

Review

# A Short Review on the Effect of Surfactants on the Mechano-Thermal Properties of Polymer Nanocomposites

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Received: 29 May 2020; Accepted: 16 June 2020; Published: 16 July 2020



**Abstract:** The recent growth of nanotechnology consciousness has enhanced the attention of researchers on the utilization of polymer nanocomposites. Nanocomposites have widely been made by using synthetic, natural, biosynthetic, and synthetic biodegradable polymers with nanofillers. Nanofillers are normally modified with surfactants for increasing the mechano-thermal properties of the nanocomposites. In this short review, two types of polymer nanocomposites modified by surfactants are classified, specifically surfactant-modified inorganic nanofiller/polymer nanocomposites and surfactant-modified organic nanofiller/polymer nanocomposites. Moreover, three types of surfactants, specifically non-ionic, anionic, and cationic surfactants that are frequently used to modify the nanofillers of polymer nanocomposites are also described. The effect of surfactants on mechano-thermal properties of the nanocomposites is shortly reviewed. This review will capture the interest of polymer composite researchers and encourage the further enhancement of new theories in this research field.

**Keywords:** surfactant; mechano-thermal; polymer; nanocomposites

## 1. Introduction

Recently, the development of polymer nanocomposites in the composite industry has grown rapidly because they have superb mechano-thermal properties and are very promising replacements for conventional polymer composites. Polymer nanocomposites are polymers incorporated with nanometer scale fillers, regardless of the origin of the materials, whether it is inorganic or organic. Synthetic polymers (examples are displayed in Table 1) are frequently utilized for the creation of polymer nanocomposites, including HDPE [1], PP [2], PS [3,4], DGEBA [5–7], PEVA [8,9], PBO [10], SR [11], PAN [12], PUA [13], etc. Synthetic biodegradable polymers (examples are also displayed in Table 1), such as PLA [14–18], PBAT [19], PBS [20], PVA [21], PCL [22], etc., are also utilized for nanocomposite preparation.

**Table 1.** Examples of synthetic polymers and synthetic biodegradable polymers used in the preparation of polymer nanocomposites.

Synthetic Polymer	Abbreviation	Synthetic Biodegradable Polymer	Abbreviation
High-density polyethylene	HDPE	Poly(lactic acid)	PLA
Polypropylene	PP	Poly(butylene adipate-co-terephthalate)	PBAT
Polystyrene	PS	Poly(butylene succinate)	PBS
Diglycidyl ether of bisphenol A	DGEBA	Polyvinyl alcohol	PVA
Poly(ethylene-co-vinyl acetate)	PEVA	Poly( $\epsilon$ -caprolactone)	PCL
Polybenzoxazine	PBO		
Silicone rubber	SR		
Polyacrylonitrile	PAN		
Polyurethane acrylate	PUA		
Thermoplastic polyurethane	TPU		
Epoxy-terminated dimethylsiloxane	EDTS		

On the other hand, nanofillers (examples are displayed in Table 2), such as MMT [2,9,12,20], Ag NPs [17,18], ZnO NPs [15], TiO<sub>2</sub> NRs [3], CNTs [10,23,24], CNFs [5,25,26], G NPs [11,13,23], GO NSs [6,27], LDHs [22], and HNTs [4], are used in the fabrication of polymer nanocomposites, as they possess a high aspect ratio, large surface area, high stiffness, and low density [17,20]. The application of bio-based nanofillers, for example, CNCs [15,18,28,29], CNPs [30], NCFs [8,19], and CNWs [7,16], also contribute to the production of nanocomposites because they are renewable and sustainable materials.

**Table 2.** Examples of nanofillers and surfactants used in the preparation of polymer nanocomposites.

Nanofiller	Abbreviation	Surfactant	Abbreviation
Montmorillonite	MMT	Hexadecyltrimethylammonium bromide	HTAB
Silver nanoparticles	Ag NPs	Didodecyltrimethylammonium bromide	DDAB
Zinc oxide nanoparticles	ZnO NPs	Sodium dodecyl sulfate	SDS
Titanium dioxide nanorods	TiO <sub>2</sub> NRs	Polypropylene glycol ethoxylated and propoxylated	Ultramic PE 105
Carbon nanotubes	CNTs	Silicon-based surfactant	Niax L-595
Carbon nanofibers	CNFs	Bis-(2-hydroxyethyl)methyltallowalkylammonium chloride	HMAC
Graphene nanoplatelets	G NPs	Polyoxyethylene octyl phenyl ether	Triton X-100
Graphene oxide nanosheets	GO NSs	Acid phosphate ester of ethoxylated nonylphenol	Beycostat A B09
Layered double hydroxides	LDHs	Lauric arginate	LAE
Halloysite nanotubes	HNTs	Poly(ethylene glycol) monooleate	PEGMONO
Expanded graphite nanoplatelets	EG NPs	Triblock copolymers of poly(ethylene oxide) and poly(propylene oxide)	Pluronic
Cellulose nanocrystals	CNCs	Oleic acid	OA
Cellulose nanoparticles	CNPs	Polysiloxane-polyether copolymer	AK8805
Nanocellulose fibers	NCFs	Stearic acid	SA
Cellulose nanowhiskers	CNWs	Palmitic acid	PA
		Sorbitan monostearate	Span 60
		Benzimidazolium-N,N'-hexadecane-2-hydroxy-ethyl bromide	BHBB
		Poly(ethylene glycol)	PEG
		Dodecylbenzene sulfonic acid	DBSA
		Sodium cholate	SC

Surfactants (examples are also displayed in Table 2), for instance, HTAB [13,20,31], DDAB [12,32], SDS [4,21], Ultramic PE 105 [19], Niax L-595 [8], HMAC [9], Triton X-100 [6,10,11,24], Beycostat A B09 [15,17,18,28], LAE [29], PEGMONO [14,16], Pluronic [7,14], OA [3], AK8805 [5], SA [2], PA [22], Span 60 [30], and BHBB [1], are commonly employed for modifying nanofillers in the preparation of polymer nanocomposites.

Surfactants have an amphiphilic character, owing to hydrophilic and hydrophobic functional groups [33,34]. Previous studies have indicated that the surfactants could act as interaction links between hydrophilic and hydrophobic polymers [35–37]. Furthermore, the presence of surfactants in polymer nanocomposites not only increased the uniformity of the nanofillers dispersion [8], but also improved the compatibility and wettability between polymer and nanofiller [11], as well as enhanced the final properties of the nanocomposites [18].

