INTERACTIONS BETWEEN POLYMERS AND CARBON NANOTUBES

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1.0 Introduction

Discovered by Iijima in 1991, carbon nanotubes (CNTs) are layers of folded graphene structured in the form of a seamless cylindrical hexagonal lattice and composed entirely of sp\(^2\) hybridized carbon atoms. A nanometer in diameter, the cylinder can be several microns (and in some instances a few millimeters) long with each end capped with half of a fullerene molecule. CNTs have been receiving an increasing amount of interest, both from industry and academia, due to their remarkable electrical (significantly more conductive than copper) and mechanical properties (e.g. a Young’s modulus, which relates to the chemical bonding of the constituent atoms, of approximately 1.2 TPa and tensile strength that ranges between 100-600 GPa) while remaining light-weight (density of 1.3 g/cm\(^3\), which is over five times lower than that of carbon-steel). Equally impressive is the extremely high aspect ratio at which CNTs exist, which can be as high as 1000, paving pathways for potentially revolutionary microelectromechanical systems (MEMS)\(^1\). CNTs can assemble either as, multiwalled nanotubes (MWNTs) comprising several coaxial cylinders bound by van der Waal forces with an interlayer distance of approximately 0.34nm, or as single walled nanotubes (SWNTs), depending on the conditions in which they are created. Resistances to tensile and compressive stress are primarily governed by in-plane \(\sigma\)-bonds while out-of-plane \(\pi\)-bonds affect the pure bending\(^2,3,4\).

Polymers and polymer matrix composite materials are being utilized in a vast range of industrial applications from aerospace composites to tissue engineering\(^5\). Their widespread use is due to their reasonably high strength and durability while remaining lightweight, flexible and easy to process. In 1994, Ajayan and his co-workers became the first group to report that further improvements to these desirable properties as well as processability can be made through the addition of CNTs\(^6\). Qian et al. showed that a mere addition of 1 wt-% of CNTs was able to improve the elastic stiffness of polystyrene by up to 42% and tensile strength by 25%; unsurprisingly, at higher CNT loadings, the increase in mechanical properties were even more pronounced\(^7\). These gains were acquired despite the fact that it is normal for CNTs to become curled and contorted when embedded in a polymer, thus are only able exhibit a small fraction of their full potential\(^3\).

Moreover, one can exploit the very high aspect ratio of CNTs, forcing them to align with one axis of the composite, allowing for very high axial conductivity and ultimately, a polymer matrix that possesses the same spectacular electrical properties that CNTs do, without sacrificing stiffness or optical clarity\(^2,8\). The conductivity of the matrix can be altered to the desired level by simply adjusting the loading of CNTs. Promising results have already been demonstrated, for example, Mamedov and his co-workers successfully created a novel, revolutionary material by filling CNTs between polymer layers; the resulting composite had a strength that was six times greater than that of carbon-fibre composites and had a hardness that matched some of the hardest ceramic materials at that time\(^9\). Notwithstanding these positive outcomes, the tensile strength of even the best polymer-CNT nanocomposites are orders of magnitude below that of pure CNT\(^10\).
2.0 Preparation of CNTs
At present, there are two widely used methods to produce CNTs: (1) laser ablation; and (2) chemical vapor deposition (CVD). The quantity and quality of CNTs that can be produced using these methods differ and hence the choice of method is dependent on the end-use of the CNTs. If a small amount of relatively defect-free CNTs are required, laser ablation will be used, while CVD is preferred when an economical means of producing large quantities of CNTs is necessary \textsuperscript{11,12}.

Discovered by Guo \textit{et al.} laser ablation replaced the comparatively low-yield and inefficient arc-discharge method for producing SWNTs which was prone to producing SWNTs with amorphous deposits. In brief, the arc discharge method involves connecting two carbon electrodes, one which acts as an anode and the other as a cathode, to generate an arc through DC current under the presence of helium gas. On arcing, the electrodes become red hot, and subsequently plasma is generated. The rod that acts as the anode is evaporated and SWNT deposits gather on the cathodic rod; the helium gas is used to catalyze the rate of deposition. The laser ablation method involves the use of an intense pulsed laser beam which is focused onto a graphite-metal composite target, vaporizing it in a chamber at roughly 1200 °C. Argon would then be bled into the chamber, which would carry the vaporized graphite into a water-cooled copper collector, downstream from the furnace, forcing condensation, and inducing the development of nanotubes \textsuperscript{13}.

MWNTs are commonly produced through chemical vapor deposition (CVD) which involves the synthesis of carbon within the 200 nm diameter pores of a template membrane made from alumina. Ethylene or pyrene are added to the CVD reactor, and at high temperatures, these compounds vaporize, decompose, and result in the formation of either carbon nanofibres or MWNTs within the aforementioned pores depending on the deposition time \textsuperscript{12}.

2.1 Dispersion of CNTs in the preparation of Polymer-CNT composites
The most common method of preparing nanotube/polymer composites involves dispersing CNT solutions - which are often chemically pretreated to improve solubility - into polymer solutions and then evaporating the solvents in a regulated manner \textsuperscript{14}. Qian and his co-workers have achieved dispersion through the use of an ultrasonic wand dismembrator, which was used to prepare a solution of toluene containing MWNTs. This solution was mixed with another solution, containing polystyrene in toluene, once again through ultrasonic agitation; the low viscosity of the polystyrene solution permitted free movement of nanotubes and toluene was subsequently removed \textsuperscript{7}.

For thermoplastic polymers, particularly those which cannot be processed using solution techniques due to incompatibility with common solvents, melt mixing has been progressively gaining widespread use. These thermoplastic polymers can include poly(methylmethacrylate) (PMMA) and polyethylene (PE). This technique takes advantage of the fact that semicrystalline thermoplastic polymers soften when heated above their melting point. The attractive forces that hold monomeric units of thermoplastic polymers easily dissociate with heating, allowing polymeric chains to slide past one another, and thus the polymer can be moulded or mixed with relative ease and then solidify when cooled, without any structural changes. However, in the case of thermosetting polymers, irreversible structural changes occur such as charring with melting, and thus mechanical agitation is not a feasible option. By applying
high shear forces while adding CNTs in a controlled manner, homogenous dispersion of nanoparticles in the polymer matrix can be achieved. Haggenmueller and co-workers melt mixed SWNTs (prepared by laser ablation) and PMMA and reported that up to 8 wt-% of SWNTs could be loaded into the polymer matrix using this technique; the team had also noticed that the CNTs had a tendency to align along the fiber axis during the extrusion process, resulting in a notable increase in mechanical properties and electrical conductivity.

Another alternative is using the monomer as the starting material and then carrying out polymersization in situ. For further details on this method, refer to the study performed by Cochet et al.

