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Mechanical properties of super honeycomb structures based on carbon nanotubes

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Abstract
As a result of repeating carbon nanotube Y junctions periodically, super honeycomb structures have recently been proposed. In this paper, the mechanical properties of these structures are investigated by using the shell model of the finite element method. The study shows that the super honeycomb structures have great flexibility and outstanding capability in force transferring; the network configuration increases the ductility of the nanomaterials. Furthermore, it can be concluded that the equivalent tensile modulus and Poisson's ratio of super structures are dependent on the number of junctions in the width direction.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Branched carbon nanotubes (CNTs), such as L, Y, and T patterns, have been observed in experiments [1]; these have generated intense attention. These nanostructures have acted as multi-terminal electronic devices and circuits [2, 3]. Recently, the CNT Y junction was used to separate negative and positive ions from a solution due to their arms having different electric properties [4]. Furthermore, the network structures are expected to strengthen the mechanical properties of nanoropes and reinforced composites compared with straight tubes. Chernozatonskii [5] has summarized recent studies on the synthesis, properties and applications of three-terminal junctions based on carbon nanotubes.

In post-production, branched CNTs can be formed by introducing defects into hexagonal structures [6]. The alternative efficient approaches are branching oriented by the template during growth [7] and synthesizing or decomposing carbon related materials with some special catalysers [8–10]. To people's surprise, Li [9] synthesized Y junctions with very straight and uniform multi-walled carbon nanotubes (MWNTs); the angles between arms were close to 120°. Similar structures based on single-walled carbon nanotubes (SWNTs) were obtained by Biró [10]. Early in 1992, Scuseria [11] had proposed the symmetric Y junction, which is composed of hexagons at the connected junction as shown in figure 1(a). Recently, based on the geometric conservation laws, Yin [12] theoretically proved that Y-branched junctions with angles of 120° and uniform branches satisfied the equilibrium state with both minimum energy and symmetric geometry. The self-assembly ability of branching nanostructures will greatly advance their practical application, and has inspired the proposal of the super honeycomb structures.

The perfect Y junction with uniform tubes and equal crossing angles is similar to the shape of the sp^2 carbon–carbon bond in graphite. By repeating perfect Y junctions periodically in a plane, the super honeycomb structure can be constructed [13]. Considering its similarity to graphite, this network structure has been named super graphite (SG). Furthermore, a super carbon nanotube (ST) can be obtained by rolling up the SG, which is similar to the transformation from a single graphite sheet to an SWNT. The geometric and electronic structure of super structures were explored by atomic calculations [13], and it was discovered that STs also hold metallic or semiconducting properties just like CNTs. The mechanical properties of super honeycomb structures are investigated in this paper.

2. Method and model

Super structures usually consist of many CNT arms, and the computational cost required to study their mechanical

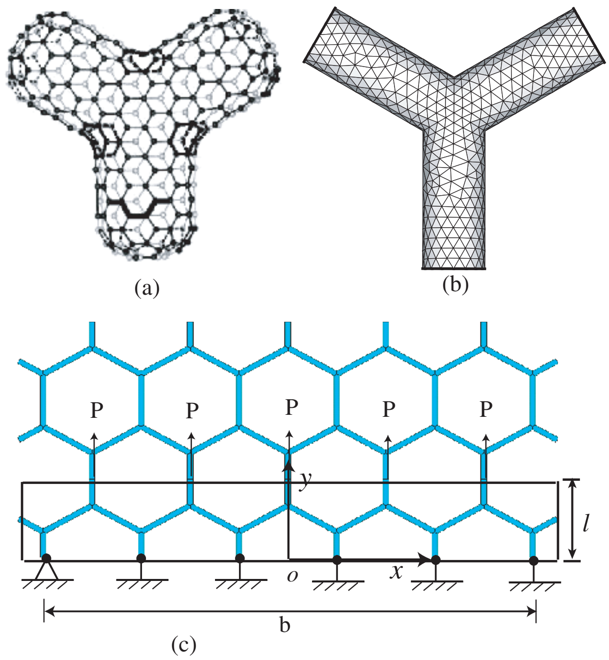

Figure 1. (a) Symmetric, armchair Y junction as proposed by Scuseria [11], reprinted from *Chem. Phys. Lett.* **195** 534, © 1992, with permission from Elsevier. (b) The mesh of Y junction. (c) A sketch of super graphite.

