Research Article

Tensile and Impact Properties of Microcrystalline Cellulose Nanoclay Polypropylene Composites

Yousef Ahmad Mubarak

Chemical Engineering Department, School of Engineering, The University of Jordan, Amman 19942, Jordan

Correspondence should be addressed to Yousef Ahmad Mubarak; ymubarak@ju.edu.jo

Received 30 August 2017; Revised 12 January 2018; Accepted 18 February 2018; Published 21 March 2018

The aim of the present work is to investigate the effects of nanoclay (NC) on the mechanical properties of polypropylene (PP)/microcrystalline cellulose (MCC) composites modified by maleic anhydride grafted PP (PP-g-MA). Polypropylene/microcrystalline cellulose nanocomposites were prepared using a twin screw Brabender Plasticorder, the weight percent of the MCC was varied at 0, 0.5, 1, 2, 5, 10, 20, and 40 wt%, and the NC content was varied at 0, 0.05, 0.1, 0.5, 1.0, and 2.0 wt%. The results showed that consistent and uniform PP/MCC nanoclay composite can be produced easily with the presence of PP-g-MA. Compression molding technique was used to produce tensile and impact testing samples; all samples were characterized by tensile and impact tests. It is observed that increasing the amount of either the MCC or the NC will decrease the tensile strength, elongation at break, and impact strength; much more reduction in the same properties was obtained in case both MCC and NC exist within PP composites. Compared with neat PP, a loss of over 75% in both elongation and impact strength was obtained for nanoclay composites which contain 60 wt% PP/40 wt% MCC. The most significant enhancement in the mechanical properties of polypropylene/microcrystalline cellulose nanocomposites is in Young’s modulus where an increment of more than twofold can be achieved for 60 wt% PP/40 wt% MCC nanocomposite. Polarized light photomicrographs showed that MCC particles play a nucleating agent rule in terms of intensity of nucleation and crystal growth acceleration.

1. Introduction

Plastics are inert and nondegradable materials and cannot break down in nature and this leads the waste to be aggregated and thereby causes environmental pollution. Due to the huge amount of plastics waste and with increasing environmental concerns to preserve our environment, ecofriendly materials have gained the attention of many researchers [1, 2]. Utilizing degradable plastics can decrease the amount of plastics in landfills that is why the use of biodegradable polymers has increased recently up to 30% of the total plastic production. Recently and to achieve this type of materials, researcher’s interest has focused on degradable thermoplastic composites reinforced with lignocellulosic based materials (e.g., kenaf, bagasse, bamboo, tobacco, and cereal straws). Such materials are favored as a new generation of reinforcing agents in thermoplastics as they represent renewable, abundant, and biodegradable natural resources [3–6].

Thermoplastics materials and composites are attractive for a variety of applications due to many features including low weight and cost, ease of processing and shaping, and corrosion resistance in addition to many other advantages. Enhancement of mechanical and physical properties of polymers was achieved by the discovery of new nanoscaled materials such as nanoclays [7], carbon nanotubes [8], and micro- and nanocellulose [9]. Thanomchat et al. [10] studied the morphology and crystallization of polypropylene/microfibrillated cellulose (MFC) composites and found that, for the PP/MFC composite, faster crystallization and higher spherulite growth rate can be achieved. In addition to that, the authors reported that the degree of crystallinity was fairly independent on the MFC-loading.

Ummartyotin and Pechyen [11] prepared polypropylene composites by integrating a small amount of cellulose of 10 μm in diameter and maleic anhydride which was employed as a coupling agent. Crystallization temperature and
compressive strength were estimated to be 130°C and 5.5 MPa, respectively, while the crystal percentage was therefore estimated to be 50%. Nakagaito et al. [12], Suryanegara et al. [13], and Iwatake et al. [14] studied microfibrillated cellulose (MFC) polyactic acid (PLA) nanocomposites. Their results revealed that MFC can reinforce PLA 40% and MFC acts as a nucleating agent and increases the crystallinity, accompanied with a tensile modulus increase by 42% [14]. Polyurethane was successfully reinforced by the addition of micron- and nanosized cellulose to the PP matrix in a work carried out by Seydiyevolu and Oksman [15]. Their results showed the importance of the nanosize reinforcement by tensile testing and dynamic mechanical testing coupled with significant thermal stability. Nakagaito and Yano [16] prepared micro- and nanocomposites of cellulose fibers and phenol formaldehyde. They modified the surface by NaOH treatment, which resulted in a superior performance of the nanosize fibers and a further improvement in the toughness and percentage elongation.