In the past few decades, many modification methods have been suggested for the purpose of increasing the mechanico-thermal properties (e.g., tensile strength, flexural strength, impact strength, degradation temperature, glass transition temperature, melting temperature, etc.) of polymer nanocomposites. The non-covalent surface modification method, by utilizing surfactants, is an effective way to modify nanofillers for enhancing the mechanico-thermal properties of polymer nanocomposites. Nonetheless, to the authors' knowledge, no short review has been made covering the work on surfactant-modified inorganic and organic nanofillers for polymer nanocomposites. That is the aim of conducting a systematic review in this paper. This short review is broad, albeit not comprehensive, but is completed with other relevant literatures.

## 2. Types of Surfactant-Modified Polymer Nanocomposites

### 2.1. Surfactant-Modified Inorganic Nanofiller/Polymer Nanocomposites

Table 3 indicates the examples of inorganic nanofillers, surfactants, polymer matrices, and preparation processes of polymer nanocomposites. An inorganic filler, such as MMT, could be modified by a cationic surfactant, like HMAC, to produce organoclay (OMMT) [9]. OMMT was incorporated into PEVA via melt blending and compression molding processes for the preparation of OMMT/PEVA nanocomposites [9]. TiO<sub>2</sub> NRs have also been used for the preparation of polymer nanocomposites. TiO<sub>2</sub> NRs could be modified or capped by an anionic surfactant, such as OA, to prevent aggregation in solution [3]. The OA-capped TiO<sub>2</sub> NRs were mixed with PS solution via the solvent blending technique, followed by a drop casting process to prepare the TiO<sub>2</sub>/PS nanocomposites [3]. Other than clay mineral and metal oxide nanomaterials, the CNTs, G NPs, and GO NSs are also categorized as inorganic nanofillers. Although carbon is an organic material, the allotropes of carbon, such as CNTs, G NPs, and GO NSs, are considered as inorganic nanomaterials [38]. CNTs could be modified by a non-ionic surfactant, like Triton X-100, to improve dispersion in a PBO matrix [10]. CNT/PBO nanocomposites were prepared through solvent-free blending and pour casting processes at an elevated temperature [10].

**Table 3.** Examples of inorganic nanofillers, surfactants, polymer matrices, and preparation processes of polymer nanocomposites.

Inorganic Nanofiller	Surfactant	Polymer Matrix	Mixing Process	Final Process	References
MMT	HMAC	PEVA	Melt blending	Compression molding	[9]
TiO <sub>2</sub> NRs	OA	PS	Solvent blending	Drop casting	[3]
CNTs	Triton X-100	PBO	Solvent-free blending	Pour casting	[10]
CNFs	AK8805	DGEBA	Solution blending	Compression molding	[5]
G NPs	Triton X-100	SR	Solution blending	Compression molding	[11]
GO NSs	Triton X-100	DGEBA	Solution blending	Pour casting	[6]

CNFs are also regarded as an inorganic nanofiller due to their preparation procedure and structure, which are the same as in CNTs, but CNFs have a larger diameter than CNTs [25]. CNFs could be modified by a silicone surfactant, like AK8805, to improve the dispersion of CNFs in an epoxy matrix, such as DGEBA [5]. CNF/DGEBA nanocomposites were prepared through solution blending and compression molding processes at an elevated temperature [5]. On the other hand, G NPs could also be modified by Triton X-100 via sonication in the solvent [11]. Modified G NPs were mixed with an SR solution through the solution blending process, followed by a compression molding process for vulcanization to obtain G NP/SR nanocomposites [11]. In addition, Triton X-100 could treat GO NSs to promote dispersion in a DGEBA matrix [6]. GO NS/DGEBA nanocomposites could also be prepared by means of solution blending and pour casting processes [6]. Table 3 demonstrates that the surfactant-modified inorganic nanofiller/polymer nanocomposites could be prepared by using typical polymer composite processing procedures without requiring complicated or complex preparation processes.

## 2.2. Surfactant-Modified Organic Nanofiller/Polymer Nanocomposites

Table 4 indicates the examples of organic nanofillers, surfactants, polymer matrices, and preparation processes of polymer nanocomposites. Organic fillers, such as CNCs, could be modified by an anionic surfactant, like Bystostat A B09, to produce surfactant-modified CNCs (s-CNCs) [15]. The s-CNCs were mixed with PLA via solution blending and solvent casting processes for the preparation of s-CNC/PLA nanocomposites [15]. CNPs have also been used for the preparation of polymer nanocomposites. CNPs could be modified by a non-ionic surfactant, such as Span 60, to improve the dispersion of hydrophilic CNPs in a hydrophobic PS matrix [30]. Span 60-modified CNPs were mixed with a PS solution via the solution blending process, followed by a solvent casting process to prepare CNP/PS nanocomposites [30]. On the other hand, NCFs could be suspended in a silicon-based surfactant, such as Nixax L-595, with dispersant oils to facilitate the dispersion of NCFs in a PEVA matrix [8]. The NCF suspension was added to the PEVA through the melt blending process, followed by a compression molding process to obtain NCF/PEVA nanocomposites [8].

**Table 4.** Examples of organic nanofillers, surfactants, polymer matrices, and preparation processes of polymer nanocomposites.

Organic Nanofiller	Surfactant	Polymer Matrix	Mixing Process	Final Process	References
CNCs	Bystostat A B09	PLA	Solution blending	Solvent casting	[15]
CNPs	Span 60	PS	Solution blending	Solvent casting	[30]
NCFs	Nixax L-595	PEVA	Melt blending	Compression molding	[8]
CNWs	Pluronic	DGEBA	Solvent-free blending	Pour casting	[7]
NCFs	Ultraric PE 105	PBAT	Solution blending	Solvent casting	[19]
CNWs	PEGMONO	PLA	Solution blending	Solvent casting	[16]

In addition, Pluronic could treat CNWs to improve the interactions between the CNWs and the DGEBA epoxy [7]. CNW/DGEBA nanocomposites could be prepared by means of solvent-free blending and pour casting processes [7]. NCFs could also be modified by a non-ionic surfactant, like Ultraric PE 105, for promoting the interfacial interaction between the NCF and PBAT phases [19]. NCFs were mixed with the surfactant and PBAT via solution blending and solvent casting processes for the preparation of NCF/PBAT nanocomposites [19]. CNWs could also be modified by a non-ionic surfactant, such as PEGMONO, to improve CNW dispersion in a non-polar PLA matrix [16]. PEGMONO-modified CNWs were mixed with PLA solution via the solution blending process, followed by a solvent casting process to prepare CNW/PLA nanocomposites [16]. Table 4 demonstrates that the surfactant-modified organic nanofiller/polymer nanocomposites could mostly be prepared through a solvent casting process by using organic solvents.

