic mean particle diameter according to

$$d = \frac{1}{n} \sum_{i=1}^{n} d_{eq,i}, \quad (6)$$

where $n$ is the total number of the particles and $A_i$ is surface area of particle $i$. The mean diameter of the particles is assumed to represent the average particle size of each sieved fraction. The mean particle sizes for the Polyamide-11 powders were 22, 42, 82 and 110 µm as shown in Fig. 5. and the main particle sizes for the PMMA powders were 280 µm as received, 202 µm after rough milling, 108 µm after 1 hour HEBM with liquid N$_2$, and 48 µm after 25 hours HEBM with liquid N$_2$, as shown in Fig 6.

**Fig.5.** Polyamide-11 fractions—equivalent diameters by scanning electron microscopy (SEM).
The particle size distributions of (PMMA/NiFe$_2$O$_4$) mixtures after high-energy ball milling (HEBM) were measured using the Malvern Process System for particle characterization, Mastersizer 2000, driven by standard operating procedures (SOPs), using SOP ISO13320-1, international standard for particle size analysis by laser diffraction (Malvern Instruments Ltd, UK). The different particle size distributions of (PMMA/NiFe$_2$O$_4$) mixtures are shown in Fig. 7.

![Graph showing particle size distributions](image-url)

**Fig. 6.** PMMA particle sizes after different milling conditions—equivalent diameters by scanning electron microscopy (SEM).
2.2 EXPERIMENTAL PROCEDURE

2.2.1 High-energy ball milling

In order to obtain a homogeneous dispersion of nanoparticles in the polymer powder in the solid state, high-energy ball milling was used. The mixtures of NiFe₂O₄ nanopowders and PMMA powders with weight per cent ratios of 1:5 and 1:1 (20% and 50%) were mechanically alloyed using a cryogenic vibratory ball mill using a 20:1 ball-to-powder weight ratio, with a continuous liquid nitrogen drip. Stainless steel vial and balls were used with a motor speed of 65 rpm. The PMMA powder was also mechanically milled for 25 hours.

Fig. 7. Nanocomposite (PMMA/NiFe₂O₄) mixtures—equivalent diameters by the Malvern-2000 process by laser diffraction.
2.2.2 High-velocity cold compaction

The powders were compacted uniaxially in a cylindrical hardened steel die with a diameter of 25 mm using a Hydropulsor powder compacting machine (Hydropulsor AB, Sweden). The dynamic compaction system fired a 25 mm diameter and 80 mm long projectile (piston) with projectile supports (relaxation assists) into the unlubricated die. The various parts of the compaction equipment are illustrated in Fig. 3. The compaction velocities were: 3.9 m/s up to 6.2 m/s, which correspond to average strain rates from $0.1 \times 10^3 \text{ s}^{-1}$ to $0.6 \times 10^3 \text{ s}^{-1}$. The average strain rate in each case was calculated by dividing the compaction velocity by the initial height of the powder bed. The different heights correspond to different geometrical factors $h/d$, (from 0.18 to 1.12) where $h$ is the height and $d$ is the diameter of the powder bed.

The total energy transferred to the powder by the piston, the Total Work of Compaction (TWC), can be calculated directly from equation (2). The pressures during the compaction process were measured by two strain gauges positioned on the piston and on the plug (Load Indicator AB/Sweden) [116].

2.2.3 Relaxation assist device

In this study, two new components have been introduced as a relaxation assist device to improve the compaction process, as shown in Fig. 3. The relaxation assists are parts of the piston and they are regarded as projectile supports. They are constructed of the same material as the piston, and the diameters are the same but the lengths are different. The relaxation assists used had lengths equal to 12, 37 and 60% of the length of the piston. The function of the relaxation assist device is to lock the powder bed in the compacted form during the compaction process.

2.3 COMPACTING PROFILES

Compaction profiling was carried out on a HYP35-4 testing machine equipped with two voltage amplifiers to amplify the output voltage from the load cells. The compaction cycle used to drive the compaction process is a one-ended compression (one piston moving) process operating over a range of velocities. Projectile velocities were measured and energies were calculated using equation (2).

Samples were prepared using four different compacting profiles in order to study the compression characterizations:
1. Samples were compacted via a single stroke, one downward post-compacting. This compacting profile is referred to as $P_{\text{post-down}}$.

2. Samples were compacted via a single downward pre-compacting stroke followed by one constant downward post-compacting stroke. This compacting profile is referred to as $P_{\text{pre}} + P_{\text{post-down}}$.

3. Samples were compacted via a single downward pre-compacting stroke followed by one constant downward primary post-compacting stroke followed by one constant secondary upward post-compacting stroke. This compacting profile is referred to as $P_{\text{pre}} + P_{\text{post-down}} + P_{\text{post-up}}$.

4. Samples were compacted via a single downward pre-compacting stroke followed by one constant upward primary post-compacting stroke followed by one constant secondary downward post-compacting stroke. This compacting profile is referred to as $P_{\text{pre}} + P_{\text{post-up}} + P_{\text{post-down}}$.

For each experiment, four to ten independent samples prepared under the same conditions were tested. All the powders were initially dry-mixed for ten minutes at room temperature in order to obtain a homogeneous particle size distribution before compaction.

### 2.4 ANALYTICAL TECHNIQUES AND MEASUREMENTS

A FASTCAM-ultima APX High-Speed Video Camera System with an electronic shuttering system up to 120,000 frames per second (fps) and PFV (Photron FASTCAM Viewer, Photron Inc., USA) and Laser sensor (M100, Measuring range 50 mm, Resolution 0.6µm) were used to study the actions of the piston and the hammer during the compaction process using the National instrument (NI LabVIEW, PC-based machine and motion-control PXI mixed-signal and Real-Time Module), as shown in Fig. 3. An image computer board camera, consisting of a computer, a light table, an adapter and a video camera with the Image J 1.33u software (IC-PCI Imaging Technology Incorporated, USA), was used to study the morphological characteristics of the compacted products. The relative dimensional changes were calculated from the position of the piston at each pressure wave, which is related to the thickness of the powder bed including the elastic deformations of the piston parts, in relation to the first pressure wave during the compaction. A sequence of pressure waves reveals the springback gradient in the die. The reorganization times were calculated from the time from the first contact between the hammer and the piston to the first rise of pressure recorded by the top strain gauge. This time is dependent on the ability of the particles to move, rotate and slide past each other before permanent deformation occurs. The time to reach the maximum pressure defines the compacting stage and the time to return to the minimum pressure defines the decompacting stage. The relative times for the compacting stage, the decompacting stage and reorganisation of the particles were calculated as fractions of the total time of the pressure wave. The time for no pressure between two consecutive waves defines the delay time, ($\tau_1$, $\tau_2$, $\tau_3$, …, $\tau_i$), as shown in Fig. 8.
Fig. 8. The pressure waveforms, the dynamic motion of the hammer and the piston plotted against time for two-gram compacted PA11 (mean particle size ≈ 22 µm and geometrical factor $h/d = 0.18$) by the strain rate $1.15 \times 10^3 \text{ s}^{-1}$ without relaxation assists.
2.4.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to study the morphological characteristics, the particle size distribution, the limit of plastic deformation and particle bonding by plastic flow at contact points. The instrument used was a Jeol JSM-5400 from Jeol, Japan. SEM is a frequently used technique in materials science research. Its strength lies in the combination of imaging with high resolution and a large depth of focus, together with the possibility of obtaining chemical and physical information.