In order to promote matrix-filler dispersion and compatibility, Spoljaric et al. [17] used poly(propylene-graft-maleic anhydride) (PP-g-MA) and MCC treated with silicone oil, stearic acid, or alkyl titanate as coupling agents in the preparation of polypropylene-microcrystalline cellulose (MCC) composites. It has been found that tensile stress-strain analysis revealed increased modulus with MCC content, PP-g-MA, alkyl titanate, and stearic acid. Also, storage modulus, loss modulus, and glass transition temperature increased with MCC concentration due to effective interaction between PP and MCC. Cellulose reinforced polypropylene composites were obtained using polyethyleneimine (PEI) as a coupling agent in González-Sánchez et al. work [18]. The author reported that the use of PEI as a coupling agent allows significant increases in both tensile strength and elongation at break. In a trial to improve mechanical properties of PP/cellulose nanofibril (CNF) composites, Yakkan [19] used a twin screw extruder to prepare the composites. It has been reported that about 87% improvement in both the tensile strength and Young's modulus was achieved.

Although cellulose and natural fibers in composite materials have many advantages, also there are some drawbacks. One of the main problems is the adhesion at the interface of the composites which leads to poor properties. However, there are many challenges to be solved for cellulose composites. To overcome the incompatibility of biocomposites, many researchers suggested the use of different coupling agents [20], such as silane [21], isocyanates [22], and titanate as coupling agents [17].

In spite of the broad works that have been done in the area of recycling or producing degradable plastics, there is a little work that has been reported on the mechanical properties of polypropylene-microcrystalline cellulose composites. This work, therefore, was intended to provide an understanding of the effect of microcrystalline cellulose on the mechanical properties of polypropylene. Since the addition of cellulose to polypropylene may deteriorate its mechanical properties, nanoclay particles will be used in combination with the microcrystalline cellulose in a trial to inhibit the effect of cellulose on polypropylene's mechanical properties.

2. Materials and Methods

2.1. Materials. The following materials were used throughout the present work.

2.1.1. Polypropylene. The polypropylene used was Moplen HP525J homopolymer, having a melting temperature between (160–163)°C and a melt flow index of 3 g/10 min; it is manufactured by PMC Polymer Products under the license of BASELL using the Spheripol process. This product has excellent processability and stretchability, high transparency and gloss, high stiffness and strength, good barrier properties, and excellent metallizability.

2.1.2. Cellulose. Microcrystalline cellulose 20μm (supplied by Aldrich Chemistry) is fine, white or almost white, odorless, and free-flowing crystalline powder. It is used in this study as it is biodegradable carries hydrophilic hydroxyl group; these groups interact with oxygen atoms from another cellulose chain. Hence, these chains build up microfibrils with a high tensile strength.

2.1.3. Nanoclay. The nanoclay (NC) used in this work was supplied by Sigma-Aldrich Chemical Co.; it is a surface modified montmorillonite clay base material and contains 25–30 wt% trimethyl stearyl ammonium with a particle size of ≤20μm.

2.1.4. Maleic Anhydride Grafted PP. Is a crystalline, isotactic, modified homopolymer supplied by Sigma-Aldrich Chemical Co. in a form of pellets. It has a density of 0.934 g/cm³, molecular weight of 9100, and Brookfield viscosity of 4.0 poise at 190°C.

2.2. Samples Preparation

2.2.1. Preparation of Composites. A Haake Poly Drive Twin Screw Brabender Plasticorder was used to prepare forty blends having various compositions of PP/MCC and clay nanoparticles. Specific materials quantities were added in sequence through a hopper and the mixing was carried out for 5 minutes, at a temperature of 220°C and a speed of 60 rpm. The resulting blend was taken from the cavity of the Brabender and left to naturally cool, and then its size was reduced using a Wanner 3-Blade Cutter to facilitate further sample preparation needed. Forty samples were prepared as shown in Table 1. To increase the combinability between the hydrophobic PP and the hydrophilic NC and MCC, 2 wt% of maleic anhydride grafted PP was used for all composites.