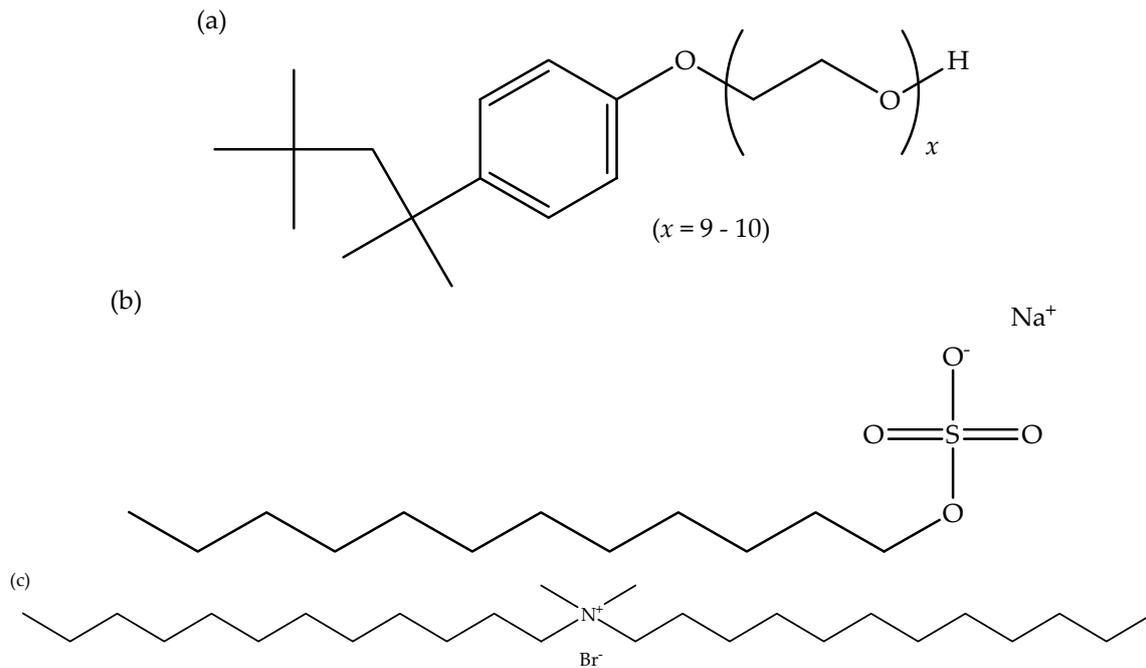
## 3. Effect of Surfactants on Mechano-Thermal Properties

### 3.1. Types of Surfactants

Surfactants have frequently been categorized into four types, namely non-ionic, anionic, cationic, and amphoteric. The categories are based on the polarity of the surfactant head group, for example, non-ionic, anionic, cationic, and amphoteric or zwitterionic. There is no charge on a head group of non-ionic surfactants, while anionic and cationic surfactants have negative and positive charges on their head groups, respectively. On the other hand, there are both negative and positive charges for the amphoteric surfactants [33]. Table 5 displays the types of surfactants, types of nanofillers, and modification methods for the preparation of polymer nanocomposites. Non-ionic surfactants, such as Triton X-100 (chemical structure showed in Figure 1a), could modify inorganic nanofillers like CNTs via an ultrasonication method to serve as a bridge between CNTs and DGEBA [24]. The NCF organic nanofiller could be modified with the non-ionic surfactant Ultraric PE 105 by mechanical stirring to improve the dispersion of NCFs in the nanocomposite [19].

**Table 5.** Types of surfactants, types of nanofillers, and modification methods for the preparation of polymer nanocomposites.

Surfactant	Type of Surfactant	Nanofiller	Type of Nanofiller	Modification Method	References
Triton X-100	Non-ionic	CNTs	Inorganic	Ultrasonication	[24]
Ultraric PE 105	Non-ionic	NCFs	Organic	Stirring	[19]
SDS	Anionic	G NPs	Inorganic	Ultrasonication	[21]
Beycostat A B09	Anionic	CNCs	Organic	Stirring	[18]
DDAB	Cationic	MMT	Inorganic	Agitation	[12]
HTAB	Cationic	CNCs	Organic	Stirring	[31]

**Figure 1.** Chemical structures of (a) Triton X-100, (b) SDS, and (c) DDAB.

An anionic surfactant, for example, SDS (chemical structure showed in Figure 1b), is commonly employed in the modification of inorganic nanofillers, such as G NPs, through an ultrasonication method to assist G NP dispersion in a PVA matrix [21]. The CNC organic nanofiller could be modified with the anionic surfactant Beycostat A B09 by mechanical stirring to obtain stable dispersions of CNCs in nanocomposites [18]. On the other hand, cationic surfactants, for instance, DDAB (chemical structure showed in Figure 1c), could be utilized for the modification of inorganic nanofillers, such as MMT, via an agitation process [12]. CNCs could be modified with the cationic surfactant HTAB, also by mechanical stirring, for the preparation of such nanocomposites [31]. Table 5 also exhibits that the non-ionic, anionic, and cationic surfactants could modify both inorganic and organic nanofillers without any limitations. However, the modification of nanofillers by amphoteric surfactants is not only complicated [39], but also limited to inorganic nanofillers, such as MMT [40,41].

### 3.2. Effect of Non-Ionic Surfactants

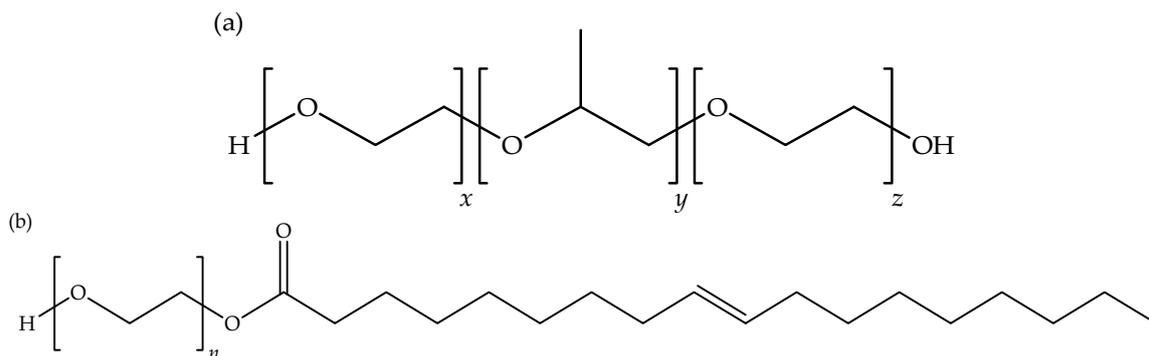
Table 6 shows the mechano-thermal properties of polymer nanocomposites modified by non-ionic surfactants. Pluronic (chemical structure showed in Figure 2a) could modify organic nanofillers like CNWs and modified CNWs have been used for the preparation of CNW/DGEBA nanocomposites [7]. The modification of CNWs has improved the mechano-thermal properties of the nanocomposites. The mechanical properties, such as tensile strength, tensile modulus, and elongation at break, of the nanocomposites have increased by up to 79%, 27%, and 77%, respectively, compared to the unmodified CNW/DGEBA nanocomposite. This is attributed to the improved dispersion and enhanced

interfacial interaction between the Pluronic-modified CNWs and the DGEBA matrix [7]. However, the degradation temperature of the nanocomposites decreased because of the presence of small aggregates of Pluronic-modified CNWs in the nanocomposites, which degraded easily in comparison with the large agglomerates. Furthermore, the glass transition temperature of the nanocomposites also decreased due to possible Pluronic micelle formation inside the DGEBA matrix [7].