behaviour is prohibitive for atomic methods. Using the molecular dynamics method, Yakobson and his colleagues [14] examined the buckling deformation of SWNTs subjected to axial compression, bending and torsion. They found that these deformations could be well explained by the thin-shell model [15] with properly chosen parameters including the thickness of wall and the elastic modulus. The thin-shell model is widely used for three-dimension objects with a quite small size in one dimension, named the thickness, in comparison with the others. Consequently, the thin-shell model is an efficient way to examine the mechanical properties of SWNTs, which are rolled up from single-atom graphite sheets, as well as the CNT structural materials. In this paper, the mechanical properties of super structures are investigated by the finite element method with the shell model.

The effect of the radius on the material properties of the thin-shell model was analysed in detail in [16]. For a tube with the smallest diameter of 0.4 nm, its elastic modulus, Poisson's ratio and thickness deviated from the limiting ones by 10%, 7%, and 7% respectively. However, the effect of the radius as well as the curvature was insignificant for SWNTs of diameters larger than 1.5 nm. Most of tubes analysed in this paper have diameters larger than 1.5 nm. Furthermore, perfect Y-branched junctions, which consist totally of hexagonal structures, are embodied smoothly in the local region of the junction. Taking these facts into consideration, the shell model with the homogeneous properties is used throughout the whole SG structures, including edges and junctions. In this paper, the thickness of the shell, the elastic modulus and Poisson's ratio are taken as the commonly used values of 0.066 nm, 5.5 TPa and 0.19, respectively [14].

The mesh of Y junctions and the representational SG were built by ANSYS software, as shown in figures 1(b), (c). Considering the uniformity in tensile deformation along the length direction (y-axis), typical structures with length l can be adopted, just like the part in the rectangle frame of the SG as illustrated in figure 1(c). The nodes on the section $y = 0.0$ are constrained by symmetry, while the nodes with $y = l$ are all constrained by the prescribed displacements along the y direction, i.e. u_y. Consequently, the tensile strain of the SG is defined as $\varepsilon_y = u_y/l$. At the same time, the two sides at the ends of the x direction are totally free. In the following discussion, the number of Y junctions in the width direction is defined as n_w, taking $n_w = 5$ as an example for the case shown in figure 1(c), and the corresponding width is b.

3. Analysis and discussion

3.1. SGs with different widths

SGs with finite widths and relatively long lengths can act as ribbons, having profound implications on the application of nanomaterials. By varying the number of Y junctions in the width direction n_w while keeping the same length of arms, the ribbons have different widths, and may show different properties when subjected to tensile deformation. Several types of SGs with $n_w = 1, 3, 5, 7, 9$ were examined. In this analysis, the SG consists of SWNTs of type (15, 15) with length of 20 nm; therefore, the length $l = 30.0$ nm and the width $b = 20\sqrt{3}\, n_w$. The displacement $u_y = 1.0$ nm is applied in steps on the SGs. Figure 2(a) illustrates the variation of tensile force F_y with the tensile strain. Apparently, the forces applied on SGs increase with the increase of n_w for a certain strain. Figure 2(b) plots the average tensile stress of the symmetric surface, which is defined as $\sigma_y = F_y/(2\pi R t n_w)$, with R the radius of the SWNT and t its thickness. If the super honeycomb structure is taken as a material, its equivalent tensile modulus can be defined as $E = \Delta\sigma_y/\Delta\varepsilon_y$. From the results plotted in figure 2(c), it can be obtained that the tensile modulus of SGs decreases with the increase of the tensile deformation. Furthermore, the reduction of the tensile modulus is dependent on the number of junctions in the width direction. It can be observed from figures 2(b), (c) that the curves of $n_w = 5, 7, 9$ are quite close to each other. Consequently, ribbons with many more junctions in the width direction are expected to behave with similar properties to that with $n_w = 9$. For the honeycomb structure with solid arms used as lightweight structures, a similar conclusion of the size effects was obtained through theoretical analysis [17]. Fitting the curve of $n_w = 9$ in figure 2(c) with a second-order polynomial function, the equivalent modulus can be expressed as

$$E = 10^4(-1.8104\varepsilon_y^2 - 0.0982\varepsilon_y + 0.013) \qquad \varepsilon_y \leqslant \tfrac{1}{30}. \quad (1)$$

The deformation in this range is mainly due to the change of angles between the arms, which results in the smaller equivalent tensile modulus of SGs compared with the Young's modulus of CNTs.

