RHEOLOGICAL DESIGN OF RECYCLED PET–CLAY NANOCOMPOSITES THROUGH ORGANOPHILIC TUNING

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Abstract

Preparation of well-dispersed recycled polyethylene terephthalate-organoclay nanocomposites with enhanced processing and mechanical properties remains a significant challenge due to the low thermal stability of organoclays. This issue is particularly critical during the melt compounding process, where high temperatures are required to process recycled PET. At elevated temperatures, organoclays, especially those modified with traditional quaternary ammonium salts, tend to degrade, releasing volatile byproducts such as ammonia and other decomposition products. This degradation not only compromises the thermal stability of the nanocomposite but also accelerates the degradation of the recycled PET matrix itself, leading to a reduction in molecular weight and deterioration of mechanical properties. The low thermal stability of organoclays is primarily attributed to the organic modifiers used to render the hydrophilic clay compatible with the hydrophobic polymer matrix. These modifiers, while effective in improving clay dispersion, often decompose at temperatures below the processing range of PET, which typically exceeds 250°C. As a result, the development of thermally stable organoclays is essential to overcome this limitation and achieve the desired improvements in nanocomposite performance. In this study, an overview of various surface modification techniques for sodium-type montmorillonite was conducted to enhance its compatibility with recycled PET. Surface modifications included the use of organic modifiers, such as quaternary ammonium salts, and other innovative approaches aimed at improving the dispersion of the clay within the polymer matrix. The thermal stability of the organoclays and the resulting nanocomposites was evaluated using melt rheology, which provided insights into the degradation behavior and processability of the materials. The results demonstrated that organoclays modified with alternative surface treatments exhibited superior performance compared to those modified with conventional quaternary ammonium compounds. Specifically, the newly prepared clays significantly suppressed matrix degradation during melt mixing, which is a common issue in the processing of PET. The findings suggest that the use of advanced surface-modified clays can open new avenues for the development of high-performance recycled PET-based nanocomposites, which can be utilized in a wide range of applications, including packaging, automotive components, and construction materials. This approach aligns with the growing demand for sustainable materials and the circular economy by adding value to recycled plastics while reducing environmental impact.

Keywords: *Recycled PET, Organoclay, Melt compounding, Rheology*

1. INTRODUCTION

Recycling of poly(ethylene terephthalate) (PET), in particular beverage bottles, is not yet satisfactorily solved. The average recovery rate of PET in Europe has improved in recent years, reaching approximately 52% in 2020, according to PlasticsEurope and PETCORE Europe [1]. In contrast, the United States lags behind, with a PET recovery rate of around 28.6% as of 2021, based on data from the National Association for PET Container Resources (NAPCOR) [2]. During the recycling process and throughout each stage of thermoplastic material reprocessing, the melt viscosity of the material tends to decrease due to chain scission, a phenomenon where the polymer chains break into shorter segments. This reduction in molecular weight directly impacts the material's rheological properties, particularly its melt strength, which is a critical parameter for successful processing. Maintaining adequate melt strength is essential to ensure the material can withstand the mechanical stresses and

deformation forces encountered during various manufacturing processes. In the case of recycled polyethylene terephthalate (PET-R), the reduction in viscosity poses significant challenges for its reuse in certain advanced processing technologies. For instance, processes such as flat-die extrusion and blow molding, which require materials with higher melt strength and viscosity to maintain dimensional stability and achieve uniform product quality, are particularly affected. The low viscosity of PET-R often leads to issues such as sagging, uneven flow, or poor mechanical performance in the final product, limiting its suitability for these applications. As a result, the use of PET-R has been largely confined to a narrower range of applications where lower viscosity is less of a concern. These include the production of staple fibers, packaging materials, thin films, and strips, which do not demand the same level of melt strength as more complex manufacturing processes. While these applications are valuable, they represent only a fraction of the potential uses for this high-performance material, leaving much of its technological potential untapped [3]. Incorporating highly dispersed silicate particles into recycled PET improves the melt consistency, thereby expanding the possibilities for further processing. The production of nanocomposites through melt mixing offers a promising approach to polymer recycling, particularly by enhancing material properties through the intercalation or exfoliation of silicate platelets within the polymer matrix. However, as far as we are aware, only a limited number of studies have been published on recycled PET-organoclay nanocomposites. The materials investigated in these studies have generally demonstrated suboptimal processing behavior and functional performance, including issues such as reduced mechanical properties and a decline in melt viscosity [4-6, 19].

In our earlier research, we investigated nanocomposites made from recycled PET and commercial organoclays (functionalized montmorillonite nanofillers), observing an increase in melt viscosity due to the formation of a physical network between the polymer and the organoclay [7]. However, a significant challenge arose with the thermal stability of the commercial organic modifiers, specifically quaternary ammonium salts, which led to degradation of the polymer matrix during the melt mixing process. The low thermal stability of these organoclays caused chemical decomposition through an α, β elimination mechanism [8-12]. To address these issues and improve both the thermal stability and delamination of the organoclays within the polymer matrix, we modified selected commercial organoclays using silanization techniques. The silanization agents included [3-(glycidyloxy)propyl]trimethoxysilane, hexadecyltrimethoxysilane, and (3-aminopropyl)trimethoxysilane [13]. The introduction of epoxy functional groups onto the silicate surface enhanced interactions between the filler and the polymer matrix while mitigating the negative effects of the silicate hydroxyl groups. Additionally, the epoxy-silanized organoclays were capable of forming direct bonds with the polymer chains, which promoted greater delamination of the silicate platelets. To completely suppress degradation reactions during compounding, we further modified sodium montmorillonite with spacers based on an imidazolium salt. This "imidazolium organoclay" was subsequently subjected to silanization to further enhance its performance [20]. In other our work [21] we functionalized montmorillonite nanofillers in a three-step functionalization process, involving the treatment with (3-aminopropyl)triethoxysilane (APTES), the grafting of initiating coatings (multifunctional peroxide initiator, [MPI]) onto clay/APTES, and the subsequent fabrication of grafted brushes using poly(butyl methacrylate) (PBMA) or poly(butyl acrylate) (PBA). This study aims to investigate the rheological behavior of recycled PET-based nanocomposites containing various surface-modified organoclays, with the objective of understanding how different modifications influence melt flow properties and processability.