**Table 6.** Mechano-thermal properties of polymer nanocomposites modified by non-ionic surfactants.

Non-ionic Surfactant	Nanofiller	Polymer Matrix	Mechanico-Thermal Properties *										References
			TS	TM	EB	FS	FM	IS	$T_d$	$T_g$	$T_m$	$T_c$	
Pluronic	CNWs	DGEBA	↑	↑	↑	-	-	-	↓	↓	-	-	[7]
PEGMONO	CNCs	PLA	↓	-	↓	-	-	-	↑	-	-	-	[14,16]
Triton X-100	CNTs	PBO	-	-	-	↑	↑	↑	-	↑	↑	-	[10]
AK8805	CNFs	DGEBA	↑	↑	-	-	-	↑	↑	↑	-	-	[5]
Triton X-100	G NPs	SR	↑	↑	↑	-	-	-	↑	-	↓	↓	[11]
Ultraric PE 105	NCFs	PBAT	↑	↑	-	-	-	-	↓	-	-	-	[19]

TS = tensile strength, TM = tensile modulus, EB = elongation at break, FS = flexural strength, FM = flexural modulus, IS = impact strength,  $T_d$  = degradation temperature,  $T_g$  = glass transition temperature,  $T_m$  = melting temperature, and  $T_c$  = crystallization temperature. \* The symbol  $\uparrow$  corresponds to an increase in the properties and  $\downarrow$  a decrease in the properties while “-” means “not available”.



**Figure 2.** Chemical structures of (a) Pluronic and (b) PEGMONO.

PEGMONO (chemical structure showed in Figure 2b) could modify organic nanofillers such as CNCs and modified CNCs have been utilized for the preparation of CNC/PLA nanocomposites [14]. The modification improved the maximum degradation temperature of the nanocomposites up to 0.6% compared to neat PLA [16]. This is attributed to the higher thermal stability of PEGMONO, which covered the surface of the CNCs and prevented the modified CNCs from decomposing quickly [14]. Nevertheless, the tensile strength of the nanocomposites decreased in comparison with the nanocomposite without PEGMONO; this is because of the presence of CNC/PEGMONO aggregates. Moreover, the elongation at break of the nanocomposites slightly decreased, as PEGMONO improved CNC interaction with the PLA matrix [14].

On the other hand, Triton X-100 could modify inorganic nanofillers like CNTs and modified CNTs have been applied for the preparation of CNT/PBO nanocomposites [10]. The modification of CNTs improved the mechano-thermal properties of the nanocomposites, such as flexural strength, flexural modulus, impact strength, glass transition temperature, and melting temperature. The flexural strength, flexural modulus, and impact strength increased by up to 31%, 10%, and 13%, respectively, compared to the unmodified CNT/PBO nanocomposite, which was due to strong hydrophobic attraction between the hydrophobic segment of Triton X-100 and the surface of the CNTs, whereas the hydrophilic segment of Triton X-100 interacted with the PBO matrix through hydrogen

bonding [10]; both interactions improved the wettability and reduced surface tension of the CNTs in the nanocomposites. Moreover, the glass transition temperature and melting temperature increased by up to 1.0% and 0.6%, respectively, which was also because of the improved interfacial interaction between the Triton X-100-modified CNTs and the PBO matrix, as well as the improved degree of dispersion of the modified CNTs in the nanocomposites [10].

AK8805 could modify inorganic nanofillers like CNFs and the modified CNFs have been used for the preparation of CNF/DGEBA nanocomposites [5]. The modification of CNFs improved the mechanico-thermal properties of the nanocomposites. The mechanical properties, such as tensile strength, tensile modulus, and impact strength, of the nanocomposites increased by up to 20%, 165%, and 15%, respectively, compared to the neat DGEBA, which was due to enhancement of the interaction between the modified CNFs and the DGEBA matrix [5]. Furthermore, the degradation temperature and glass transition temperature of the nanocomposites also increased by up to 4.5% and 2.7%, respectively, because of the better dispersion of CNFs caused by the enhanced interaction [5].

Triton X-100 could also modify inorganic nanofillers such as G NPs and modified G NPs have been utilized for the preparation of G NP/SR nanocomposites [11]. The modification of G NPs improved the tensile strength, tensile modulus, and elongation at break by up to 20%, 5.4%, and 22%, respectively. This is attributed to the capability of the surfactant to act as a bridge between the G NPs and the SR matrix, which subsequently improved the compatibility and wettability of the graphene platelets and this provided a good adhesion to the SR [11]. The maximum degradation temperature of the nanocomposites also improved by up to 3.0% due to the good Triton X-100-G NP/SR interface interaction that offered a better barrier effect [11]. Nonetheless, the melting temperature and crystallization temperature of the nanocomposites insignificantly decreased compared to the nanocomposite without Triton X-100 because of Triton X-100 does not link with the crystal structure.

On the other hand, Ultraric PE 105 could modify organic nanofillers like NCFs and modified NCFs have been applied for the preparation of NCF/PBAT nanocomposites [19]. The modification of NCFs slightly improved the mechanical properties of the nanocomposites, such as tensile strength and Young's modulus, by up to 8.9% and 4.4%, respectively, compared to the unmodified NCF/PBAT nanocomposite. The minor increase was probably related to the excess of Ultraric PE 105 in the nanocomposites, which influenced the exerted force on the nanocomposites [19]. Moreover, the degradation temperature of the nanocomposites decreased because Ultraric PE 105 has a lower molecular weight than PBAT, which consequently affected its thermal stability [19]. Table 6 clearly displays that the modification of inorganic and organic nanofillers by non-ionic surfactants improved the mechanico-thermal properties of the prepared polymer nanocomposites, regardless of the type of the non-ionic surfactant.