2.2.2. Preparation of Tensile Testing Samples. Tensile testing samples were prepared by a hot compression molding (Carver Auto Series Press). Each processing cycle gives 14 tensile samples using a copper square mold. Overhead projector sheets were used to prevent the composite tensile testing samples from sticking to the machine surface. The hot press molding temperature was set at 220°C and the hot pressing cycle lasts for five minutes to ensure complete melting of the composite particles. Molten samples under compression were
Figure 1: Dimensions of the tensile testing sample.

Figure 2: Dimensions of the impact testing sample.

Table 1: Composition of PP/MCC nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP wt%</th>
<th>MCC wt%</th>
<th>NC wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>100</td>
<td>0</td>
<td>0, 0.1, 0.5, 1.0, 2.0</td>
</tr>
<tr>
<td>G2</td>
<td>99.5</td>
<td>0.5</td>
<td>0, 0.1, 0.5, 1.0, 2.0</td>
</tr>
<tr>
<td>G3</td>
<td>99</td>
<td>1</td>
<td>0, 0.1, 0.5, 1.0, 2.0</td>
</tr>
<tr>
<td>G4</td>
<td>97.5</td>
<td>2.5</td>
<td>0, 0.1, 0.5, 1.0, 2.0</td>
</tr>
<tr>
<td>G5</td>
<td>95</td>
<td>5</td>
<td>0, 0.1, 0.5, 1.0, 2.0</td>
</tr>
<tr>
<td>G6</td>
<td>90</td>
<td>10</td>
<td>0, 0.1, 0.5, 1.0, 2.0</td>
</tr>
<tr>
<td>G7</td>
<td>80</td>
<td>20</td>
<td>0, 0.1, 0.5, 1.0, 2.0</td>
</tr>
<tr>
<td>G8</td>
<td>60</td>
<td>40</td>
<td>0, 0.1, 0.5, 1.0, 2.0</td>
</tr>
</tbody>
</table>

The prepared impact samples were analyzed via a 6545 Ceast Impact Tester. The sample was cantered for testing, and a 7.5 J pendulum hammer was used to hit the sample. The energy needed for breaking each of the samples was recorded for further calculations; the results are expressed in energy lost per unit of thickness (J/m) at the notch or energy lost per unit cross-sectional area at the notch (J/m²). Approximately 10 replicates of each sample were tested; the average of these results was used to represent the final result.

3. Results and Discussion

The dispersion of the microcrystalline cellulose and the nanoclay particles in the polypropylene matrix in addition to their effects on the tensile and impact properties will be presented and discussed in this part.

3.1. MCC and NC Particles Dispersion. Although a twin screw Brabender Plasticorder was used to prepare the composites, it has been found that when the concentration of MCC is high, the obtained PP/MCC composites were not perfect and homogenous in terms of MCC particles distribution. Figure 3 shows the distribution of the MCC particles within the PP matrix at different MCC concentration. Photomicrographs A, B, and C show the good distribution of the MCC particles, while micrographs D, E, and F show the poor distribution of the MCC particle. The images prove that, at MCC concentration less than 5 wt%, the particles are well dispersed within the matrix and there is no agglomeration while at high concentration (≥5 wt%) the agglomeration of the particles and the poor dispersion are clearly seen. This
poor distribution can be attributed to the fact that MCC is hydrophilic in its nature whereas PP is hydrophobic, and this caused a weak interaction and compatibility [25, 26].

To enhance the interfacial adhesion between polar hydrophilic MCC and nonpolar hydrophobic synthetic polypropylene, maleic anhydride grafted polypropylene (PP-g-MA) is used. The anhydride groups of MAPP are prone to compatibilizing with hydrophilic MCC particles, thereby promoting the dispersion and surface wetting of MCC particles in the PP matrix. These groups can also improve the interfacial adhesion between the MCC particles and PP. Similar phenomenon was observed by Gao et al. [27] and Zhou et al. [28]. Figure 4 presents PP/MCC composites after inclusion of 2 wt% of PP-g-MA. The photomicrographs show the good dispersion of the MCC particles within the PP matrix and disappearance of the agglomeration except for PP/40 wt% MCC composites, where agglomeration did not disappear totally. As a result of this finding, all PP/MCC composites used in the present study were mixed with 2 wt% PP-g-MA.