2. EXPERIMENTAL

2.1. Materials and methods

All chemical compounds were purchased from Fluka or Aldrich in sufficient purity. The synthesized compounds were characterized by elemental analysis, and melting point, if possible. The MMT-IM and MMT-IME organoclays have been synthesized using the molar excess of modifiers in order to achieve maximal modification efficiency.

Recycled poly(ethylene terephthalate) from colour-sorted beverage bottles (PET-R), with the intrinsic viscosity 0.73 dl/g was supplied by Polymer Institute Brno, Ltd., Czech Republic. Virgin bottle grade PET Elixir (PET-V) with the intrinsic viscosity 0.8 dl/g was delivered by EKO PET, Inc., Czech Republic.

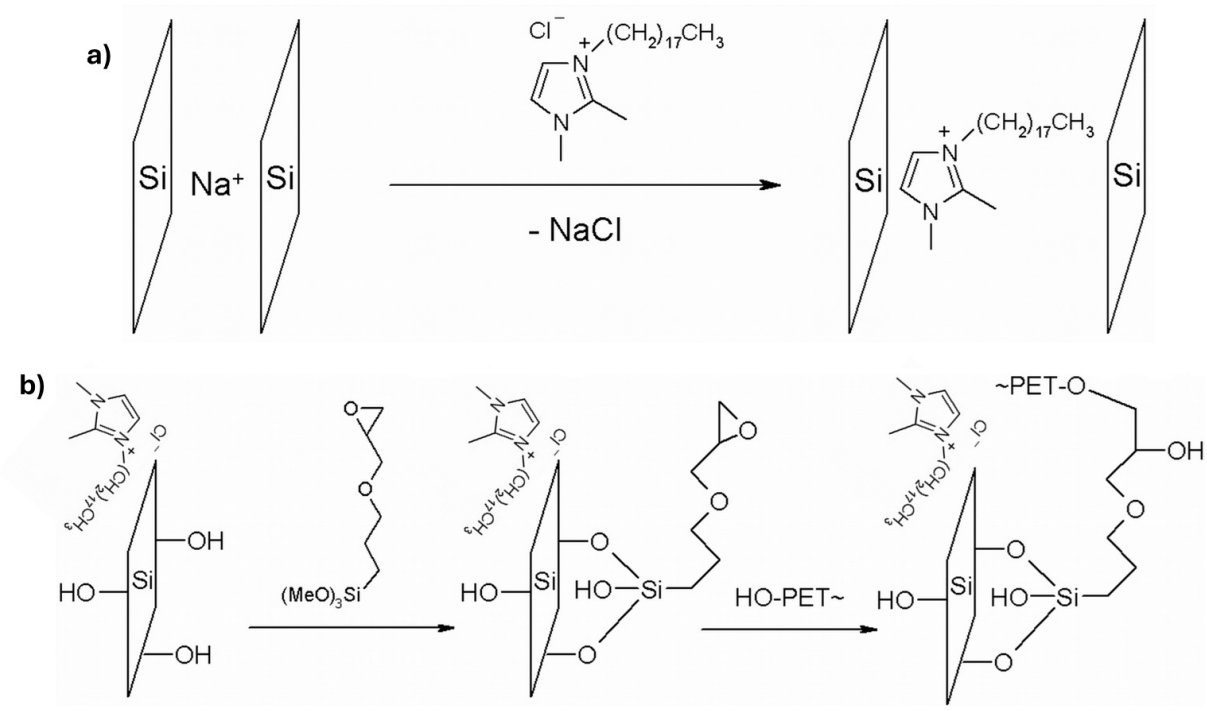
2.2. Synthesis of 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium chloride [14]

1,2-dimethyl-1H-imidazole (18 g, 0.188 mol) was suspended in 1-chloroctadecane (65 g, 0.225 mol) and the mixture was homogenized by stirring at 100 °C for 12h. The reaction mixture was cooled to 50 °C and shaken with 200 ml of benzene. Precipitated crystals were filtered off, washed with a small amount of benzene and dried under vacuum (Scheme 1). The yield was 49.3 g (68 %) and the melting point 93-95 °C [20].

2.3. Funtionalization of clay with 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium (MMT-IM) (Scheme 1a)

Cloisite Na^+ (20.6 g of dry matter) was stirred in 1000 ml of deionized water and the suspension was kept at room temperature for 12 h. The suspension was heated at 80 °C under vigorous stirring and the warm (60 °C) solution of 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium chloride (7.85 g, 20.38 mmol) in 200 ml water was slowly added. The thick suspension was stirred for 90 min at 80 °C, filtered off while hot and washed with a high amount of boiling water. The filtration cake was suspended in 1000 ml of hot water (80 °C) and vigorously stirred for 1 h. The final suspension was filtered off, washed and the described procedure was repeated. The properly washed organoclay was air-dried and then in dried under vacuum at 110 °C (Scheme 1). The yield of the product was 25.6 g.

Elemental analysis (Perkin Elmer CHNSO Analyzer Series II 2400): Found C 20.70 %, H 3.83 %, N 1.60 %, ash 68.39 %. The 23 % fraction of organic phase was calculated from TGA measurement [20].



