

# P O L I M E R Y

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

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## Microcellular polymer and composites

### Part II. PROPERTIES OF DIFFERENT TYPES OF MICROCELLULAR MATERIALS<sup>\*\*)</sup>

#### MICROCELLULAR POLYMERS AND COMPOSITES. PART II. PROPERTIES OF DIFFERENT TYPES OF MICROCELLULAR MATERIALS

**Summary** — The paper is the review of microcellular polymer materials (polyolefins, polycarbonates and other thermoplastics) and microcellular composites reinforced with mineral fillers or natural fibers. The effects of type of foamed material, kind of foaming agent used and the foaming process conditions on mechanical properties, morphology and useful properties of various plastics were evaluated. The examples of microcellular materials characterized with low density and simultaneously high dimensional stability, stiffness and good strength characteristics, in relation to weight, were given. These advantageous features promote the wide applications of microcellular polymer materials among others in automotive industry, industrial casings, sports equipment, transport as well as in decorative and textile industries.

**Key words:** microcellular polymers, polyolefins, polycarbonates, thermoplastics, microcellular composites, foaming agents, properties, applications.

#### MIKROPOROWATE POLIMERY I KOMPOZYTY. Cz. II. WŁAŚCIWOŚCI RÓŻNYCH TYPÓW TWORZYW MIKROPOROWATYCH

**Streszczenie** — Artykuł stanowi przegląd publikacji o mikroporowatych materiałach polimerowych (poliolefiny, poliwęglany oraz inne termoplasty), jak również o mikroporowatych kompozytach wzmocnionych napełniaczami mineralnymi i włóknami naturalnymi. Oceniono wpływ rodzaju spienianego materiału, typu używanego środka spieniającego i warunków prowadzenia procesu na właściwości mechaniczne (rys. 1), morfologię (rys. 2—4) i właściwości użytkowe (rys. 5) różnych tworzyw. Podano przykłady materiałów mikroporowatych charakteryzujących się małą gęstością, a jednocześnie wysoką stabilnością wymiarową wyrobów, sztywnością i wysokimi w odniesieniu do wagi wskaźnikami charakterystyk wytrzymałościowych. Te korzystne cechy sprzyjają szerokim zastosowaniom mikroporowatych materiałów polimerowych między innymi w przemyśle samochodowym, obudo-

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wach instalacji przemysłowych, sprzęcie sportowym, transporcie jak również w przemyśle dekoracyjnym i włókienniczym.

**Słowa kluczowe:** polimery mikroporowate, poliolefiny, poliwęglany, termoplasty, kompozyty mikroporowate, środki spieniające, właściwości, zastosowanie.

In paper [1] we described most popular technologies of production of microcellular plastics with use of physical or chemical foaming agents. In this part we characterize different types of microcellular polymers and composites produced.

## MICROCELLULAR THERMOPLASTICS

### Microcellular polyolefins

Polyolefins are the most frequently used and dominant polymers in the industrial applications. The following polymers belong to the polyolefin group: polypropylene (PP) and polyethylene (PE), forming a number of different types, e.g. high molecular weight polypropylene and many types of PE like: very low-density PE (PE-VLD), low-density PE (PE-LD), linear low-density PE (PE-LLD), high-density PE (PE-HD) and ultra high-molecular weight PE (PE-UHMW). PP and PE find the most significant and important applications. Both PP and PE are the polymers of today and tomorrow which belong to the engineering category [2].

Mechanical properties, morphology and application of microcellular polyolefins are influenced by variable properties of materials as well as the following conditions of foaming process, namely [3–5]:

- kinds of materials: homo or copolymer, block copolymer, linear, branched, crosslinked polymer or blend,
- grade of crystalline and density of the foam,
- melt temperature and viscosity during melting,
- type and amount of blowing agents,
- weight reduction size and foam structure.

In general, the cellular structure of semi-crystalline polymer foams is difficult to control, compared to that of amorphous polymer foams. That is already well known that the cells formation take place mostly in the amorphous regions of the polymers what is after-effect of diffusion and absorption processes. The semi-crystalline polymers may have very complex textures, which are strongly dependent on the processing conditions, in particular, the thermal history [6]. With a growing crystallinity of polyolefins, approximately 41 %, the cell structure seems to be non-uniform. It is believed that due to the high injection rate of polymer melt, at increased content of the blowing agent and high viscosity of polymer matrix, the relatively fine, closed and uniform cell structure is formed. On the other hand, the slowly cooled samples with a higher degree of crystallinity produced non-uniform foam structure with a large cell size [6].

Matuana *et al.* [7] studied microcellular foams of PP and found that microcellular PP could be successfully

produced by adding the appropriate nucleating agents into the formulation. He also reported that microcellular foamed ethylene-propylene copolymer could be produced without a nucleating agent at temperature above the melting point because of the lower surface tension in the copolymer [7].

