Review Processes and influencing parameters of the solid particle erosion of polymers and their composites

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The solid particle erosion behaviour of polymers and polymeric composites has been reviewed. Attention was paid to the effects of testing variables (e.g., erodent type, size and flux, impact angle) and target material characteristics (e.g., crystallinity, crosslink density, reinforcement content and arrangement). The occurring failure mechanisms were classified and discussed. Various predictions and models proposed to describe the erosion rate (ER) were listed and their suitability was checked. Recommendations were given how to solve some open questions related to the structure—erosion resistance relationships for polymers and polymeric composites. © 2002 Kluwer Academic Publishers

1. Introduction

Solid particle erosion is a dynamic process that occurs in different machine-parts due to the impingement of solid particles. The exposed components undergo material removal and surface degradation. Similar to other tribological processes, solid particle erosion is also a combined process: the mechanical load may be associated with secondary thermal, chemical and physical reactions between the counterparts involved in the tribological system [1]. Attempts to understand the basic mechanisms of the erosion started in the last half of the 20th century and have been continued to the present. All these years the interest of the scientists was concentrated on conventional materials and especially metals. Finnie [2] after 40 years involvement with erosion presented in 1995 an article on the past and the future of erosion. In this article, the influencing parameters and dominating mechanisms during solid particle erosion were reviewed on the erosion response of metals and ceramic materials. In the same year another article was published by Meng et al. [3] providing information about the existing wear models and prediction equations. This article was more general as it discussed all the frictional phenomena termed to 'wear' including also the solid particle erosion. The main conclusion of this publication was that no universal predictive equation exists.

Nowadays polymers and related composites are extensively used as structural materials in various components and engineering systems due to their excellent specific (i.e., density related) properties. In comparison with metals they offer some extra benefits, like easy processability and designer freedom in shaping (especially with thermoplastics). The anisotropic behaviour of the fibre reinforced polymers (FRPs) may be very useful for given application. However, compered with metals, composites present different and significantly more complex damage- and failure-mechanisms, which affect also the safety of the related parts. Examples of the application of polymer composites are pipelines carrying sand, slurries in petroleum refining, helicopter rotor blades, pump impeller blades, high speed vehicles and aircrafts, water turbines, aircraft engine blades, missile components, canopies, radomes, wind screens and outer space applications. In such applications, one important characteristic is the erosion behaviour as these parts operate very often in dusty environments [4–7].

This is the reason "why" in the last three decades the erosion behaviour of polymers and related composites has been intensively studied. Different trends in the erosion have been observed, depending mainly on the experimental conditions and the target material properties. It is widely recognised that polymers and polymeric composites present a rather poor erosion resistance. Their erosion rates (ERs) are considerably higher than metals. The erosion resistance of polymers is two or three orders of magnitude lower than that of metallic materials. Furthermore, none of the models proposed for conventional materials can be adopted to predict reliably the erosion behaviour of polymers and polymeric composites [3].

The absence of valid predictive models intensify the need of creating a data base which informs about the erosion behaviour of polymers and polymeric composites. Review articles on this topic are—to our knowledge—very scare and the last survey of sand and rain erosion of composite materials was made almost two decades ago by Tsiang [4]. Therefore, this article attempts to review the solid particle erosion response of polymers and their composites by considering the dominating mechanisms and the most discussed influencing parameters of external (erosion conditions) and internal nature (target material characteristics). It was not our intention, to compare directly the erosion response of the materials since the existing results differ in terms of absolute ER (mass loss of the target/mass of the erodent) and/or in the dominating mechanisms due to the different experimental conditions used. In case of analogies, conclusions derived from studies on conventional materials are also considered.

2. Erosion types

The material removal during erosion is dependent on many interrelated factors that include the properties and structures of the target material, the macroexposure and microexposure conditions and the physical and chemical characteristics of the erodent particles. The combination of all these factors, sometimes exceeding 20 in number, results in erosion rates that are peculiar to specific sets of conditions. Additional difficulties arise from the fact that the different processes occur simultaneously during erosion.

In respect to the impact angle (a), solid particle erosion is divided in [8]:

- erosion at normal impact angles ($a \approx 90^{\circ}$)
- erosion at oblique impact angles ($0^{\circ} < a < 90^{\circ}$)

A low impact angle favours wear processes similar to abrasion because the particles tend to track across the worn surface after impact. A high impact angle causes wear mechanisms which are typical of solid particle erosion.

A great difference in the classification of various materials in respect to their erosive wear exists, when the variation in the impact-angle and -time is regarded. Fig. 1 shows typical erosion diagrams as a function of impact-time and -angle, respectively. The erosion mechanisms can be categorised as ductile and brittle, which do not directly match with the traditional grouping of materials according to their failure [4]. It can be seen in Fig. 1 that in ductile mode of erosion the maximum material removal occurs at low impingement angles whereas if the maximum is found at high impingement angles then brittle erosion dominates. Regarding the variation of the material removal with the impact time, Fig. 1 indicates that ductile erosion may involve an incubation period whereby the weight of the target increases first before settling down to a steady state. For normal impacts, this is due to the initial embedding of particles in the target surface. After the subsequent removal of these particles, steady state erosion is established [4, 5, 9, 10]. At glancing impacts during the incubation period other processes occur. The impact energy is mainly dissipated in roughening the target surface [5, 11–13]. The roughening process includes a high degree of plastic deformation of the polymer under compressive and tensile stresses. This results, in little surface bumps as the material is pushed away from the incident impact site.

Elastomers may show maximum erosion at oblique impact angles similar to the ductile response, but they present a much lower weight loss compared to that observed for ductile thermoplastics. At normal impacts it may happen that the material does not reach a steady state. Failure is progressing however even if no mass reduction of the polymer occurs (the deformed material is pushed away from the site of impingement) [13]. The differences in the erosion behaviour can be traced to material removal mechanisms which can range from tearing and fatigue for rubbers, through cutting and chip formation for ductile metals and polymers, to crack formation and brittle fracture for ceramics, glasses and brittle polymers [14].