Figure 5 shows photomicrographs of PP/NC composites uploaded with different weight fractions of nanoclay. The micrographs revealed that the nanoclay particles are distributed well in the PP matrix without any agglomeration. The main reason behind this dispersion is the modified surface of the nanoclay used in the present study.

The distribution of 5 wt% MCC and different weight fractions of NC particles in the grafted PP matrix is presented.
in the micrographs of Figure 6. It is clearly seen that both types of particles are dispersed in a good manner without agglomeration; the addition of the NC particles does not alter the dispersion of the MCC particles. Similar results were observed for PP composites uploaded with different weight fractions of MCC.

3.2. Effect of Clay Nanoparticles. Figures 7 and 8 present the yield strength, Young’s modulus, percentage elongation, and impact strength of polypropylene as a function of nanoclay percentage. The addition of 2 wt% of nanoclay resulted in a reduction in both the yield strength by about 11% and the elongation at break by about 19% while Young’s modulus increased by 49%. On the other hand, the impact strength decreased by 35% at the maximum nanoclay concentration used. The addition of the nanoclay to the neat PP increases the brittleness of PP and this causes the yield strength, elongation at break, and impact strength to decrease. The brittleness increases the toughness of PP and hence Young’s modulus increases. Since PP has a hydrophobic nature and the nanoclay has a hydrophilic property, the usage of maleic anhydride grafted PP increased the compatibility and hence the adhesion between the components of the composite [29–31].

3.3. Effect of Microcrystalline Cellulose. The effects of the microcrystalline cellulose on the mechanical properties of polypropylene are shown in Figures 9 and 10. It is clearly seen that as the weight fraction of the microcrystalline cellulose increases, the yield strength, elongation to break, and impact strength are all decreases. At the maximum MCC used in the study, it has been found that the reduction values in the parameters are 33%, 67%, and 45%, respectively. Figure 9 reveals that Young’s modulus value increases as the concentration of MCC increases; an increment of 18% was achieved at the maximum concentration of MCC.

The obtained results show that MCC plays nearly the same role as the NC but with greater effects in terms of reduction in the yield strength, elongation at break, and impact strength. This result complies with the results obtained by Yang and Gardner [32], where incompatibility between the hydrophilic cellulose filler and hydrophobic matrix polymer was given as a reason for the reduction in the yield strength. Young’s modulus values continuously increased as MCC loading increased because the MCC is more brittle than the PP polymer [33]. Also, the elongation at break values continuously decreased as MCC loading increased because of the increased brittleness of the composites [32].

Figure 11 proves the efficiency of MCC particles in nucleation of the crystallization process of polypropylene. Using a polarized light microscope, the presented images were taken during an isothermal process at 145°C for a virgin polypropylene and for polypropylene/microcrystalline cellulose composite. The difference in intensity per unit area
and the size of the crystals for samples containing MCC particles when compared with neat PP is clearly seen.

3.4. Combined Effects of MCC and Nanoclay. Yield strength, Young's modulus, elongation at break, and impact strength of PP/MCC nanoclay composites are presented in Figures 12–15 as a function of nanoclay weight fraction. Compared with a neat polypropylene, the addition of nanoclay to the PP/MCC composites leads to further reduction in the yield strength and a maximum reduction reaches 85% at the highest MCC weight fraction employed in this study and this can be seen clearly in Figure 12. The elongation at break did not improve at all by the nanoclay addition; PP/MCC nanoclay composites behave like a brittle material and lost about 76% of its elongation at break when compared with the virgin polypropylene. Figure 14 reveals that Young's modulus increased from 0.6 GPa for the neat polypropylene to 1.43 GPa for composites consist of 60 wt% PP and 40 wt% MCC nanoclay composites. Further deterioration in the impact strength is shown in Figure 11 and 73% reduction in the impact strength was obtained for PP/MCC nanoclay composites when a 2 wt% of the nanoclay is added to a 60 wt% PP and 40 wt% MCC composite.