2.4.2 Density analysis

The relative green density, \( D \), calculated as the ratio of the apparent density of the compacted polyamide-11 to the theoretical density of polyamide-11 [117] was used as a measure of the degree of compression [8].

The apparent density was calculated by applying the Archimedes principle using n-hexane as the liquid medium, according to

\[
\text{Apparent density} = \frac{\text{Mass in air}}{\text{Mass in air} - \text{Mass in n-hexane}} \times \text{Density of n-hexane}, \quad (7)
\]

the density of n-hexane being taken as 0.66 g cm\(^{-3}\).

A Mettler Toledo AE100 balance and a Mettler density determination kit 33360 were used for the measurements.
3 RESULTS AND DISCUSSION

3.1 THE EFFECT OF HIGH-VELOCITY COLD COMPACTION STAGES AND CONDITIONS ON THE COMPACTED POLYMER POWDER BED

Many techniques can be used for processing powders at room temperature or elevated temperature. At room temperature, the high-velocity technique is more energy-efficient and permits faster cycle times than conventional processing, since the relatively slow heating and cooling stages are eliminated \([1, 5, 7]\). Common problems are a low green density and an inhomogeneous density distribution in the compacted powder bed (compacted material). During the cold forming of plastics, the most important parameter is pressure. The disadvantage of the technique is the loss of pressure at the bottom of the die as result of friction between the plastic powder particles and the container wall \([6]\).

3.1.1 Compactibility characteristics

3.1.1.1 The effect of pre-compacting

The effect of the pre-compacting stroke on the relative green density is shown in Fig. 9. Compaction of polyamide-11 by a single stroke, \(P_{\text{post-down}}\), is insufficient to achieve an adequate density at an energy level less than 100 J/g, as shown in Fig. 9a. One stroke occurs under a relatively short time, and this is not sufficient to reorganize and deform the particles both elastically and plastically. Since powders have different initial densities, they have different initial adequate densities \([1]\).

Compaction with different pre-compacting energies followed by a constant post-compacting energy (300 J/g), \(P_{\text{pre}} + P_{\text{post-down}}\), leads to a higher density than the single stroke, \(P_{\text{post-down}}\), profile. This is attributed to an increasing densification and increasing particle-to-particle bonding and possibly to an interlocking of particles with increasing pre-compacting energy. To raise the pre-compacting energy, with constant mass of the stroke, is not always an advantage and the density sometimes develops unpredictably as shown in Fig. 9b. As the pre-
Results and discussion

compacting energy increases the compacting time decreases, and the particles—particularly the coarse particles—have less time to move and slide past each other. As a result, the porosity between powder particles increases and finally the apparent density decreases.

![Graph showing the relative green density plotted against compaction energy of a two-gram compacted PA11 (different particle size distributions) by: (a) one downward post-compacting $P_{\text{post-down}}$ profile, (b) a single downward pre-compacting stroke followed by one constant downward post-compacting (300 J/g), $P_{\text{pre}} + P_{\text{post-down}}$ profile.]

**Fig. 9.** The relative green density plotted against compaction energy of a two-gram compacted PA11 (different particle size distributions) by: (a) one downward post-compacting $P_{\text{post-down}}$ profile, (b) a single downward pre-compacting stroke followed by one constant downward post-compacting (300 J/g), $P_{\text{pre}} + P_{\text{post-down}}$ profile.

### 3.1.1.2 The effect of post-compacting

The distribution of force within the powder mass and the pressure loss during compaction have a major influence on the density distribution and on the quality of the compacted material.

In this investigation, attempts were made to compensate for the pressure loss by changing the post-compacting quantity and direction using different compacting profiles such as $P_{\text{pre}} + P_{\text{post-down}} + P_{\text{post-up}}$ and $P_{\text{pre}} + P_{\text{post-up}} + P_{\text{post-down}}$, without changing either the geometrical die design or the geometrical factor.

The effect of post-compacting quantity and direction on the relative green density is shown in Fig. 10. The $P_{\text{pre}} + P_{\text{post-down}} + P_{\text{post-up}}$ compacting profile leads to a higher relative green density, as shown in Fig. 10a. The maximum relative green density increase achieved by this compacting profile was 17.5 % higher than that achieved when compacting by a single stroke, $P_{\text{post-down}}$, profile, and 0.63% higher than when compacting by a $P_{\text{pre}} + P_{\text{post-down}}$ profile. The results achieved with a $P_{\text{pre}} + P_{\text{post-up}} + P_{\text{post-down}}$ compacting profile are shown in Fig. 10b. The maximum relative green density increase achieved with this profile was 17.6 % higher than that achieved by a single stroke, $P_{\text{post-down}}$ compacting profile and 0.66 % higher than that achieved by a $P_{\text{pre}} + P_{\text{post-down}} + P_{\text{post-up}}$ compacting profile.
Fig. 10. The relative green density plotted against compaction energy of two-gram compacted PA11 (different particle size distributions) by: (a) a single downward pre-compacting stroke followed by one constant downward primary post-compacting stroke (300 J/g) followed by one constant secondary upward post-compacting stroke (300 J/g). $P_{\text{pre}} + P_{\text{post-down}} + P_{\text{post-up}}$ profile, (b) a single downward pre-compacting stroke followed by one constant upward primary post-compacting stroke (300 J/g) followed by one constant secondary downward post-compacting stroke (300 J/g). $P_{\text{pre}} + P_{\text{post-up}} + P_{\text{post-down}}$ profile.

The difference in total relative green density achieved by pre-compacting followed by a single post-compacting and by pre-compacting followed by double post-compacting was very small, regardless of the post-compacting profile used.

Changing the pressure direction leads to evenness, homogeneity and densification on the surfaces as well as in the density distribution in the compacted powder bed. The pressure and density distribution between the upper and lower surface were more uniform when using the $P_{\text{pre}} + P_{\text{post-up}} + P_{\text{post-down}}$ profile than when using the $P_{\text{pre}} + P_{\text{post-down}} + P_{\text{post-up}}$ profile.