Blending is commonly used to enhance certain properties of the polymer. It has been shown, that the presence of another phase in polyolefins has a great influence on the microfoaming of PE-HD and PP in micromolecular batch processing. Also, the mechanical properties, which have been decreased by blending, were improved by foaming. The experiments made by Park *et al.* [8] showed that the notched Izod impact strength values of foamed PE/PP (90/10) and PE/PP (10/90) were three times higher than those of unfoamed ones. The cell causes a kind of stopping device which retard subsequent propagation [8]. It was also the effect of blending on the foam processing of PE-HD/*i*-PP. The microcellular foaming of the materials was greatly enhanced by blending and strongly affected by the interface in the blends. All blends were foamed with a fine cellular structure. Although the impact strength was deteriorated by blending, it was improved significantly by introducing a microcellular foam structure into the material [9].

Microcellular polyolefin production by MuCell technology is increasing as the processing leads to further effective development and the materials will find applications as fibers, sheets, films and packagings.

MuCell process belongs to the physical foaming system. The microcellular MuCell process consists in the introduction of carbon dioxide or nitrogen as a supercritical fluid (SCF) into a polymer melt to produce a microcellular foam [10]. Essentially the process involves the creation of a single-phase solution formed by adding supercritical atmospheric gas (CO<sub>2</sub> or N<sub>2</sub>) to a polymer melt. This single-phase solution is then injected into the mold. The amount of material that is injected into the mold is less than the part volume. This process is guided by following four steps: creation of a single-phase solution, homogeneous nucleation, cell growth, and part formation [11].

Currently the Trexel takes steps to intensify the development of polyolefin foams through internal projects. Primarily closed cell microstructures have been produced with cell sizes of 10 to 60 microns. Now there is a method to make microfoam with cell size in the range of 15 microns. The elongation at break of MuCell PP sheets were 30 % greater than control sample [12].

The cell morphology had a strong relationship with the impact strength. To improve the impact strength,

well-developed uniform microcellular structure is needed with small cell size and high cell-population density [7]. Recent studies have shown that the void fraction and cell morphology of microcellular PE-HD/PP blends were strongly dependent on the processing parameters. Blends decreased in crystallinity of both PE-HD and PP what facilitated a microcellular process. Pure materials did not foam so well at any conditions. The notched impact strength increased with higher temperature of foaming at long foaming time. Improvement in impact strength was associated with well-developed microcellular morphology [13].

The nature of the process is such that the advantages of traditional foaming techniques can now be applied to the parts not previously considered for foaming. In addition, the cell structure achieved in the MuCell process is significantly smaller and more uniform. This presentation will address the use of MuCell foaming technology in PP applications for various automotive and business machine injection molded products [14].

Worldwide there are a lot of manufactures of polyolefin foam and is still growing with their increased requisition. The most persuasive reasons to use the polyolefin foams are their satisfy properties.

They require special processing techniques and that is why their cost per unit volume is higher that of low density polystyrene or polyurethane foams [15]. Even the polyolefins weight savings are rarely sufficient to drive investment in the MuCell process. Those applications which can benefit most from applying the MuCell process to polyolefins are those where quality issues can be resolved, substantial cycle time can be reduced, or when a higher cost material can be converted from polyolefin [14].

PP sheet was also produced in MuCell process, which at first had a wall thickness of 3 mm and final thickness of the sheet was measured equal to 10 mm. The wall thickness achievable in this process may be three to four times bigger than the initial thickness [16].

The general experiments of polyolefin which are mentioned lead to obtain the relationship between the process technology and the foam properties. In general, the cellular structure of semicrystalline polymer microfoam is difficult to control, compared to that of amorphous polymer foams. According to the literature presented, polyolefins' microfoams can be prepared with closely controlled density and cell structure.

### Microcellular polycarbonate

Polycarbonate (PC) is often viewed as the quintessential engineering thermoplastic, due to its combination of toughness, high strength, high heat-deflection temperature and transparency. Polycarbonate offers good color ability and chemical resistance, along with very high rigidity for a resin with such a good ductility. It is the one of the most moisture-sensitive thermoplastics. Physical

properties are significantly reduced if the resin is not dried well prior to processing [15].

In the beginning of nineties Kumar *et al.* created microcellular structure in PC with the high solubility of CO<sub>2</sub> [16]. The injection molding process of microcellular PC using physical blowing agent (MuCell technology) has been demonstrated by Bledzki *et al.* [17]. The major aim of the both processes was to produce microcellular structure with extremely large number of bubbles with cell size under 10 μm, which was evidently obtained and controlled by producing the foams showing a wide range of foam density [17–19]. The research carried out to investigate the expansion behavior of extruded polycarbonate foams blown with supercritical CO<sub>2</sub> to achieve low density microcellular foams. The expansion behavior of PC foam was interpreted by the amount of gas retained in the cell structure in consideration of the cell opening, cell-to-cell diffusion, and melt stiffening [20].