It is obvious that the addition of nanoclay particles to the PP/MCC composites did not improve the yield strength, elongation at break, or the impact strength. Increasing the amount of the MCC and the NC leads to a large amount of agglomerated particles among the composite samples, which
might explain the brittle behavior due to stress concentrated points and nonuniform stress transfer. Also, increase in filler loading (NC and MCC) restricted the mobility of the polymer chains and this presumably caused a decrease in the elongation at break. This obtained result is in good agreement with previous research results that attributed this reduction to the numerous irregularly shaped microvoids or microflaws in the composite structure [34–36]. On the other hand, the increase in nanoclay and MCC content restricted the mobility of the PP chain and this was reflected in tensile Young’s modulus values, the more the weight fraction of nanoclay added to the PP/MCC composite, the higher Young’s modulus obtained [37, 38].

The presence of both MCC and nanoclay particles within PP composites enhances the nucleation and accelerates the growth of the crystals. Thus, the intensity of the crystals per unit area increases dramatically and the size of the final crystals is much smaller as shown in Figure 16. It is concluded that MCC and nanoclay particles can play similar rules as nucleating agents.

To summarize the effect of the combined additives on the mechanical properties of polypropylene, the loss and gain percentages were calculated and presented in Table 2; negative values mean loss while positive values mean gain. It is clearly seen that, for all combinations of PP/MCC/NC, the yield strength, elongation at break, and impact strength
Figure 7: Yield strength and Young's modulus of neat PP as a function of nanoclay wt%.

Figure 8: Elongation at break and impact strength of neat PP as a function of nanoclay wt%.

Figure 9: Yield strength and Young's modulus of neat PP as a function of MCC wt%.
values are all negative (loss) while Young's modulus values are all positive (gain). Increasing the weight fraction of NC, MCC, or the combination of both of them leads to a further loss in the yield strength, elongation at break, and impact strength and leads to further gain in Young's modulus.

For example, increasing the weight fraction of the NC within the PP/NC nanocomposites from 0 to 2 wt% increases the loss in the yield, elongation, and impact strength to 11.4, 18.7, and 35.0, respectively. Increasing the weight fraction of the MCC within the PP/MCC composites from 0 to 40 wt% increases the loss in the yield, elongation, and impact strength to 32.9, 67.4, and 45.4, respectively. On the other hand, increasing the weight fractions of both the NC from 0 to 2 and increasing the MCC from 0 to 40 increase the loss further in the yield, elongation, and impact strength to 57.1, 76.1, and 72.9, respectively. Regarding the gain achieved by the addition of either the NC or MCC or both is represented by Young's modulus, where increasing the weight fractions of both NC
Figure 12: Yield strength PP/MCC composites as a function of NC wt%.

Figure 13: Elongation at break of PP/MCC composites as a function of NC wt%.

Figure 14: Young's modulus of PP/MCC composites as a function of NC wt%.

Figure 15: Impact strength PP/MCC composites as a function of NC wt%.

from 0 to 2 and increasing the MCC from 0 to 40 increase the gain in Young's modulus to 138.3.

It seems that the addition of the NC particles to the PP/MCC composite turns the whole composite to a more brittle one and hence does not improve the mechanical properties if we excluded Young's modulus. Generally speaking, the addition of the MCC deteriorates polypropylene's mechanical properties more than the deterioration caused by the addition of the NC. The existence of both of the NC and the MCC in polypropylene composites deteriorates its mechanical properties more.

4. Conclusions

Polypropylene/microcrystalline cellulose nanoclay composites can be produced easily with the presence of a small quantity (2 wt%) of maleic anhydride grafted polypropylene. The most significant improvement in mechanical properties of MCC reinforced polypropylene nanoclay composite is in Young's modulus. The elongation at break and the impact strength decreased dramatically when both MCC and nanoclay particles exist together in the composite. Compared with neat PP values, PP composites containing 40 wt% MCC and 2 wt% nanoclay lost about 75% of both values of elongation at break and impact strength. Although maleic anhydride grafted PP is used but it could not prevent the agglomeration of MCC particles at very high concentration and enhance the adhesion within the matrix. The addition of the hydrophilic nanoclay and MCC to polypropylene increased the brittleness of the resulting composites and hence decreased the yield strength, the elongation at break, and the impact strength due to the restricted mobility of the polymer chains in addition to the formation of numerous irregularly shaped microvoids or microcracks within the composite as the quantity of NC and MCC increases. Polarized light microscope images prove that MCC and nanoclay particles are both played similar rules in terms of intensity of nucleation, acceleration of growth, and crystal size and type.
Figure 16: Isothermal crystallization images at 145°C for 95 wt% PP/5 wt% MCC nanoclay composite after (a) 5 minutes, (b) 10 minutes, (c) 20 minutes, and (d) 30 minutes [magnification = 133x].