The relative green density was influenced more by the pre-compacting effect than by the post-compacting quantity and direction. The surface morphology, density distribution and the quality of the surfaces of the compacted powder beds were influenced to a greater extent by the post-compacting direction. The maximum relative green density was achieved by all the compaction profiles when the pre-compacting energy was ca. 100 J/g. This indicates that the particle behavior is independent of particle size and the geometrical $h/d$ factor.

The pressure loss for a geometrical factor of $h/d = 1.12$ at the bottom of the die during the secondary post-compacting was 35.3% of the applied pressure at the top with the $P_{\text{post-down}} + P_{\text{post-up}}$ profile and 21.5% with the $P_{\text{post-up}} + P_{\text{post-down}}$ profile.
3.1.2 Springback gradient

During the compaction process, the polymer powder undergoes a high compressive strain which ultimately leads to consolidation and densification of the material. The process can be divided into two stages, the compacting and the decompacting stages. In the compacting stage, the material is compressed and the density of the material increases to a maximum value. After the maximum pressure has been reached and the piston starts to withdraw (the decompacting stage), the compressive stresses relax and the material expands due to the elastic energy stored in the material. During this springback stage, the density decreases. Most of the springback phenomenon occurs during the decompaction stage, within the die, rather than after ejection [118].

A typical example is shown in Fig 8. This figure shows the pressure wave forms and the motion of the hammer and of the piston when compacting PA11 (mean particle sizes ≈ 22 μm) with the geometrical factor h/d = 0.18 and strain rate 1.15×10³ s⁻¹ without relaxation assists. During the decompacting stage, the hammer returns to its original position and the piston follows it, as a result of the release of elastic energy stored in the powder bed. The new position of the piston is higher than the initial position before the stroke with the same gap to the bottom surface of the hammer, as shown in Fig. 8 regions a and b. Immediately after the first pressure wave, the compaction process is interrupted and there is a delay between the successive pressures wave. In this case, the delay time between the first peak and the second peak was 12.2 ms. During the first delay, the compacted volume was maximally 195% (Fig. 8 region a) of the initial volume of the powder bed before compaction. In this volume, during the delay time, the polymer powders are less restricted and dimensional changes occur which depend on the characteristics of the powder material and on their kinetic energies. The hammer withdraws faster than the piston, and the piston moves back faster than the compacted powder bed due to the longer natural relaxation time of the compacted material. During each delay period, there is a springback, until the end of the pressure wave. The first instantaneous springback is difficult to repair during the following pressure waves because the pressure decreases from peak to peak until the process ends.

Several studies have proposed that high-velocity compaction (HVC) is a continuous process but in these studies the complex nature of the pressure waves within the compacted materials has not been considered [32] and the process analysis has been limited to the first peak of the pressure waves [27, 28].

In contrast, the results of this study reveal that the high-velocity compaction process is not a continuous process, but rather that it includes several interruptions that are likely to have a great influence on the compacted material. The subdivisions of the high-velocity pressure waves have an important function and they should not be underestimated. The nature of the multiple waves and peak-to-peak delay times at different strain rates are shown in Fig. 11.
Results and discussion

Fig. 11. The pressure wave forms recorded by two strain gauges (upper and lower-strain gauge) for PA11 by: (a) velocity 4.82 m/s and strain rates ($1 \times 10^3$, $0.4 \times 10^3$ and $0.25 \times 10^3$ s$^{-1}$) for mean particle size $\approx 42$ µm, (b) velocity 5.3 m/s and strain rates ($1.15 \times 10^3$, $0.5 \times 10^3$ and $0.3 \times 10^3$ s$^{-1}$) for mean particle size $\approx 80$ µm, (c) velocity 6.2 m/s and strain rates ($1.5 \times 10^3$, $0.6 \times 10^3$ and $0.35 \times 10^3$ s$^{-1}$) the mean particle size $\approx 100$ µm.
3.1.3 Stick-slip mechanisms

The dynamic dry frictional force system is very complex and the result depends on many factors, including the types of metastable states in the system, the times needed to transform between states, and the properties of the device, the compacting machine, that imposes the stress on the powder bed and the powder properties [119]. At low compaction rates, the motion often becomes intermittent. This instability is caused by the irregular nature of both the particle-particle and the particle-wall frictional forces, developed at very low stress, so that the system alternately sticks and slips forward (the stick-slip mechanism). At high compaction rates and therefore at a high velocity, the frictional force is basically independent of contact speed and the system usually slides smoothly (sliding mechanism) [104, 105].

The stick-slip mechanism at the die wall during low-energy and low-velocity pre-compaction is shown in Fig. 12. This figure shows the first reflecting wave form for the pressure wave forms recorded by two strain gauges (upper and lower strain gauges) when compacting PA11 (mean particle sizes 42 and 82 µm) at a velocity of 3.9 m/s, at compaction rates of \(0.6 \times 10^3\), \(0.2 \times 10^3\) and \(0.1 \times 10^3\) s\(^{-1}\), and with the geometrical factors \(h/d = 0.2, 0.5\) and 1.12. The beginning of the compacting stage comprises several stages that involve a reorganization of the particles, elastic deformations at particle contact points and plastic deformations or fragmentation in the case of brittle powder materials. Similar stages are seen in metal compaction [120-124]. The principle differences in the case of polymer particles arise from the specific nature of the small particle reorganization and friction, as well as from the early transfer from elastic to plastic deformation when the particle shape is irregular, due to the high stresses which develop on small contact areas between particles. This early transfer means that the elastic limit is overcome at a relatively low compaction pressure, generally in the upper part of the powder bed. Under these conditions, at a low compaction rate, the particles follow the common cyclic limit conditions in the horizontal plane (x and y-directions) and there is more opportunity for the particles to move, rotate and slide past each other [50]. As a result of such particle-particle and particle-wall rearrangements, the powders stick. After a further increase of pressure, the compaction advances at a rapid rate until the powders stick again and so on. The stick-slip phenomenon during low-energy and low-velocity pre-compaction is shown in Fig. 12 a-f.

During the reorganization stage, a longer time is needed for the large particles to move, rotate and slide. Nevertheless, the elastic energy absorption by large particles takes more time than the absorption by small particles due to their relatively large diameter and mass. As a result, the relative time of the reorganization stage increases and the stick-slip phenomenon is observed more with increasing particle size, as shown in Fig. 12 c and f. Stick-slip processes should be avoided because they lead to macroscopic defects in the compacted product.
Results and discussion

Fig. 12. The first reflecting wave form for the pressure wave forms recorded by two strain gauges (upper and lower-strain gauge) when compaction PA11: (a, b and c) mean particle sizes 42 µm at velocity 3.9 m/s, compaction rates $0.6 \times 10^3$, $0.2 \times 10^3$ and $0.1 \times 10^3$ s$^{-1}$, with the geometrical factors $h/d = 0.2, 0.5$ and 1.12 respectively. (d, e and f) mean particle sizes 82 µm at velocity 3.9 m/s, compaction rates $0.6 \times 10^3$, $0.2 \times 10^3$ and $0.1 \times 10^3$ s$^{-1}$, with the geometrical factors $h/d = 0.2, 0.5$ and 1.12, respectively.
3.1.4 **Coefficient of sliding friction, sliding coefficient**

The coefficient of sliding friction characterizes the interaction between the powder and the wall of the die. During high-velocity compaction, the coefficient of sliding is irregular and describes the ability of the powder to be uniformly densified during the whole of the compaction process. Its numerical value can vary in the range $0 < \eta < 1$, as shown in Fig. 13. Reorganization and sliding in polymer powders are severely controlled due to the large particle-particle and particle-wall frictional forces, which depend on the nature of the powder and on the compaction conditions.