3. Processes during solid particle erosion

As stated above, solid particle erosion includes cutting, impact and fatigue processes. The local energy concentration of the erodent on the impacted surface is crucial for the erosive wear [1, 10, 15–18]. This depends on characteristics of the erodent particles (size, shape, hardness, mass) and on those of the target material. Apart from these factors, the impact-angle, -velocity and –flux rate are of crucial influence. Hitting of a particle corresponds to a certain impact force imposed on the material surface. During impact, the initial energy of the particle is converted into different energy terms. The following cases present a simplification of the expected phenomena [18]:

3.1. Normal, elastic impact

The initial energy of the particle is reconverted into elastic energy and during the rebound phase again into kinetic energy of the particle. Some rubbers show such



Figure 1 Typical behaviours in erosion schematically.

behaviour, where no erosive wear is observed, in case of normal impact. Erosive wear occurs only after longer erosion duration due to thermal decomposition. Tearing or separation of the macromolecules is the result when the impact comes from sharp edged particles. Almost elastic impact prevails when high-strength, hard materials, are impacted with particles of low initial energy (low velocity and/or low mass of the erodent).

3.2. Normal, plastic impact

This case is not very common in practice, since the entire energy is hardly converted into plastic deformation without fracture initiation.

3.3. Normal, elastic/plastic impact

This type of impact is most frequent. A certain amount of the initial energy remains to one or both impact partners in form of plastic energy, whereas the largest part of the initial energy is converted into heat by internal friction. The kinetic rebound energy of the particle is accordingly reduced. Single impact does not generally cause fracture. Only repeated impacts by many particles on the same impact site can cause "dislocations" of the material from the site of impingement. After a given overall deformation the material strength is exceeded. Small micro-fractures may develop inside the material, which entail material removal.

The amount of the plastic energy is determined from the properties of the target material and the erosive particle. The smaller the ductility of the impact partners, the smaller generally the number of stress cycles up to failure is, and the greater the amount of energy carrying fracture (and therefore erosive wear) is. This is obvious from the comparison of materials that show ductile and brittle behaviour, respectively. The latter ones display a greater erosive wear when the initial energy of the impacting particle is enough to create stresses that exceed the strength of the material. The larger the ductility, the smaller the impact-force and -stresses are.

Regarding the erosive wear of elastomers a much lower amount of kinetic energy will be absorbed on impact. This depends on the rebound resilience of the elastomer. It is intuitive that the impact stresses play a crucial role in the erosive wear of elastomers. Attention should be payed to the fact that the nature of the deformation induced in a roughened surface by an irregular particle is quite sophisticated. At normal incidence, as Poisson's ratio for rubber is approximately 0.5, the surface tensile stresses due to an impacting particle will be predominantly frictional in nature. The tensile stresses in the surface arising from the frictional forces due to particle impact cause fine cracks to grow progressively into the surface. Material loss occurs when these cracks intersect. A reduction in friction via lubrication would lower the tensile stresses on the surface, leading to reduction in the ER [16].

Another process proposed for elastomers involves a build-up of steady strain on the surface owing to incomplete strain relaxation between impacts. Following this concept, it is supposed that the straining produced by a single impact is insufficient to cause material removal. Accordingly, successive impacts are necessary to raise the strain to a level linked to material removal. This mechanism would explain the greater erosion resistance observed for more resilient elastomers [19, 20].

3.4. Oblique, elastic/plastic impact

This is one of the most general type of impact. It differs from the normal impact, because of the onset of microcutting and micro-ploughing mechanisms. The material is deformed similar to normal impact but it is additionally cut and ploughed, in particular by sharp edged erodents. The micro-cutting and micro-ploughing phenomena are mainly related to the hardness of the particles, which can penetrate into the target surfaces. The softer erodent material leads to micro-cracking at higher impact angles, while a harder one mainly cause plastic deformation.

The particles deform ductile materials due to their arranged movement perpendicular and parallel to the surface. This means that both parallel and perpendicular velocity components transfer accordingly the initial energy in deformation energy. This is one of the reasons for the increased erosive wear of materials following the 'ductile mode,' found at low to middle impact angles. Because of the friction, the particles "shift" in the contact area and also rotate. The amount of energy initiated due to this process is however of subordinated importance.

Brittle materials are not so easily cut by the particles. The energy transfer parallel to the surface direction can take place, contrary to the ductile materials, only by friction forces. Thus the energy transfer is accordingly small. Only the perpendicular component of the velocity or the respective part of the initial energy determine the energy that goes into the material. The mechanism of the erosion is the same as in case of 90°-impact therefore the well-known constant reduction of the erosive wear at small impact angles. If the coefficient of friction of the impact partners is high then it is expected that also the horizontal part of the impact force can transfer energy on the material which will lead to deviations from the aforementioned erosive wear behaviour. The consequence is an increase of the internal stresses, which at middle to high angles of impingement causes an erosive wear maximum.

Elastomers eroded at glancing incidence show formation of tears and cracks perpendicular to the erosion direction. A series of ridges, running transversely to the impact direction, is produced during the initial stage of erosion. Impacting particles slide over the surface and deform the ridges, causing the growth of fatigue cracks from the base of each ridge. It can be assumed that the growth of these fatigue cracks is the rate-determining step in the erosion wear process driven by tensile stresses [21].

Stachwiak *et al.* summarised schematically the known mechanisms of the erosive wear [12]. Part of this presentation is undertaken in Fig. 2 (note that the case of atomic erosion is excluded). This short description of the processes in the micro area shows that both the experimental conditions and the material properties determine the type of the dominating mechanisms,



Figure 2 Possible mechanisms of solid particle erosion; (a) abrasion at low impact angles, (b) surface fatigue during low speed, high impingement angle, (c) brittle fracture or multiple plastic deformation during medium speed, large impingement angle, (d) surface melting at high impact speeds, (e) macroscopic erosion with secondary effects (after [12]).

the energy conversion, as well as the extent of the accommodated stresses.

4. Influencing parameters

Although some of the influencing parameters of solid particle erosion are already mentioned, Fig. 3 summarises the most important ones.

It has been stated that the effects of the various parameters on the solid particle erosion behaviour are interrelated therefore, it is not easy to distinguish the individual influencing parameters. Nevertheless, in the next paragraphs some obvious trends will be reviewed based on literature data.

4.1. Experimental conditions 4.1.1. Effect of erodent velocity

The velocity (v) of the erosive particle has a very strong effect on the wear process. If the velocity is very low then stresses at impact are insufficient for plastic deformation to occur and wear proceeds by surface fatigue [12]. When the velocity increases, the eroded material may deform plastically upon particle impact. In this regime, wear is caused by repetitive plastic deformation. At brittle wear response, wear proceeds by subsurface cracking. At very high particle velocities melting of the impacted surface may even occur.