Table 2: Yield strength, elongation at break, and impact strength % loss and Young's modulus % gain of polypropylene/nanoclay as a function of MCC wt%.

<table>
<thead>
<tr>
<th>MCC%</th>
<th>NC wt%</th>
<th>Yield strength loss</th>
<th>NC wt%</th>
<th>Yield strength loss</th>
<th>NC wt%</th>
<th>Yield strength loss</th>
<th>NC wt%</th>
<th>Yield strength loss</th>
<th>NC wt%</th>
<th>Yield strength loss</th>
<th>NC wt%</th>
<th>Yield strength loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>-0.6</td>
<td>0.5</td>
<td>-14.5</td>
<td>1</td>
<td>-18.8</td>
<td>2</td>
<td>-26.7</td>
<td>5</td>
<td>-45.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-11.4</td>
<td>1.0</td>
<td>-30.7</td>
<td>2.0</td>
<td>-40.0</td>
<td>0.0</td>
<td>-5.0</td>
<td>0.5</td>
<td>-26.9</td>
<td>1</td>
<td>-34.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>0.1</td>
<td>-40.0</td>
<td>0.5</td>
<td>-6.7</td>
<td>0.5</td>
<td>-5.0</td>
<td>1</td>
<td>-34.2</td>
<td>1</td>
<td>-7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33.3</td>
<td>0.5</td>
<td>-6.7</td>
<td>1</td>
<td>-34.2</td>
<td>2</td>
<td>-9.7</td>
<td>2</td>
<td>-37.5</td>
<td>2</td>
<td>-14.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>62.7</td>
<td>1</td>
<td>-34.2</td>
<td>2</td>
<td>-14.5</td>
<td>5</td>
<td>-42.9</td>
<td>5</td>
<td>-37.5</td>
<td>5</td>
<td>-23.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>109.5</td>
<td>2</td>
<td>-37.5</td>
<td>5</td>
<td>-23.1</td>
<td>10</td>
<td>-49.2</td>
<td>10</td>
<td>-43.6</td>
<td>10</td>
<td>-26.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>138.3</td>
<td>10</td>
<td>-43.6</td>
<td>10</td>
<td>-26.9</td>
<td>20</td>
<td>-51.8</td>
<td>20</td>
<td>-46.6</td>
<td>20</td>
<td>-30.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>202.4</td>
<td>20</td>
<td>-46.6</td>
<td>20</td>
<td>-30.4</td>
<td>40</td>
<td>-57.1</td>
<td>40</td>
<td>-49.1</td>
<td>40</td>
<td>-34.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>104.0</td>
<td>40</td>
<td>-49.1</td>
<td>40</td>
<td>-34.9</td>
<td></td>
<td>-18.3</td>
<td></td>
<td>-18.3</td>
<td></td>
<td>-18.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MCC%</th>
<th>Elongation at break loss</th>
<th>MCC%</th>
<th>Impact strength loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.5</td>
<td>-4.3</td>
<td>-7.8</td>
<td>-9.8</td>
</tr>
<tr>
<td>1</td>
<td>-3.5</td>
<td>-10.9</td>
<td>-13.0</td>
</tr>
<tr>
<td>2</td>
<td>-8.7</td>
<td>-10.0</td>
<td>-19.6</td>
</tr>
<tr>
<td>5</td>
<td>-13.0</td>
<td>-26.1</td>
<td>-27.4</td>
</tr>
<tr>
<td>10</td>
<td>-26.1</td>
<td>-36.1</td>
<td>-34.8</td>
</tr>
<tr>
<td>20</td>
<td>-60.9</td>
<td>-57.4</td>
<td>-63.0</td>
</tr>
<tr>
<td>40</td>
<td>-67.4</td>
<td>-74.8</td>
<td>-76.1</td>
</tr>
</tbody>
</table>
Conflicts of Interest

The author declared that they have no conflicts of interest.

References