![Sliding Coefficient](image)

**Fig. 13.** The sliding coefficient plotted against time over the whole of the compaction process, for compacted PA11 (8 g, mean particle size $\approx 110 \mu m$ and geometrical factor $h/d = 0.75$) at a compaction velocity of 6.2 m/s and a strain rate of $0.35 \times 10^7$ s$^{-1}$.

During the first pressure wave, at the beginning of the compaction stage, the sliding coefficient is relatively low due to the increase in the radial–to–axial stress ratio until the maximum pressure has been reached. A much better transfer of the pressure throughout the powder bed and a lower loss of pressure lead to a higher sliding coefficient due to the overall friction during the compaction process. The sliding coefficient was found to be proportional to the density. Since the stress ratio tended to reach a constant value when the pressure reached a certain level at the top of the pressure wave, the continuous rise in the sliding
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coefficient during the first pressure wave at the compaction stage as the density increased was
due mainly to a decrease in the friction coefficient. A more homogeneous density distribution
in the compacted powder and a smaller loss of pressure during compaction have a major
influence on the sliding coefficient and on the quality of the compacted material.

The effect of the particle size distribution on the sliding coefficient for compacted PA11 (8 g,
mean particle size $\approx 22, 42, 82$ and $110 \mu m$ and geometrical factor $h/d = 0.75$) at a compaction
velocity of 6.2 m/s and a strain rate of $0.35 \times 10^3 s^{-1}$ is shown in Fig. 14. The large particles
take a longer time than the small particles to move, rotate and slide due to their relatively
large diameter and mass, since the elastic energy absorption by the large particles takes more
time. As a result, the value of the sliding coefficient decreases and the friction coefficient
increases. Eventually a springback occurs, where the density decreases due to the release of
elastic energy, i.e. the ability of the material to absorb energy in an elastic form without
permanent deformation during the compaction stage [87].

![Graph showing the sliding coefficient against the sequence of pressure waves for compacted PA11](image)

**Fig. 14.** The sliding coefficient plotted against the sequence of pressure waves for compacted
PA11 (8 g, mean particle size $\approx 22, 42$ and $82 \mu m$ and geometrical factor $h/d = 0.75$) at a
compaction velocity of 6.2 m/s and a strain rate of $0.35 \times 10^3 s^{-1}$ with and without relaxation assists.
3.2 THE EFFECT OF HIGH-VELOCITY COLD COMPACTION STAGES AND CONDITIONS ON THE COMPACTED POLYMER-BASED NANOCOMPOSITE

Several methods have been used to produce polymer nanocomposites, such as sol-gel reaction [63], intercalative polymerization [64], and polymerization via melt processing [65], depending on the nature of the nanoparticles and on the manner of synthesizing the polymeric matrices. These composites are dispersed, usually by conventional methods of polymer processing; in the melt [66], for example, by casting [67-70], injection moulding [71-73] or extrusion [74-78]. It is however extremely difficult to disperse the nanoparticles homogeneously in the polymer matrix because of the easy agglomeration of nanoparticles and the high viscosity of the polymer. On the other hand, the production of blends by solution processing often generates environmental concerns regarding solvent removal and disposal. The possibility of blending polymers in the solid state by e.g. mechanical milling (MM) or mechanical alloying (MA) of polymers by ball milling[79, 80] is thus an attractive alternative since many of the problems presently encountered could be avoided altogether [81]. High-energy ball milling (HEBM) [82, 83] a low-cost technique for the manufacture of polymer/metal composite powders [84, 85], is followed by high-velocity cold compaction [86, 87].

In this part of the study, PMMA was chosen as a basic material for the preparation of polymer nanocomposites because it has favourable physical properties: exceptional transparency, easy thermoforming, great machinability, and resistance to ageing. PMMA is used in many engineering constructions, for example in aviation, the nuclear power industry, machinery equipment, sanitary equipment, windscreens, impact protection, etc. Attempts has been made to explore the efficacy of preparing composite powders of nickel-ferrite (NiFe$_2$O$_4$) nanopowders and ultrafine poly(methyl methacrylate), PMMA, by co-milling the mixture of PMMA and NiFe$_2$O$_4$ in the solid state by low-temperature mechanical alloying, and producing polymer nanocomposite (PMMA/NiFe$_2$O$_4$) using high-velocity cold compaction.

3.2.1 Preparation of composite powders in the solid state, the effect of high-energy ball milling on the composite powders

High-energy ball milling (HEBM) has been used to improve the compatibility between different components, polymer/metal nanocomposite powders, by mechanical alloying. The efficiency of the high-energy ball milling is determined by the collision probability of powders and milling media (balls), the impact force, the oscillating frequency and the amplitude of the equipment. A high ball/powder weight ratio and long milling time are required to achieve ultrafine or nano-sized powders.
The effect of milling time on the particle size distribution of the PMMA powders is shown in Fig. 6. In the initial stage, the particle size decreases with increasing milling time and the amount of coarser particles increases more than the amount of finer particles. This is due mainly to the agglomeration of the smaller particles and to the pulverization of larger particles. Pulverization and agglomeration occur concurrently and an equilibrium state is reached. Later, a rapid reduction in the mean particle size occurs (from 280 µm, as received, to 202 µm, after rough milling, to 108 µm, after 1 hour HEBM with liquid N₂, and to 48 µm after 25 hours HEBM with liquid N₂).

The effect of milling time on the particle size distribution of the PMMA/NiFe₂O₄ blends is shown in Fig. 7. It is possible to obtain a good distribution of fillers in the polymer matrix in the solid state when fillers and polymers are co-milled. As the NiFe₂O₄ nanopowder content increases, the reduction in the particle size is more effective. With 20 % NiFe₂O₄, the mean particle size was reduced from 33.3 µm after 10 hours co-milling to 17.1 µm after 20 hours co-milling and with 50 % NiFe₂O₄, the mean particle size was reduced from 13.4 µm after 10 hours co-milling to 5.1 µm after 20 hours co-milling. During mixing, these agglomerates can be broken down into their constituent primary particles, provided that the energy of the collisions between the relatively different particle sizes, large (PMMA) particles and small nanoparticles, is sufficient to overcome the agglomerate strength. This condition results in a homogeneous dispersion of nanoparticles in the polymer powder, and the NiFe₂O₄ powder is relatively well dispersed on the PMMA surface. Finally, the PMMA particles are covered with a layer of NiFe₂O₄ particles.