Stabilization of the CNTs is also equally important. Due to their extremely high surface area and extended π electron system, CNTs have a strong tendency to agglomerate. Agglomeration leads to a reduction in mechanical properties primarily because stress transfer to individual nanotubes takes place more inefficiently. A range of techniques have been used to reduce agglomeration including sonication and mechanical stirring. However, the most effective method to date is the surface functionalization of CNTs which stabilizes the dispersion, prevents re-aggregation while promoting coupling with the polymer matrix. The downside of surface functionalization is an effective deterioration in the intrinsic properties of CNTs; covalent functionalization, e.g. addition of -COOH or –OH groups on the surface of nanotubes using strong oxidizing agents such as HNO₃, has shown to fragment CNTs through the introduction of atomic defects and internal stresses. Thus, if surface functionalization is performed, compromises will have to be made depending on the end use of the composite. Notwithstanding the reduction in intrinsic properties of CNTs, studies on acid functionalization of CNTs have demonstrated noticeable improvements in interfacial bonding between CNTs and the polymer, resulting in improvements in Young’s modulus and mechanical strength when compared to the polymer by itself. In addition, one research group reported that covalent functionalization may not reduce the intrinsic properties of CNTs as dramatically as other studies have stated, provided that the electronic structures of the functional group that CNTs are modified with are similar to that of the polymer. In this study, modification of CNTs with methyl and phenyl groups facilitated greater interaction with poly(phenylacetylene) (PPA) and thereby prevented slipping in the composite. By increasing the concentration of the functional groups in the CNT, the group observed even further improvement in interaction, and through this, one could assume enhanced load transfer between the CNT and polymer. Complementing the results of this study was the investigation by Zhen and his co-workers who functionalized 5% of CNT surfaces with carboxylic (–COOH), amide (–CONH₂), alkyl (–C₆H₁₃) and phenyl (–C₆H₅) groups which were then to form composites with polyethylene (PE). Their results showed an across-the-board improvement in adhesion to the polymer matrix post-functionalization, relative to the pristine CNT. This improvement was attributed to a dramatic increase in contact area between the nanotube and the polymer matrix upon functionalization. The aromatic ring structure of the phenyl group was able to impart the greatest improvement in adhesion, likely due to its ability to align almost parallelly in the radial direction of the CNT surface. These findings along with those of Frankland et al., suggest that lower levels of functionalization (≤10%) have negligible impact on the mechanical properties of CNTs while significantly improving dispersion and load transfer ability via chemisorption.


2.2 The addition of surfactants to improve dispersion
As mentioned in the previous heading, achieving good interfacial interaction is critical towards developing composites with greatly improved mechanical properties. Surfactants can aid in dispersion without imparting the deleterious effects of covalent modifications on CNTs. In a study by Gong and co-workers, the surfactant, polyoxyethylene 8 lauryl, was successfully used in the addition of 1 wt-% CNTs in polymers which in turn, helped improve the glass transition temperature from 63 °C to 88 °C while a 30% increase in elastic modulus was also observed. The authors mentioned that these improvements were achieved despite complete homogenous dispersion not being achieved. Another sample was tested without the addition of the surfactant, and the CNTs by themselves did not impart a noteworthy improvement on thermomechanical properties of the composite 27. Moore et al. studied a range of aqueous dispersions using anionic, cationic and non-ionic surfactants. The group concluded that, for non-ionic surfactants, the size of the hydrophilic group was directly proportional to the extent of nanotube dispersion, attributing to the fact that larger hydrophilic groups are able to provide greater steric stabilization, and thus, if one can tailor the size of this group, one is able to fine-tune suspendability 28.

3.0 Mechanical Properties
According to Khaled Mezghani et al. the reinforcement of mechanical property for polymer/CNT composites varies with the concentration of CNT. They have done a series of mechanical experiments on linear low density polyethylene (LLDPE)/CNT composites with different CNT loading of 0.08, 0.3 and 1 wt%. They used chemical vapour deposition process to fabrication the composites, and gained well aligned and distributed CNT in LLDPE matrices. Error! Reference source not found.1 show the alignment of CNTs in LLDPE 29.

![Figure 1 Aligned CNT produced by CVD process](image)

The experiment result show that when concentration of CNT is 1 wt%, it is indeed increase the tensile strength; however, when the concentration change to 0.08 and 0.3 wt%, the tensile strength actually
decrease from 254Mpa to 209MPa and 224Mpa respectively, the results are plotted in Error! Reference source not found..

The concentration of CNT also has impacts on toughness and ductility of the LLDPE/CNT composites. With 0.08 and 0.3 wt% CNT, the ductility increase to 107% and 127% respectively, and the toughness increase by 63% and 105% 29.

Wenhan Guo et al. also did some experiment to test the mechanical properties of polymer/CNT composites. They used acrylic acid as a model monomer to fabricate aligned CNT/polymer thereby obtaining CNT/PAA. They claimed the tensile strength of the CNT/PAA composite fibers has been increased by up to 31% compared with those prepared by the direct incorporation of PAA under the
some experimental condition. They also find that the tensile strength of the CNT/PAA composite fibers first increases and then decreases with increase in the monomer concentration. The tensile strength reaches a peak point at monomer concentration of 8 mol/L, and then starts to decrease.\cite{30}

(I find no articles that related to the compression strength of Polymer/CNT strength)

Table 1 Increments in the mechanical properties of common resins with the addition of CNTs \cite{3}

<table>
<thead>
<tr>
<th>Polymer (matrix)</th>
<th>CNT Type</th>
<th>CNT content (wt-%)</th>
<th>% increase in tensile strength</th>
<th>% increase in Young's modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Purified MWNTs</td>
<td>1.00</td>
<td>25</td>
<td>42</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Pristine SWNTs</td>
<td>1.00</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>HD-Polyethylene</td>
<td>Pristine MWNTs</td>
<td>5.00</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>LD-Polyethylene</td>
<td>Pristine MWNTs</td>
<td>10.00</td>
<td>56</td>
<td>89</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>Pristine MWNTs</td>
<td>5.00</td>
<td>75</td>
<td>40</td>
</tr>
<tr>
<td>Polyethylene Oxide</td>
<td>Phenoxy-grafted MWNTs</td>
<td>1.50</td>
<td>440</td>
<td>230</td>
</tr>
<tr>
<td>PMMA</td>
<td>Purified SWNTs</td>
<td>8.00</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Nylon-6</td>
<td>Pristine MWNTs</td>
<td>1.00</td>
<td>120</td>
<td>110</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>Pristine SWNTs</td>
<td>0.10</td>
<td>9</td>
<td>20</td>
</tr>
</tbody>
</table>