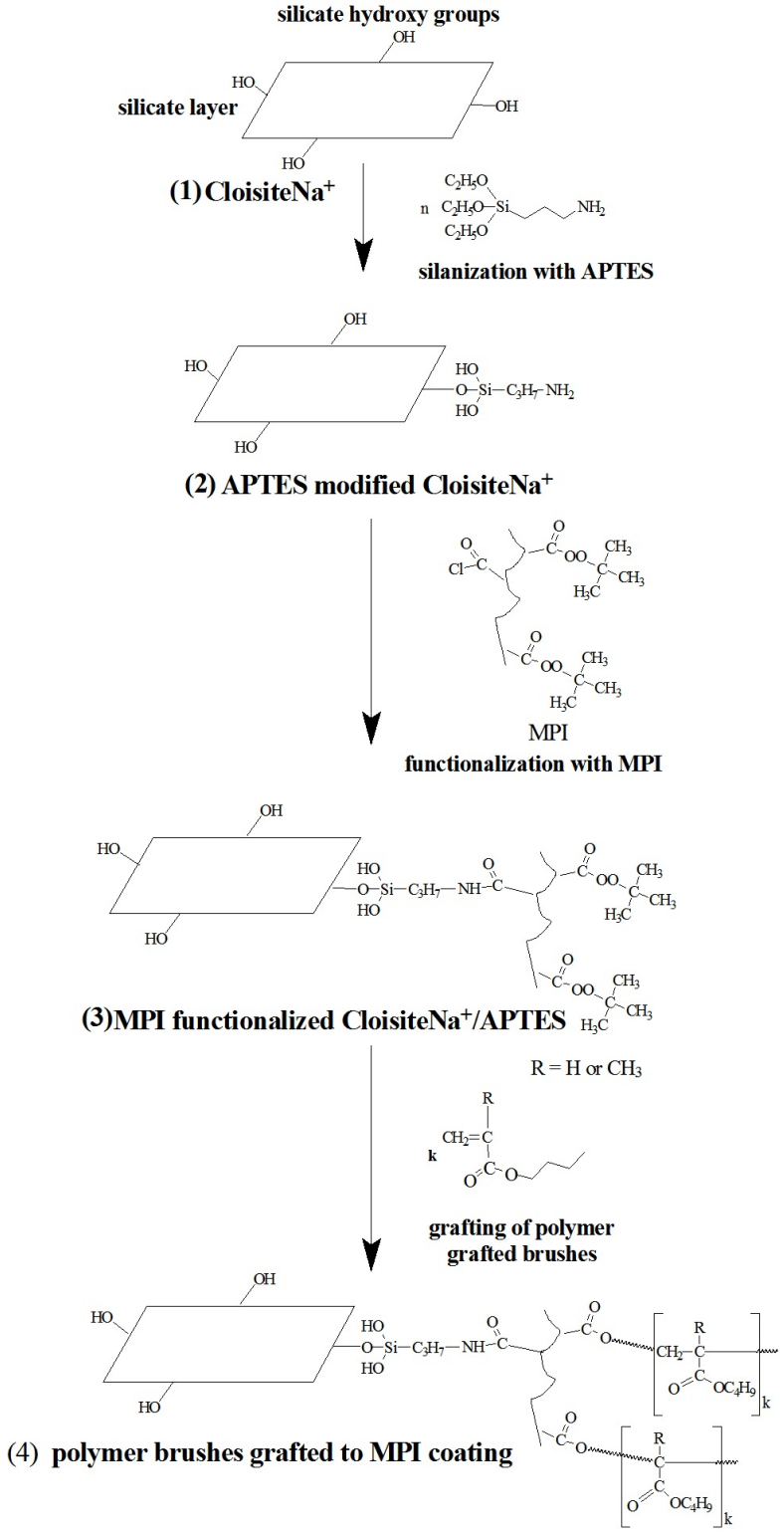
Scheme 1. Ion exchange reaction for the functionalization of sodium montmorillonite (Na^+-MMT) with 1,2-dimethyl-3-octadecylimidazolium chloride to form organo-modified MMT (MMT-IM) (a); Subsequent surface grafting of epoxy-functional silane onto MMT-IM, followed by reaction with hydroxyl-terminated PET to anchor PET chains onto the clay surface (b).

2.4. Epoxy-silanization of 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium organoclay (MMT-IME) (Scheme 1b)

The MMT-IM organoclay (1 g) was suspended in 50 ml of a methanol-water mixture (10:1) and [3-(glycidyloxy)propyl]trimethoxysilane (0.3 g) was added. The mixture was stirred at room temperature for two days and the precipitate was filtered off and thoroughly washed with methanol. The solid was dried under vacuum at 50 °C for 4 h. This procedure has been performed according to scheme 1 [20].

2.5. Functionalization of the clay with APTES (MMT-APTES) (Scheme 2)

1. Modification of clay fillers. 1 g of clay nanoparticles in the form of a powder is placed in 100 ml of distilled water, with constant stirring, a freshly prepared solution containing 1 g of APTES in 100 ml of distilled water is added. Intensive mixing is carried out for 30 minutes at room temperature.



Scheme 2. Stepwise modification of Cloisite Na^+ with polymer brushes: (1) Silanization of the silicate surface with 3-aminopropyltriethoxysilane (APTES); (2) Covalent immobilization of photoreactive copolymer MPI via amide bond formation; (3) Preparation of MPI-functionalized Cloisite Na^+/APTES; (4) Induced grafting of side-chain polymer brushes from the MPI layer, forming surface-grafted polymer coatings.

2.6. Modification of the APTES functionalized clay with oligoperoxide initiator (PET/MMT-Initiator) (Scheme 2)

After modification, ungrafted silane molecules are removed by washing the obtained substance several times with water and subsequent centrifugation. After that, the obtained substrate interacts with a multifunctional initiator based on a peroxide-containing oligoperoxide with chloride groups. For this, 100 ml of a 1% solution of the initiator in anhydrous dixane is mixed with the amino-functionalized substrate. Stir intensively for 24 hours.

2.7. Grafting polymerization from clay surface (PET/MMT-PBA and PET/MMT-PBMA) (Scheme 2)

The surface initiated by the initiator was placed in a metal cylinder with a stirring system, then filled with a 0.1 M solution of the corresponding monomer (butyl acrylate or butyl methacrylate) in methanol. Samples are polymerized at a temperature of 90°C for 24 hours with constant stirring. After the polymerization time, the samples are removed and washed with ethanol and water [21].

2.8. Preparation of nanocomposites

Organoclay powder was dried at 80 °C and PET pellets at 110 °C in an oven overnight. Polymer was compounded with 5 wt. % of organoclay in a co-rotating twin-screw microextruder (DSM Research, Netherlands) at 255 °C under nitrogen. The mixing time was 10 min at a speed of 200 rpm. Immediately after blending cycle, the nanocomposite melt was injected into a form at 260 °C using DSM micro-injection equipment.