The shrinking strain in the width direction ε_x, defined as the change of the width relative to the original one, b, is plotted versus the tensile strain in figure 3(a). It is well known that the Poisson's ratios of materials are mostly smaller than 0.5. However, Poisson's ratios of SGs, defined as $\upsilon = -\Delta\varepsilon_x/\Delta\varepsilon_y$, are larger than 1.0 and behave nonlinearly, as shown in figure 3(b). With the increase of the tensile strain,

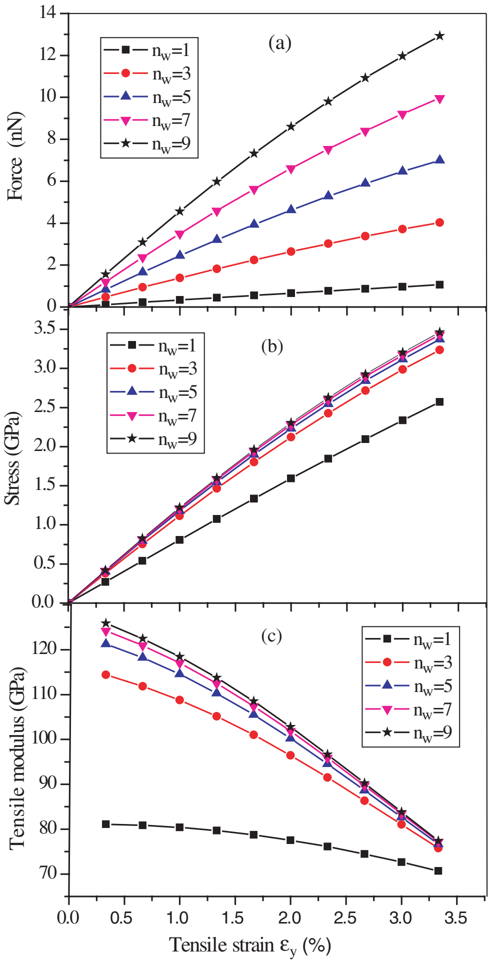

Figure 2. The variation of the tensile force in (a), the tensile stress in (b), and the tensile modulus in (c) versus the tensile strain. The parameter n_w represents the number of Y junctions along the width direction.

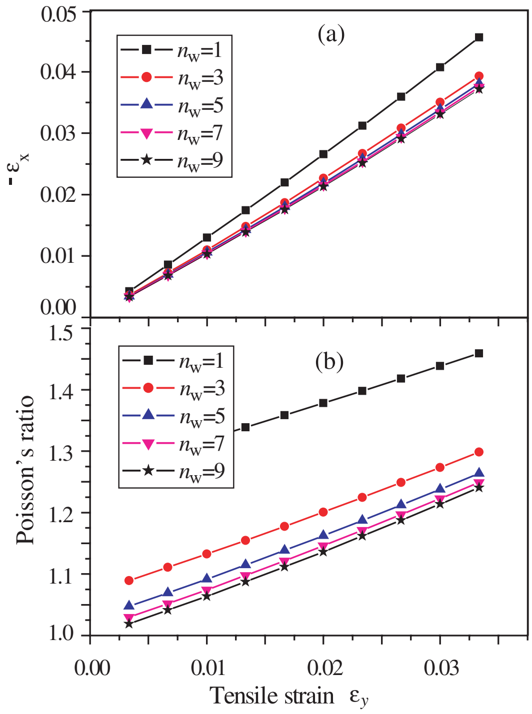

Figure 3. The variation of the shrinking strain in the width direction in (a), and Poisson's ratio in (b) versus the tensile strain.

the rotation of arms seems to be easier. Fitting the curve of $n_w = 9$ in figure 3(b) with a linear polynomial function, the approximate expression for the Poisson's ratio is

$$\upsilon = 7.3981\varepsilon_y + 0.9908 \qquad \varepsilon_y \leqslant \tfrac{1}{30}. \qquad (2)$$

The connection of the Y junction based on SWNTs has different properties from the general joint of a framework such as a rigid connection or hinge joint; thus the beam element cannot be used to analyse super structures. Based on the above discussion, the mechanical behaviour of super honeycomb structures is similar to that of a membrane structure with great flexibility. Consequently, the complex deformation of SGs can be analysed by using a membrane element with the nonlinear material properties given in equations (1) and (2).