4.0 Thermal Properties

SWNTs have exceptionally high thermal conductivity, with a value of approximately 3500 W/m.K along its axis at room temperature, making it many times more conductive than conventional filler materials such as carbon black, silver and ceramic powder.\cite{31} Being light-weight, corrosion resistant and easy to process, thermally conductive polymer composites have the potential to replace metallic parts in a vast range of applications including heat exchangers and electric motors. However, at present, the remarkably high thermal conductivity of pure SWNTs is not observed in nanocomposites. The underlying reason is that there is enormous interfacial thermal resistance between the CNTs and the polymer matrix that surrounds it, thereby undermining the capacity of the composite to conduct heat through phonons.\cite{32} In addition, imperfect physical contact between the polymer matrix and CNT serve only to exacerbate the effects of interfacial resistance. Phonons, which are quantized modes of vibration that take place within a rigid crystal lattice are the main means through which heat conduction occurs in polymers. The conductivity of polymers are many orders of magnitude smaller than that of CNTs and typically range from 0.2 W/m.K to 0.5 W/m.K depending on polymer crystallinity. The more amorphous
the polymer, the lower the phonon mean free path, and thus, conductivity will be lower. The Debye equation is often used to calculate the thermal conductivity of polymers, and it is written as follows:\[ \lambda = \frac{C_p v l}{3} \]

Whereby \( C_p \) is the specific heat capacity per unit volume, \( 'v' \) is the average phonon velocity and \( 'l' \) is the phonon mean free path.

Much of the research thus far have reported that the improvement to thermal conductivity conferred by the addition of CNTs is well below what theory would predict, suggesting that careful control of the micro- and nanostructure is crucial to maximize the benefits of nanoparticle addition. Another key issue is that phonons in polymers intrinsically have a very low mean free path, the free path on CNTs are several orders of magnitude larger, thus, even with perfect dispersion of CNTs, efficient heat conduction may not be observed. Detailed knowledge about the physical mechanism behind thermal conduction in nanocomposites, which is yet to be elucidated, is crucial if one is to leverage the outstanding properties of CNTs in CNT-polymer composites. Thus far, it is clear that in order to make progress, CNT dispersion must be homogenous and form an effective conductive path while thermal resistances at the CNT-polymer and CNT-CNT interfaces must be brought to a minimum. The latter is said to be the chief limiting factor towards progress and overcoming this necessitates further research in this promising field.

5.0 Electrical Properties for use as sensors

The electrical conductivity of polymers can be enhanced by several orders of magnitude through the addition of, as little as, 0.1 wt% CNTs, upon which percolation threshold is achieved. Percolation occurs when an interconnected conducting nanotube network is formed, changing the nature of the polymer from an insulator to a conductor. This addition has no adverse impact on the mechanical and optical properties of the polymer. Computational studies have revealed that the primary reason why this threshold is so much lower than that for metallic particles and carbon fibers is because of the extremely high aspect ratios of CNTs. It is important to bear in mind that the type of polymer and degree of alignment can also have a small but significant impact on the percolation threshold.

Sensors are devices which measure physical and chemical properties such as temperature, concentration, and stress, and then transduce the reading into an electrical signal which can be displayed by an instrument. Due to the remarkable intrinsic properties of CNTs (viz. small size, exceptional strength, very high electrical and thermal conductivity), they have the potential to revolutionize the sensor industry.

Dharap and co-workers took advantage of the fact that the electrical properties of CNTs change when subject to strains and developed a CNT film sensor that could be used for strain sensing on a macro scale. The SWNTs incorporated into the film were randomly oriented, thus creating a film that was
isotropic in nature, and one that allowed the measurement of strains at multiple locations simultaneously. The group observed an almost linear correlation between voltage across the film with tensile and compressive stresses \(^{36}\). In a study by Kong \textit{et al.}, it was shown that the electrical resistance of SWNTs changes considerably upon exposure to gases such as oxygen (O\(_2\)), ammonia (NH\(_3\)) and nitrogen dioxide (NO\(_2\)). The nanotube sensors were also reported to have response times that was, at worst, an order of magnitude faster than solid state sensors, and thereby, the researchers were able to unveil the promising potential for advanced, miniaturized chemical sensors based on CNTs which could be used for detecting the leakage of explosive gases, environmental monitoring, biomedicine, and the likes \(^{37}, \, ^{38}\).

The study by Wang and co-workers made use of MWNTs functionalized with polymers to develop sensors that would electrically respond to the presence of organic vapors such as methanol, chloroform and tetrahydrofuran. As gas was adsorbed onto the polymer film causing swelling, or when charge transfer occurred between the adsorbed molecules and the CNTs, the conductive pathway was altered reversibly, and this produced a change in electrical response of the composite. Their results showed that CNT-polymer nanocomposites exhibited enhanced gas sensitivity than CNTs by themselves \(^{39}\). These findings were congruent with those by An \textit{et al.} who compared the resistance response of PPy, SWNTs and SWNT/PPy nanocomposites \(^{40}\). Their results were as follows:

![Figure 4 Change in sensitivity at a nitric oxide concentration of 3000 ppm as a function of gas exposure time (40)](image)

The above diagram shows that the nanocomposite has greater sensitivity than the pure materials, highlighting that the added benefits of nanoparticles towards enhancing conductivity when dispersed in a polymer matrix. Also inferred from these results was that CNTs alone did not have exceptionally high sensitivity. It has been reported that CNTs did not exhibit a sensing response to all gases, but only to those with high adsorption energy, or those that are capable of interacting with CNTs \(^{41}\).

### 6.0 Mechanisms underpinning CNT-polymer interactions

In order to effectively utilize CNTs in composite applications, they must be dispersed homogenously throughout the matrix. Furthermore, their application in structural reinforcement, particularly in the
form of composites with polymers, is going to depend on the interfacial characteristics, i.e. ability to transfer the load from the matrix to the nanotubes. To achieve this, good interfacial bonding at the CNT-matrix interface is of chief importance, and understandably, failure of good adhesion nullifies the advantageous properties that CNTs impart, viz. high tensile strength while maintaining a desirable elastic modulus. Three key mechanisms of load transfer have been identified, and are described as follows:

(i) Micromechanical interlocking:
Localized regions of non-uniformity along a CNT, e.g. variations in diameter and bends at places where non-hexagonal defects are present, aid the adhesion of CNTs to polymer by mechanical interlocking. For example, in the case of CNT pullout, additional mechanical work will have to be exerted on the CNT and the polymer for them to slip past one another compared to CNT-polymer making contact along a smooth surface.

(ii) Chemical bonding:
Two types of interaction can take place between the nanotubes and polymer matrix: (1) ionic bonding; and (2) covalent bonding. Chemical bonding improves interfacial interaction, facilitating stress transfer far more effectively than physical adsorption would.

(iii) van der Waals forces:
CNTs exhibit an even distribution of charge and therefore the composite is often devoid of any electrostatic interactions, and thus, in the absence of the stronger chemical bonding mentioned in (ii), van der Waals forces predominate. In this case, the strength of interfacial binding depends largely on the geometrical conformation of the CNT with respect to the polymer.