Table 1. Types of PET Nanocomposites and Corresponding Organoclay Modifications

Nanocomposite name	Organoclay Type	Modification Steps
PET/MMT	MMT	MMT
PET/MMT-IM	MMT-IM	Modified with 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium chloride (ionic liquid) via cation Exchange
PET/MMT-IME	MMT-IME	MMT-IM further functionalized with [3-(glycidyloxy)propyl]trimethoxysilane (epoxy silanization)
PET/MMT-APTES	MMT-APTES	Surface treated with (3-aminopropyl)triethoxysilane (APTES) in water
PET/MMT-Initiator	MMT-Initiator	MMT-APTES reacted with peroxide-containing oligoperoxide initiator in dioxane
PET/MMT-PBA	MMT-Brush (PBA)	MMT-Initiator used for grafting of poly(butyl acrylate) brushes via surface-initiated polymerization
PET/MMT-PBMA	MMT-Brush (PBMA)	MMT-Initiator used for grafting of poly(butyl methacrylate) brushes via surface-initiated polymerization

2.9. Melt rheology

An ARES 3 Rheometer (Advanced Rheometric Expanded System, from Rheometric Scientific, Inc., U.S.A.) with the 25-mm parallel-plate geometry was employed for rheological characterization. Dynamic frequency sweep measurements were performed at 270 °C under nitrogen at the strain level 2 % (nanocomposites) or 30 % (neat matrices), respectively.

3. RESULTS AND DISCUSSION

Commercially available organo-modified montmorillonite nanofillers (organoclay) are widely used for the preparation of polymer nanocomposites due to their improved compatibility with hydrophobic polymer matrices and enhanced dispersion behavior. These nanoclays are typically surface-modified with quaternary ammonium salts, which increase the interlayer spacing and render the clay organophilic. Among the most commonly used are Cloisite® series clays (BYK Additives), such as Cloisite® 6A, 10A, 15A, 20A, 25A, 96A, and 30B, which differ in the structure and functionality of the organic modifiers (Figure 1).

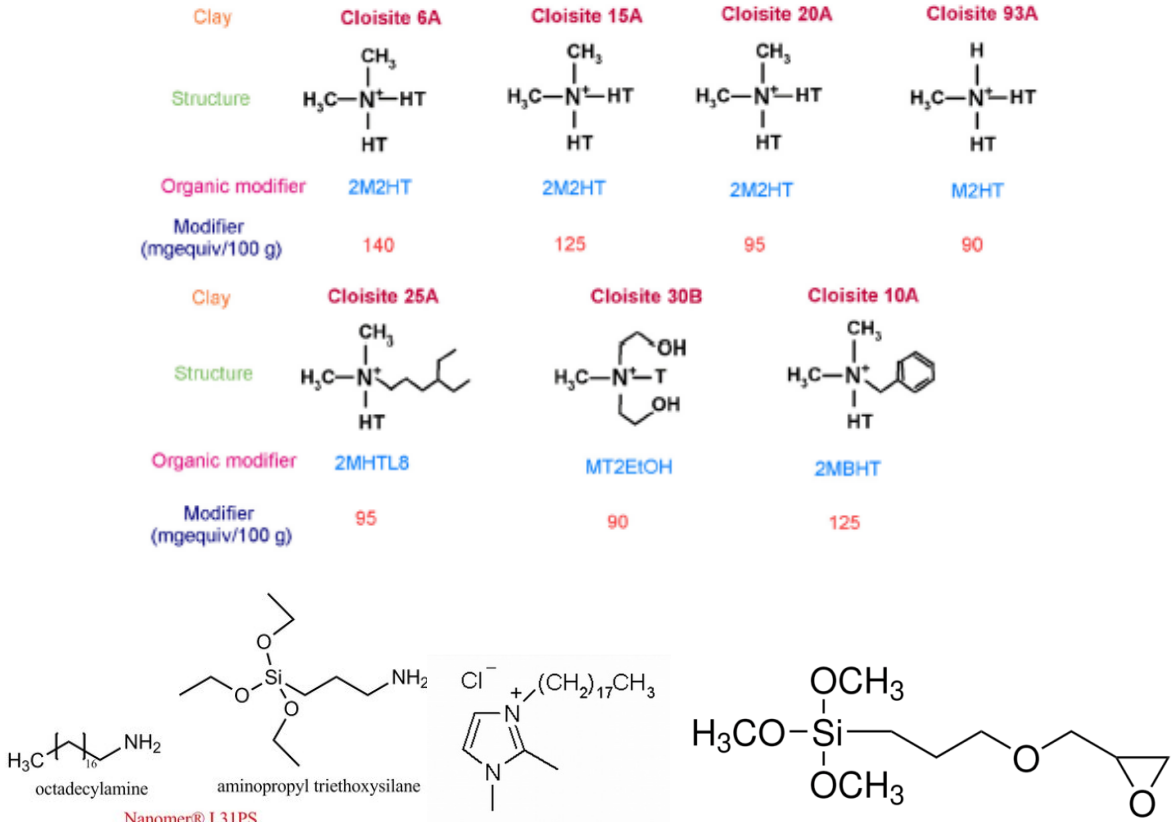


Figure 1. Examples of the commercially available and used by as clay modifies

The "A" series uses non-functional quaternary ammonium modifiers, some with these clay have same chemical nature but different amount of modifier. HT means hydrogenated tallow, which is a mixture of long-chain alkyl groups, mainly C16 (hexadecyl), C18 (octadecyl), and

C18:1 (oleyl). Cloisite® 6A is modified with dimethyl di(hydrogenated tallow) ammonium. Hydrophobic, used with nonpolar polymers like polyolefins. Cloisite® 10A is modified with dimethyl benzyl hydrogenated tallow ammonium. Slightly more polar and more thermally stable. Suitable for vinyl polymers and rubbers. Cloisite® 15A is modified with dimethyl di(hydrogenated tallow) ammonium. Common type, hydrophobic, but less thermally stable. Used in polypropylene and LDPE. Cloisite® 20A is modified with dimethyl di(dehydrogenated tallow) ammonium. Similar to 15A but more thermally stable. Used in polyolefins and polyesters. Cloisite® 25A is modified with methyl tallow bis(2-hydroxyethyl) ammonium. Has hydroxyl groups, more compatible with polar polymers like polyamides and polyesters. Cloisite® 96A is modified with trimethyl stearyl ammonium. Very hydrophobic, used in nonpolar systems such as polyethylene and rubber. Cloisite® 30B is modified with a hydroxyl-functionalized quaternary ammonium salt and is particularly suited for polar polymers