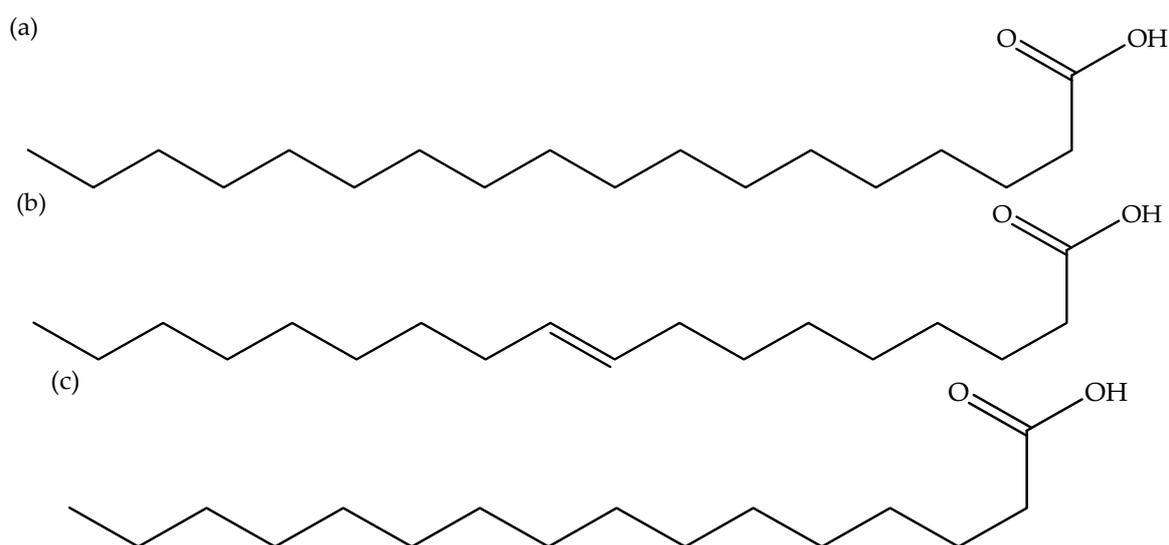
### 3.3. Effect of Anionic Surfactants

Table 7 shows the mechanico-thermal properties of polymer nanocomposites modified by anionic surfactants. SA (chemical structure showed in Figure 3a) could modify inorganic nanofillers like MMT and modified MMTs have been used for the preparation of MMT/PP nanocomposites [2]. The modification of MMT improved the mechanico-thermal properties of the nanocomposites. The mechanical properties, such as tensile strength, elongation at break, and impact strength, of the nanocomposites increased by up to 5.3%, 125%, and 50%, respectively. This is due to the dispersion state of SA-MMT being very good [2]. In contrast, the Young's modulus of the nanocomposites decreased because the tougher the composites, the less stiff their character. The melting temperature of the nanocomposites slightly increased by up to 1.0% due to the strengthening of mechanical properties of the nanocomposites. However, the crystallization temperature of the nanocomposites decreased compared to the nanocomposite without SA because of the very good dispersion of SA-MMT in the nanocomposites [2].

**Table 7.** Mechano-thermal properties of polymer nanocomposites modified by anionic surfactants.

Anionic Surfactant	Nanofiller	Polymer Matrix	Mechanico-Thermal Properties *										References
			TS	TM	EB	IS	SM	LM	$T_d$	$T_g$	$T_m$	$T_c$	
SA	MMT	PP	↑	↓	↑	↑	-	-	-	-	↑	↓	[2]
OA	TiO <sub>2</sub> NRs	PS	-	-	-	-	↓	↑	↑	↓	-	-	[3]
PA	LDHs	PCL	↓	↑	-	↑	↑	↑	-	↓	↓	↑	[22]
SDS	HNTs	PS	-	-	-	↑	↑	-	↑	↓	-	-	[4]
Beycostat A B09	CNCs	PLA	↑	↑	↓	-	-	-	↓	↓	↓	↓	[18]
SDS	G NPs	PVA	↑	↑	↑	-	-	-	↑	-	↓	↑	[21]

TS = tensile strength, TM = tensile modulus, EB = elongation at break, IS = impact strength, SM = storage modulus, LM = loss modulus,  $T_d$  = degradation temperature,  $T_g$  = glass transition temperature,  $T_m$  = melting temperature, and  $T_c$  = crystallization temperature. \* The symbol  $\uparrow$  corresponds to an increase in the properties and  $\downarrow$  a decrease in the properties while “-” and  $\updownarrow$  mean “not available” and “unchanged”, respectively.

**Figure 3.** Chemical structures of (a) SA, (b) OA, and (c) PA.

OA (chemical structure showed in Figure 3b) could modify inorganic nanofillers, such as TiO<sub>2</sub> NRs, to prevent the agglomeration of TiO<sub>2</sub> NRs and modified TiO<sub>2</sub> NRs have been utilized for the preparation of TiO<sub>2</sub> NR/PS nanocomposites [3]. The modification of TiO<sub>2</sub> NRs improved the loss modulus of the nanocomposites by up to 22% compared to neat PS. This is attributed to the PS chains becoming softer due to the presence of OA-modified TiO<sub>2</sub>. [3]. Moreover, the glass transition temperature of the nanocomposite decreased because of the soft PS chains caused by the OA molecules. In addition, the storage modulus of the nanocomposite decreased due to the plasticization effect of OA, which is present at the TiO<sub>2</sub> NR surface [3]. Nevertheless, the maximum degradation temperature of the nanocomposites increased by up to 1.3% because the thermal stability of the TiO<sub>2</sub> NRs was more than 400 °C.

On the other hand, PA (chemical structure showed in Figure 3c) could modify inorganic nanofillers like LDHs and modified LDHs have been applied for the preparation of LDH/PCL nanocomposites [22]. The modification of LDHs improved the mechano-thermal properties of the nanocomposites, such as tensile modulus, impact strength, storage modulus, and crystallization temperature. The tensile modulus and impact strength properties increased by up to 12% and 65%, respectively, compared to the neat PCL, which was due to the reinforcement property of the PA-modified LDHs (PA-LDHs), and they could also act as an impact strength modifier in the nanocomposite system. Moreover, the storage

modulus of the nanocomposites increased by up to 9.1%, which was because of a favorable dispersion and interaction between the PA-LDH nanofiller and the PCL matrix [22]. The loss modulus of the nanocomposites also increased by up to 10% due to the plasticizing effect of the PA-LDHs. Additionally, the crystallization temperature of the nanocomposites increased by up to 3.0%, which could possibly be attributed to the PA-LDHs, which acted as heterogeneous nucleation sites in the PCL matrix. However, the tensile strength of the nanocomposites decreased because of the presence of tactoids at a high content of PA-LDHs, which may act as stress concentrations [22]. In addition, the glass transition temperature of the nanocomposites also decreased due to improved PCL chain mobility, and it is probable that it would enhance in free volume.