A numbers of studies on the microcellular PC have exposed a widely correlations between mechanical properties and variation of density. The morphology as well as mechanical properties of microcellular PC products were influenced by different process variables [17], such as injecting velocity, type and concentration of the blowing gas (N<sub>2</sub>, CO<sub>2</sub>), mold and melt temperature, geometries of the final products — part thickness not least the intended density or weight reduction. The material characteristic according to ASTM and ISO can be determined, but until now they were not applicable to more complex part. The following trends generally applied: the absolute values of the modulus of elasticity, tensile strength, yield stress and elongation are decreased by microfoaming; they often decrease in a linear relationship with the density or weight of the part [21]. The density and weight can be reduced up to twice [22].

The effects of the cell size, cell structure and density on the mechanical properties have been also investigated. It was found that the PC-CO<sub>2</sub> system offers a wide range of foam densities and significant variation in the average cell size at a given density [23]. Microcellular nucleation in PC-CO<sub>2</sub> followed to the lowering of the glass transition temperature ( $T_g$ ) of the original material. This process is observed below  $T_g$  of neat polycarbonate [19, 24–26]. The mechanical properties of amorphous polymers are affected by dissolved gas [25]. It was also found that concentration of foaming agent, such as CO<sub>2</sub> or n-pentane, as well as processing temperature and pressure influenced the solubility and diffusivity on the nucleation mechanisms [27].

Since PC foams are highly susceptible to cell opening, the expansion behaviors of PC foams were significantly affected by the amount of gas lost through openings in the cell walls. The expansion ratio increased as the content of CO<sub>2</sub> increased [28].

It observed that the notched impact strength of neat PC depended significantly on the part thickness (with a

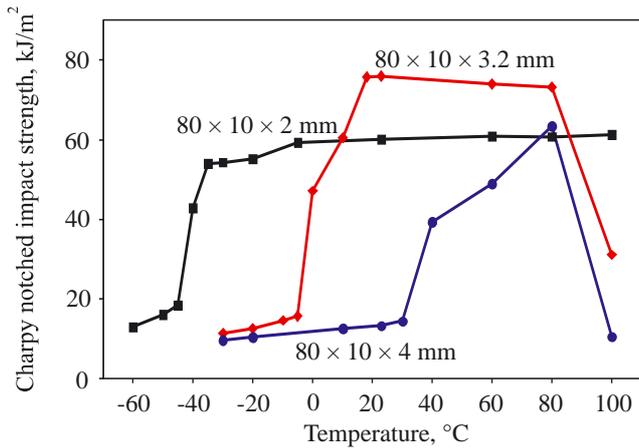


Fig. 1. The influence of the temperature on Charpy notched impact strength of test bars of different (2 mm, 3.2 mm and 4 mm) thickness (DIN EN ISO 179); annealing time was 2 h [29]

though brittle transition at thickness increase), temperature of investigation, notch radius and obviously on the processing parameters (Fig. 1). That is also already well known, that the polycarbonate is very sensitive to sharp notches and scratches [17, 21, 29].

The effect of residual CO<sub>2</sub> as blowing agent on the impact strength of polycarbonate foams appears to be negligible after 2 weeks of distortion while the effect of N<sub>2</sub> after 10 days [30].

The investigations of Izod notched impact strength made by Kumar *et al.* [30, 31] were carried out according to ASTM D256-93a, which recommended a notch radius of 0.08 mm with using 2.7 Joule capacity hammer. Under these conditions, it can be observed that the sharp notch radius causes an increased in Izod impact strength of PC microfoam with density as well as cell size at a given

density. In comparison with compact PC, Izod impact strength of microcellular foam was 60 percent more related to density. It is also important to remark that the compact PC at the same time demonstrates brittle break behavior. Regarding to cell size, the highest impact strength occurred at cell size of 18 μm [31].

Microcellular PC has only significantly higher notched impact strength than compact PC if the compact PC shows brittle fracture under the same conditions. A higher toughness of the microfoams under the same conditions is primarily the result of the crack stopping mechanisms in the core structure and the ductile fracture of the thin, compact surface layer [29, 32]. The experimental results revealed that it is important to note the parameters as well as the investigation conditions by comparison impact properties of neat PC with microcellular PC. The 3.2 mm sample of PC shows ductile fracture at room temperature and brittle at -30 °C temperature. The 4 mm sample of PC with brittle fracture at room temperature shows other properties what have been significantly changed owing to microfoaming. In this way PC microfoam has higher notched impact strength than compact PC [32].

The results of the Izod impact test showed that by addition of 3 wt. % of PP to neat PC, the impact strength at lower temperature increased by around factor five in comparison with pure PC. During the typical processing the well dispersed PP in PC matrix has been obtained in spite of poor compatibility of the components and different thermal expansion coefficients [33, 34]. It was found that the tensile strength at break as well as yield strength is directly proportional to the foam density or equivalently, volume fraction of the cell [35–37].