(iv) Thermal expansion:
A less significant mechanism, mentioned sometimes in literature, is the difference in coefficients of thermal expansion which is shown to promote the ability of stress transfer between the CNTs and polymers. This increased ability of stress transfer can be attributed to thermal residual radial stress and deformation along to tube which occurs when the polymer is cooled from its melt; this compressive radial stress increases the effective contact area between the CNT and the polymer and thereby promotes closer interaction, and further enhances the mechanical interlocking mentioned in (i).

7.0 Modelling and Simulation
The characterization of structure and the manipulation of CNT/polymer composite fabrication have posed a tremendous challenge to researchers worldwide. Thus, computer modeling and simulation are heavily relied upon to predict and design material properties. The use of modeling and simulation allows us to better understand: (1) the thermodynamics and kinetics that govern the formation of polymer nanocomposites; (2) dynamics of the nanocomposite structure and the molecular structure at the interface; (3) how rheological behavior of the polymer varies with CNT addition; and (4) molecular mechanisms through which nanoparticles are able to reinforce the polymer composites. The three most
widely used methods of modeling and simulation are molecular mechanics (MM), molecular dynamics (MD) and Monte Carlo (MC) \(^{44}\).

### 7.1 Continuum mechanics based models

Continuum modeling is based on an assumption that the CNT molecular structure is an equivalent solid cylinder. Yang seunghwa has established a continuum model for Zigzag CNTs with parameters of (5,0), (10,0), (15,0) and (20,0).

![Figure 5 Continuum modelling of CNTs from molecular modelling](image)

### 7.2 Molecular Dynamics Simulations

MD allows us to simulate a system of interacting particles through a range of time intervals. This simulation provides us with data such as atomic position, velocities and forces, using which, we can ascribe mechanical and thermodynamic properties (e.g. pressure and heat capacity) to our molecular of interest \(^{44}\). We can also acquire structural and dynamical information about the interface and gain a better understanding of how interfacial attraction is influenced by chemical composition and structure of the polymer \(^{5}\). Through this, we can also derive our understanding of how load transfer takes place at the molecular level \(^{45}\).

A MD study was performed by Yang et al., who sought to examine the influence of specific monomer structure of polymers and their influence on the strength of interaction in CNT/polymer composites \(^{19}\). Their findings using poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV), polystyrene (PS), PPA, and poly(p-phenylenevinylene) (PPV) were congruent with several studies, who too had made the same conclusion that polymers with a backbone comprising aromatic rings show promising, non-destructive, non-covalent binding to CNTs while improving its solubilization \(^{46,47,48}\). The aforementioned polymers were chosen primarily for their increased affinity for physisorption onto CNTs, which as explained earlier, promote enhanced interfacial binding between CNT and the polymer without introducing the deleterious effects of chemical functionalization on CNT. PS is a relatively flexible polymer that contains σ-bonds between repeating units which facilitate easy rotation around the axis of the backbone, in contrast, PPA is far more rigid due to its π-conjugated backbone. Conjugation occurs when we have a series of alternating single and double bonds which results in the overlapping of p-orbitals. PPV is a linear, rigid molecule with a conjugated aromatic ring in its backbone while PmPV is a
substituted form of PPV that is more flexible due to an added dihedral angle between the two phenyl rings. MD was used to deduce interaction energy, whose magnitude correlates positively with strength of binding, between CNTs and each of these four polymers. The results highlighted the importance of the specific monomer structure on attractive interaction.

![Figure 6](image)

Figure 6 Intermolecular interaction between polymers and single walled carbon nanotubes [19]

![Figure 7](image)

Figure 7 Radial distribution functions (RDFs) between carbon atoms in PmPV (left) and PMMA (right) molecules and the longitudinal axis of the CNT integrated into the composite. Solid lines represent backbone, dashed lines represent side chains [46].

The RDF tells us how atomic density varies as we move further away from the longitudinal axis of the CNT. The above figure shows us that the backbone aromatic rings in PmPV are closer to the CNT surface than the carbon atoms in side chains; the discrepancy is particularly conspicuous at \( r = 10 \). When comparing this graph to the one on the right, we see why the PMMA/CNT model is stated to have lower interaction energy. This observation strengthens the findings by Yang and his co-workers who speculated that the phenyl rings align parallel to the CNT surface, in turn, leading to higher interaction energy.

Although the mechanism underlying this attractive interaction is yet to be elucidated, it has been hypothesized that the hexagonal arrangement of the graphene sheets is isomorphic to the atomic arrangement of the carbon atoms comprising aromatic rings. These aromatic rings are believed to
interact with the graphene surface via sp\textsuperscript{2} hybridized atoms \cite{46}. Perhaps this is the very type of isomorphism that drives the CNTs to form aggregates. Further tests by the authors were performed by calculating the dihedral angles between the surface and the plane of the aromatic rings and it was concluded that polymers with aromatic rings in their backbone (rather than side-chains), i.e. PmPV and PPV, were able to align to the surface of the CNTs and stack parallel. This was not the case for PS and PPA whose aromatic rings were vertical to the surface of the CNT, and the required contortions to make these side chains align with the CNT surface were energetically unfavorable. It was suggested by the authors that polymers such as PmPV, PPV and the like can be used as scaffolds in amphiphilic copolymers to promote an increase in interfacial binding between the polymer matrix and CNT \cite{19}.

Further MD studies have unveiled important information about the mechanism of interaction between the polymer, PPV, and CNT. The first step of this mechanism involves PPV “discovering” the presence of the CNT, and subsequently, a portion of the polymer chain is adsorbed onto the CNT surface. Within moments, the polymer chain begins to wrap around the CNT in a helical fashion, extending along the entire length of the CNT in a manner that would greatly optimize \(\pi-\pi\) interaction. This extensive wrapping was not observed in polymers such as PS, which has a far more flexible backbone than PPV, however its aliphatic side chains hinder its interactions with the CNT, and ultimately, the polymer preferentially undergoes intrachain coiling \cite{49}. Tests on polypyrrole (PPy), which has two aromatic rings in its backbone, added weight to aforementioned study; it was shown once again that the presence of aromatic rings encouraged extensive interaction with the CNT through helical wrapping and discouraged intrachain coiling \cite{5}. Foroutan and Nasrabadi made similar findings; their results (see figure 3) showed that the closely spaced aromatic rings in polythiophene (PT) and PPy interacted even stronger, through \(\pi-\pi\) stacking, than what PmPV did with the CNTs \cite{50}.