3.2.2 The effect of high-velocity cold compaction conditions on the compacted nanocomposite

Compression of the powder bed, high-velocity cold compaction, leads to stress concentrations at the contact between grains. When the stress concentrations exceed the yield strength, the grains deform plastically. The change in shape of the grains allows them to pack more tightly together and decreases the porosity of the powder bed. This process can be divided into compacting and decompacting stages. In the compacting stage, the material is compressed and the density of the material increases to a maximum value. After the maximum pressure has been reached and the piston starts to withdraw (the decompacting stage), the compressive stresses relax and the material expands due to the elastic energy stored in the material. The beginning of the compacting stage consists of several stages that involve a reorganization of the particles, elastic deformations at particle contact points and plastic deformations/fragmentation. During the reorganization stage, a longer time is needed for the large particles to move, rotate and slide. Nevertheless, the elastic energy absorption by large particles takes more time than the absorption by small particles due to their relatively large diameter and mass. The reorganization of small particles is dependent on the specific nature of small particle reorganization and friction and the early transfer from elastic to plastic deformation when the particle shape is irregular, due to the high stresses which develop on small contact areas between particles. This early transfer means that the elastic limit is overcome at a
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relatively low compaction pressure, generally in the upper part of the powder bed. As a result, the top surface of the product becomes uneven. Nevertheless, the energy absorption by the particles which have more contact points per surface area, i.e. small particles, is greater than that by the larger particles. Consequently, the particles which have inadequate contact points with other particles will be less obstructed. They can withdraw more freely than the other parts of the compacted powder bed and this leads to the pull-out phenomenon, capping phenomenon and inhomogeneous morphology on the top surface of the compacted material shown in Fig. 15.

During co-milling, the agglomerates can be broken down into their constituent primary particles, provided that the energy of the collisions between the larger PMMA particles is sufficient to overcome the agglomerate strength. This condition therefore leads to the formation of a coating layer in which the nanopowder is relatively well dispersed on the PMMA surface. On the other hand, the nanopowder behaves as a cushion, and squeezing between the larger particles decreases the milling effect. Finally, it is clear that the break-up of agglomerates takes place gradually: the longer the mixing time, the greater is the degree of dispersion of the nanopowder. The effect on the morphology of the top surface of the compacted material of compacting with different milling systems is shown in Fig. 16: (i) mechanical milling of PMMA for 25 hours HEBM with liquid N\textsubscript{2} and later drying mixing with NiFe\textsubscript{2}O\textsubscript{4} nanopowders at 20% weight per cent for 10 minutes at room temperature, (ii) mechanical milling of the mixture of NiFe\textsubscript{2}O\textsubscript{4} nanopowders and PMMA powders for 10 hours HEBM with liquid N\textsubscript{2} at 20% weight per cent at constant strain rate.
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Fig. 15 Top surface of 2-g compacted PMMA with geometrical factor \( h/d = 0.2 \), compaction energy 300 J/g, and strain rate \( 1.34 \times 10^7 \) s\(^{-1} \) with mean particle size (a) 202 µm, after rough milling, (b) 108 µm, after 1 hour HEBM with liquid N\(_2\), (c) 48 µm, after 25 hours HEBM with liquid N\(_2\).
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**Fig. 16.** The effect of different milling systems on the morphology of the top surface of 2-g compacted nanocomposite (NiFe$_2$O$_4$/PMMA) with a 1:5 weight per cent ratio, 20%, geometrical factor $h/d = 0.2$ and strain rate $1.34 \times 10^3$ s$^{-1}$; (a) 25 hours HEBM of PMMA with liquid N$_2$ and later dry-mixing with NiFe$_2$O$_4$ nanopowders with a 1:5 weight per cent ratio, 20%, for 10 minutes at room temperature. (b) 10 hours HEBM of a mixture of NiFe$_2$O$_4$ nanopowders and PMMA powders with liquid N$_2$. 
After the maximum pressure has been reached, the piston starts to withdraw and the bottom wall reflects the particles, the powder bed, to begin the decompacting stage with the inverse velocity, the boundary velocity [86]. The upper piston ultimately returns towards its original position and the particles, the powder bed, follow it. The movable top wall of the mould takes over in this case. However, the top wall of the mould moves faster than the compacted powder bed, due to the plastic response of the compacted material. In the case of the homogeneous dispersions of nanoparticles (NiFe₂O₄) in the polymer powders (PMMA), the two materials have the same average velocity. Due to material heterogeneities, a large elastic response, and non-homogeneous particle velocities, the stress field is not uniform. Stress concentrations arise at the contacts between grains. When the stress concentration exceeds the yield strength, the grains deform plastically and squeeze out some of the nanoparticles. Changing the post-compacting profile, the pressure direction, leads to uniformity, homogeneity and densification on the surfaces in the compacted powder bed [87]. The effects of post-compacting conditions, with the effect of the milling time on the morphology, the nature of the heterogeneities, of the top surface of the compacted composite powders are shown in Figs. 17 and 18.

3.3 THE EFFECT OF RELAXATION ASSISTS DEVICES ON THE COMPACTION PROCESS

To improve the compaction process, a relaxation assist device has been developed. The relaxation assists are parts of the piston and they are regarded as projectile supports. They are constructed of the same material as the piston, and the diameters are the same but the lengths are different, as shown in Fig. 3. The function of the relaxation assist device is to lock the powder bed in the compacted form during the compaction process.