SDS could modify inorganic nanofillers such as HNTs and modified HNTs have been used for the preparation of HNT/PS nanocomposites [4]. The modification of HNTs improved the mechanico-thermal properties of the nanocomposites. The mechanical properties, for example, impact strength and storage modulus, increased by up to 203% and 39%, respectively, with the addition of HNTs compared to neat PS. This is because the HNTs could improve of the stiffness of the nanocomposites [4]. Furthermore, the degradation temperature of the nanocomposites also increased by up to 14% due to the entrapment of decomposition products by the HNT lumen. Nonetheless, the glass transition temperature of the nanocomposites decreased because of the presence of interactions between the HNTs and PS [4].

Beycostat A B09 could modify organic nanofillers like CNCs and modified CNCs have been utilized for the preparation of CNC/PLA nanocomposites [18]. The modification of CNCs improved the mechanical properties of the nanocomposites, such as tensile strength and tensile modulus. The tensile strength and tensile modulus increased by up to 63% and 50%, respectively, which was attributed to the Beycostat A B09 efficiently dispersing CNCs in the PLA matrix [18]. However, the decrease in the elongation at break of the nanocomposites was due to the CNCs initiating considerable local stress concentrations and then failure at lowered strain values. Moreover, the decrease in crystallization temperature was because of the presence of Beycostat A B09 on the CNC surface, which caused a better dispersion of the CNCs in the PLA matrix, which certainly increased the nucleation effect on the nanocomposites [18]. Nonetheless, the other thermal properties, for instance, the glass transition temperature and melting temperature, decreased insignificantly compared to the nanocomposite without Beycostat A B09.

On the other hand, SDS could also modify inorganic nanofillers like G NPs and modified G NPs have been applied for the preparation of G NP/PVA nanocomposites [21]. The modification of G NPs improved the mechanical properties of the nanocomposites, such as tensile strength and tensile modulus, by up to 75% and 154%, respectively, compared to neat PVA. The substantial increases were due to the SDS aiding the dispersion of G NPs, which maximized the load transfer from PVA to the G NPs. Moreover, the elongation at break of the nanocomposites also increased by up to 53% because of the slippage of the intercalated state of G NP dispersion in the PVA matrix during tensile testing [21]. Additionally, the degradation temperature and crystallization temperature of the nanocomposites also increased by up to 0.8% and 1.6%, respectively, even at a low content of SDS-modified G NPs. This due to a heterogenous nucleating effect, which was caused by the adsorption of SDS into the G NPs [21]. Nevertheless, the melting temperature of the nanocomposites decreased, which was related to the decrease in their degree of crystallinity. Table 7 clearly displays that the modification of inorganic and organic nanofillers by anionic surfactants improved the mechanico-thermal properties of the prepared polymer nanocomposites, regardless of the type of anionic surfactant.

#### 3.4. Effect of Cationic Surfactant

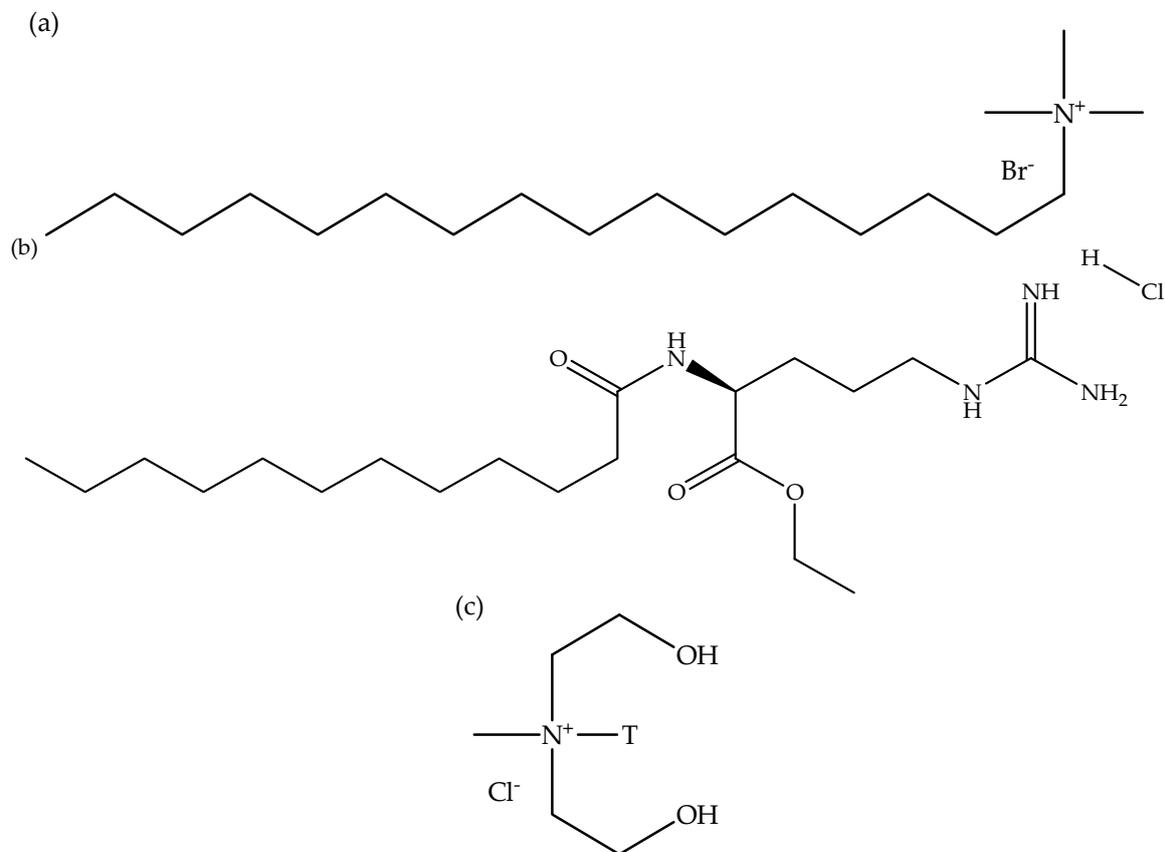
Table 8 shows the mechanico-thermal properties of polymer nanocomposites modified by cationic surfactants. HTAB (chemical structure showed in Figure 4a) could modify inorganic nanofillers like MMT and modified MMTs have been used for the preparation of MMT/PBS nanocomposites [20]. The modification of MMT improved the mechanico-thermal properties of the nanocomposites. The mechanical properties, such as tensile strength, tensile modulus, elongation at break, flexural

strength, flexural modulus, and impact strength, of the nanocomposites increased by up to 34%, 7.3%, 210%, 34%, 3.6%, and 66%, respectively, compared to the unmodified MMT/PBS nanocomposite. This is due to the presence of trimethyl groups in HTAB that eased the MMT dispersion and offered a better reinforcement effect. Additionally, the high aspect ratio of HTAB-modified MMTs provided a higher surface area to interact with the PBS matrix [20]. Furthermore, the melting temperature also improved by up to 2.3% because of the higher degree of crystallinity of the nanocomposites. In addition, the crystallization temperature also increased by up to 6.5% due to the improved modified MMTs and the PBS matrix interactions and better filler dispersion [20].

