



Effects of Maize-cobs Nanofiber on Mechanical and Morphological Properties of HDPE/ HD-g-MAH / Org-MMT Nanocomposites

Jamila Baba Ali¹ Abdullahi Danladi¹, Musa Muhammad Bukhari¹, Paul Mamza², Zurina Binti Mohamad³

¹ Faculty of Engineering, Department of Polymer and Textile Engineering,

Ahmadu Bello University, P.M.B 1044 Samaru, Zaria, Kaduna State, Nigeria.

² Department of Chemistry, Ahmadu Bello University, P.M.B 1044 Samaru, Zaria, Nigeria.

³ Faculty of Engineering, School of Chemical and Energy Engineering,
Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.

Abstract

The objective of this research was to investigate the potential of waste biomass residue as reinforcement for polymers to produce composites as an alternative to synthetic fillers. Bio nanocomposites were produced using Sammaz-14 variety maize cobs Nano cellulose (MC-NF)/High Density Polyethylene (HDPE) / high-density polyethylene grafted maleic anhydride (HD-g-MAH) / organic montmorillonite (Org-MMT). The nanocomposites were compounded with a two-roll mill and fabricated using the injection molding machine. The mechanical (Tensile strength, tensile modulus, and Flexural strength, Flexural modulus), as well as morphological (FE-SEM) properties of the biocomposites, were investigated. The effect of the addition of 1-5% of MC-NF with 2 wt % of Org-MMT and 3% maleic anhydride grafted polyethylene in HDPE were studied. From the results, 2% of Org-MMT was enough to improve the exfoliation and dispersion of the filler in the matrix and 3% incorporation of HD-g-MAH increased the adhesion and reduce the surface tension between the fiber and matrix. hence, creating excellent interfacial adhesion within the composite's structures, the tensile strength and modulus increased from 19.18 MPa for pure HDPE to 20.24 Mpa (5.5%) at 5 % MC-NF filler loading and stiffness (modulus of elasticity) increased up 52%. Flexural strength and modulus increased from 15.57Mpa for pure HDPE to 17.99 MPa (18.60%) at 5% filler loading and Flexural modulus also increased from 1.99MPa to 2.27MPa (14.07%). The addition of MC-NF improves the mechanical properties up 3% after which the strength starts declining but stiffness steadily increased up to 5% filler loading.

Keywords: Bio Nanocomposites, High-Density Polyethylene, HD-g-MAH, Maize cob Nano Cellulose, Organic Montmorillonite.

1. Introduction

With an increasing demand for high-performance structural materials, recently, research has been focused on manufacturing materials with enhanced properties that have insignificant or no changes in the production materials, the processes of production, and the quality of products. In an attempt to achieve the aforementioned objectives, researchers and industries are investigating various areas of utilizing bio-composites with different natural fibers and additives. In the past decade, there have been many exertions to produce agro-based fiber composites to replace other non-biodegradable or synthetic products (Naveen et al.,2019). Use of natural fiber in composites has recently gained more attention because of its biodegradability and recyclable, low cost, availability, abundance, low density, acceptable properties, ease of production, among others. These natural fibers produce better mechanical strength when used with thermosets, elastomers or thermoplastics. The overall



properties of particulate filled polymer composites very much depends on the nature and treatments applied on the fibre, particles size and type, particle-matrix interfacial bonding, and particle loading (Jai et al.,2018).

High-density polyethylene is the most commonly used commodity polymer after polypropylene and LDPE, HDPE does not contain any polar groups in its structure, as such, uniform distribution of the fibers in HDPE may not be accomplished. thus, to achieve compatibility, it is crucial to add a compatibilizer which will initiate interaction between the hydrophilic and hydrophobic phases thus, increasing interfacial bonding between the filler and matrix, reduce the interfacial tension and improve dispersion and homogeneity within the structure (Araujo et al.,2008).

Montmorillonite is the widely used nano clay with polymers. It belongs to the Smectite family with 2:1-layer type i.e (it contains two tetrahedral sheets and one octahedral sheet) and 0.5-12-layer charge. The silicate layers are connected by weak dipole and van der Waals forces. Na⁺ or Ca²⁺ dwelling in the interlayers can be exchanged by organic cations such as trimethylammonium stearyl ions through ion-exchange reaction to make the hydrophilic-layered silicate organo-modify to permit it compatibility with polymers Faheem Uddin (2018).