Figure 3 Parameters influencing the solid particle erosion.

From medium to high velocities, a power law [12], can describe the relationship between wear rate and impact velocity:

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = k\upsilon^n \tag{1}$$

where m is the mass of the worn specimen, t is the duration of the process, k is an empirical constant, n is a velocity exponent.

The characteristics of the erodent and that of the target material determine the value of the exponent 'n'. It has been stated that 'n' varies in the range of 2-3 for polymeric materials behaving in a ductile manner, while for polymer composites behaving in brittle fashion the value of 'n' is in the range of 3-5 [6, 22].

4.1.2. Effect of erodent characteristics

A key aspect of the erosion problem is related to the erodent characteristics. Variations in particle size and shape can cause fundamental changes in the erosion response [12]. Transitions in wear mechanisms were traced to a change in the shape, hardness or size of the erodents [12, 15]. If the eroding particles are blunt or spherical then plastic deformation is favoured, if the particles are sharp then cutting and brittle fragmentation are more likely. A blunt particle has a mostly curved surface approximating to a spherical shape while a sharp particle consists of flat areas joined by corners with small radii which are critical to the process of wear [12].

It is assumed that the ER is independent of particle size above a critical value [15, 23, 24]. This critical value is observed between 100–200 μ m, however, it is dependent on the exposure conditions and the particle-target interaction [13, 24]. Up to this critical value,

experimental results showed that with increasing size of the erodent also the ER increases.

The existence of this critical value has been attributed to a range of factors [24], i.e.,

(i) Strain rate effects, due to small particles: it has been shown that strain rates are higher for smaller than for larger particles. This results in increased stresses of the target material when bombard with smaller particles.

(ii) Differential work hardening due to erodents of various particle size. It has been suggested that a surface layer of 50–100 μ m "hardens" more than the bulk material. Hence, small particles will encounter a layer with a significantly higher flow stress than the bulk material, whereas large particles should penetrate in this layer. Above the critical size, the influence of this layer should be negligible.

The opposite trend is observed after this threshold size, because of the increased possibility of particle collisions as the erodent size increases. Another possible reason is that less number of particles reached the sample per unit weight of erodent when the particles impacting the sample had larger sizes. In that case the larger particles became less effective and that results in a lower ER [25].

The erodent fracture toughness may influence the erosive procedure if fragmentation of the erodent occurs during impact. When a particle breaks to several fragments, the initial energy and therefore the stresses on the surface are distributed over a larger area. Additionally, these cleavage-processes reduce the part of the energy getting into the material. From energetic view, the fracture of the particle has a wear-reducing effect. However, if the erodent fragments produced have sharper edges, compared to the original particles, then wear may also increase [18].

The effect of erodent hardness depends mainly on the particular mode of erosive wear taking place, e.g., ductile or brittle. In the brittle mode the effect of particle hardness is much more pronounced than in the ductile mode. It is usually believed that hard particles cause higher wear rates than soft ones, but it is impossible to isolate hardness completely from other features of the particle (e.g., shape). Even if the particle is hard, but relatively blunt, then it is unlikely to cause severe erosive wear [12].

With respect to the size and type of the erodent material, two trends may hold for harder and/or more brittle material. The erosive wear increases the higher the hardness of the erodent and the larger the erosive particle size are (until a level of saturation is reached in both cases) [13]. In ductile polymers, however, the situation may be quite different. Due to the relatively low hardness no pronounced effects of changes in the hardness of the usually much harder erodent materials should be expected [13].

From the above analysis it is obvious that it is often difficult to distinguish whether a transition in the ER variation originates from the experimental conditions or from the material characteristics. The existence of the threshold size along with the effect of other significant erodent characteristics, i.e., erodent shape and hardness, were recently examined on the example of a model material. As model material served an Epoxy Resin (EP) modified with different amount of hygrothermally decomposed polyurethane (HD-PUR). This system was selected because it was recently shown that the properties of the EP/HD-PUR systems could be set between those of crosslinked thermosets and rubbers via the HD-PUR amount [26]. This means that with these systems the possible transitions can be examined in terms of material and erodent characteristics at the same time. Therefore the EP/HD-PUR systems were eroded with a range of erodents [27].

Fig. 4 presents the ER results of the EP/HD-PUR systems for four different erodents. In Fig. 4 the variation



Figure 4 ER variation as a function of impact angle for the different erodents. HD-PUR modifier content: (a) 0, (b) 40 and (c) 80 wt%.

of the ER is illustrated as a function of the impact angles at constant modifier content. Generally, the harder and more angular erodents (i.e., corundum) are more erosive than the less hard and less angular (i.e., glass beds) erodents. The classification of the erodents in respect to their erosive efficiency is as follows: corundum1 > corundum2 > steel grit > glass beads. Ashift in the angle referred to the maximum ER of the unmodified EP is observed from 90° towards 30° when sharp, angular erodents (i.e., corundum, steel grit) instead of round ones (i.e., glass beads) were used (cf. Fig. 4a). On the other hand all types of erodents led to a maximum ER at 30° for the EP/HD-PUR systems with 80 wt% modifier (cf. Fig. 4c). Hardness and size of the erodent have a larger influence at low modifier content (up to 40 wt%) (cf. diagrams a and b in Fig. 4) and at low impact angles. The effect of these two parameters is lower as the modifier content and the impact angle increase. This becomes clear when someone compares the diagrams b and c in Fig. 4. At 30° impact the size of the erodent seems to play an important role (look the difference between the ERs achieved by corundum1 and corundum2, respectively). The effect of erodent hardness however, is lower. Comparing the ER results of corundum2 and steel grit hardly any difference exits, especially when the impact angle approaches 90°. As impact angle comes close to 90°, the effect of the erodent size is also minimised (see Fig. 4b and c). These findings coincide with the theoretical trends reported above, that the critical value of the erodent size is in the range of 100–200 μ m. Above this value the ER is independent of the erodent size or decreases with increasing erodent size. Finally, the arguments [12, 13, 24] that in brittle mode the effect of particle hardness is more pronounced than in ductile mode, are also confirmed by the results collated in Fig. 4.

4.1.3. Effect of erodent flux rate

The particle flux rate (i.e., the mass of impacting material per unit area and time) is another controlling parameter of the erosive wear rate. Theoretically, the ER should be independent of the flux of particles striking a target since (it is assumed that) all the particles hit the target with the same velocity and angle of impact. In practice, however, significant effects of particle flux on measured ER were observed [12, 20, 28, 29].