such as polyesters and polyamides. T means tallow-based long alkyl chains (C16–C18). Similar chemical structure have organoclays, which are sold under the brand name Nanomer® clays (Nanocor). Only commercially available Nanometer I.30E clay included surface-modifying substances other than quaternary ammonium salts. These commercially available nanofillers provide a reproducible and industrially relevant basis for nanocomposite design, facilitating the development of high-performance materials with tailored mechanical, thermal, and barrier properties. However, a significant challenge arose with the thermal stability of the commercial organic modified clay with quaternary ammonium salts, which are thermally unstable above 200 °C, undergoing a Hofmann degradation at this temperature which led to degradation of the polymer matrix during the melt mixing process. The low thermal stability of these organoclays caused chemical decomposition through an α, β elimination mechanism (Fig. 2) [8-12]. When this occurs, the polymer/clay interface is destroyed and the material can thermally rearrange to give a microcomposite structure, thus nullifying any gains achieved by the original nanocomposite structure [(10) (a) Shah, R.K., Paul, D.R., Polymer, 2006, 47, 4084. (b) Nassar, N., Utracki, L.A., Kamal, M., Intl. Polym. Proc., 2005, XX, 423. (c) Gilman, J.W., Jackson, C.L., Morgan, A.B., Harris, R., Manias, E., Giannelis, E.P., Wuthenow, M., Hilton, D., Phillips, S.H., Chem. Mater., 2000, 12, 1866].

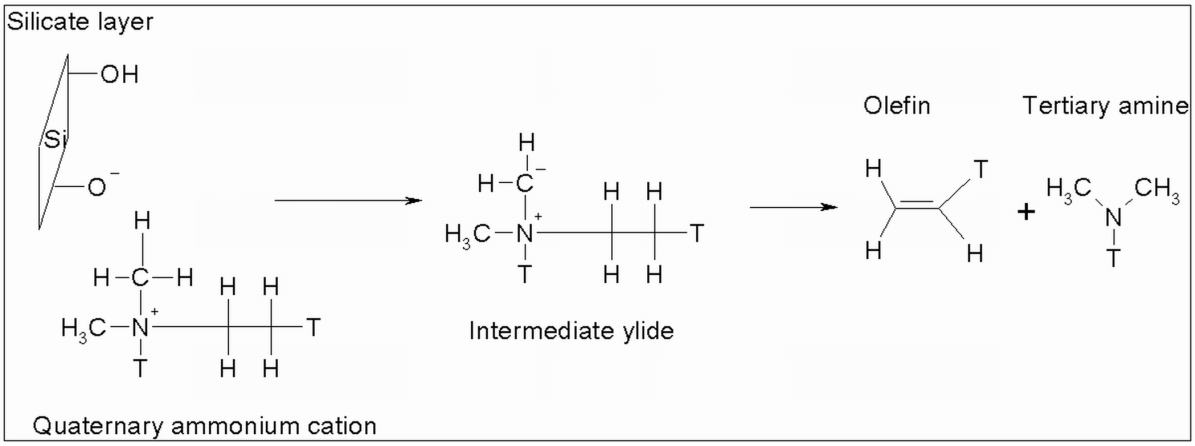


Figure 2. Thermal degradation mechanism of quaternary ammonium cations in organoclay via the Hofmann elimination pathway. The degradation proceeds through the formation of an ylide intermediate, resulting in the generation of an olefin and a tertiary amine, leading to the loss of organic modifier and affecting nanocomposite thermal stability.

To address these issues and improve both the thermal stability and delamination of the organoclays within the polymer matrix in last years are using two approaches. First, its application of the clay intercalated with imidazoliums which have great promise, capable of handling temperatures 300 °C and available in a variety of structures that can be tailored to the polymer nanocomposite application [(a) Gilman, J.W., Awad, W.H., Davis, R.D., Shields, J., Harris, Jr., R.H., Davis, C., Morgan, Multifunctional Polymer-Clay Nanocomposites A.B., Sutto, T.E., Callahan, J., Trulove, P.C., DeLong, H.C., Chem. Mater., 2002, 14, 3776. (b) Bottino, F.A., Fabbri, E., Fragala, I.L., Malandrino, G., Orestano, A., Pilati, F., Pollicino, A., Macromol. Rapid Commun., 2003, 24, 1079. (c) Wang, Z.M., Chung, T.C., Gilman, J.W., Manias, E., J. Polym. Sci. Part B., 2003, 41, 3173. (d) Davis, R.D., Gilman, J.W., Sutto, T.E., Callahan, J.H., Trulove, P.C., De Long, H.C., Clays and Clay Minerals, 2004, 52, 171.]. And second approach functionalization of the clay using silanization techniques. In particular, functional silanes bearing epoxy or amino groups were employed to covalently anchor thermally stable organic moieties onto the surface of the montmorillonite platelets. This approach not only prevented the premature decomposition associated with quaternary ammonium salts but also enhanced interfacial compatibility between the clay surface and the polymer chains. Furthermore, silane modification created additional opportunities for covalent bonding or hydrogen bonding

interactions with reactive polymer functional groups, thus promoting better dispersion and exfoliation of the clay within the polymer melt. Moreover, to enhance further the structural integration and functional performance of the nanocomposites, a dual-modification strategy was implemented in this work where functionalizing clay with 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium chloride (MMT-IM), followed by epoxy-silanization (MMT-IME), was chosen to modify the hydrophilic clay surface into an organophilic and chemically reactive material suitable for advanced polymer nanocomposites. Other strategy included fabrication of the grafted polymer brushes but organoclay that was fabricated in the intermediate stages was also used for production of the PET nanocomposites and their rheological properties were studied in the details. At synthesis, first clay was modified with (3-aminopropyl)triethoxysilane, introducing reactive amino groups onto the surface. These functionalized clays were then reacted with peroxide-containing oligoperoxide initiators, enabling surface-initiated radical polymerization. The subsequent grafting of polymer brushes, such as poly(butyl acrylate) or poly(butyl methacrylate), resulted in a brush-like architecture that provided steric stabilization and improved interfacial adhesion with the thermoplastic matrix. This strategy significantly improved clay dispersion, reduced aggregation during melt processing, and enhanced the mechanical and thermal properties of the resulting nanocomposites (see Scheme 2).

In this study we studied in details of the rheological behavior of the PET-R nanocomposites with different types of the organoclays: PET-R/MMT, PET-R/MMT-IM, PET-R/MMT-IME, PET-R/MMT-APTES, PET-R/MMT-Initiator, PET-R/MMT-PBA, PET-R/MMT-PBMA.