The interfacial properties of the polymeric composites can be inciting to better interfacial adhesion/bonding through the use of compatibilizers. Compatibilizers can react with hydroxyl group in natural fibres and the polymers by providing a connection across the interface. Studies of the effect of PE-g-MAH in fiber reinforced composites have been reported by Leila et al.,2019) they reported an increase in the tensile strength and Young's modulus of composites with the addition of PE-g-MAH.

Bio-based nanoparticles (CNPs) have a wide area of applications because cellulose materials can assemble themselves into a defined structure in multiple scales from macro to nano. Its abundance, high strength and stiffness, low weight/density, biodegradability, recyclability and non-toxicity are some unique properties of cellulosic materials which make them promising candidates for use in bio-composite production (Mochane et al.,2018)

Maize cob is abundant, it has high strength and stiffness, low weight, and biodegradable, it is non-toxic, cheap, readily available, easy processable. These useful features make it an attractive or valuable useful biomass for various applications. The use of maize cob in the area of composites has seldom been reported. However, (Moreno et al.,2018; Suresh et al.,2020) among others have reported on its use in composites.

The objectives of this study are to fabricate bio nanocomposites with high-density polyethylene, maize cob nano cellulose, 3% PE-G-MAH, and 2% Org-MMT, to investigate the effect of the MC-NF in 2% of Org-MMT and determine the mechanical and morphological properties of these biocomposites.

2. Materials and Methodologies

Materials used

Nano clay (Org-MMT) 0.885 g/cm³, surface modified with trimethyl ammonium stearyl purchased from sigma Aldrich Germany, Maize cobs (SAMMAZ-14 Maize cob variety) obtained from Institute for Agricultural Research, Federal Ministry of Agriculture and Rural Development. Ahmadu Bello University, Zaria-Nigeria, Maize cob nano cellulose (isolated by NaOH pre-treatment followed by ball milling with 86 ± 15 nm which has an onset temperature of 281 oC and degradation temperature of 386 oC, Polyethylene (HDPE) grade no: H16178-M170306D and HD-g-MAH (Orevac 18360) purchased from Lotte Chemicals, Johor Malaysia.

Methodologies

Table 1. Composite Formulations

S/ N	HDPE (wt.%)	MC- NF (wt.%)	HD-g- MAH (wt.%)	Org- MMT (wt.%)
1	100	0	0	0
2	94	1	3	2
3	93	2	3	2
4	92	3	3	2
5	91	4	3	2
6	90	5	3	2

Composites Preparation

Interfacial compatibility between polymer matrices (HDPE & grafted copolymer PE-g-MAH) and nanofiber (MC-NF) is critically important for manipulating nanostructure and various properties of the polymer biocomposites, hence, the need for proper compounding of these materials to achieve a good dispersion of the fillers in the matrix. However, mechanical properties significantly depend on the dispersion of fillers particles in the polymer. In this research, maize cob nano fiber (MC-NF) was utilized as functional reinforcing filler, Org-MMT was used as an additive to modify the properties of the matrix and enhanced the dispersion of the fillers in the matrix whereas, the PE-g-MAH was incorporated as a compatibilizer whose role is to create linkage or site for interaction/bonding between the phases i.e fibre and polymer and hence, provide fibre/matrix interfacial adhesion.

Compounding/Mixing

The mixing was carried out in an open mixer, using two-roll-mill with 150g capacity at a temperature of 190 oC with a roller nip distance of 1.4mm. Melting 12g HD-g-MAH /10 min and 17g HDPE/ 10 min at a roller speed of 60 rpm for 20 min.

Crushing/Granulating

Plastic granulator SLM, 50 FY (Wenzhou Zhingang co. Ltd China) was used for crushing the compounded samples to a smaller size, suitable for use on the mini plastic injection molding machine. The granulated or crushed samples were fabricated using the Nissei horizontal injection molding machine in the polymer processing lab Universiti Tun Hussein Onn Malaysia.

Fabrication/ Injection Moulding

The crushed samples in the form of pellets were fed into the Nissei horizontal Injection Molding machine whose temperature was set at 140 oC, 160 oC and 190oC, (for the hopper, barrel i.e heating and mixing chamber and the nozzle temperature respectively) after a complete cycle, the molded samples were ejected from the mold cavity by the pins. Molding was carried out in a semi-automatic mode, the complete processes happened in approximately 10min/cycle. The fabricated samples were conditioned according to ISO 291 before the characterization.