It has been reported that erosive wear rate was proportional to the flux rate up to a certain threshold value of the flux rate. This limit is believed to be the result of interference between rebounding- and arriving-particles [12]. This effect is rationalised in terms of a first-order particle collision model where the collisions removed the incident particles from the erosion process [29]. This collision effect may be significant, even for relatively low values of flux. The limiting particle flux rate is highly variable, ranging from as low as 100 kg/m²s for elastomers to as high as 10000 kg/m²s for erosion against metals by large and fast particles. The wear rates decrease marginally when the limiting flux is exceeded [12, 20].

Although the effect of erodent flux has been mainly attributed to the above mentioned interaction, there are

other mechanisms that can take place and affect the erosive wear. Darkened areas are often observed on the surface of eroded sample which created a debate about their generation. Some studies state that this is due to a chemical change of the surface possibly associated with localised heating (which further leads to mechanical softening or surface melting). This heating allows the embedding of particles in the material surface. It has been suggested that the weight loss occurs once the surface is saturated with particles and degraded [5]. Although this could be a good explanation for the above phenomenon, it was observed that the darkened areas were not affected by ultrasonic cleaning of the sample in acetone, implying that other reasons should hind behind this phenomenon [21]. Environmental degradation is one rational proposal. Environmental conditions are known to affect the abrasion and fatigue of rubber. Silica and glass, with a large amount of adsorbed water, may cause extensive degradation. Alumina, with a smaller amount of adsorbed water, causes less degradation. Silicon carbide, which is virtually free from adsorbed water, has a negligible effect on ER. The process can be regarded as a series of transient reactions occurring after each impact. As the flux increases, the time between impacts in the related surface decreases. So, the degradation reaction will have less time to occur before the next impact, and thus the degree of degradation and hence the amount of erosion will be reduced [20].

From the above analysis it is clear that a specific flux should be adjusted in order to avoid effects of particle interaction and environmental degradation on the erosion of a given material [28].

4.2. Target characteristics

The effect of the experimental conditions was above briefly presented. In the next paragraphs the effects of the target characteristics will be considered.

4.2.1. Polymers

Material characteristics exert a strong effect on erosive wear and have been extensively studied. It has been found that there is no general recipe for high resistance to erosive wear. Because of the different erosive wear mechanisms that can take place, wear resistance can be theoretically achieved by materials of different characteristics. In some cases the material can be extremely hard and tough so that the impacting particle is unable to make any impression on the surface. Alternatively, the material can be highly elastic so that the kinetic energy of the particle is harmlessly dissipated. Difficulties with materials optimisation for wear reduction arise from the fact that a material can show different behaviour depending on the impact angle and the experimental conditions (cf. Fig. 4). The choice of the ideal properties may also be compromised by other considerations such as maximum operating temperature or material transparency, etc. [12].

The solid particle erosion behaviour of polymers [9, 13, 17, 30–36] and elastomers [16, 20, 21, 37, 38–43] is extensively studied and cited in literature. Attempts have been made in these studies to

correlate the erosion resistance of polymers with morphological-, mechanical-, thermomechanical- and fracture-characteristics.

4.2.1.1. Morphological properties. In the area of polymer morphology the crystallinity as well as the physical and chemical network characteristics of the polymers have been suggested as controlling parameters. The influence of physical and chemical network characteristics on the wear behaviour of elastomers has been intensively followed in the past. The nature of the base components and their relative ratio [44–46], the molecular weight of the elastomer [47, 48], the presence of crosslinks [50], the degree of phase separation between soft and hard segments and the effect of annealing on this degree are the most discussed characteristics [37, 51, 52].

Concerning the effect of crystallinity, it has been stated that amorphous polymers show more brittle features, while semicrystalline have a more pronounced viscoelastic character, therefore the first erode usually faster than the latter ones [13, 53]. In order to verify these results and to extend the knowledge on this field, medium density polyethylene (PE) samples were examined [27]. Five grades of PE with different crystallinity (PE1, PE4 and PE5) and crosslinking degrees (PE1, PE2 and PE3) were selected. The ER results did not confirm the trends mentioned above. An increase in the crystallinity led to a steep increase of the ER (cf. Fig. 5a). Nevertheless, the effect of crystallinity is more pronounced at low impact angles. As the impact angle proceeded to 90° the crystallinity has less influence on the ER. Note that these PEs were produced by different catalysts resulting different molecular characteristics an thus crystallisation behaviour. This is a hint that even the supermolecular arrangement (lamellae thickness, density of the molecules etc.) may have a strong effect on the ER.

Chemically, crosslinked thermoplastics. In the above mentioned samples (PE1, PE2 and PE3), different crosslinking rates achieved by varying the amount of crosslinking agent during the composition. Note that the changes in the crosslinking led to simultaneous changes also in the crystallinity. The presence of crosslinking improved the erosion resistance at high impact angles (cf. Fig. 5b). At normal impact (90°) the erosion resistance of the crosslinked samples is outstanding. The presence of crosslinking deteriorated the erosion resistance at low impact angles. It has been stated in literature that the crosslinked material requires a higher strain energy density to initiate crack growth while crack growth starts in the non crosslinked material at quite low strain energy densities. It is expected that this increase in the fracture toughness would translate into better wear resistance under those conditions where the wear mechanism is limited to fatigue crack growth.

Three characteristic specimens of the PE materials were selected (i.e., PE1, PE2 and PE5) and their eroded surfaces were observed by SEM. The surface topography of PE1 and PE2 at 15° impact angles is very similar



Figure 5 ER variation as a function of the impact angle for PE samples of various (a) crystallinity-(due to the morphology) and (b) crosslinking-degrees (achieved by adding different amounts of crosslink agent). Note: crystallinity was determined by differential scanning calorimetry by accepting 288 J/g for the 100% crystalline PE.

to that of specimens under sliding wear by a blade indenter (cf. Fig. 6). PE5 shows, because of its more amorphous nature, more cutting characteristics with chips formation than PE1 and PE2. The chip formation is better resolved in higher magnification in Fig. 7a. For the same sample (i.e., PE5) interlinking of lateral or radial cracks is observed at 90° impact angle (cf. Fig. 7b).