3.2. SGs based on SWNTs with different radii

In order to explore the influence of the radius of the arms on the tensile deformation, SGs based on SWNTs (18, 18), (15, 15), (12, 12) and (10, 10) are examined: their radii R are equal to 1.22, 1.0, 0.814, and 0.678 nm. The other geometrical parameters are the same for all SGs: n_w equals 5 and the length of the arms is 20.0 nm. It can be concluded from the results illustrated in figure 4(a) that the Poisson's ratio of SGs is independent of the radius of the arms. The SGs with larger radius have higher tensile stress than those with smaller radius, as shown in figure 4(b). It can be observed from figure 4(c) that the tensile modulus of SGs decreases with the increase of tensile strain. Moreover, the reduction of the tensile modulus of the larger radius arm is more significant than that of the smaller one. Considering that the SGs have the same variation of angles between arms, the differences existing in the reduction of tensile modulus are mainly due to the different degree of weakening at the joint of the tubes. Actually, SWNTs with radius larger than 1.0 nm can exist in a collapsed configuration due to the effect of van der Waals interaction [18], which may accelerate the weakening of the junction.

3.3. Large tensile deformation

A large tensile strain of 0.26 was applied step by step on the SG with $n_w = 3$, which consists of SWNTs of type (15, 15) with length of 20.0 nm. Figure 5(a) shows the nonlinear relation between the tensile force applied and the strain of the SG. In the first phase with $\varepsilon_y \leqslant 0.02$, the SG almost behaves linearly due to the small strain and the slight rotation of the arms. With the increase of deformation, the slope of the curve decreases slowly because of the visible change of angles, and a local flattened deformation occurred at the connected region. The stress concentration at the connected region can be observed from the distribution of von Mises stress[1] as

[1] The von Mises stress is a scalar measure of the stress state at any point within a body, which is defined as $\sigma_{vm} = \frac{1}{\sqrt{2}}\sqrt{(\sigma_{xx}-\sigma_{yy})^2 + (\sigma_{yy}-\sigma_{zz})^2 + (\sigma_{zz}-\sigma_{xx})^2 + 6(\sigma_{xy}^2+\sigma_{yz}^2+\sigma_{zx}^2)}$, where σ_{ij} are the stress components.

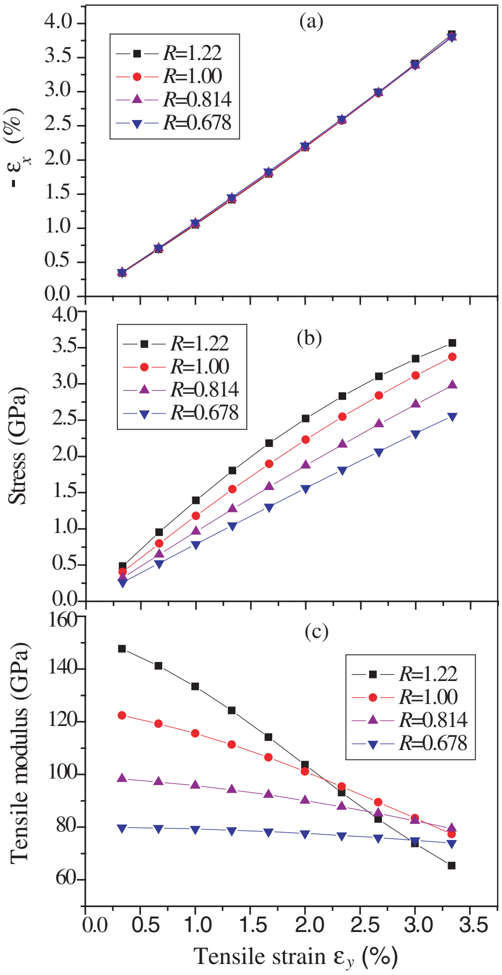

Figure 4. The variation of shrinking strain in the width direction (a), the tensile stress (b), and the tensile modulus (c) of the SGs based on different SWNTs with radius of 1.22, 1.0, 0.814, and 0.678 nm, respectively.