Characterization

Mechanical testing: Tensile tests were done using the universal tensile testing machine which was loaded with 5KN at room temperature according to ISO 527-2, with a crosshead speed of 2mm/min. An average of five (5) samples were analyzed and results were recorded accordingly.

Flexural tests or the three-point bending test was conducted according to ISO 178:2003. The Universal Material Testing Machine was loaded with a 10KN load cell. Five (5) rectangular beam samples were tested at a

support span length of 70mm, the width 9.5mm and thickness of 4.5 were measured and used correctly according to standard at room temperature.

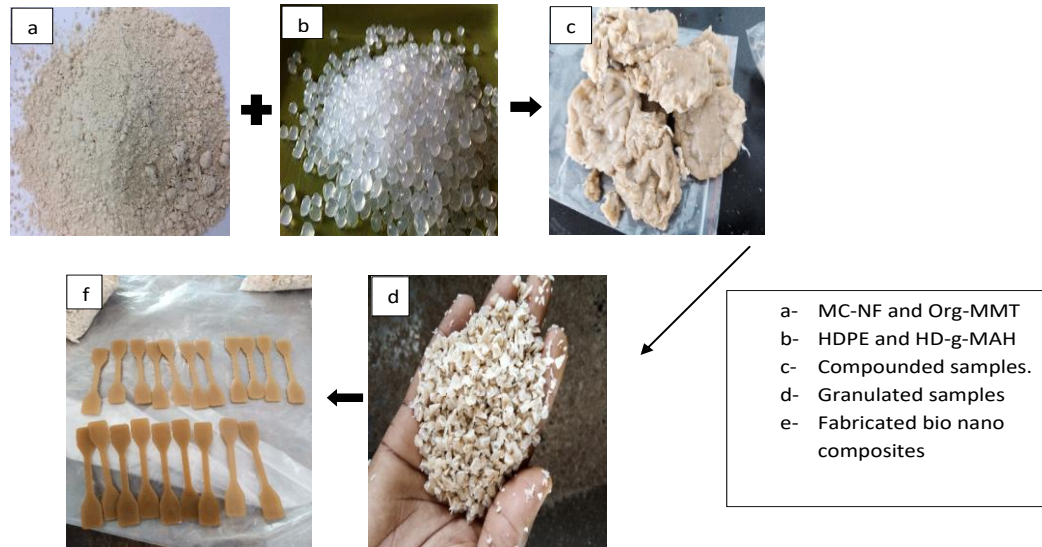


Figure 1. Graphical presented of the fabrication processes

Field emission electron microscopy (FE-SEM): The fabricated bio nanocomposites were examined using a field emission scanning electron microscope (FE-SEM). The sample of about 0.5x0.5cm was carefully placed on the aluminium stub, which has a double-sided adhesive carbon tape. Samples were coated with a layer of platinum using an automated platinum sputter coater. The analysis was performed at an accelerating voltage of 5 kV with a working distance of 4 mm. The micrographs were taken at different magnifications and are shown in figure 6.