Chemically, crosslinked thermosets. The EP/HD-PUR systems aimed to explore the role of the erodent characteristics were also employed to understand the role of crosslinking. Modification of EP by increasing HD-PUR amount resulted in a network of reduced crosslink density. The fracture-toughness (K_c) and energy (G_c) of the EP/HD-PUR systems were found to vary with their crosslink density. This fact enabled the investigation of the erosive behaviour as a function of the network characteristics and the fracture mechanical response of these modified EPs.

Fig. 8 illustrates the direct influence of the crosslink density (v) on ER of the modified systems. The variation of the ER seems to be a step-wise function of v, the shape of which is nearly independent to the impact angle. For all impact angles, the ER-v variation starts with a plateau and is followed by a steep increase of the ER with increasing v up to a specific v value. Above this v value a second plateau is observed. As the impact angle is decreasing from 90° to 30°, the first plateau becomes progressively smaller and even disappears at 30° impact. The second plateau shows an adverse trend

PE-5



2mm

2mm

Figure 6 SEM micrographs of the PE samples at 15° impact angle.



Figure 7 SEM micrographs of PE5 eroded at (a) 15° and (b) 90° impact angles.



Figure 8 ER variation as a function of the crosslink density (v) for the EP/HD-PUR systems.

getting progressively larger as the impact angle moves towards 30° (cf. Fig. 8). The physical interpretation of these findings is not easy, as v is a direction independent material property while ER is a direction dependent one. The existence of the two plateau indicates that for extreme values of the crosslinking density, i.e., for highly- and low-crosslinked systems, the crosslink characteristics do not practically influence the ER. The steep increase in the ER that separates the two plateau signifies that the change in the crosslink density is associated by a transition in the erosion failure mode.

Fig. 9 depicts the ER and fracture energy (G_c) as a function of v along with the ER at 90 and 30° impact angles. ER and G_c tend to vary adversely to one other when considering their change as a function of v. For high crosslink density values, G_c only slightly changes

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Figure 9 ER and fracture energy (G_c) versus crosslink density (v) for the EP/HD-PUR systems.

while for the same range of v the ER at 30 and 90° impacts presents the above mentioned plateau. As a consequence, the increasing resistance to erosion can be attributed to the increment in G_c . The absence of the first plateau in case of 30° impacts (cf. Fig. 9) implies that a slight variation in G_c may have an important influence on the erosion resistance at oblique impacts.

Physically and chemically crosslinked polyurathanes. Many studies are focused on the effect of morphology on the wear response of polyurethanes (PUR). Note that PUR exhibits outstanding erosion resistance. The special interest arises from the fact that even within a particular group, such as PUR elastomers, some grades behave much better than others. In PURs, structures capable of producing the network required for rubbery behaviour can be either of chemical (knots are given by crosslinks), or physical nature (knots are produced by phase segregation and subsequent crystallisation resulting in "hard domains"). The latter PURs are termed thermoplastic polyurethanes (TPUs). Their physico-mechanical characteristics mostly depend on their constituent monomers (type, ratio, etc.). By this way TPUs of different hardness (controlled by the crystallinity, i.e., hard segment content) can be produced.

Preliminary studies of similar TPUs with varying percentage hard segments (crystallinity) indicate that the lowest hard segment content gives the lowest ER. However, the mechanical integrity becomes a problem with decreasing hard segment content. Hence a combination of chemistry and morphology should be used to optimise TPU properties for a given loading environment. General conclusions about the correlation between the physical and chemical structure and the erosion response cannot yet be obtained. A previous study aimed at discovering possible correlation between material characteristics and ER involved six TPUs and twelve crosslinked PURs. Because these trials include not only the morphological properties but also the mechanical, thermomechanical, etc. properties of these materials, the results will be summarised in paragraph 4.2.1.4.

4.2.1.2. Thermal and thermomechanical properties. From the thermal and thermomechanical point of view, the thermal conductivity and the glass transition temperature (T_g) seem to be important control parameters of solid particle erosion. The localised deformation caused by the erosive impact of a particle on a target material and the adiabatic conditions prevailing at high strain rates in a material of low thermal conductivity may generate high temperatures. The maximum temperature depends on the amount of work that is done on the target material and the specific heat and density of the material. The work done is a function of the maximum pressure during impact and this, in turn, is influenced by the target- and particle-hardness. The temperature rise is lower if heat can flow away from the impact site faster than it is being generated [30, 31]. High temperatures may briefly soften the material [30, 53, 54]. This may create a thermal stress field which is superimposed upon the mechanical stress field of the deformation. This will have important repercussions since it is acknowledged that the development and relaxation of the plastic zone at an impact site is associated with viscoelastic extrusion and fracture in polymers. These damage modes ultimately account for degradation and material loss [30].

Nevertheless, the assumption of perfectly adiabatic conditions needs to be carefully examined. An indication of the adiabatic situation existing in polymers will be the deformed region after relaxation. If this region is larger than the indentation crater depth then likely an adiabatic situation exists. In praxis, a small value of the hardness ensures that only small temperature rises may be expected and thermal degradation of the surface of a plastic material will not be expected to affect strongly the erosion [30].

Model material for thermal effects and their role is usually PE [30, 31]. PE has a low thermal conductivity, thus if the particles arrive fast enough then heat accumulates in the surface [30]. Earlier studies on the temperature rise in PE stated that the maximum temperature rise would remain insufficient for localised melting. It was estimated that thermal effects would become significant at a flux rate of ca. 180 kgm⁻²s⁻¹ [31]. These effects were verified in a recent study [27] where the flux rate even at 15° impact angle was definitively lower (82 kgm⁻²s⁻¹) than this value (see the ER results in Fig. 5). As confirmed by the scanning electron microscopic (SEM) pictures of the eroded surfaces in Figs 6 and 7, the thermal effects were less dominant.

With reference to the influence of T_g on the erosion resistance of polymers the following trends have been observed:

(i) Erosion is higher for polymers with a glass transition temperature (T_g) above room temperature (RT) relative to those with a T_g below RT [13].

relative to those with a T_g below RT [13]. (ii) For T_g below RT, the wear rate decreases the greater the difference between the experimental temperature and T_g is [13, 19].

4.2.1.3. Mechanical properties. Aim of a designer with polymers and composites is usually to improve the mechanical performance of the related engineering part or construction. Similar to other tribological procedures, improvements in mechanical properties do not always coincide with superior erosive resistance. A large number of studies [9, 12, 13, 32–34, 37–42, 48, 54–56] was focused to clarify possible relations between mechanical properties and ERs, however, with less success.