The increase in fatigue life in related to the saturation concentration of CO<sub>2</sub> and, consequently the yield strength. These effects may be due to the changes both in

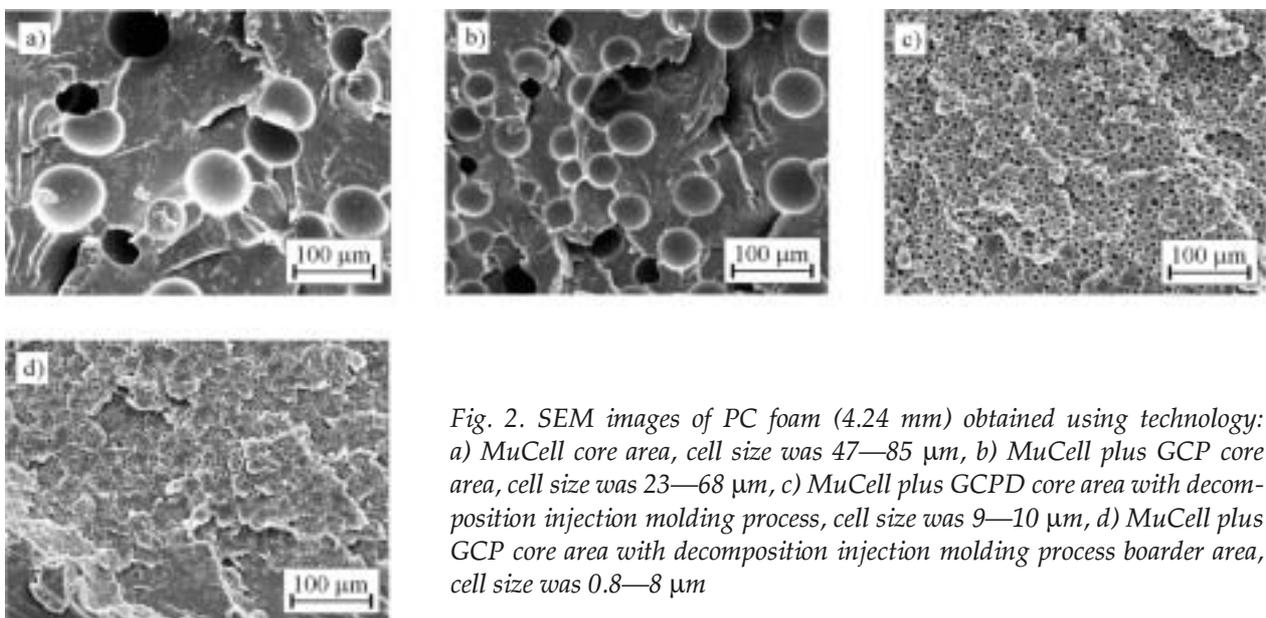


Fig. 2. SEM images of PC foam (4.24 mm) obtained using technology: a) MuCell core area, cell size was 47–85 μm, b) MuCell plus GCP core area, cell size was 23–68 μm, c) MuCell plus GCPD core area with decomposition injection molding process, cell size was 9–10 μm, d) MuCell plus GCP core area with decomposition injection molding process boarder area, cell size was 0.8–8 μm

the properties of the polymer and the state of pre-existing internal flaws or cracks [38]. It has been also found that the fatigue life of microcellular PC increased with decreasing relative foam density. The differences in the fatigue behaviors of microcellular and solid polycarbonate results directly from the geometry of the foam blunting either the leading craze crack growth or non uniform stress and strain [16, 39].

As PC is used in many load-bearing applications, knowledge of the creep behavior of microcellular PC is of special interest. It was found that the creep strain of the foam contains a higher viscoplastic component compared to the unfoamed material [40, 41].

The mechanism of nucleation phenomenon in the solid state microcellular foam is identified as a solid state failure process [24]. Kumar *et al.* has also investigated the tensile properties as functions of cell size. It was observed that average cell size brought not so significant changes of tensile behavior. The stiffness, strength and toughness demonstrated no definite trends with cell size change of microcellular PC [42]. On the other hand increase in mechanical properties such an elongation and impact behavior of the microcellular PC could be correlated with CO<sub>2</sub> concentration [43].

The Figure 2 shows the fracture pattern (made by cryogenic crushing of PC) showing very fine gas bubbles distributed by the application of gas counter pressure (GCP) process with the precision mold opening. The reason of this is the impulsive pressure relief of melt during increasing volume of cavity [32].

The industry of microcellular foam injection molding of PC faces several serious challenges. There are different kinds of processing to produce PC microfoams. Microcellular PC foams properties produced in injection molding process depend on the temperature, thickness and processing parameters. It was shown that PC was very sensitive to sharp notches and scratches.

### Other microcellular thermoplastics

The development of microcellular poly(ethylene terephthalate) (PET) was increased for packaging, automotive and also for aerospace applications. The CO<sub>2</sub>—crystallized PET foams show the highest bubble nucleation densities in the solid state process. Thus CO<sub>2</sub> induced crystallization can be employed to obtain the smaller bubbles than are seen in low crystalline or amorphous PET foams [44].