3. Results and Discussion

Mechanical tests

Tensile Strength and Tensile Modulus

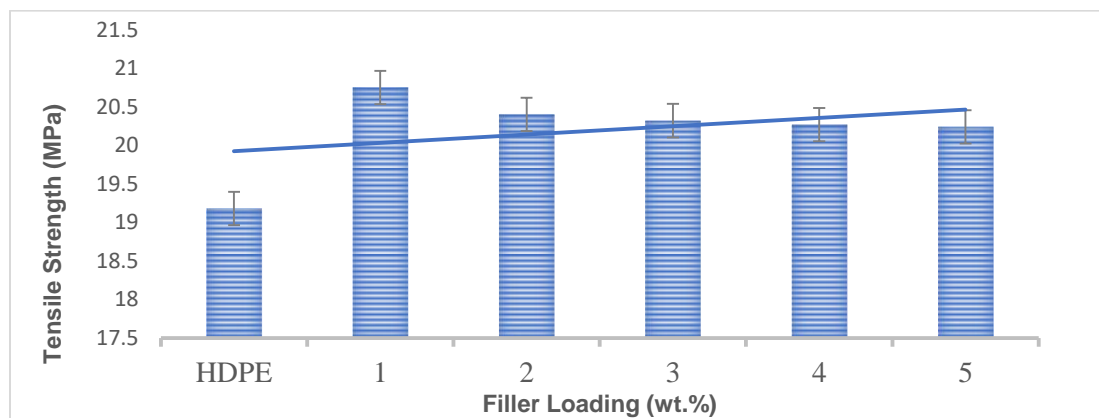


Figure 2. Tensile Strength against filler loadings for HDPE/MC-NF/Org-MMT/HD-g-MAH bio nano composites

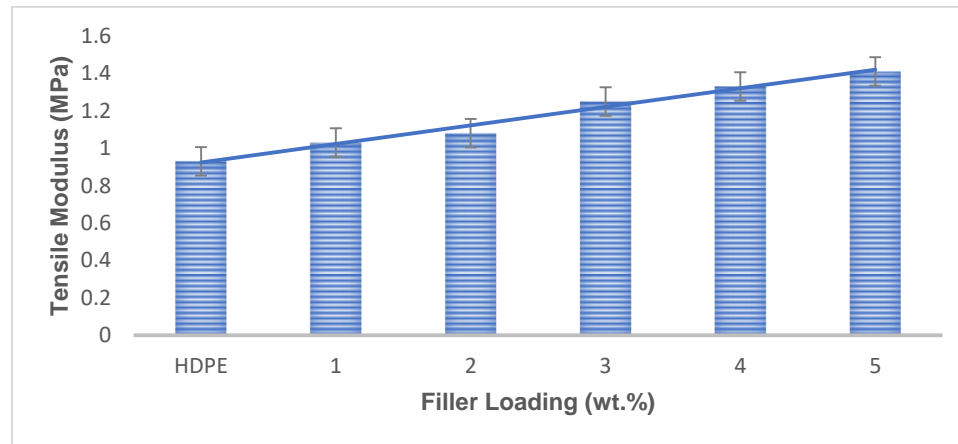


Figure 3. Tensile Modulus against filler loadings for HDPE/MC-NF/Org-MMT/HD-g-MAH bio nano composites

The most important factors affecting the properties of fiber-reinforced composites are the polymer/polymer interfacial tension, fiber/ matrix interfacial bonding/ adhesion, these are determined by several factors such as the nature of the polymer, fiber components/properties, the processing and fabrication methods, product design and fiber treatments i.e, chemical or mechanical treatments (Kamarudin et al.,2018).

In this study, the Tensile strength, the tensile modulus was studied and the results are depicted above in Figures 2 and 3. From the results above, it was observed that the tensile strength and tensile modulus or modulus of elasticity significantly increased as the filler loading (MC-NF) increased in HDPE. It was found that, by adding 1%, 2%,3%,4% and 5% of MC-NF in 2% Org-MMT/ 3% HD-g-MA in HDPE, the tensile strength of bio nanocomposites increased with 8.2%,6.4%,5.6% and 5.5% respectively and stiffness (modulus of elasticity) increased up 52% at 5% filler loading. The increase in tensile strength and modulus shown by the fabricated bio nano composites compared to the neat HDPE could be attributed to the nucleating effect of PE-g-MA, which may have created strong interfacial adhesion and also reduced interfacial tension between the fillers and matrices. PE-g-MAH as a grafted copolymer has been used effectively as a compatibilizer in polymer composites because of the three (3) hydrogen bond acceptor sites in maleic anhydride (MAH) which makes it easy to interact/ link and bond with cellulosic fibers which has abundant of hydrogen (Zhai et al.,2004; Fatimah et al.,2015; Adamu et al.,2020) Hence, creating dispersion, adhesion, and compatibility between systems containing a hydrophilic filler and hydrophobic polymer.

Manjunath et al.,2017; Mohamed et al.,2018, reported Similar findings of an increase in tensile strength and modulus with the addition of 1-3% of MMT, they attributed these improvements to the good dispersion and strong interfacial adhesion between the materials. From the results in figure 2 and 3, Org-MMT served as an additive which has modify the properties of these nanocomposites by improving the dispersion and overall strength of the material. This however, proves that the nano composites will be able to withstand/ resist more stretching and pulling before rupturing compared to the neat HDPE.