shown in figures 5(c) and (e). Before the strain reaches 0.22, the deformation mainly comes from the change of angles between the arms, which embody the great flexibility of the net structure. When the tubes rotate significantly and incline in the length direction, they begin to be stretched. As measured from the configuration in figure 5(d), the angles between the arms are 162°, 162°, and 36°, respectively. Consequently, the tensile force increases rapidly in the final phase. The deformation of this structure is just like the fishing net: a remarkable change of angles between arms occurs before the arms are stretched; this finally results in a high value of tensile modulus. Coluci [13] also predicted similar properties for super structures in their work.

The junction modelled in this paper lacks smoothness compared to the atomic model, which increases the stress concentration. Moreover, a transformation at atomic level such as recombination of bonds and the van der Waals interaction should be included when the angles between arms are significantly changed. These deformations are beyond the range of elastic deformation, and thus need further analysis. However, the presented analysis predicts that the SGs are ductile materials and that they still have a high value of the ultimate tensile strength when the net structures are significantly changed.

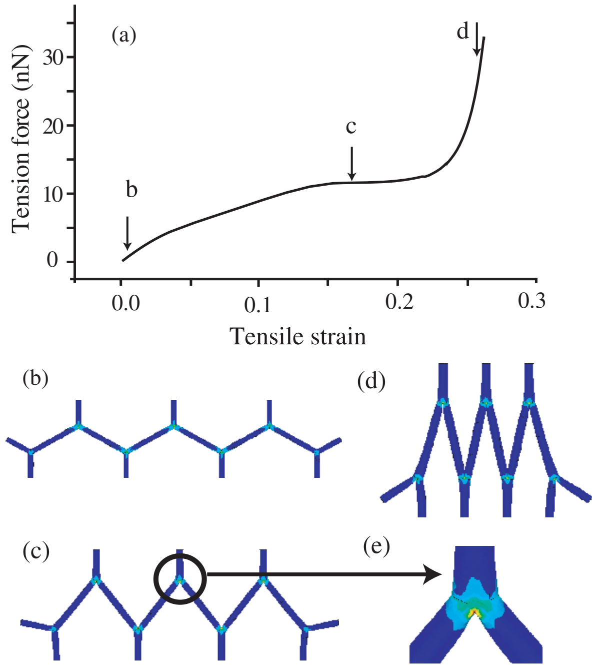

Figure 5. (a) The total tensile force versus the tensile strain along the length direction. ((b), (c),(d)) The configurations of SGs subjected to three different values of tensile strain, which are indexed by 'b', 'c', and 'd' respectively in (a); and the various colours illustrate the distribution of von Mises stress. (e) The local amplified region within the circle of (c).

3.4. The ability of force transferring for SGs

Generally speaking, the connection of straight tubes mainly depends on the weak van der Waals interaction between tubes. SWNTs bundles or nanoropes seem to present a big problem for any force transferring between tubes. For branching structures, the tubes are connected by strong bonds into the network, which greatly strengthens the ability for transferring force. From the distribution of von Mises stress described in figure 6(a), it can be concluded that if even only one of the tubes is subjected to the tensile force, the force can be transferred to the other tubes through junctions. The region of SGs bearing loads becomes a triangle with a vertex at the point of the applied force, as shown in figure 6(a). When defects exist in SGs, the force can stay away from the defects and be transferred to other tubes. Figure 6(b) shows the distribution of von Mises stress of an SG with defects under a tensile load. When one arm is broken in the SG with $n_w = 5$, its bearing capacity is reduced by 8.3% when subjected to a tensile strain of 0.033. The arrangement of SWNTs in networks through the junctions can significantly improve the global mechanical properties. Nanoropes or reinforced composites based on branched structures will have better mechanical properties compared with those of straight SWNTs. Furthermore, large scale super structures do not require long tubes, but can consist of relatively short tubes with many junctions.