Rheological studies

Understanding the rheological behavior of PET nanocomposite melts is essential for optimizing processing conditions and ensuring the performance of the final material. The incorporation of nanoclay significantly alters the viscoelastic properties of the polymer matrix, often increasing melt viscosity, elasticity, and shear-thinning behavior due to the formation of a percolated filler network and enhanced polymer–filler interactions. These changes directly affect the flow, orientation, and dispersion of the nanofillers during melt mixing and shaping, which in turn influence the morphology, mechanical strength, and barrier properties of the nanocomposites.

Rheological studies also provide indirect insight into the degree of intercalation or exfoliation of the clay platelets within the polymer matrix. For example, an increase in complex viscosity or storage modulus at low frequencies typically indicates the formation of a nanostructured network or improved filler dispersion. Moreover, assessing the thermal and shear stability of the nanocomposite melt is particularly important for PET, which is processed at relatively high temperatures (>250 °C), where thermally unstable components, such as some organic modifiers, may degrade and negatively affect flow behavior and final material properties.

Therefore, rheological characterization serves not only as a diagnostic tool for evaluating the dispersion state and structural organization of nanofillers but also as a critical step in predicting and controlling processability, ensuring reproducibility, and guiding the design of high-performance PET-based nanocomposites.

Dynamic rheological behavior of the prepared nanocomposites was investigated in the region of linear viscoelasticity. The dynamic strain sweep test ($G'(\gamma)$) revealed the linearity region of 1–100 % strain (the matrices) or 1–15 % strain (the composites), respectively.

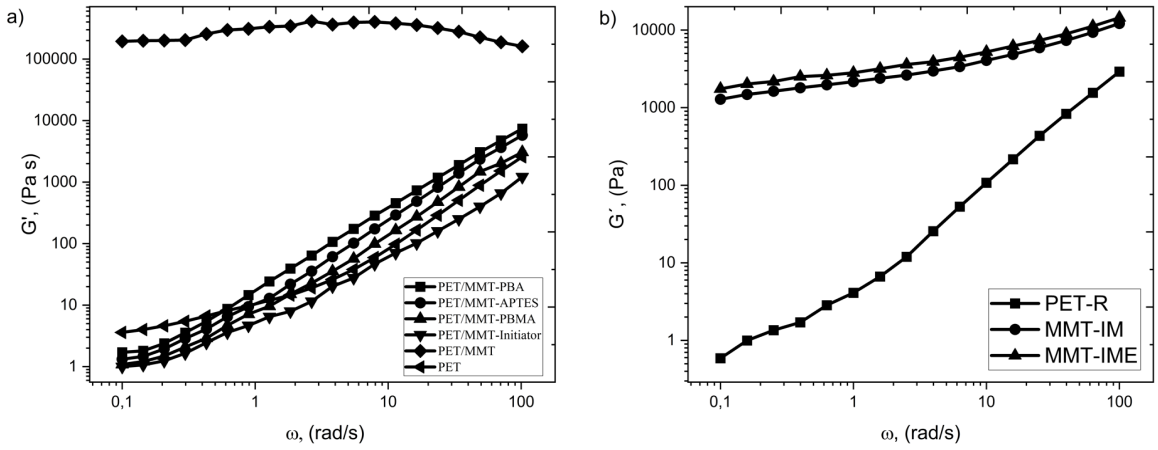


Figure 3. Dependence of the storage modulus (G′) on frequency (ω) for PET-based composites

The storage modulus (G′) of PET-based composites shows clear frequency-dependent enhancement of the elastic response across all modified systems. Figure 3a shows that samples containing functionalized nanoclays, especially PET/MMT-PBA and PET/MMT-PBMA, have significantly higher G′ values than neat PET, particularly in the low-frequency region. This indicates effective filler dispersion and strong interfacial interactions that restrict polymer chain mobility [21,22,26]. PET/MMT exhibits the highest G′ values, suggesting the formation of a rigid, percolated network. However, its response may be associated with excessive filler aggregation and constrained relaxation [26]. PET/MMT-APTES and PET/MMT-Initiator demonstrate enhanced stiffness to a lesser extent, reflecting moderate structural reinforcement.

Figure 3b shows that recycled PET (PET-R) has the lowest G′ values, which are nearly linear across the frequency range. This is typical of a highly amorphous or degraded polymer matrix with reduced chain entanglement [28]. In contrast, the MMT-IM and, especially, the MMT-IME composites exhibit markedly higher G′ values throughout the frequency spectrum. This indicates the formation of a more organized internal network and improved elastic recovery. This is attributed to efficient matrix–filler interactions and nanoscale structuring [26]. The MMT-IME system, in particular, demonstrates a reinforced polymer architecture that can resist deformation and reinforce the synergistic effect of interfacial modifiers.

These observations confirm that combining nanofillers with targeted surface chemistry significantly improves the elastic behavior of PET composites by promoting structural integrity and interfacial compatibility [21,22,26].

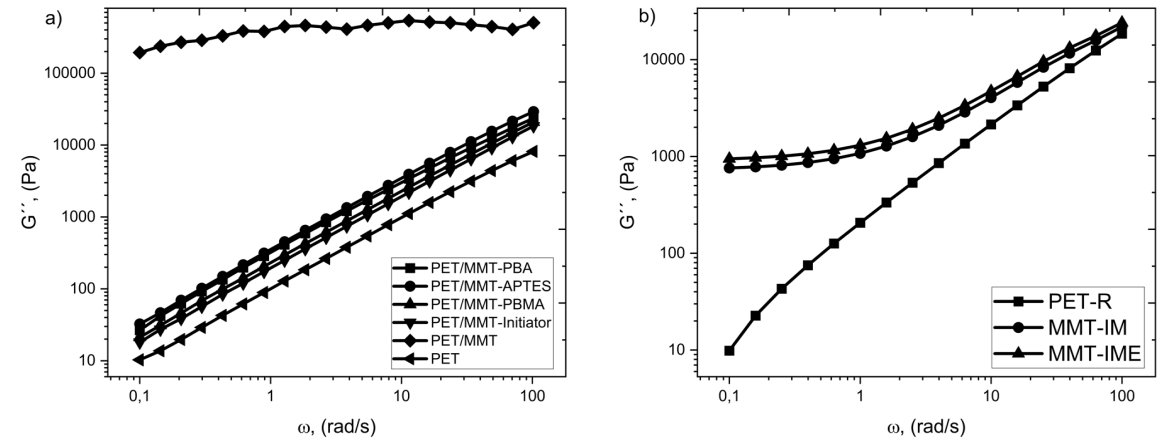


Figure 4. Loss Modulus (G″) Dependence on Angular Frequency (ω) for PET-Based Nanocomposites