Flexural Strength and flexural Modulus

Figure 4 and 5 above showed the results for flexural strengths of HDPE/MC-NF nano composites. The flexural strength for pure HDPE is 15.57MPa, while those for its composites were higher and increases with addition of filler.

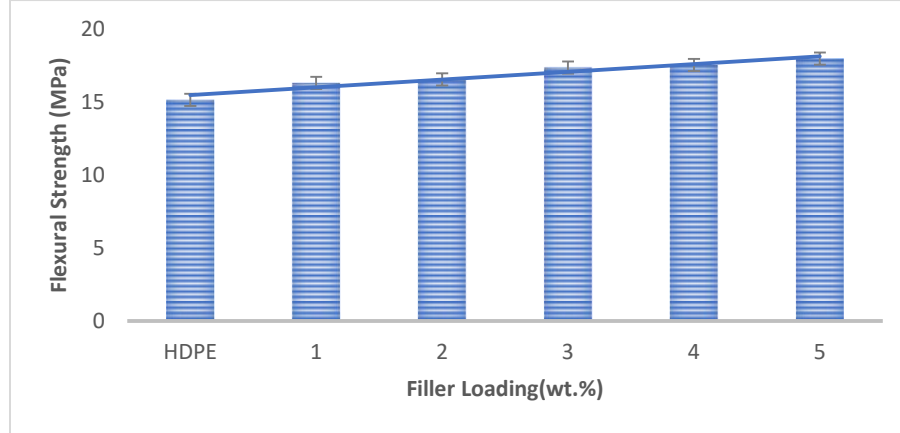


Figure 4. Flexural Strength against filler loadings for HDPE/MC-NF/Org-MMT/HD-g-MAH bio nano composites

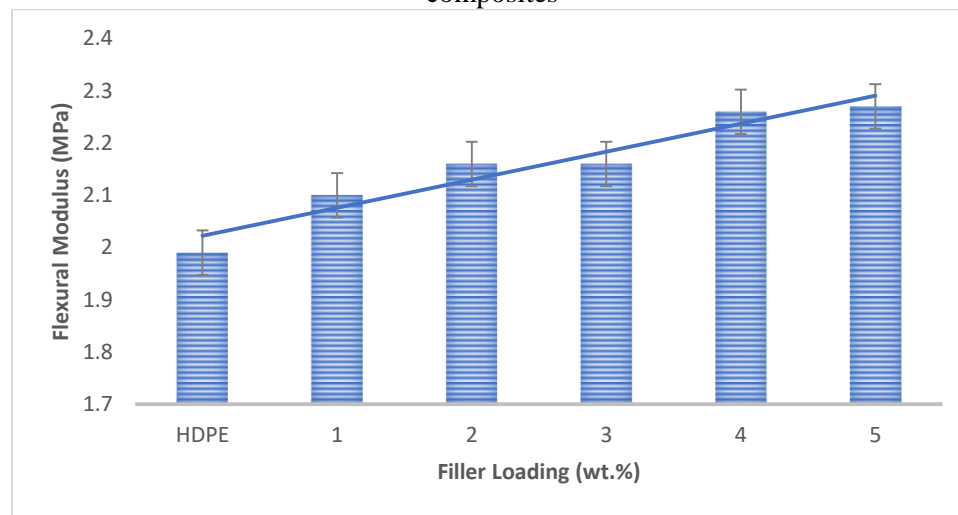


Figure 5. Flexural Modulus against filler loadings for HDPE/MC-NF/Org-MMT/HD-g-MAH bio nano composites

As the filler loading increases from 1%/2%,3%,4% and 5% of MC-NF in the matrix structure with 3% HD-g-MA /2% Org-MMT for all the fabricated samples, the flexural strength increased to 16.32 MPa (7.58%), 16.57 MPa (9.23%), 17.38 MPa (14.57%), 17.55 MPa (15.68%) and 17.99 MPa (18.60%) respectively. Just like the strength of this fabricated bio nanocomposites, the flexural modulus increased with an increase in filler content. Flexural modulus for pure HDPE was found to be 1.99 MPa but with 1% to 5% addition of MC-NF the modulus increases to 2.10MPa (6%), to 2.27 MPa (14.07%) respectively. Similar to tensile strength, the increase in flexural strength and stiffness of these nanocomposites with an increase in filler loadings could be due to the excellent interaction, good exfoliating and compatibilizing effects of Org-MMT and PE-g-MAH and proper dispersion of these fillers in the matrix structure as shown in the FESEM micrographs provided below which resulted to good interfacial bonding between fillers and matrices. However, nano particles have a high surface area for interaction and bonding with polymer at lower loadings. These results prove that alkaline pre-treatment of fibers enhanced resin-filler penetration at the interface by providing more link for filler/matrix crosslinking which reduces the effect of fiber/filler agglomeration.