To explain the role of specific monomer structure on intermolecular interactions, the authors focused on the \(\varepsilon\)-parameter (bond energy at equilibrium distance between) of the constituent atoms of the monomer. This hypothesis states that the higher interaction energy observed with PT, when compared to PPy, is a result of the higher energy parameter of the sulfur atom (\(\varepsilon = 0.202\) kcal/mol) while nitrogen in PPy has a value of only 0.043 kcal/mol. The difference of interaction energy between poly(2,6-pyridinylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PPyPV) and PmPV arises solely because of
their unidentical monomer structure. The nitrogen has a lower ε than that of carbon (ε = 0.056 kcal/mol), resulting in reduced van der Waals interaction and as a consequence, lower intermolecular interaction. Aside from this, the isomorphism of PmPV allows it to align better with CNT surface. Polymers with flexible backbones such as PMMA and PP tended to coil within themselves, leading to the least amount of wrapping around the CNT, suggesting the presence of either an enthalpic or entropic barrier that bolsters intrachain coiling. In a molecular mechanics study performed by Lordi and Yao, it was concluded that the polymer’s ability to form helices around around the CNT is important towards building ultrastrong composites, to a far greater extent, than interfacial binding energy and frictional forces are.

The radius of the CNT is another factor that could play a role in affinity. A CNT of larger radius will possess reduced curvature, allowing for improved alignment of aromatic rings in polymers with the CNTs, and thus significantly improved π-π interactions. A study by Zhen and co-workers showed that attractive interaction between CNTs and polymers (viz. polyethylene, polypropylene, PS and polyaniline) does indeed increases as a function of CNT radius, and just as theory would dictate, the increase was more profound in the polymers with aromatic groups. During the study, the group also discovered the importance of chirality of the CNT on interaction energy, inferring that the armchair (10,10) crystal lattice configuration of the nanotubes may be the superior form for reinforcement; this is because the group observed that adhesion energy decreased when chiral angle became smaller and approached that of a zig-zag conformation (see figure 4). Chen and his colleagues had also made identical findings. The abovementioned orientation and alignment of ring planes parallel to the CNT surfaces were observed for both PS and polyaniline (PANI), both of which have aromatic groups, in the side chain and backbone respectively. Unsurprisingly, in comparison to PE and polypropylene (PP), both of which had an interaction energy of -13 kcal/kmol with the CNT, PS and PANI displayed a noticeably higher interaction energy of -20 kcal/kmol.

The following diagram shows the temperature dependence on interaction energy:
As we can see in the above diagram, temperature has a rather weak influence on interaction energy for PS and PP, while its influence is noticeably stronger for the two polymers which contain an aromatic ring. Several other groups have also made this observation. B. Arman et al. conducted a MD simulation on the response of phenolic resin/CNT composites to shock wave loading. They preformed the simulation with the large-scale atomic/molecular massively parallel simulator (LAMMPS) package. Periodic boundary conditions are applied along all three directions in nonshock simulations but only along the two directions orthogonal to the shock direction in shock simulations.

![Figure 10 Influence of CNT chirality on adhesion [48].](image1)

B. Arman et al. conducted a MD simulation on the response of phenolic resin/CNT composites to shock wave loading. They preformed the simulation with the large-scale atomic/molecular massively parallel simulator (LAMMPS) package. Periodic boundary conditions are applied along all three directions in nonshock simulations but only along the two directions orthogonal to the shock direction in shock simulations.

![Figure 11 Monomers of phenolic resin, methylol phenolic and epoxy](image2)
They constructed a unit configuration of amorphous phenolic resin with XENOVIEW (6) via randomly placing 64 polymeric chains into a 2.7×2.9×10 nm³ supercell. Each such polymeric chain contains eight monomers (as show in Error! Reference source not found.6 (a) and Error! Reference source not found.7 (a)). This unit configuration contains 7296 atoms, and then it was replicated by 2×2×8, after that, the resulting configuration is further equilibrated at ambient condition with a time (t) step of 0.25fs and reaches a density of ρ₀ = 1.12 g/cm³, and is adopted as the projectile for shock simulations. A CNT composite unit configuration consists of a capped single-wall CNT with (10, 0) chirality embedded in phenolic resin containing 64 polymeric chains, and is 2.9×2.9×10 nm³ in edge lengths. The CNT is ~0.78 nm in diameter and 7.8 nm long. The phenolic resin chains are introduced randomly around the CNT. The van der Waals distance between the resin and CNT is 0.34 nm. This van der Waals distance thus induces the excluded volume between the CNT and the resin matrix, as shown in Error! Reference source not found. (b). The composite unit is first equilibrated at 0.1 K with the constant-volume-temperature (NVT) ensemble for 40 ps, followed by thermal annealing procedure at constant volume, where the system is heated with a ramp rate of 0.03 k/fs to 2000 k, equilibrated at 2000 k for 20 ps and then cooled to 300 k with the same ramp rate. The annealing procedure is repeated twice. Replications of the composite unit by 2×2×8 and 2×20×1 are adopted to construct configurations for longitudinal and transverse shock loading of the composites, respectively. The corresponding edge lengths are 5.7×5.9×84.1 nm³. The resulting configurations are then equilibrated for 125 ps with the constant-pressure-temperature ensemble at ambient conditions (ρ₀ = 1.18 g/cm³) for shock simulations.

The shock simulations are performed on pure phenolic resin and the CNT-resin composites along the longitudinal and transverse directions. The stress (σ₁) evolutions, plotted in the traditional x-t diagrams, illustrate wave propagation and interaction, which result in the shocked and unshocked regions as well as the release fan originated on the free surface (Error! Reference source not found. and Error! Reference source not found.). The shock (Hugoniot) states, deformation, and related structural changes in pure resin and composites are examined.
Figure 13 x-t diagrams for phnolic resin (a), and longitudinal loading (b) and transverse loading (c) of the CNT resin composites ($u_p=2$ km/s). Color coding is based on $\sigma_{11}$. O: unshocked; S: shocked; R release fan.
In 2008, Liu and his team made some novel discoveries by considering repeat unit arrangements (RUAs) of polymers in an MD simulation study, and calculating the interaction energy of SWNTs with PPA in ten different conformations, including two geometric isomers of PPA: transPPA and cisPPA.

As can be seen in the above table, transPPA3 and cisPPA4 have the greatest interaction with SWNTs while transPPA8 and cisPPA5 have the weakest. PPA of course is a rigid polymer due to its backbone constituted by π-bonds. Having the same hybridization in electronic structure as those in SWNTs, the
phenyls in PPA side chains play a critical role in the interaction between PPA and SWNT. Yang et al. had shown that the polymer would have a stronger interaction with SWNT depending on the number of aromatic rings in the polymer approaching the SWNT surface. The torsion angle between the planes of aromatic rings was also determined to be important, with ideal values approaching $0^\circ$ or $180^\circ$. TransPPA3 and cisPPA4 are structured in such a way that there is a very large interval between adjacent phenyl groups, which in turn, makes the backbone very flexible and limit interaction between the phenyl groups. It is this relatively high backbone flexibility that permits bending around the CNT surface, and consequently, all parts of the polymer are able align themselves proximally to the CNT surface, in particular, the phenyl groups. The weak interaction of transPPA8 and cisPPA5 is a result of three closely interacting phenyl groups in the former and two in the latter, which effectively distances the polymer from the CNT. Through this discovery, we can see the great influence of RUAs on interaction energy, and the importance of how interaction between phenyl groups can degrade overall performance of the composite. This knowledge allows us to fine-tune our polymer in accordance with the desired mechanical properties of our composite.