3.3.1 Pull out phenomenon

The degree of plastic deformation and particle bonding by plastic flow at the contact points depends on the amount of energy that can be absorbed by the powder particles. In the high-velocity compaction process, the kinetic energy is proportional to the applied pressure.
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Fig. 17. The top surface of 2-g compacted nanocomposite (NiFe$_2$O$_4$/PMMA) at a 1:5 weight per cent ratio, 20%, 10 hours HEBM with liquid N$_2$, and geometrical factor $h/d = 0.2$ after a constant single downward pre-compacting stroke, strain rate $0.6 \times 10^3$ s$^{-1}$ followed by a constant post-compacting, strain rate $1.2 \times 10^3$ s$^{-1}$ with different directions and different profiles: (a) one constant downward post-compacting stroke, $P_{\text{post-down}}$, (b) one constant primary downward post-compacting stroke followed by one constant secondary upward post-compacting stroke, $P_{\text{post-down}} + P_{\text{post-up}}$, (c) one constant primary upward post-compacting stroke followed by one constant secondary downward post-compacting stroke, $P_{\text{post-up}} + P_{\text{post-down}}$. 
Fig. 18. The top surface of 2-g compacted nanocomposite (NiFe₂O₄/PMMA) at a 1:5 weight per cent ratio, 20%, 10 hours HEBM with liquid N₂, and geometrical factor h/d = 0.2 after a constant single downward pre-compacting stroke, strain rate $0.6 \times 10^3$ s⁻¹ followed by a constant post-compacting, strain rate $1.2 \times 10^3$ s⁻¹ with different directions and different profiles: (a) one constant downward post-compacting stroke, $P_{\text{post-down}}$, (b) one constant primary downward post-compacting stroke, followed by one constant secondary upward post-compacting stroke, $P_{\text{post-down}} + P_{\text{post-up}}$, (c) one constant primary upward post-compacting stroke followed by one constant secondary downward post-compacting stroke, $P_{\text{post-up}} + P_{\text{post-down}}$. 
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It is possible to increase the kinetic energy by increasing the hydraulic force or by increasing the distance between the hammer and the top surface of the piston. It is difficult to increase the hydraulic force without changing the design and/or initial parameters of the machine. The disadvantage of increasing the distance between the hammer and the top surface of the piston is that it leads to an increase in the compaction velocity at constant hydraulic force and hammer mass. As the piston velocity increases, the ability of the particles to move, rotate and slide past each other decreases as a result of the shorter time available for this process [91]. Nevertheless, the energy absorption by the particles which have more contact points per surface area, i.e. small particles, is greater than that by the larger particles. This increase in the energy absorption at contact points results in plastic deformations and plastic flow, although the effective dwell time is reduced.

An early transfer from elastic to plastic deformation and plastic flow occurs in powders where the particle shape is irregular, because high stresses develop on small contact areas between particles. This early transfer cases the elastic limit to be overcome at a relatively low compaction pressure, generally in the upper part of the powder bed. These particles form contorted and deformed particle layers in the compacted powder bed.

When the piston moves down, the top wall of the compacted powder bed also moves down (compacting stage) to a point of maximum compaction, and this is followed by the inverse movement which begins the decompaction stage. The piston ultimately returns towards its original position and the compacted powder bed follows it. During faster compaction, the withdrawal time of the piston is shorter than the natural relaxation time of the compacted material and the piston moves back faster than the compacted material. Different post-compacting profiles, i.e. different energy distributions between the upper and lower parts of the compacted powder bed, lead to different movements of the particles and of the particle layers. The use of relaxation assists reduces the difference between these velocities in the powder bed and gives the compacted powder bed a more homogeneous opposite velocity during the decompacting stage and probably more time to slow down the stress relaxation.

Particles which have inadequate contact points with other particles will be less obstructed. They can withdraw more freely than the deformed particle layers and start the pull-out phenomenon. In addition, the deformed particle layers withdraw more rapidly than the other parts of the compacted powder bed and start the capping phenomenon. The effect of compacting with different energies and different velocities on the morphology of the top surface of the compacted material without and with relaxation assists is shown in Fig. 19 and Fig. 20, respectively.
**Fig. 19.** The top surface of compacted PA11 (20-30 µm) without relaxation assists compacted with: (a) low energy, 180 J/g at velocity 4.83 m/s, (b) higher energy, 300 J/g at velocity 6.23 m/s.

**Fig. 20.** The top surface of compacted PA11 (20-30 µm) with relaxation assists compacted with: (a) low energy, 180 J/g at velocity 4.83 m/s, (b) higher energy, 300 J/g at velocity 6.23 m/s.
3.3.2 Springback gradient

In this part of the study, a relaxation assist device has been used to reduce the instantaneous springback and to increase the understanding of the springback gradient in a die. The lengths of the assists were 12, 37 and 60% of the length of the piston. The upper relaxation assist was located above the polymer powder bed, below the piston, where the top strain gauge was positioned, and the lower relaxation assist was located below the polymer powder bed, above the plug, where the bottom strain gauge was positioned. The function of the relaxation assists is to lock the powder bed during the compaction process. The compaction process with and without the relaxation assist device is shown schematically in Fig. 21. Without the assists, particles can withdraw more freely, leading to dimensional changes, during the decompacting stage.

![Diagram of compaction and decompaction stages](image)

**Fig. 21.** Compacting and decompacting stage: (a) without relaxation assists, (b) with relaxation assists.
The pressure wave forms, dynamic motion of the hammer and the piston when compacting PA11 (mean particle sizes \(\approx 22 \, \mu m\)) with the geometrical factor \(h/d = 0.18\) and strain rate \(1.15 \times 10^3 \, s^{-1}\) with relaxation assists 12, 37 and 60% of the length of the piston, are shown in Fig. 22 a, b, and c, respectively.

During compaction, all collisions between different parts of the piston, the relaxation assists, and the hammer were elastic without permanent deformation. The ability to absorb energy in a elastic collision without permanent deformation is a material property. During the decompacting stage, the lower relaxation assist relaxes rapidly and strikes the powder bed upwards due to the pure elastic energy which is stored in the lower relaxation assist during the compacting stage. The piston withdraws faster than in the case of compacting without the relaxation assist due to the elastic collision between the piston and the upper relaxation assist.

The high speed camera showed that the position of the piston after the first pressure wave, during the first delay time, was 61% higher in the case of the relaxation assist with a height of 37% than without the relaxation assist, and the delay time between the first peak and the second peak decreased from 12.2 ms to 11.58 ms with the 37% relaxation assist and to 8.58 ms with the 60% relaxation assist.

The collision between the upper relaxation assist and the powder bed is not elastic, because of the permanent plastic deformation which occurs within the powder bed during the compacting stage. The upper relaxation assist probably relaxes against the powder bed, and is in direct contact with the powder bed. Consequently, the powder bed is held between the two relaxation assists without any gap during the delay time. This locking action improves the compaction process by reducing the expansion of the compacted volume until the powder bed is subjected to the next pressure wave.

The relative dimensional changes during the sequence of the pressure waves for two-gram compacted PA11 (mean particle sizes \(\approx 22 \, \mu m\)) with and without relaxation assists (12, 37 and 60% of the length of the piston) are shown in Fig. 23. The first instantaneous springback was found to increase with decreasing height of the relaxation assists. During the first pressure wave, the dimensional changes take place more rapidly without than with the relaxation assists. Furthermore, the final dimensional change was greater without than with the relaxation assists.
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Fig. 22. The pressure wave forms, the dynamic motion of the hammer and the piston plotted against time for two-gram compacted PA11 (mean particle size \( \approx 22 \, \mu m \) and geometrical factor \( h/d = 0.18 \)) with a strain rate of \( 1.15 \times 10^3 \, s^{-1} \) with relaxation assists (a) 12\%, (b) 37\% and (c) 60\%. 
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Fig. 23. The relative dimensional change plotted against the sequence of pressure waves for two-gram compacted PA11 (mean particle size ≈ 22 µm and geometrical factor h/d = 0.18) with a strain rate of 1.15×10³ s⁻¹ with and without relaxation assist (12, 37 and 60% of the length of the piston).