The loss modulus (G″) characterizes a material's energy dissipation capacity and viscous response under oscillatory shear. Across all PET-based nanocomposites, G″ increases with rising frequency, indicating typical viscoelastic behavior. Figure 4a shows that the PET/MMT sample has the highest G″ values, which may suggest a highly constrained polymer matrix. However, these values could also reflect excessive filler aggregation that limits relaxation mechanisms [26]. Functionalized systems, particularly PET/MMT-PBA and PET/MMT-PBMA, exhibit elevated G″ values, especially at low and intermediate frequencies. This behavior indicates improved interfacial interaction and an enhanced capacity to dissipate mechanical energy through internal friction [21, 26]. PET/MMT-APTES and PET/MMT-Initiator composites show moderate G″ increases, suggesting improved but less developed filler–matrix coupling compared to unmodified systems.

In contrast, the neat PET sample displays the lowest G″ values, which are indicative of weak energy dissipation and poor internal structural organization. This behavior is consistent with a linear amorphous polymer lacking reinforcement. Figure 4b shows similar trends for recycled PET (PET-R), which also exhibits low G″ values and minimal frequency dependence due to reduced entanglement and molecular degradation [26].

Introducing modified montmorillonite (MMT-IM and MMT-IME) significantly increases the loss modulus; MMT-IME shows the highest G″ values across the frequency range. This suggests the formation of a robust dissipative network within the composite, supported by enhanced interfacial bonding and nanofiller dispersion [23,26]. These improvements underscore the pivotal role of surface modifiers in shaping the viscoelastic and dissipative properties of PET-based nanocomposites.

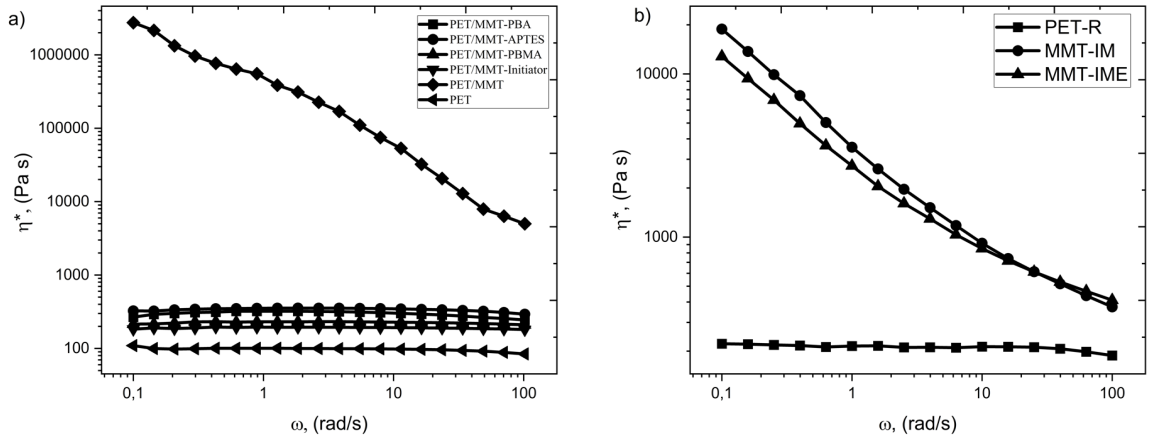


Figure 5. shows the dependence of complex viscosity (η*) on angular frequency (ω) for PET-based nanocomposites with different modifiers

Plots of complex viscosity (η*) versus angular frequency (ω) demonstrate the shear-thinning behavior characteristic of polymer melts. Across all samples, η* decreases with increasing frequency, reflecting reduced resistance to flow under high shear. Figure 5a shows that the PET/MMT nanocomposite exhibits the highest η* values, possibly due to excessive filler loading or aggregation. These factors restrict molecular mobility and increase viscosity [26]. However, the behavior is anomalously elevated at low frequencies, suggesting rigid structure formation that resists deformation.

In contrast, functionalized systems that incorporate polymer brushes (PET/MMT-PBA and PET/MMT-PBMA) or APTES demonstrate lower and more stable η* values. This indicates better nanofiller dispersion and balanced network formation [21,22,26]. These samples maintain moderate structural integrity while allowing sufficient chain mobility for processability. The PET/MMT-APTES and PET/MMT-Initiator composites also display reduced viscosity compared to unmodified MMT,

which is consistent with improved interfacial control. The neat PET sample shows the lowest η* values, indicating minimal structural organization and a lack of viscoelastic enhancement.

Figure 5b further illustrates the impact of montmorillonite modification. Recycled PET (PET-R) exhibits the lowest η* values across the frequency range, which is consistent with polymer chain degradation and reduced molecular cohesion [26]. The MMT-IM and MMT-IME systems demonstrate significantly higher η* values, with MMT-IME exhibiting the highest viscosity overall. This reflects the formation of a more cohesive, structured network that resists flow and dissipates energy more effectively. This is attributed to optimized nanostructuring and interphase interactions [23, 26]. These findings reinforce the role of combined chemical modifiers in improving the structural and processing properties of PET nanocomposites.