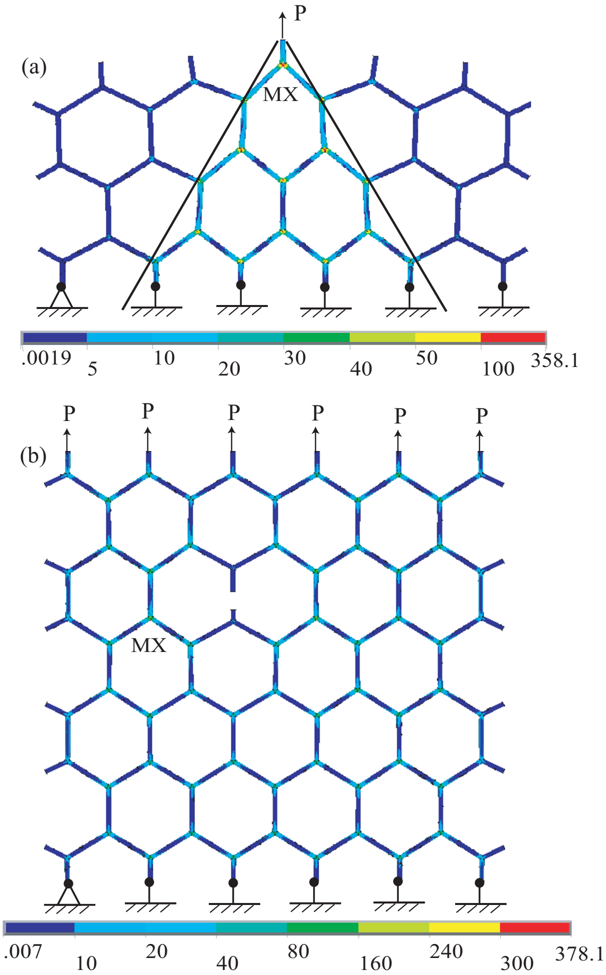

Figure 6. (a) The von Mises stress distribution of SG when only one tube is applied to the tensile load. (b) The von Mises stress distribution of SG with one tube broken; the place indexed with 'MX' has the maximum stress.

3.5. Super carbon nanotubes

Wang [16] analysed the dependence of the material parameters of SWNTs on the diameter of tubes. They reported that SWNTs with large radius have the same tensile modulus as a graphite sheet while those with relatively small radius have a slightly reduced modulus. Furthermore, the Poisson's ratios of graphite sheets and SWNTs with diameter larger than 1.5 nm are very close. Analogously, when SGs are wrapped into tubes, the tensile modulus and Poisson's ratio of STs can be predicted on the basis of SGs just like the relationship of graphite sheets and SWNTs.

Higher-order super nanotubes have been proposed by Coluci [13] and Yin [12]. SWNTs can be considered as the fundamental unit, and the STs discussed in this paper are the first-order ones, denoted as $ST^{(1)}$. The $ST^{(k)}$ can be considered as the arms of the $ST^{(k+1)}$, just like the relationship of SWNTs and $ST^{(1)}$. The order of super structures can be enlarged gradually, and thus carbon fibres on a macroscopic scale may be constructed. More recently, Pugno [19] evaluated the strength, toughness and stiffness of super nanotubes, as well as the related fibre-reinforced composites. Using hierarchical equilibrium analysis, the material parameters of $ST^{(k)}\forall k$ could be obtained from the fundamental unit, i.e. SWNTs, and the matrix filled, which is a plus for filled STs. The effects of the local flattened deformation in the junction and the arms' rotation seem to be ignored in their analysis. However, in this paper, STs have great shrinking in the radial direction and behave more flexibly than SWNTs, which is due to the rotation rather than the stretching of the arms. Then STs are stiffened when the arms are stretched finally, as shown in figure 5. At the same time, local deformation and stress concentration in junctions are observed in this analysis. It should be noted that the length of arms is 20 nm in this study, which is expected to have an effect on the mechanical properties of super structures.

4. Conclusion

The development of carbon nanotube Y junctions has stimulated the proposal of super graphite and nanotubes. The network structures are expected to provide useful applications not only in nanoelectronics but also in fibre-reinforced composites. Using the shell model with equivalent parameters, the mechanical properties of super structures have been examined. The study shows that they possess great flexibility and outstanding capability for transferring force. The tensile modulus and Poisson's ratio are dependent on the number of junctions along the width direction. Approximate expressions for the material parameters have been obtained for SGs with many junctions in the width direction. Moreover, the equivalent tensile modulus of a Y junction with relatively large radius arms decreases more significantly than that of one with small radius.

Acknowledgments

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