Morphological analysis

Field emission electron microscopy (FE-SEM)

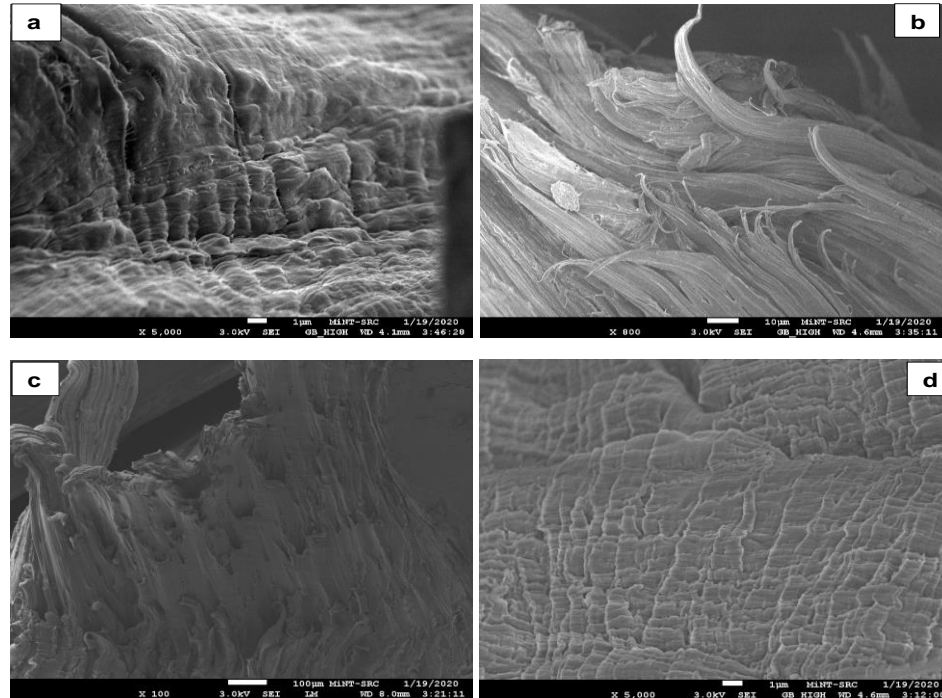


Figure 6. Micrographs of (a) 5% (b) 1% (c)3% (d) 0% MC-NF loading at different magnifications

The tensile fracture surface was used to examine the morphology of the fabricated samples. The micrographs a, b and c showed good dispersion and the exfoliation of the fillers within the matrix structures, at 1%, 3%, and 5% MC-NF loading while (d) showed micrograph of pure unreinforced HDPE showing smooth surface. It was observed that bio nano composites had no noticeable agglomeration, voids, gaps, and cracks or pull-outs. Showing good surface adhesion between fillers and matrix, confirming the reason for the increased observed in the tensile strength and tensile modulus as well as flexural strength and flexural modulus.

4. Conclusion

Bio based nano composites of MC-NF/2% Org-MMT/ HPDE/ HD-g-MAH were successfully prepared by injection molding technique. The effect of MC-NF on the mechanical and morphological properties of HPDE and HD-g-MAH reinforced MC-NF were determined. It was observed that the tensile and flexural properties of the bio nano composites prepared by injection molding technique increased with an increase in filler (MC-NF) content up to 5.5% and 52% at 5% MC-NF loading for tensile strength and modulus respectively. flexural strength and modulus also increased up to 18.60% and 14.07% at 5% filler content, due to adequate dispersion of the fillers in the matrix and strong/good interfacial adhesion between the phases, evidence in the FESEM micrographs provided above. The fabricated nanocomposites can be used where strength is required e.g in building and construction (partition walls, shelves, staircase handle) as well as the automotive interior.



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