3.3.3 Delay time, relative time of the pressure wave and relative green density

The delay time, relative time of the pressure wave components (compaction stage, decompaction stage and reorganisation time) and the value of the relative green density are plotted against the height of the relaxation assists in Fig. 24.

With increasing height of the relaxation assists, the pressure wave requires more time to transfer through the piston and the upper relaxation assist. Furthermore, the ability of the particles to move, rotate and slide past each other before some permanent deformation take place increases. As a result, the polymer powder bed reaches a higher relative green density.

Consequently, with the better particle rearrangement and more closely packed material, the height of the powder bed is decreased and the pressure wave requires less time to reach the maximum value. As a result, the relative time of the compacting stage decreases (the time needed to reach the maximum value of the pressure related to the time of the pressure wave) with increasing height of the relaxation assists. During the decompacting stage, more time is needed to release the elastic energy stored in the upper and lower relaxation assists during the
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compacting stage. As a result, the relative time of the decompacting stage increases with increasing height of the relaxation assists.

The delay time decreases with increasing height of the relaxation assists due to the elastic collision between the lower relaxation assist and the plug, which means that the locked powder bed is in a higher position when the powder bed is subjected to the next pressure wave and the elastic collision between the upper relaxation assist and the piston, and this causes the piston to withdraw rapidly and meet the hammer in a shorter time. As a result, the powder bed has less time to relax and change its dimensions before it is subjected to the next pressure wave. By avoiding the first instantaneous springback, the powder bed attains a higher density as shown in Fig. 24. Ultimately, the interruption of the process decreases, and the powder bed relaxes during the whole compacting time with less change in dimensions, as shown in Fig. 23.

Fig. 24. The delay time, the relative time of the pressure wave components (compaction stage, decompaction stage and reorganisation time) and the value of the relative green density plotted against the height of the relaxation assists (the height of the relaxation assist related to the height of the piston).
3.3.4 Stick-slip mechanisms

In this part of the study, the function of the relaxation assist device is to lock the powder bed in the compacted form during the compaction process. When the relaxation assists are used, the pressure wave requires more time to transfer through the piston and the upper relaxation assist, and the ability of the particles to move, rotate and slide past each other increases. As a result, the polymer powder bed reaches a higher relative green density and a more closely packed material [86]. The better particle rearrangement and more closely packed material mean that the height of the powder bed is decreased and the pressure wave takes a shorter time to reach the maximum value, so that the time of the compaction stage becomes shorter and the relative time of the stick-slip phenomenon during compaction stage is reduced. The time needed to transfer from the intermittent stick-slip state to the smooth sliding state is reduced and the powder bed slides smoothly, as shown in Fig. 25.

![Fig. 25](image.png)

**Fig. 25.** The pressure wave forms recorded by two strain gauges (upper and lower-strain gauge) for five-gram compacted PA11 at velocity 6.2 m/s and strain rates $0.6 \times 10^3$ s$^{-1}$ with a mean particle size $\approx 110$ µm and the geometrical factor $h/d = 0.45$: (a) without relaxation assists, (b) with relaxation assists.
3.3.5 Sliding coefficient

Immediately after the first pressure wave, the compaction process is interrupted and there are delays ($\tau_1$, $\tau_2$, $\tau_3$, ..., $\tau_i$) between the successive pressure waves, as shown in Fig. 10. During these delay periods, the polymer powders are less restricted and dimensional changes occur which depend on the characteristics of the powder material and on their kinetic energies [86, 87]. The use of relaxation assists lead to a more homogeneous opposite velocity and a better locking of the powder bed in the compacted form with less change in dimensions, and less springback. The powder bed then attains a higher density and slides more smoothly, as shown in Fig. 14. Without the assists, particles which have inadequate contact points with other particles are less obstructed and they can then withdraw more freely than with the assists and this introduces dimensional change.

3.3.6 Compacted nanocomposites

In this part of the study, the relaxation assist device has been used to improve the compaction nanocomposites. The lengths of the assists were 37% of the length of the piston. The upper relaxation assist was located above the polymer powder bed, below the piston, where the top strain gauge was positioned, and the lower relaxation assist was located below the polymer powder bed, above the plug, where the bottom strain gauge was positioned, as shown in Fig. 3. During compaction, all collisions between different parts of the piston, the relaxation assists and the hammer were elastic without permanent deformation. The ability to absorb energy in an elastic collision without permanent deformation is a material property.

Different post-compacting profiles, i.e. different energy distributions between the upper and lower parts of the compacted powder bed, lead to different movements of the different particles and of the different particle layers. The function of the relaxation assists is to lock the powder bed during the compaction process. The use of relaxation assists reduces the difference between these velocities in the powder bed and gives the compacted powder bed a more homogeneous opposite velocity during the decompacting stage. During the decompacting stage, the lower relaxation assist relaxes rapidly and strikes the powder bed upwards due to the pure elastic energy which is stored in the lower relaxation assist during the compacting stage. Furthermore, the piston withdraws faster than in the case of compacting without the relaxation assist, due to the elastic collision between the piston and the upper relaxation assist. The collision between the upper relaxation assist and the powder bed is not elastic, because of the permanent plastic deformation which occurs within the powder bed during the compacting stage. The upper relaxation assist probably relaxes against the powder bed, and is in direct contact with the powder bed [86]. The difference between compaction without and with relaxation assists is shown in Figs. 26 and 27, respectively. It is also shown in Fig. 21.
Fig. 26. Compaction process without relaxation assists, first reflecting wave form and first interruption, first time-delay $\tau_1$. 
Fig. 27. Compaction process with relaxation assists, first reflecting wave form and first interruption, first time-delay $\tau_1$. 
Immediately after the first pressure wave, the compaction process is interrupted and there are delays ($\tau_1$, $\tau_2$, $\tau_3$, …, $\tau_i$) between the successive pressure waves, as shown in Fig. 10. During these delay periods, the composite powders are less restricted and dimensional changes occur which depend on the characteristics of the composite powders and on their kinetic energies [87]. Using the relaxation assists, the powder bed is held between the two relaxation assists without any gap during the delay time. This locking action improves the compaction process by reducing the expansion of the compacted volume and by reducing the difference between the opposite velocities, a more homogeneous opposite velocity, due to the nature of the heterogeneities in the powder bed, composite powder, until the powder bed is subjected to the next pressure wave [125].