Resilient moldable beads that retain blowing agent can be prepared from an amorphous polyester resin. The polyester foam remedies the deficiencies of existing bead products. This foam has a low thermal conductivity as well as excellent dynamic cushioning [45].

Most of the microcellular processes using two stages concerned polystyrene [46]. Some kinds of experiments showed also mixtures of polystyrene (PS) and blowing agents by extrusion process [47—50]. The relationships

between the mechanical properties and morphology have been studied for various bubble sizes and percentage of foaming for high impact polystyrene (PS-HI) [51]. PS is available to foam in two forms: extruded PS and PS expanded to molded forms. There are light, closed cell foams with low thermal conductivities and excellent water resistance [15]. The experiments have shown the influence of soluble additives at levels just below their solubility limit and high gas saturation pressures gave the most acceptable foams with smaller the cell size [52, 53]. In the polymer processing it is also important the viscosity of polymer/SCF solution. The effect of pressure on the viscosity of PS/CO<sub>2</sub> solution was observed [54, 55]. The effects of dissolved supercritical CO<sub>2</sub> on the viscosity and morphology were also investigated for the blend/CO<sub>2</sub> solutions. It was observed that the cell structure of foamed PE/PS blends showed a typical dependence on pressure and CO<sub>2</sub> concentration. Increase in these both parameters led to a smaller cell size [56]. The experimental results showed that the cell density of extruded PS foams was influenced by the geometry of the die due to its effects on the pressure profiles along the die and pressure drop rate across the die [57—59].

It was demonstrated that microcellular poly(vinyl chloride) (PVC) was formed in solid state process. This experimental program showed that the foam structure alters significantly by using different concentrations of plasticizers and additives [6, 60]. PVC foams are of two types: open-cell foams which are soft and flexible as well as closed-cell foams which show rigid behavior [15]. The impact strength of PVC foam was found to decrease linearly with relative density [61]. Park *et al.* [62] reported the microcellular PVC showing unique cell morphology and mechanical properties. It was found that there is a significant effect of amount of void fracture on the tensile and impact properties. The notched Izod impact strength of microcellular PVC increased with the void fraction increased. On the other hand as increasing of void fraction the decrease in tensile strength and modulus decrease.

The poly(methyl methacrylate) (PMMA) foams made by two stage batch process have been characterized using different methods conditions which were directly linked with desired mechanical properties. The expansion ratio and elastic modulus, tensile strength and elongation at break decreased with increasing foaming time and saturation pressure [63].

Microcellular foaming by injection molding is used also for such resin as acrylonitrile butadiene styrene terpolymer (ABS) or PC/ABS which are challenges for further attainments [20, 64, 65]. MuCell technology is used to reduce injection pressure and melt temperature to improve quality of in-mold decorated parts. PC/ABS is one of the materials used in these applications [20].

The studies on the effects of the crystallinity and morphology of semicrystalline polymers on the microcellular morphology have been done. For all the studies on

semicrystalline polymers such as PE-HD, polybutylene (PB), PP and PET, higher crystallinity was obtained at lower rate of cooling [60].

The gas supersaturation technique was used for production of microcellular polymers like PS, styrene-acrylonitrile copolymer (SAN) and PC. Dissolved nitrogen gas had some effect on the deformation behavior of PS and SAN [66]. The PS and SAN were used to study the impact properties. Microcellular foams were tested at various impact conditions by using different notch radius [67].

Microcellular semicrystalline polymers such as poly(ethylene terephthalate) are very promising for engineering applications because of their unique properties, particularly at higher densities. The results of experiments presented considerable insight into the mechanisms controlling the cell nucleation during microcellular processing of amorphous and semicrystalline polymers [68, 69].

The effects of processing parameters on the mechanical properties of PMMA were investigated [70]. Recent studies on the PMMA/CO<sub>2</sub> foams suggest that there is also possibility to expand further the primary foam and obtain secondary foam with smaller cell size [71].

Microcellular injection molded structure of polyoxymethylene (POM) was also investigated. The greatest effects on all the measured properties were observed at higher injection speed [72].

The ability to produce such a family of microfoams opens the possibility to explore the effect of cell size on the properties of cellular materials. Microcellular thermoplastics are prepared using different processes: injection molding, extrusion and so on. Due to their energy absorption closed-cell polymeric foams are predominantly used in packaging, impact and sandwich applications. It is important to note that the foam properties are influenced by two factors: the solid walls and gases inside the cells. The comparison of all of presented microfoams shows significant differences as results of different processing conditions such as temperature, injection speed, kind and content of blowing agents and so on.

#### MICROCELLULAR REINFORCED POLYMER

Reinforced foamed polymeric material offer a unique combination of dimensional stability, rigidity, and low specific gravity. In addition, they exhibit excellent strength to weight ratios. The reinforced foams will also have higher heat capabilities, greater flexural strength, and improved fatigue characteristics in comparison with a non reinforced foam [73, 74]. Introduction of the reinforcing filler actually improves the properties in two ways. The filler contributes an increase in strength of the material and also acts as a nucleating agent to promote more uniform and complete foam formation.