The following mechanical properties are the most discussed ones when their correlation with the erosive wear response was tackled:

Hardness, tensile-strength and -modulus of elasticity, fracture toughness, yield stress and (after yield stress is exceeded) yield strain, rebound resilience, friction coefficient, ultimate-strength and -elongation etc. Tearing energy is also a decisive parameter for the erosion resistance of elastomers. This parameter can change the erosion mechanism from progressive fatigue crack growth to single-cycle tensile failure of the rubber. It is well known that the crack growth rate in fatigue is dependent on tearing energy. The critical frictional input work in erosion is similar to the critical tearing energy in fatigue. Both of them are in good agreement with the fracture energy. The erosion mechanism changes from mechanical fatigue to direct tearing according to the critical frictional input work [40, 50].

Generally impact wear does not relate to the work of the friction forces. Nevertheless, if wear is due to fatigue, the influence of the friction forces should be considered and the coefficient of friction under impact, should be found. There are three types of external friction, namely static friction, kinetic friction (in motion) and dynamic friction (under impact). In dynamic friction energy dissipation is usually characterised by the portion of energy loss at impact [57]. Various trends have been observed in the erosion behaviour in respect to the above parameters not only between different categories of materials (thermosets, thermoplastics, elastomers), but also within the same category. This is likely due to the following reasons:

- The strain rates in the impact of erosive particles are very high, whereas the mechanical properties used in the correlation are measured at much lower strain rates. In addition the stress state accommodated during the mechanical and erosion tests may be completely different [3, 36, 48, 53].
- The properties of worn surface layers differ from those of the bulk material because of thermal-, mechanical- and chemical-degradations during erosion [12, 14, 20, 28, 30, 54, 55, 58].
- Some properties are related to the experimental conditions and thus strongly interrelated [3].

Friction coefficient and hardness, for example, seem to change dramatically during solid particle erosion. The friction coefficient depends significantly on the impact angle. For elastomers, it decreases with increasing angle of attack, while for plastics at small and medium angles of particle hitting usually slightly increases and then, as in case of elastomers, decreases to zero as normal impact is approached. A variation in the friction coefficient within the smaller angle range is probably caused by a change in load. Indeed, with an increase in the impact angle equivalent to a load increase, the friction coefficient for elastomers is lowered. This is usually observed in normal sliding. On the other hand the coefficient of friction for plastics increases slightly. This is observed when a plastic is imposed to increasing load. From this standpoint, the friction coefficient of plastics should steadily increase with the impact angle; however, above 40° - 60° the friction coefficient begins to decrease. It may be assumed that the reason for this phenomenon is a shortened path of movement of the particle over the surface [57].

An increased hardness seems to be important for the erosion resistance when the erosion process takes place at oblique angles and brittle erosion prevails. Conversely, elastomeric materials show generally better erosion resistance at lower values of hardness. However, a better correlation of the ER with hardness has been experimentally found when the surface hardness during erosion was considered. This was obtained by estimating the degree of work hardening and softening by heat generation [54].

4.2.1.4. Empirical relationships. As already confirmed, the influence of selected material properties on the erosion base on literature data is quite confusing. This led the scientists to introduce empirical relationships in order to distinguish the possible modes of erosion and to propose combinations of material parameters to prevent or to minimise the erosion effects.

It has been suggested [22, 59] that the parameter $\eta = \frac{2 \times ER \times H}{\rho \times v^2}$ (ER: erosion rate, *H*: Hardness, ρ : density, v: impact velocity), known as erosion efficiency, is a valuable tool as it can be used to identify the brit-

tle and ductile erosion response of various materials. Ideal micro-ploughing involving just the displacement of material from the crater without any fracture (and hence no erosion) has zero erosion efficiency. Alternatively, in case of ideal micro-cutting, η is unity. When erosion occurs by the formation of a lip and its subsequent fracture, the erosion efficiency is in the range 0 to 1. In contrast, as happens with a brittle material, if the erosion takes place by material spalling and removal of large chunks (e.g., by interlinking of lateral or radial cracks) then the erosion efficiency may be even greater than 100%.

The "brittleness index" in the form of hardness/fracture toughness (H/K_c) has been proposed as an indicator for the erosion resistance of materials of different fracture energy classes [60]. A modified correlation in the form of $H^{0.5}/K_c^2$ has been found to work well in describing the erosion resistance of brittle target materials [61]. For polymers, better correlations have been found by the combined term of hardness and fracture energy (G_{Ic}). For polymer composites under severe abrasive wear conditions, an expression in the form ($H^{1/2}/G_{Ic}$) has been proposed. This correlated well with the wear rate due to friction [62]. Its modified version (i.e., H/G_{Ic}) seems to hold for the erosive wear of polymers [13].

According to the Ratner-Lancaster equations [63], the wear rate is proportional to $1/\sigma_u \varepsilon_u$ where σ_u and ε_u are the ultimate tensile stress and elongation of the polymer, respectively. The term $\sigma_u \varepsilon_u$ is a rough measure of the area under the stress-strain curve to fracture and therefore gives an estimate of the energy to fracture. Similar to this correlation, the combination of high yield stress and strain, was also used. The latter term correlated with the resistance to crack initiation and propagation under very complex (fatigue and/or impact) loading conditions.

Finally, good correlation of the erosion resistance has been found with rebound resilience (RR) within the elastomer group of materials. The ER is found empirically to be proportional to the quantity (1-RR)^{1.4}. This quantity represents the fraction of the initial energy of the impacting particle which is absorbed by rubbers and is therefore available, at least in principle, to cause permanent deformation or fracture, and hence erosion [38]. The above empirical relationships may give satisfactory results within a group of materials, but they have no universal applicability.

As already mentioned, the erosion behaviour of PUR elastomers is of special interest. In order to verify the above mentioned trends for this group of materials, a statistical program was applied and all possible correlations were examined between ER and material properties listed in Table I. Combination of material properties and empirical equations already mentioned right above, like the quantity (1-RR)^{1.4}, or the combination of high yield stress and strain high yield stress were additionally examined [27]. Alike the results presented for the abrasive wear of polyurethane elastomers [46] a lack of correlation among polyurethane chemistry, standard mechanical properties and erosion resistance was found.