In the case of the nano-composite (coarse viscoelastic polymer particles with fine elastic nano-metal particles), the nanoparticles are much more rigid than the polymer particles and most of the macroscopic deformation results from the deformation of the polymer particles. Within the composite powder bed, the stress distribution, particle size distribution, and opposite velocities are not uniform, due to material heterogeneities within the composite, and most of the plastic deformation is concentrated within the polymer particles. In contrast, the smaller particles, nano-metal particles, allow equilibration throughout the whole powder bed, which is thus able to flow more easily as a whole [126].

The particle velocity is very sensitive to particle size, and the largest particles generate the highest stresses. In this case, the coarse composite has the highest shear, while the fine composite has the lowest. Consequently, the coarse microstructure inhibits flow, while the fine composite can more easily flow as a whole. In general, without the assists, particles which have inadequate contact points with other particles are less obstructed and they can then withdraw more freely than with the assists, and this introduces dimensional changes, pull-out, springback, capping and delamination, due to a breakdown in the product during and/or after the decompacting stage. The effects of the relaxation assist on the nanocomposite compacted by high-velocity cold compaction are shown in Fig. 28.
Fig. 28. The top surface of 2-g nanocomposite (NiFe$_2$O$_4$/PMMA) compacted at a 1:1 weight per cent ratio, 50%, 20 hours HEBM with liquid N$_2$, and geometrical factor $h/d = 0.2$ by high velocity cold compaction: (a) strain rate $1 \times 10^3$ s$^{-1}$ without relaxation assist (b) strain rate $1.34 \times 10^3$ s$^{-1}$ without relaxation assist, (c) strain rate $1.34 \times 10^3$ s$^{-1}$ with relaxation assist, (d) strain rate $1.34 \times 10^3$ s$^{-1}$ with relaxation assist.
The results presented in this investigation show that the compaction of polymer powders and polymer-based nanocomposites by high-velocity cold compaction and using relaxation assists lead to a higher relative green density than conventional pressing. Achieving this density depends on the nature of the particle behavior regardless of particle size and geometrical characteristics. The relative green density is more influenced by pre-compaction step characteristics than by the post-compaction step characteristics. However, the difference in relative green densities achieve by pre-compacting followed by single post-compacting and by pre-compacting followed by double post-compacting are very small, regardless of the post-compacting profile used. Furthermore, the pressure and density distribution differences between the upper and lower surfaces are influenced more by post-compacting quantity and direction than by the pre-compacting characteristics. For this particular material, the early transfer from elastic deformation to plastic deformation means that the elastic limit is overcome at a relatively low compaction pressure, generally in the upper part of the powder bed.

During high-velocity cold compaction, the frictional force system is very complex and depends on many factors. At low compaction rates, the motion often becomes intermittent due to a stick-slip mechanism. At high rates the system usually slides smoothly. Both mechanisms depend on the nature of the powder and on the compaction conditions. The stick-slip phenomenon occupies a shorter time. The time needed to transfer from the intermittent stick-slip state to the smooth sliding state is reduced and the powder bed slides smoothly, with a higher sliding coefficient and lower friction. A much better transfer of the pressure throughout the powder bed and a smaller loss of pressure lead to the higher sliding coefficient due to the overall friction during the compaction process. At the beginning of the compaction stage, the sliding coefficient was decreased due to an increase in the radial–to–axial stress ratio until the maximum pressure had been reached. Since the stress ratio tends to reach a constant value when the pressure reaches a certain level at the top of the pressure wave, the continuous rise in the sliding coefficient with increasing density is caused mainly by a decrease in the friction coefficient. More homogeneous density distributions in the compacted powder and the smaller pressure loss during compaction have a major influence on the sliding coefficient and on the quality of the compacted material.
Conclusions

The preparation of polymer-Nanofiller, poly(methyl methacrylate) and nickel-ferrite, by high-energy ball milling at low-temperature followed by high-velocity cold compaction has been shown to be a suitable and low-cost technique for the manufacture of polymer/metal composite products. It is possible to obtain a good distribution of fillers in a polymer matrix, homogeneous dispersions of nanoparticles (NiFe$_2$O$_4$) in the polymer powders (PMMA), in the solid state when fillers and polymers are co-milled. During co-milling, the squeezing of nanoparticles between the larger particles decreases the milling effect. Furthermore, a longer mixing time leads to a higher degree of dispersion of the nanopowder on the PMMA particle surfaces. The NiFe$_2$O$_4$ nanopowder content also increases, and the reduction in the particle size is more effective. In the case of a heterogeneous material, elastic responses, particle sizes and field stress distributions, and opposite velocities are irregular. Consequently, the different post-compacting profiles, i.e. different energy distributions between the upper and lower parts of the compacted powder bed, lead to different movements of the different particles and of the different particle layers. Uniformity, homogeneity and densification on the surfaces in the compacted powder are influenced more by post-compacting magnitude and direction.

The relaxation assist device, a novel technique which has been successfully developed in this investigation, leads to an improvement in the compaction of powders, polymer powders and polymer-based nanocomposites, by giving a more homogeneous opposite velocity and a better locking of the powder bed in the compacted form with less change in dimensions in the case of both the homogeneous and heterogeneous materials. Consequently, the movement of the particles is reduced, the powder bed attains a higher density and the total elastic springback is minimized. Accordingly, a much better transfer of the pressure throughout the powder bed and a smaller loss of pressure lead to a more homogenous stick-slip of the particles and a higher sliding coefficient due to the overall friction during the compaction process. The results presented in this investigation shows that the high-velocity compaction process is a non-continuous process, the delay times between the pressure waves being strongly dependent on the strain rate, and the delay times can be decreased by increasing the height of the relaxation assists. Furthermore, the relative times of the compacting stage, decompacting stage and reorganisation of the particle can be controlled by altering of the height of the relaxation assists.
5 SUGGESTION FOR FUTURE WORK

The processing of polymer and polymer-based powder composites by high-velocity cold compaction (HVC) is a complex process. The properties of the final products can be varied over a wide range by a suitable choice of process variables. This work illustrates the effects of these process variables and parameters on the properties of the final products, and it shows the influence on the coefficient of friction of the sliding speed, contact pressure, die surface conditions, polymer particle size, degree of compaction and time, and that it is possible to obtain a good distribution of fillers in a polymer matrix, and a homogeneous dispersions of nanoparticles in the polymer powders, but these factors are not fully understood. Consequently, no equation of state has been presented to describe the relationships between molecular structure, solid-state properties and mechanical properties, and no equation of state has been presented to describe the relationship between the coefficient of friction and these factors. Therefore, more work needs to be done to investigate the structure development during processing so as to establish processing—structure—property correlations for the solid-state processing of polymers and their mixing. Mathematical equations and models are needed that can describe the processability of material in large-scale manufacturing processes. These models must be validated to ensure efficacy, accuracy and consistency.
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