### 7.3 Molecular Mechanics (geometry optimization)

### 7.4 Monte Carlo Models

The MC technique is one that is founded on probability and statistics. A MC simulation comprises three steps: (1) the physical problem of interest is translated into a statistical model; (2) the statistical model is computed by a numerical stochastic sampling experiment; and (3) statistical methods are used to analyze the acquired data, through which we can determine vital information about equilibrium properties such as free energy and phase equilibrium.

MC simulations have revealed that both van der Waals and π-stacking (aromatic groups interacting with CNTs) play a noteworthy role in promoting the helical wrapping of polymers around CNTs. Kusner’s group observed that there is a narrow range of two parameters, chain stiffness and curvature of CNT surface, for which ordered helical wrapping of polymers occur around the CNT. Beyond this range, the undesirable aggregation of CNTs is observed.

To further understand the mechanism by which polymers wrap around CNTs, Gurevitch and Srebnik used MC to build upon Kusner’s work. The group reported that as long as CNT diameter is sufficiently large, van der Waals interactions were sufficient to ensure that the polymer wrapped around the CNT surface in a helical manner, which was found to be the preferred conformation. The driving force for this adsorption was found to be entropic as the CNT radius was the sole factor that influenced energetic gain. The energetic gain of adsorption was greater than the entropic loss upon adsorption of the polymer chain.
7.5 Simplification of Modelling Model

For simplification of the modelling model, there is an assumption that the CNT molecular structure is an equivalent solid cylinder. Under this assumption, the simulation method is called continuum micromechanics.

According to Seunghwa Yang et al., without surface treatment of nanofillers, smaller nanoparticle-reinforced cases have shown a more enhanced reinforcing effect than other cases, even at the same volume fractions. This is due to the interphase formed by the immobilized surrounding matrix polymer. Thus, an equivalent nanocomposite microstructure was modelled as a three-phase structure consisting of a particle, matrix, and an additional phase-effective interphase that contains information about the size effect, however, this model have a problem called Eshelby inclusion problem. To modify and simplify the model, Seunghwa Yang et al. applied a method of effective particle suggested by Yannase and Ju as an alternative to replace Eshelby tensor. The following figure shows the original Eshelby tensor and simplified Eshelby tensor.
7.6 Interaction Energy, Rotational Moment and Pullout Energy

The interaction energy, $\Delta E$, is used to quantify the interfacial bond strength between the polymer and SWNT. $\Delta E$ can be defined as the energy difference between the total energy contained in the polymer/SWNT composite and the sum of the energies contained in individual molecules comprising the SWNTs and polymer matrix:

$$\Delta E = E_{\text{total}} - (E_{\text{SWNT}} - E_{\text{polymer}})$$

These values are extracted with the aid of molecular dynamics simulations (explained in further detail later in this review). In general, in the absence of significant chemical variations in the backbone...
structure of the polymer, there is a positive correlation between interaction energy and molecular weight \(^4\).  

Moment of inertia calculations can also provide us with useful information towards understanding the wrapping behavior of polymers as a function of time, and is given by \(^5\):

\[
MI = \sum_{i=1}^{n} m_i r_i^2
\]

Using the above equation, the moment of inertia of each polymer involved in the study can be compared relative to the longitudinal axis of the CNT, whose atoms are held fixed, as a function of time. The equation simply states that the rotational moment of inertia is equivalent to the sum of masses of polymer chains multiplied by square of their distance, perpendicularly, from the longitudinal axis of the CNT. The particle number is represented by \(i\), the mass of the \(i\)th particle by \(m_i\), and distance of the particle from the CNT axis by \(r_i\). The larger the moment of inertia, the greater the amount of intrachain coiling; this corresponds to a reduced degree of helical wrapping of the polymer around the CNT.

Pullout energy is also reported in literature, where experiments are conducted with a fully embedded CNT being pulled out of the polymer matrix \(^5\). This allows for the calculation of interfacial shear stress of the composites. It is calculated as follows:

\[
E_{\text{pullout}} = E_2 - E_1
\]

\[
= (\Delta E_2 + E_{\text{SWNT2}} + E_{\text{Polymer2}}) - (\Delta E_1 + E_{\text{SWNT1}} + E_{\text{Polymer1}})
\]

\[
= (\Delta E_2 - \Delta E_1) + (E_{\text{SWNT2}} - E_{\text{SWNT1}}) + (E_{\text{Polymer2}} - E_{\text{Polymer1}})
\]

\(E_1\) and \(E_2\) are the potential energies of the composite before and after the pullout simulation respectively.

The following equation allows us to use the pullout energy to calculate the interfacial shear stress, \(\tau_i\):

\[
E_{\text{pullout}} = \int_{x=0}^{x=L} 2\pi r (L-x) \tau_i dx = \pi r L \tau_i L^2
\]

\[
\tau_i = \frac{E_{\text{pullout}}}{\pi r L^2}
\]

\(L\) and \(r\) represent the length and outer radius of the CNT respectively; and \(x\) is used to represent the coordinate along the longitudinal axis of the CNT \(^24\).
8.0 Reference List


## 9.0 Appendix A

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
<th>Molecular formula</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>((C_8H_8)n)</td>
<td><img src="image1" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(phenylacetylene)</td>
<td>PPA</td>
<td>((C_8H_6)n)</td>
<td><img src="image2" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>PE</td>
<td>((C_2H_4)n)</td>
<td><img src="image3" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene)</td>
<td>PmPV</td>
<td>((C_{32}H_{44}O_2)n)</td>
<td><img src="image4" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(p-phenylenevinylene)</td>
<td>PPV</td>
<td>((C_8H_6)n)</td>
<td><img src="image5" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(methylmethacrylate)</td>
<td>PMMA</td>
<td>((C_5O_2H_8)n)</td>
<td><img src="image6" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>PPy</td>
<td>((C_8H_8N_2)n)</td>
<td><img src="image7" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Polythiophene</td>
<td>PT</td>
<td>((C_4H_4S)n)</td>
<td><img src="image8" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(2,6-pyridinylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene)</td>
<td>PPyPV</td>
<td>((C_{31}H_{44}O_2N)n)</td>
<td><img src="image9" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Polyaniline</td>
<td>PANI</td>
<td>((C_6H_4NH)n)</td>
<td><img src="image10" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Polypropylene</td>
<td>PP</td>
<td>((C_3H_6)n)</td>
<td><img src="image11" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>
9.1 Appendix B

Foreword: Consideration of the chemical structure of monomeric units to predict properties of the polymer has its limitations; especially the mechanical behavior of the polymer, i.e. chemical structure only contributes partly and indirectly towards the mechanical properties. A more direct role is played by the supramolecular structure, which is the physical arrangement of the chain molecules in respect to one another. Nonetheless, I have tried my best to present the likely properties of a polymer using the chemical structures of the monomers I had been provided with, however I do encourage the reader to bear in mind that thermal and mechanical properties are influenced considerably more by length (degree of polymerization) than by specific chemistry.