The use of layered silicate nanoparticles *i.e.*, clay to reinforce the polymers have drawn a great deal of atten-

tion recently. Polymer nanocomposites contain layered silicates that are dispersed at a nanoscale level in the polymer matrix. In comparison with conventional micro-sized filler particles used in foaming processes, nanometer-sized clay particles in fact offer unique properties. In other words, the large surface area of clay nanoparticles with their extremely fine dimensions, and close contact between particles and polymer matrix greatly alter the cell nucleation and growth behaviors.

Addition of the nanoclay into a neat resin has been found improving the mechanical properties of the resulting nanocomposites and their microcellular injection molded products [75]. The observed improvement in mechanical properties could be attributed to the fact that the nanoclay would not only enhance the properties but also act as a nucleating agent altering the cell nucleation and growth behaviors during the microcellular injection molding process. The presence of nanoclay also increases the maximum weight reduction, presumably because of a higher degree of gas dissolution in the nanocomposite. A higher weight reduction can be attributed to the more nucleation sites available and higher viscosity and stiffness of the matrix, leading to less severe cell coalescence. In addition, the microcells in neat resins tend to be rough on the inner surface, while the nanocomposites show a much smoother surface.

The effect of nanoclay on the cell development and crystallization behavior of polyamide 6 (PA 6) in microcellular injection molding process was investigated [75, 76]. It was found that the presence of nanoclay greatly reduced the cell size (20–30  $\mu\text{m}$  with nanoclay while 70–80  $\mu\text{m}$  without nanoclay) and increased the cell density when compared to a neat resin processed under identical molding conditions. In addition, cell size distribution at the sprue center was, in general, the largest, gradually decreasing towards the skin for both neat resin and nanocomposite. The presence of a nanoclay increased the crystallization rate. But with extra addition of nanoclays into the polymer matrix, the crystallization rate is reduced. Nanocomposites containing the proper amounts of nanoclays show the maximum crystallization activation energy and produce finer and denser microcell structures what leads to better mechanical properties.

An optimum content and dispersion of nanoclay for microcellular PE-LD/clay nanocomposite foam was illustrated [77] and the study has revealed the following: when a small amount (less than 0.1 wt. %) of clay was added to PE-LD with maleic anhydride grafted polyethylene (MA-PE), the cell density was improved significantly (above  $10^9$  cells/cm<sup>3</sup>). The optimum content of clay was 0.02–0.1 wt. %, which corresponded to an extremely high cell density. However, above the critical content of 0.05 wt. % clay, a decrease in cell density occurred, and no distinct effect of clay was observed in terms of cell density for the PE-LD nanocomposite filled with 5 wt. % clay, which showed an intercalated structure. Exfoliated clay particles not only greatly improved

the cell density but also decreased the cell size in the nanocomposites.

Rubber particles are also used now in microcellular polymer composites [78]. The small addition of core-shell rubber also reduced the cell size (60  $\mu\text{m}$  to 35  $\mu\text{m}$ ) and increased the cell density of microcellular injection molded PA 6 parts, in comparison to their neat resin counterparts. On the other hand, at higher core-shell rubber loading, the cell size and density were found to be similar to that of the neat resin.

Glass fibre reinforced PP foams are also manufactured in the MuCell process for a seal construction unit (33 % glass fibre, weight reduction around 20 % in comparison to nonfoamed unit) [79].

#### MICROCELLULAR NATURAL AND WOOD FIBRE REINFORCED POLYMERS

Many new innovative technologies are now being introduced and reintroduced for foam processing. Often called microcellular foaming, the new technologies utilise a number of approaches to achieve fine cellular structures with double digit weight and cycle time reductions. The key to the innovative technologies is computer process control, good tool design including counter pressure, static melt mixing and new chemical foaming agents.

On the other side, one of the fastest developing reinforcing materials for plastics is also one of the oldest: wood fibre. The processing of polymer (PVC and blends of PP-PE-HD)/wood fibre composites of microcellular foamed structures through a batch foaming process [80–86] was investigated. The batch foaming process used to generate the cellular foamed structures in the composites is not likely to be implemented in the industrial production of the foams because it is not cost-effective. The microcellular batch foaming process is time consuming due to the multiple steps in the production of foamed samples.

The manufacture of the PVC [87–91], PS [92–94], PE-HD [95, 96] and PP [97] wood fibre composite foams in a continuous extrusion process was also investigated considering the factor design, moisture as a foaming agent, effect of foaming agent (endothermic and exothermic), critical processing temperature, cellular morphology and cell density.

Park *et al.* [98] have experimented with two system configurations (tandem extrusion system *vs.* single extruder system) for wood fibre/polymer composites to demonstrate the system effect on the cell morphology and foam properties. The system configuration had a strong effect on the cell morphology, and the tandem extrusion system is a highly effective for fine-celled foaming of PE-HD/wood fibre composites compared to single screw extruder system.