**Table 8.** Mechano-thermal properties of polymer nanocomposites modified by cationic surfactants.

Cationic Surfactant	Nanofiller	Polymer Matrix	Mechano-Thermal Properties *											References
			TS	TM	EB	FS	FM	IS	SM	$T_d$	$T_g$	$T_m$	$T_c$	
HTAB	MMT	PBS	↑	↑	↑	↑	↑	↑	-	-	-	↑	↑	[20]
LAE	CNCs	PLA	↑	↑	↑	-	-	-	↑	-	↑	↑	↓	[29]
HMAC	MMT	PEVA	-	-	-	-	-	-	↑	-	-	↓	↓	[9]
HTAB	G NPs	PUA	-	-	-	-	-	-	↑	↑	↑	-	-	[13]
BHHB	MMT	HDPE	↑	↑	↓	-	-	-	↑	↑	-	-	-	[1]
DDAB	MMT	PS	↑	↑	↑	-	-	-	-	↑	-	-	-	[32]

TS = tensile strength, TM = tensile modulus, EB = elongation at break, FS = flexural strength, FM = flexural modulus, IS = impact strength, SM = storage modulus,  $T_d$  = degradation temperature,  $T_g$  = glass transition temperature,  $T_m$  = melting temperature, and  $T_c$  = crystallization temperature. \* The symbol  $\uparrow$  corresponds to an increase in the properties and  $\downarrow$  a decrease in the properties while “-” means “not available”.



**Figure 4.** Chemical structures of (a) HTAB, (b) LAE, and (c) HMAC.

LAE (chemical structure showed in Figure 4b) could modify organic nanofillers such as CNCs and modified CNCs have been utilized for the preparation of CNC/PLA nanocomposites [29]. The modification of CNCs increased the tensile strength, Young's modulus, and strain at break by up to 91%, 78%, and 58%, respectively. This could probably be attributed to the result of improved crystallinity and the enhanced dispersion/interface compatibility of LAE-modified CNCs within the PLA matrix. Additionally, the storage modulus of the nanocomposites increased by up to 69%; this could be associated with the creation of a stiff continuous modified CNC percolation network and the modified CNCs, which prompted the limitation of the PLA chain movement [29]. Furthermore, the glass transition temperature and melting temperature also improved by up to 15%, and 1.4%, respectively, due to the increased modified CNC dispersion and interface compatibility, which efficiently restricted the movement of PLA chains. In contrast, the crystallization temperature of the nanocomposites decreased compared to the nanocomposite without LAE because of the strong nucleating effect of modified CNCs, which promoted crystallization [29].

On the other hand, HMAc (chemical structure showed in Figure 4c) could modify inorganic nanofillers like MMT and modified MMTs have been applied for the preparation of MMT/PEVA nanocomposites [9]. The modification of MMT improved the mechanical properties of the nanocomposites, such as storage modulus. The storage modulus of the nanocomposites increased by up to 340%, due to strong HMAc-modified MMT and PEVA interactions compared to the nanocomposite without HMAc [9]. However, the melting temperature of the nanocomposites decreased due to the presence of HMAc, which offered interactions between the modified MMTs and the PEVA matrix [9]. Moreover, the crystallization temperature of the nanocomposites also decreased because the crystallization kinetics were altered by modified MMTs, which diminished the crystal perfection of the PEVA matrix.

HTAB could also modify inorganic nanofillers like G NPs and modified G NPs have been used for the preparation of G NPs/PUA nanocomposites [13]. The modification of G NPs improved the mechanico-thermal properties of the nanocomposites. The storage modulus of the nanocomposites increased by up to 104% compared to the neat PUA; this could be attributed to a high aspect ratio of HTAB-modified G NPs with high surface areas dispersed evenly in the PUA matrix and forming strong interfacial interactions with the matrix via hydrogen bonding [13]. Furthermore, the degradation temperature of the nanocomposites improved by up to 23% due to the high thermal stability of modified G NPs that acted as an efficient physical barrier, which hindered thermal decomposition by slowing down the vaporization of volatile molecules. Moreover, the glass transition temperature of the nanocomposites also increased by up to 554% because of the physical barrier effect of the crumpled modified G NPs, which induced mechanical interlocking with PUA chains, and subsequently confined segmental movements at the modified G NP–PUA interface [13].

BHBB could modify inorganic nanofillers such as MMT and modified MMTs have been utilized for the preparation of MMT/HDPE nanocomposites [1]. The modification of MMT improved the tensile strength and Young's modulus by up to 31% and 66%, respectively, compared to the neat HDPE; this is attributed to the homogeneous distribution and a large aspect ratio of BHBB-modified MMTs that induced the strong interfacial interaction between modified MMTs and the HDPE matrix for better interfacial stress transfer efficiency. Nonetheless, the elongation at break of the nanocomposites significantly decreased because of the cross-section of HDPE resisted deformation, which was efficiently reduced by the modified MMTs [1]. The storage modulus of the nanocomposites increased by up to 99% because an interconnected network of modified MMTs within the HDPE matrix formed, which restricted the long-range movement of HDPE chains. Moreover, the degradation temperature of the nanocomposite improved by up to 5.3% because the modified MMTs acted as a mass transport barrier to the volatile products generated during thermal decomposition [1].

On the other hand, DDAB could also modify inorganic nanofillers like MMT and modified MMTs have been applied for the preparation of MMT/PS nanocomposites [32]. The modification of MMT improved the mechanical properties of the nanocomposites, such as tensile strength, Young's modulus,

and elongation at break, by up to 32%, 30%, and 18%, respectively, compared to the unmodified MMT/PS nanocomposite. The increases were related to the exceptional dispersion of DDAB-modified MMTs in the PS matrix and the remarkable adhesion between the modified MMTs and the PS [32]. Moreover, the degradation temperature of the nanocomposites also increased by up to 7.1%, possibly because DDAB, with two long alkyl chains, could provide outstanding thermal stability [32]. Table 8 clearly displays that the modification of inorganic and organic nanofillers by cationic surfactants has improved the mechanico-thermal properties of the prepared polymer nanocomposites, regardless of the type of the cationic surfactant.