Polymers

Polyethylene

Polyethylene is a linear, thermoplastic polymer, and as its name implies, is produced through the polymerization of ethylene. Thermoplastic polymers are those without cross-links between the chains. The absence of cross-linking allows the polymer to be flexible and have relatively low melting points. The reason behind the low melting point is that intermolecular forces between the ethylene monomers are considerably weaker than covalent cross-links, allowing the attractive forces to dissociate by warming. This dissociation allows the chains to slide relative to one another, and thus the polymer can be molded without much difficulty. Once polyethylene is cooled, the aforementioned intermolecular forces undergo reformation. There is no net chemical change as a result of heating thus polyethylene can be recycled several times.

![Diagram of polymers](image)

**Figure 1.** The above diagram shows how covalent cross-links can greatly reduce flexibility and resist molding through thermal means. [1]
The dissociation energy required to overcome the covalent cross-linkages (shown in figure 1) ranges from approximately 50-200 kcal/mol while the dissociation energy required to disrupt the bonds that hold the individual polymer chains together is more than one order of magnitude smaller with a range of 0.5-7 kcal/mol [2].

The physical characteristics of polyethylene are strongly influenced by the arrangement of the molecular chain of monomers. Branching off the main chains are side chains which can be of varying lengths. The presence of these side chains can affect the density, tensile strength, flexibility, hardness, brittleness and melt viscosity of the final product, and concomitantly, the classification of polyethylene. Greater branching will reduce net linearity of the polymer chains and thus the polymer will pack with less efficiency (and thus with more voids), resulting in polyethylene of lower density and strength, but with greater flexibility [3]. The following table summarizes the differences in physical properties between the highly branched low-density polyethylene (LDPE) and the relatively linear high-density polyethylene (HDPE):

<table>
<thead>
<tr>
<th>Property</th>
<th>LDPE</th>
<th>HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat deflection temperature (1820 kPa; °C)</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>Maximum resistance to continuous heat (°C)</td>
<td>40</td>
<td>80</td>
</tr>
<tr>
<td>Coefficient of linear expansion (cm/cm²·C, 10⁻⁵)</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Compressive strength (kPa)</td>
<td>2 × 10⁴</td>
<td></td>
</tr>
<tr>
<td>Impact strength (Izod: cm-N/cm of notch)</td>
<td>No break</td>
<td>50</td>
</tr>
<tr>
<td>Tensile strength (kPa)</td>
<td>5 × 10³</td>
<td>3 × 10⁴</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>0.91</td>
<td>0.96</td>
</tr>
</tbody>
</table>

**Figure 2.** General physical and mechanical properties of LDPE and HDPE [4]

**Figure 3.** Molecular structures of LDPE and HDPE [8]

*Poly(propylene)*

Polypropylene is a thermoplastic polymer comprising monomers of propylene. Its crystallinity lies between that of LDPE and HDPE and thus it is moderately tough while remaining flexible. The primary difference between polyethylene and polypropylene is the presence of a methyl group in polypropylene
subunits. This methyl group facilitates the production of three distinct polypropylene structures, viz. isotactic, syndiotactic and atactic \[^5\]. Much of polypropylene produced commercially today is isotactic, i.e. the methyl group is located on the same side of the molecular backbone. Isotacticty confers polypropylene with enhanced physical properties which include improved stiffness and higher distortion temperature. This is because an isotactic polypropylene molecule is able to pack together far more tightly than one that is atactic (where methyl groups occur randomly and on different sides of the backbone), resulting in a crystalline polymer framework that is denser and less porous. Another advantage of having a crystalline structure is, because more polymer chains are tightly packed in the crystalline region than in amorphous areas, the effective stress on each polymer chain is reduced and in effect, we have a polymer with superior resistance to stress \[^2\].

The following table summarizes the key physical properties of isotactic polypropylene (iPP).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat deflection temperature (1820 kPa; °C)</td>
<td>55</td>
</tr>
<tr>
<td>Maximum resistance to continuous heat (°C)</td>
<td>100</td>
</tr>
<tr>
<td>Coefficient of linear expansion (cm/cm-°C, 10^-5)</td>
<td>9</td>
</tr>
<tr>
<td>Compressive strength (kPa)</td>
<td></td>
</tr>
<tr>
<td>Flexural strength (kPa)</td>
<td>5 x 10^4</td>
</tr>
<tr>
<td>Impact strength (Izod: cm-N/cm of notch)</td>
<td>27</td>
</tr>
<tr>
<td>Tensile strength (kPa)</td>
<td>3.5 x 10^4</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>100</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>0.90</td>
</tr>
</tbody>
</table>

*Figure 3.* General physical and mechanical properties of iPP \[^4\].

**Poly(acrylonitrile)**

Polyacrylonitrile is a synthetic polymer based on acrylic acid that is commonly used to produce carbon fiber. Strong electrostatic forces between adjacent, highly polar, nitrile groups (C≡N) of the same polymer molecule restricts the rotation of bonds, leading to the formation of a rigid helical chain, and consequently, polyacrylonitrile has a high melting point of 317 °C \[^2\][^7]. As a result of certain exothermic reactions that take place intrinsically, the polymer tends to degrade at temperatures well below its melting temperature and therefore it can only be polymerized in a select few organic solvents \[^6\].

**Poly(styrene)**

Polystyrene is a brittle, rigid, amorphous, aromatic polymer acquired from the polymerization of styrene solution in ethyl benzene with the presence of benzoyl peroxide. Transparent, stable and resistant to moisture, it is a thermoplastic polymer with a glass transition temperature of approximately 100 °C. This relatively high glass temperature, rigidity and brittleness are attributable to the resistance of the bulky phenyl-containing units to movement. As with all thermoplastic polymers, increasing the chain length and thus creating polystyrene of higher molecular weight, an improvement in strength and toughness will be observed however its melt viscosity will simultaneously increase, making processing considerably
more energy intensive. The abovementioned transparency of polystyrene is a result of its amorphousness which is attributable to the presence of large phenyl groups that prevent the chains from packing into dense crystalline arrangements which would subsequently scatter incident light, making the polymer opaque \[4\]. The reason behind this is that crystalline polymers are in fact two-phases systems with a crystalline phase dispersed in amorphous matter. When light passes through these two phases with different refractive indices, much of the light is scattered at the interphase, moreover, dense crystalline areas have a higher refractive index than amorphous regions, thus light will be absorbed.