The microcellular foaming in an injection molding process was [99–107] investigated for polymers con-

taining wood fibre and also flax fibre [108]. The advantage of this injection molding process is that by using conventional injection molding machine and different chemical foaming agents (exothermic, endothermic and endo/exothermic) the shaped parts (sandwich structure) can be prepared, containing compact outer skin and foamed cores showing different physical and mechanical characteristics.

The microscopic observations as well as microcell classifications of microcellular wood fibre reinforced PP composites [109] showed that exothermic foaming agent gave better performance considering cell size, diameter, distance and polydispersity compared to endothermic and endo/exothermic chemical foaming agents (CFA). The presence of 2 wt. % of exothermic foaming agent led to finer cellular structure in comparison to the other content (5 wt. %), at same wood fibre content (Fig. 3). It is also notable that an optimum of CFA content depends on the CFA type, wood fibre type and also wood fibre content. From micrographs, it is also seen that the microcells can orient themselves depending on the direction of flow.

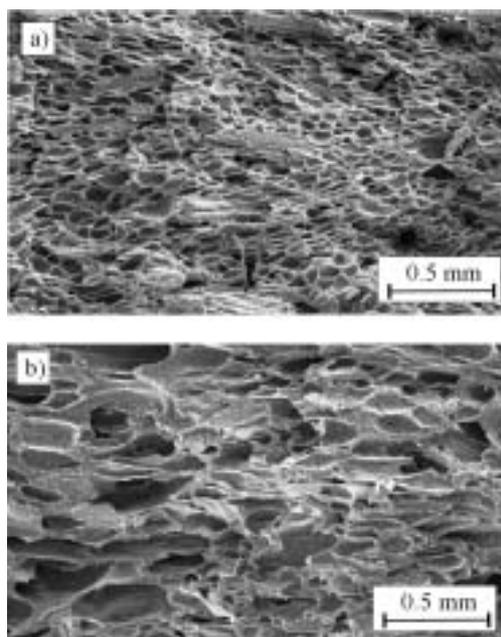


Fig. 3. Effect of exothermic foaming agent content on the structure of hard wood fibre-PP microcellular composites (wood fibre content 30 wt. %): a) 2 wt. %, b) 5 wt. %

The density of the microcellular composite is reduced 30 % at most compared to non foamed composites which is achieved with using exothermic foaming agent (density decreased to 0.71  $\text{g}/\text{cm}^3$ ). The coupling agent — maleic anhydride grafted PP (MA-PP 5 %) in the microcellular wood fibre-PP composites shows a great influence on the fibre-matrix adhesion and on the cell size distribution, as well as on the mechanical characteristics (tensile strength improved around 80 %).

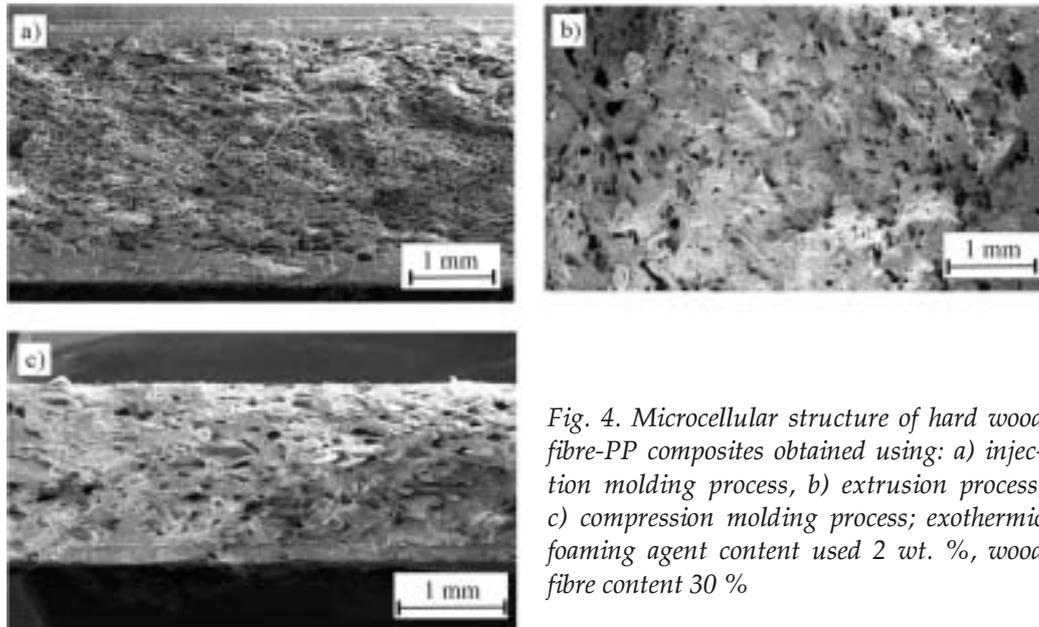


Fig. 4. Microcellular structure of hard wood fibre-PP composites obtained using: a) injection molding process, b) extrusion process, c) compression molding process; exothermic foaming agent content used 2 wt. %, wood fibre content 30 %

It is also found that the microfoams show smooth surfaces compared to the non foamed composite [110]. This is reached by outer non foamed zone and due to the internal pressure of the microcellular foam structure. With the use of endothermic foaming agent, the surface roughness is reduced by nearly 70 % compared to non foamed composites. Due to the microfoaming the odour concentration of the wood fibre reinforced composites can be reduced. It is also notable that the odour concentration of the composites is effected by the processing time of the different processes.