TABLE I Characteristic properties of the polyurethane elastomers tested

	ρ (g/cm ³)	H (Shore A)	σ at $\varepsilon = 100\%$ (MPa)	σ at $\varepsilon = 300\%$ (MPa)	σ_u (MPa)	Eu (%)	τ _R (kN/m)	RR (%)	$\alpha_{\rm TH} \ (10^{-6} \ {\rm K}^{-1})$
PUR-1	1.26	95	10.6	15.8	42	692	67	61	176
PUR-2	1.26	83	4.3	7.8	50	660	31	65	192
PUR-3	1.26	70	2.5	4	42.3	650	15.5	52	229
PUR-4	1.21	87	6.6	16	42	410	30	50	142
PUR-5	1.23	86	5.6	9.5	35	550	40	52	170
PUR-6	1.24	94	10	17	53	432	65	34	159
PUR-7	1.24	72	6	11	52	800	_	75	174
PUR-8	1.07	70	2.7	6.5	11.6	430	11.5	53	184
PUR-9	1.03	80	3.5	6.7	11.7	460	19.3	50	180
PUR-10	1.11	70	2.7	6	12	530	15	54	217
PU-11	1.20	55	1.8	3.6	21.2	495	_	45	211
PU-12	1.13	97	9.6	21.2	32.6	394	84.4	52	169
TPU-1	1.14	92	8.5	16	50	550	85	_	167
TPU-2	1.20	93	7	20	55	550	95	_	150
TPU-3	1.21	91	7	20	55	550	90	_	160
TPU-4	1.21	89	7.2	12.6	50	530	66	_	164
TPU-5	1.23	90	8	16	37	525	122	47	143
TPU-6	1.20	92	8	20	50	500	100	36	189

Note. $\tau_{\rm R}$: tear resistance, $\alpha_{\tau\eta}$: thermal expansion coefficient.

4.2.2. Polymeric composites

Polymer composites are often used as structural components where erosive wear occurs. Differences in the erosion behaviour of various types of composite materials are caused by the amount, type, orientation and properties of the reinforcement on the one hand and by the type and properties of the matrix and its adhesion to the fibres/fillers on the other.

Studies made on the erosive wear of composites refer more on fibre-reinforced polymer (FRP) and less on filler-reinforced-systems. The effect of fillers is considered more as modification of the matrix and less as reinforcement, possibly because of the low percentage of fillers. Similar to polymers, the interrelated phenomena occurring during erosion do not allow us to derive general conclusions about the influence of various parameters. The situation becomes more complicated if the geometrical aspects of the microstructure are considered.

It appears that the factors governing ERs in FRPs are mainly influenced by (a) whether the matrix is thermosetting or thermoplastic, (b) the brittleness of the fibres and (c) the interfacial bond strength between the fibres and the matrix [6]. The following sequence in the erosion process of fibre reinforced composites has been reported [43]:

(i) erosion and local removal of material in the resin rich zones

(ii) erosion in the fibre zones associated with breakage of fibres

(iii) erosion of the interface zones between the fibres and the adjacent matrix

Since the matrix has been removed first, the erosion characteristics of resin materials are the prime factor for the resistance of composites. During the erosion process the fibres are exposed to the erosion environment subsequent to the removal of matrix. Thus the toughness of exposed fibres directly affects the erosion mechanisms of composites. The effect of fibre reinforcement has been classified in importance as fibre material, fibre content, reinforcement type (i.e., length, diameter etc.) and fibre orientation. Further continuation of the erosion damages the interface between the fibres and the matrix. This damage is characterised by the separation and detachment of broken fibres from the matrix. The material with the strongest interface strength showed the best erosion resistance [64, 65]. The existence of interleaves in laminated composites was also beneficial (because of the better adhesion between the adjacent layers) for the erosion resistance [66].

Generally composites with thermosetting matrix erode in a brittle manner. A totally different scenario is observed in the thermoplastic matrix composites. The matrix is uniformly grooved and cratered with local material removal showing a clear tendency for ductile mode of erosion [4, 6, 17, 22, 64, 67, 68].

It has been also stated, that short fibre reinforced composites show a better resistance to erosion compared to unidirectional endless fibre reinforced ones (UD). In a randomly oriented short fibre composite a reasonable proportion of the fibres is oriented such that they were nearly aligned with the direction of the impinging particles [6]. On the contrary, in UD composites, when the resin is removed practically nothing remains to support the exposed fibres, which are thus more easily broken and removed.

Many studies report on the role of fibre orientation on the solid particle erosion of UD composites [6, 25, 46, 64, 67–73]. Different trends have been reviewed for the role of this parameter. It is claimed that the fibre removal is due to bending of the unsupported fibres when the surrounding matrix is removed. Additionally, as the fibre orientation angle changes, the shape of the exposed fibre also changes. The exposed shape is a geometrical aspect that depends mainly on the impact angle, while the bending resistance of the fibres depends on the art of the fibre- and matrix-material and on their bonding. Therefore, it would be more sound to consider the role of fibre orientation in a group of other parameters (i.e., angle of impingement, fibre/matrix adhesion, fibres ductility) and not as an individual parameter.

Finally the role of fibre content can also not be insulated from other parameters like the fibre brittleness. Studies on the role of fibre content [69, 74–76] suggest that the inclusion of brittle fibres in both thermosetting and thermoplastic matrices led to compositions with lower erosion resistance.

5. Averaging rules and predictions

A crucial parameter for the design with composites is the fibre content. In order to obtain the favoured material properties for a particular application, it is important to know how the material performance changes with the fibre content under given loading conditions. Right above the role of the fibre content was discussed. Nevertheless, it is not definite how the fibre content affects the erosive wear rate (ER) of a composite. When designing with composites it is important to know what will be the overall ER in the combined multiphase material if the ERs of the individual constituent are given. The main question is the following:

Is the erosion process in a composite controlled by the erosion properties of the individual constituents and what is the 'averaging law' imposed by the microstructure?