**Poly(ethylene oxide)**

Polyethylene oxide is a linear, non-ionic, partially crystalline polymer of ethylene oxide which can have a vast range of physical properties which vary according to chain length and degree of crystallinity \[10\]. Low molecular mass polymers of ethylene oxide are clear, transparent liquids. With increasing chain length, and therefore molecular mass, the poly(ethylene oxide) goes from becoming a soft waxy solid to a hard wax, and eventually to a tough thermoplastic whose melting temperature can vary from 30-65 °C \[8\]. At low temperatures, hydrophilic interactions are dominant, making poly(ethylene oxide) one of the most hydrophilic polymers available \[10\].

**Poly(methyl methacrylates)**

Poly(methyl methacrylate) (PMMA) is a widely used alkyl methacrylates that is most commonly sold as an amorphous, atactic polymer that has excellent light transparency (92%), giving rise to transparent films and moldings. Unlike corresponding poly(alkyl acrylates), poly(methyl methacrylate) contains two substitutes on every alternate carbon atom, which in turn, restricts chain mobility and ultimately makes the polymer comparatively less flexible while conferring it greater tensile strength. The methyl group on the α-carbon on each monomeric unit helps to increase the stability of PMMA towards chemical (e.g. hydrolysis) and light-associated degradation \[4\][9]. The methyl group also prevents close packing of the polymer chains and this is the primary reason why PMMA is amorphous and transparent. As implied previously, PMMA is a thermoplastic polymer and thus its carbon backbone is comprised of very strong covalent bonds while the molecules comprising the polymer are held by significantly weaker Van der Waals’ forces allowing the plastic molecules to slide by one another without breaking the primary, covalent bonds.
The following table summarizes the key physical properties of PMMA:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat deflection temperature (1820 kPa; °C)</td>
<td>95</td>
</tr>
<tr>
<td>Maximum resistance to continuous heat (°C)</td>
<td>75</td>
</tr>
<tr>
<td>Coefficient of linear expansion (cm/cm·°C, 10⁻⁵)</td>
<td>7.0</td>
</tr>
<tr>
<td>Compressive strength (kPa)</td>
<td>1 × 10⁵</td>
</tr>
<tr>
<td>Flexural strength (kPa)</td>
<td>9.6 × 10⁴</td>
</tr>
<tr>
<td>Impact strength (Izod: cm·N/cm of notch)</td>
<td>21</td>
</tr>
<tr>
<td>Tensile strength (kPa)</td>
<td>6.5 × 10⁴</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>4</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Figure 4:** General physical and mechanical properties of PMMA [4]

**Nylon-6**

Nylon-6 is produced through the ring-opening polymerization (ROP) of caprolactam at 533 K under the presence of nitrogen. Because each monomeric unit consists of six carbon atoms, it is named nylon-6, in accordance with the naming system given for nyons. Consistent with the property of most polyamides, Nylon-6 is tough, translucent and semi-crystalline (i.e. they contain crystalline and amorphous phases); its toughness is a result of the strong hydrogen bonds present in its backbone. The net effect of crystallinity is an increase in yield and tensile strength, abrasion resistance and enhanced elastic properties and shear modulus. However, it also leads to a reduction in impact strength and moisture absorption. Fortunately, crystallinity of Nylon-6 can be controlled such that the final product contains the desired balance of the aforementioned properties. A low degree of crystallinity is achieved when Nylon-6 is rapidly quenched below room temperature from a molten state, or it can also be achieved through chemical means, e.g. by the use of unsymmetrical monomers such that efficient packing cannot occur. Most commercially produced Nylon-6 has a degree of crystallinity that ranges between 45-55% and thus fibers produced with this polymer are tough, elastic while possessing high tensile strength [11].

**Poly(ethylene terephthalate)**

Poly(ethylene terephthalate) (PET) is a thermoplastic, aromatic polymer synthesized through step-growth polycondensation (i.e. random reaction of two functional groups of monomers) of ethylene glycol and terephthalic acid. The formation of this polymer involves two reaction steps: (1) esterification of terephthalic acid with ethylene glycol whereby the –COOH groups of the former react with –OH groups of the latter; and (2) transesterification reaction which ensues in the melt phase. PET that is used in the production of bottles is amorphous in nature and thus it appears transparent. The concentrations of the reactive species determine the chain length of the final product and consequently also influence molecular mobility and viscosity of the product when melted [12]. Depending on the processing or rate at
which the molten polymer is cooled, PET can exist either as amorphous or semi-crystalline, with the former state producing a transparent polymer \[^4\]. The presence of the aromatic ring (from terephthalic acid) confers the polymer with considerable strength and stiffness, hence they are commonly used in the manufacture of fabrics due to their superior resistance to wrinkling.

The following table summarizes the key physical properties of PET:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat deflection temperature (1820 kPa; °C)</td>
<td>100</td>
</tr>
<tr>
<td>Maximum resistance to continuous heat (°C)</td>
<td>100</td>
</tr>
<tr>
<td>Crystalline melting point (°C)</td>
<td></td>
</tr>
<tr>
<td>Coefficient of linear expansion (cm/cm°C, 10^-5)</td>
<td>6.5</td>
</tr>
<tr>
<td>Compressive strength (kPa)</td>
<td>8.6 × 10^4</td>
</tr>
<tr>
<td>Flexural strength (kPa)</td>
<td>1.1 × 10^2</td>
</tr>
<tr>
<td>Impact strength (Izod: cm-N/cm of notch)</td>
<td>26</td>
</tr>
<tr>
<td>Tensile strength (kPa)</td>
<td>6.2 × 10^4</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>100</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.35</td>
</tr>
</tbody>
</table>

**Figure 4:** General physical and mechanical properties of PET \[^4\]

**Poly(acetylene)**

Poly(acetylene) is a linear polymer of acetylene units formed at elevated temperatures and pressures. The backbone of this polymer is composed of strong carbon-carbon double bonds (typically arranged in *trans* configuration) which significantly increase the attractive forces between each monomer in a chain and thus results in a strong, inflexible polymer. The packing of poly(acetylene) monomers is highly dependent on the process used to manufacture them and thus it is difficult to label properties monomeric units of acetylene \[^13\].

**Poly(pyrrole)**

Polypyrrole is a highly conductive, amorphous polymer formed though the oxidative polymerization of pyrrole monomers. The polymeric chain can be either linear or can form a planar ring structure comprising up to ten pyrrole rings and thus the properties of the polymer can vary widely \[^14\][^15]. However, regardless of polymeric structure, like poly(acetylene), the backbone of poly(pyrrole) comprises carbon-carbon double bonds which greatly enhance the attractive forces between the monomer chains and this make the polymer stiff and inflexible.

Please note: Much of literature conducted on poly(pyrrole) focused on its electrical properties, thus it was exceptionally difficult to acquire information on how its chemical structure related to its physical and mechanical properties.
References