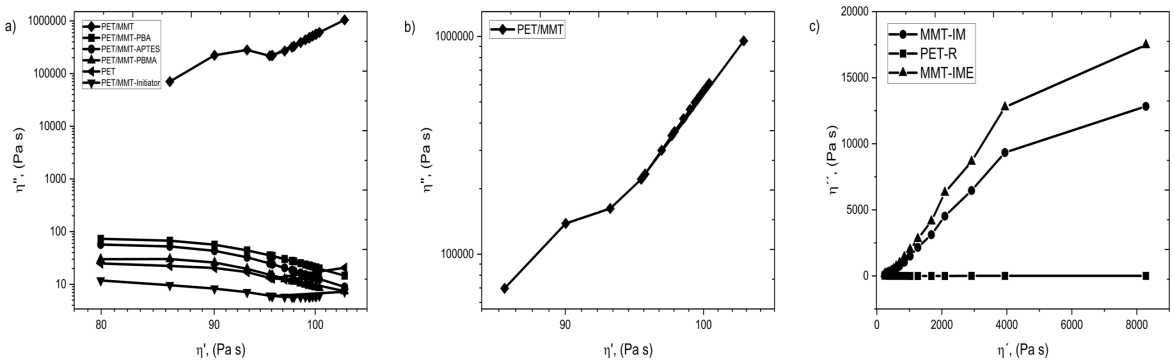


Figure 6. Cole–Cole plots of imaginary viscosity (η″) versus real viscosity (η′) for PET-based nanocomposites

These plots demonstrate the significant impact of surface modification on the viscoelastic behavior of PET-based nanocomposites. Functionalized systems that incorporate Cloisite Na^+ along with APTES and polymeric modifiers (MPI-graft-PBA and MPI-graft-PBMA) demonstrate increased η″ values and a notable decrease at high η′ values. This trend indicates the presence of a well-developed internal network that weakens under deformation. The MPI-graft-PBA sample shows the most pronounced peak and subsequent drop in η″, reflecting efficient interphase coupling and structural responsiveness. In contrast, systems modified only with APTES or APTES/MPI display smoother transitions, indicative of moderate interfacial interactions.

Interestingly, the PET/MMT sample with unmodified Cloisite Na^+ (Figure 6b) exhibits anomalous behavior, with η″ increasing continuously alongside η′. This suggests ineffective dispersion, probable agglomeration, and weak matrix–filler interactions [21]. The neat PET sample exhibits a typical viscoelastic profile with no evident structural reinforcement effect [23].

On the other hand, the MMT-modified samples in Figure 6c (MMT-IM and MMT-IME) demonstrate a steady increase in η″ with rising η′, which is typical of highly structured polymer networks [22,24]. The MMT-IME system consistently exhibits higher η″ values than the MMT-IM system, signifying superior energy dissipation and optimized nanostructuring. In contrast, the PET-R sample shows nearly flat behavior with negligible η″, indicating a viscous-dominated response and reduced elasticity, which is a common characteristic of recycled, partially degraded polymers due to chain scission and decreased entanglement density [23].

In general, these results show that adding montmorillonite, especially with specific organomodifiers, greatly improves the flexibility and resilience of PET nanocomposites. This is achieved by enhancing the bonding between phases and the stability of the network structure [21,22,24].

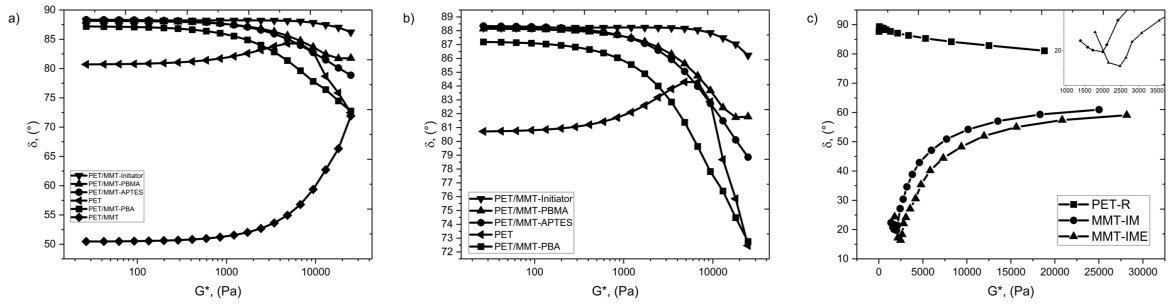


Figure 7. Van Gurp–Palmen Plots (δ vs. G*) for PET-Based Systems

These plots demonstrate the significant influence of nanofiller modification on the viscoelastic behavior of PET-based composites. Recycled PET (PET-R) (Figure 7c) exhibits high phase angle (δ) values ranging from 80 to 89°, indicating a predominantly viscous response with a negligible elastic contribution [23]. The low associated complex modulus (G*) confirms the weak internal structure typical of highly amorphous or degraded polymers.

In contrast, nanocomposites incorporating montmorillonite (MMT), especially MMT-IME, exhibit substantially reduced δ values (20–60°). This signifies a transition toward viscoelastic behavior and an increase in the elastic response. The MMT-IME system shows the lowest δ values and the highest G*, suggesting enhanced chain entanglement, interfacial interaction, and improved nanostructural integrity [22,25,26].

Furthermore, surface modification using interfacial agents (e.g., APTES) or grafted copolymers (PBA or PBMA) in PET/MMT systems (Figure 7a) results in a sharp decrease in δ and an increase in G*, indicating an effective transition from a viscous regime to a structured, viscoelastic one [22]. The PET/MMT-PBA composite exhibits the most significant decrease in δ (from ~90° to ~50°), reflecting highly efficient interphase bonding. Conversely, pure PET and PET/MMT without modifiers exhibit flat or erratic δ behavior, consistent with poor filler dispersion and weak structural coherence [23].

Together, these results highlight the importance of tailored surface chemistry and interfacial compatibilization in improving the rheological properties of PET nanocomposites.

4. CONCLUSIONS

Nanocomposites based on recycled PET with enhanced thermal stability and improved processability were successfully developed. Rheological analysis demonstrated a characteristic shear-thinning behavior upon the addition of organoclays, along with a noticeable increase in melt viscosity across the entire range of measured shear rates compared to unfilled PET matrix. These thermally stable organoclays offer potential for use in the production of multilayer beverage bottles without the need for polyamide blending, thereby simplifying the recycling process for such multilayer packaging. Compared to the unfilled PET matrix, the melt strength of all nanocomposite systems was significantly improved due to the formation of a three-dimensional physical network created by the dispersed silicate platelets. Additionally, nanocomposites incorporating organoclays with polymer brushes exhibited excellent thermal stability, showing no signs of degradation, while maintaining processability comparable to that of pure recycled PET. This combination of properties opens up opportunities for employing recycled PET in a wider range of processing technologies, expanding its potential applications and contributing to more sustainable material use.

ACKNOWLEDGEMENT

This research has been supported by the LIT Institute of Technology at Johannes Kepler University Linz, project number: LIT-2022-11-SEE-123.

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