The linear (LROM) and inverse (IROM) rule of mixture have been proposed for the prediction of the ER. The linear (LROM) and inverse (IROM) rule of mixture have been proposed for the prediction of the ER. Equations 1 and 2 describe the LROM and the IROM, respectively:

$$ER_{c} = w_{f} \times ER_{f} + w_{m} \times ER_{m}$$
(2)

$$\frac{1}{\mathrm{ER}_{\mathrm{c}}} = \frac{w_{\mathrm{f}}}{\mathrm{ER}_{\mathrm{f}}} + \frac{w_{\mathrm{m}}}{\mathrm{ER}_{\mathrm{m}}} \tag{3}$$

where subscripts c, f and m mean composite, fibre and matrix respectively, whereas ER and w denote the erosion rate and the weight fraction of the related material. These two rules of mixture have also been proposed to model the abrasive wear of UD fibre reinforced composite materials [76, 77]. Unlike to the erosive wear, the applicability of these rules to the abrasive wear was limited as a steady state process was supposed to hold. To refute this limitation a new model was proposed [78], which suggested that the abrasive wear behaviour is quasi-steady state in nature. In this study, it was found that other processes such as reinforcement debonding, reinforcement fracturing and wear scarring (chip removal) beside abrasion are likely to occur in a non-steady state manner. Two mechanisms, each representing the two extremes of the quasi-steady state wear behaviour (maximum and minimum fibre wear resistance, respectively) were described. These rules took under consideration the modulus of elasticity E_i of the constituent phases, using further a linear and an inverse rule of mixture for the calculation of the E-modulus of the composite [78].

The LROM and IROM were first evaluated for a multiphase AL-Si alloy [79]. The same rules of mixture were adopted for a glass-fibre reinforced epoxy composite [72]. The key aspect in the problem of the 'averaging law,' is the size of the impact site in comparison to the size of the microstructural phase [79]. This work enlightened and discussed the different cases arising from the microstructure of the composite and from the behaviour of each constituent. Generally an increase of the fibre/filler content leads to an increase to the ER. This is due to the fact that usually the erosion resistance of the fibres is lower than that of the matrix. A further reason is the quality of the bonding of the reinforcement with the matrix [43, 65, 67, 69, 73, 80]. In case of particulate composites the interface between matrix and filler is not only weak but may also promote subsurface crack propagation. This will accelerate further the ER. Such phenomena have been reported in case of rubbers reinforced with fillers [19, 81].

However, a composite material may also show a better resistance to erosion with increasing reinforcement content. This has been observed for instance in an aramid fibre (AF) reinforced epoxy [25]. A plausible reason for this behaviour lies in the behaviour of AF, which fibrillates during failure, thereby absorbing significantly more energy than the brittle matrix. In case of particulate systems, when the amount of filler is enough to modify the properties of the composite then a positive influence of the filler content on the ER of the composite can be expected.

The effects of fibre content on the erosive wear behaviour is mostly studied for thermosetting matrix systems. As different mechanisms of material removal govern the erosion of thermoplastic matrix composites, a recent study evaluated whether or not the proposed rules of mixtures can be used for glass fibre/ polypropylene (GF/PP) composites [68]. For the case of erosion at low impact angles (30°) the modified rules of mixture [78] were additionally evaluated.

Generally the results showed that the linear rule of mixture and the inverse rule of mixture provide good bounds for the experimental ER. The inverse rule of mixture deliver generally better results. The modified rules of mixture proposed for the case of abrasion do not hold for the erosive wear. The applicability of the LROM in some of the experimental results [68] verified the already existing remark [79], that although generally the IROM predicts better the ER of multiphase systems, when the two constituents are continuous and linear aligned along the incident erodent particle beam direction, the LROM approach works well.

In engineering applications a structural part is not only subjected to solid particle erosion but also to stress- and deformation- profiles, oscillations and impacts. Therefore it should be sufficiently resistant also to these solicitations. Additionally to material removal the FRPs can show strength and stiffness degradation which results in reduced durability of the construction. There was no study until very recent referring to the residual properties of the polymeric composites after solid particle erosion. Results after solid particle erosion of interleaved and non-interleaved CF/EP with various stacking sequences [66] implied that the solid particle erosion can be considered as a repeated impact procedure. The damage growth under erosion was likely similar to that of impact fatigue. A semiempirical approach, initially developed for the prediction of the residual strength after single impact, was adopted and evaluated for solid particle erosion. The model takes into account the inherent material properties, the initial and post-impact tensile strength of the material and the visco-elastic response (mechanical damping) of the non-impacted material. The model predicted well both the impact energy threshold and the residual strength after solid particle erosion (impact). Results showed that for impact energy values lower than a characteristic threshold the damage induced did not affect the residual tensile strength of the materials. It was also established that this threshold depends on the orientation of the plies, the existence of interleaves and on the energy absorption capacity of the material.

A latter study verified the applicability of the above mentioned model in a composite system which shows a typical ductile type of erosion [82]. The model predicted well both the impact energy threshold and the residual strength after solid particle impact also in case of UD-GF/PP at both Pa (parallel) and Pe (perpendicular) erosion directions. The erosion direction did not influence the onset of the strength degradation, it affected, however, the ultimate residual strength. Erosion in Pa-direction resulted in maximum material removal and maximum loss in the tensile strength. A comparison between CF/EP and UD-GF/PP systems showed that the strength degradation onset appeared almost immediately in the latter case but the UD-GF/PP preserved a greater amount of its initial tensile strength compared to that of CF/EP systems.

6. Suggestions on future work

The present study was aimed at reviewing the solid particle erosion response of polymers and their composites focusing on the dominating mechanisms, the most discussed influencing parameters and the different trends observed in the literature. Although a great amount of work has already been devoted to this topic many questions are still open.

As confirmed above, there exists a lack of correlation between material properties and ER. At the beginning of this article the need of determining the exact conditions during solid particle erosion and estimating the polymer properties under these specific conditions was enlightened. More precisely, it would be interesting to estimate the temperature profile and the strain rates during solid particle erosion and to try afterwards to estimate the material properties under the same experimental conditions.

The dynamic character of solid particle erosion suggests the need to determine the dynamic-mechanical properties of the materials under the erosion dominating frequencies. There are many indications that the frequency-dependent loss factor is a key parameter. It is known for polymers that the viscoelasticity has a dramatic effect on their properties. Therefore it is of great importance to find out and determine especially the thermomechanical and fracture characteristics of the materials in the requested frequency range. Because of the complexity of erosion (interrelated properties and mechanisms) the possibility of creating a data base including the wear response and material properties under the same experimental conditions would be very straightforward. For data mining various mathematical methods or tools, like neural networks, could be used. The use of neural networking has already been applied to predict tribological properties of polymeric composites [83, 84]. All these suggestions could possibly direct to a better correlation between material characteristics and ER.

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