A comparative study of wood fibre reinforced PP composites obtained in extrusion, injection and compression molding was done [111, 112]. Injection molding process showed better achievement compared to extrusion and compression molding process in maximum properties, especially in cell size, shape and distribution (Fig. 4). Chemical foaming agent content strongly influenced the density reduction in extrusion and compression molding processes, whereas it was nearly the same in the injection molding process. Density was reduced around 30 %, 20 % and 22 %, decreased to  $0.741 \text{ g/cm}^3$ ,  $0.837 \text{ g/cm}^3$  and  $0.830 \text{ g/cm}^3$  for injection molding, extrusion and compression molding processes, respectively [111].

Microcellular wood fibre reinforced composites exhibit also reduced surface roughness compared to non foamed composites. This is reached by outer non foamed zone and a smaller surface irregularity due to the microcellular foam structure and also resulting internal pressure of the microfoam. Figure 5 shows that endothermic foaming agent maximally reduced surface roughness (around 70 %) compared to other chemical foaming agents. This is may be due to the slow nucleation of the process by endothermic foaming agent and to the thickness of the outer zone of the composites.

Natural fibre (jute and flax fibre) reinforced epoxy foams [113] and polyurethane microfoams [114] were also investigated in compression molding process.

Nowadays, nanoparticles (*i.e.* clays) are used in microcellular wood fibre reinforced polymer composites [115, 116] in extrusion process. The results indicate that the addition of nanoparticles generally decreases the cell size, increases cell density and facilitates foam expansion. For pure PE, the addition of clay has a small effect on the crystallinity of PE. However, for the PE-wood fibre composites, the addition of nanoclay significantly reduces the crystallinity of PE. The PE-nano composite did not show any distinctively low diffusivity compared to that of PE. Moreover, when the wood fibre was added to the PE or PE/nano matrix, there was no distinct difference between the wood-PE or wood-PE-nano composites. The addition of clay did not change a lot the diffusivity of  $\text{CO}_2$  in the composites and the foam material

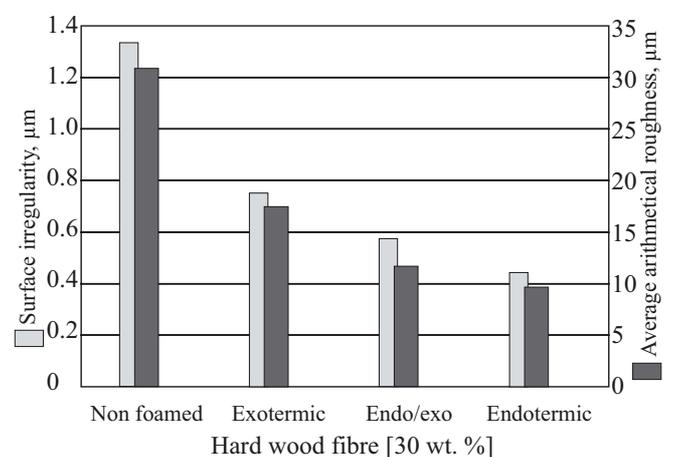


Fig. 5. Surface roughness (irregularity and average arithmetical roughness) of the non foamed and microfoamed composites

with nano particles showed good char formation when it was burned.

The specific characteristics of wood fibre reinforced polymer is significantly improved by the microcellular structure. Since the presence of microcells in the composite structure, the density is substantially reduced. The microcellular wood fibre reinforced polymer composites represent a specific group of the wood-polymer composites, which find versatile applications in various sectors and their specific characteristics are more favourable in the comparison to the non foamed composites.

Microcellular foams and their processing change the fundamental cost structure through the following sources of economic benefits. The operating costs can be reduced through cycle time reduction, reduced scrap and reject rates and lower energy consumption. By the purchase of smaller and fewer machines, fewer and less expensive molds, the capital costs will be lowered. Through the component density reduction, thinner design and material substitution, the material costs can be reduced. It is also benefited to use thermoplastic materials which are flatter, straighter, free of sink marks and dimensionally improved.

Numerous applications are envisioned for microcellular plastics. Current efforts towards commercialization are focused on automotive, construction, food packaging and industrial foams markets. Although commercialization of microcellular foams has been slow so far, one can believe that with continuing worldwide efforts to address the manufacturing challenges, the next decade will see the potential of these novel materials realized in many areas.

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