### 3.5. Effect of Surfactants on Thermal Conductivity

Table 9 displays the effect of different types of surfactants on the thermal conductivity of polymer nanocomposites. The thermal conductivity of G NP/SR nanocomposites increased by up to 14% when the G NPs were modified with Triton X-100. The increase is due to the modified G NPs that have a good dispersion and good interface in the nanocomposites [11]. The thermal conductivity of CNT/PS nanocomposites increased by up to 202% when the CNTs were modified with a non-ionic surfactant, such as PEG (chemical structure showed in Figure 5a). The increase is because the modified CNTs have a more even dispersion character, which was acquired through ultrasonic dispersion with PEG [42]. The thermal conductivity of CNT/SR nanocomposites increased by up to 38% when the CNTs were modified with an anionic surfactant like DBSA (chemical structure showed in Figure 5b). The increase is because the modified CNTs have a good homogeneity, which creates a large interface area with SR [43].

On the other hand, the thermal conductivity of CNT/TPU nanocomposites increased by up to 2971% when the CNTs were modified with an anionic surfactant, such as SC (chemical structure showed in Figure 5c). The increase is because the modified CNTs were smaller and had a fine distribution that generated effective interactions with the TPU matrix [44]. The thermal conductivity of EG NP/PEVA nanocomposites increased by up to 137% when the EG NPs were modified with SDS. The increase is because the modified EG NPs have a better dispersion, which formed the constant EG NP pathways [45]. The thermal conductivity of GO NS/EDTS nanocomposites increased by up to 404% when the GO NSs were modified with HTAB. The increase is because the modified GO NSs formed a thin, finely dispersed layer, which created an uninterrupted heat flux pathway and interacted with the EDTS matrix [46]. Table 9 clearly shows that the modification of inorganic nanofillers by non-ionic, anionic, and cationic surfactants has increased the thermal conductivity of the prepared polymer nanocomposites.

**Table 9.** Effect of different types of surfactants on the thermal conductivity of polymer nanocomposites.

Surfactant	Nanofiller	Polymer Matrix	Thermal Conductivity	References
Triton X-100	G NPs	SR	↑ (14%)	[11]
PEG	CNTs	PS	↑ (202%)	[42]
DBSA	CNTs	SR	↑ (38%)	[43]
SC	CNTs	TPU	↑ (2971%)	[44]
SDS	EG NPs	PEVA	↑ (137%)	[45]
HTAB	GO NSs	EDTS	↑ (404%)	[46]

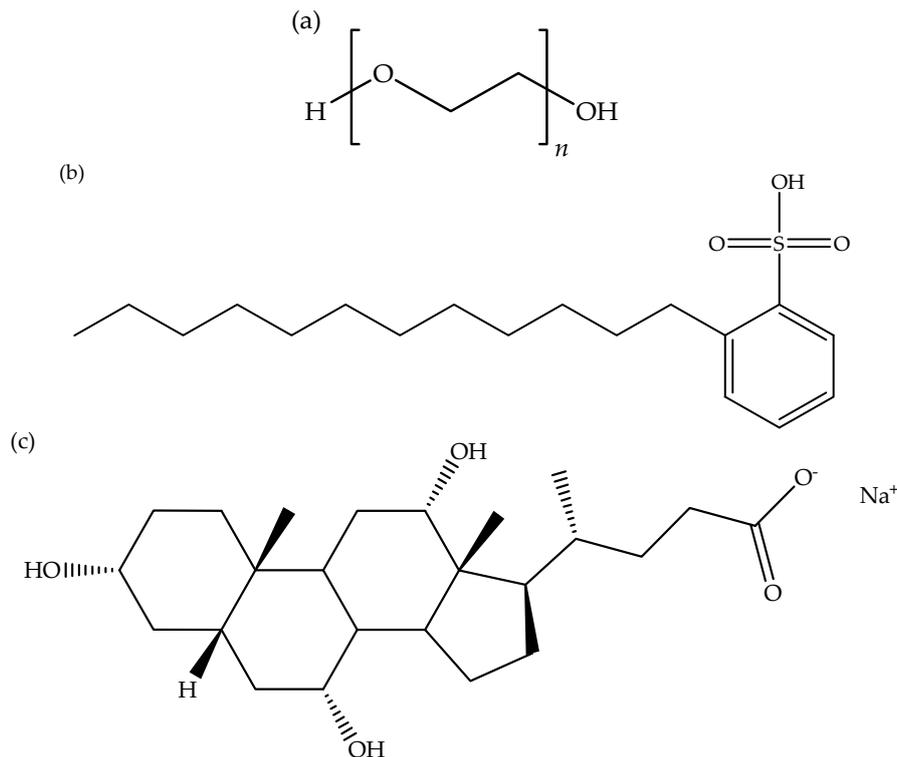


Figure 5. Chemical structures of (a) PEG, (b) DBSA, and (c) SC.

#### 4. Conclusions

Nanofillers, polymer matrices, preparation procedures, and the mechanico-thermal properties of polymer nanocomposites modified with surfactants have been briefly reviewed in this paper. The primary mechanico-thermal properties, for instance, tensile strength, flexural strength, impact strength, degradation temperature, glass transition temperature, and the melting temperature of the nanocomposites, have also been described in this short review. Surfactants have regularly been applied for the modification of nanofillers because they possess an amphiphilic character. Surfactants utilized for different types of polymer nanocomposites are mostly based on their chemical structures. In addition, non-ionic, anionic, and cationic surfactants have been the three most significant surfactants for the improvement of the mechanico-thermal properties of polymer nanocomposites. Non-ionic surfactants are typically used in the modification of organic nanofillers, such as nanocelluloses. Anionic and cationic surfactants are frequently employed in the modification of inorganic nanofillers, like metal oxides, MMT, etc. The proper modification of nanofillers by surfactants could improve the dispersion of the nanofillers in the polymer matrices. Moreover, the surfactant-modified inorganic and organic nanofillers could effectively form strong interactions between the nanofillers and the polymer matrices. This short review might be beneficial, not only for polymer composite researchers, but also be useful for the commercialization of polymer nanocomposites for various applications.

**Author Contributions:** Conceptualization, A.A.S. and S.N.A.M.J.; methodology, A.A.S.; validation, A.A.S. and S.N.A.M.J.; formal analysis, S.N.A.M.J.; investigation, A.A.S.; resources, S.N.A.M.J.; data curation, A.A.S.; writing—original draft preparation, A.A.S.; writing—review and editing, S.N.A.M.J.; project administration, A.A.S.; funding acquisition, S.N.A.M.J. All authors have read and agreed to the published version of the manuscript.

**Funding:** This short review was funded by the Universiti Putra Malaysia under the Grant Putra IPM Scheme (project number: GP-IPM/2017/9579900).

**Acknowledgments:** The authors would like to thank the Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia.

**Conflicts of Interest:** The authors declare no conflict of interest. The funder had no role in the design of the review; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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