Development of High Performance Elastomer ‘Tafthren®’

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High performance elastomer ‘Tafthren®’, which exhibit distinguished miscibility with polypropylene, has been developed by precise stereochemical and sequencial control of polyolefins with new homogeneous catalyst developed in Sumitomo chemical Co., Ltd.

Many important properties of polypropylene, like flexibility, heat resistance, scratch resistance, transparency, adhesion properties and so on, could be improved remarkably by the addition of Tafthren®, that could not be improved by the utillization of conventional olefinic elastomers or plastomers as modifiers. In addition, Tafthren® is expected as an environmentally friendly material, because Tafthren® is comprising from substantially same component as polypropylene, so recycle becomes easier than conventional modifier used systems.

In this article, some of the practical features and practical application examples of Tafthren® will be introduced.

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Introduction

Polyolefins, represented by polypropylene and polyethylene, have been widely used in a variety of applications like automobile parts, electronics parts, packaging films and industrial parts. because of their excellent practical features like heat stability and reduction in enviromental load. 1)

When these materials are used in various applications, the various modifications described in the following are generally performed in order to satisfy performance requirements. Primary structure control (co-polymerization with the other comonomers, control of stereo-regularity, molecular weight distribution, composition distribution), addition of various functional polymers, various inorganic and organic fillers and so on are used.

Particularly in the development of high performance automobile parts or high performance films, specific functional polymers are effectively utilized to improve or achieve the practical properties desired for each usage.

For example, when polypropylene is used for materials in automotive parts, materials with excellent property balance in high rigidity and impact resistance at low temperature are required; however it is difficult to achieve the required performance just by controlling the polymer structure in the polymerization stage, so various specific elastomers, such as EPR, EPDM, and hydrogenated styrenic block-copolymers, have been utilized to improve the property balance of composites. On the other hand, since control of the dispersion structure (morphology) and the interactions at the domain-Matrix interface in the blends is also an important factor in determining the physical properties of polymer blends, development of new elastomer which exhibit superior modification capabilities have been anticipated. 2), 3)

The high performance elastomer ‘Tafthren®’ which exhibits superior miscibility with polypropylene has been developed by precise stereochemical and sequential control of polyolefins with a new homogeneous catalyst developed at Sumitomo Chemical Co., Ltd. recently.

Tafthren is currently used in many applications because of its unique characteristics as follows: superior softineing capability of the polypropylene resin (comparable to soft PVC) while maintaining a heat deformation temperature as high as if of polypropylene were used 4)–9).

Characteristics and Applications of Tafthren

1. Structure and Basic Properties of Tafthren

(1) Structure of Tafthren

In this article, basic characteristics and practical applications of Tafthren will be introduced.

The new polypropylene based elastomer "Tafthren," which exhibits superior compatibility with polypropylene resin, has been developed utilizing Sumitomo Chemical's new homogeneous catalyst technology. As shown in **Fig. 1**, EPR domains of a submicron-order could be observed in EPR blended articles, while no distinguishable domains could be observed in Tafthren blend articles. Even in the samples using over 50 vol% of tafthren as a blending component, no elastomer domain composed of Tafthren could be observed. In addition, matrix-domain phase inversion generally takes place in conventional immiscible elastomer blend systems when over 50 vol% elastomer is blended in; however, it is interesting that, when Tafthren is used as elastomer component, no distinguishable domains or phase inversion could be observed even when over 50 vol% of Tafthren was blended in.10) Several examples of polypropylene resin modification by Tafthren will be shown in following paragraphs.

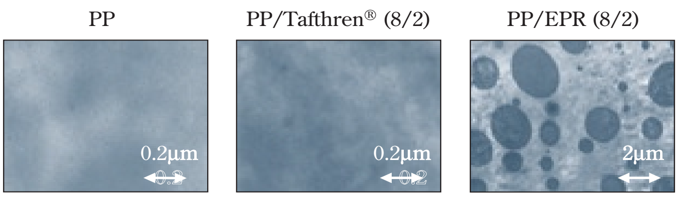


Fig. 1 TEM Images of PP and PP/elastomer blends

(2) Basic characteristics of Tafthren

① Softening effect

In **Fig. 2**, relationship between Flexural modulus (FM) and the amount of elastomer added is shown. As shown in Fig. 2, the FM of polypropylene could be lowered more drastically by the addition of smaller amount of Tafthren than when the conventional elastomer used.

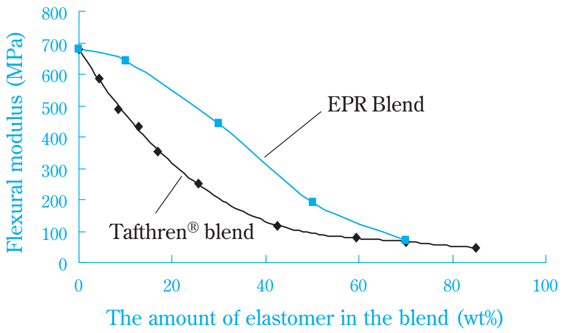


Fig. 2 Flexural modulus of PP/elastomer blends

② Transparency improvement

In **Fig. 3**, the relationship between the amount of Tafthren in the blend and transparency (Haze) is shown. As shown in Fig. 3, transparency can be improved when the amount of Tafthren added is increased. As revealed in Fig. 1, in Tafthren blended samples, no distinguishable domains over the sub-micrometer size, which bring about scattering of light in the visible wavelengths and affect the transparency of composites, have been observed in TEM images.

In addition, as the amount of Tafthren in the blends is increased, the fraction of the crystallizable component (polypropylene resin) in the blend decreases. From these results, it could be understood that there were improvements in transparency with Tafthren blending.

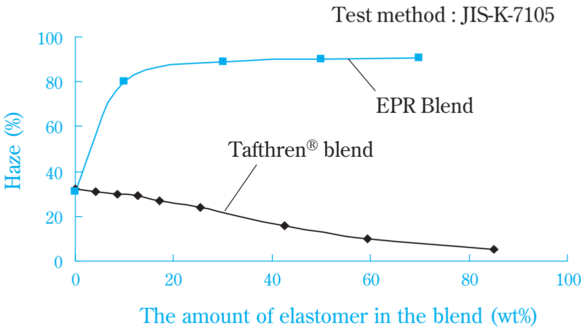


Fig. 3 Transparency of PP/elastomer

③ Improvement of heat resistance

In **Fig. 4**, a chart of DSC (differential scanning calorimetry) measurements of Tafthren-polypropylene blended articles is shown. No significant change in fusion enthalpy and Tm in DSC charts is observed, even when larger amounts of Tafthren were used. From these results it could be inferred that Tafthren does not affect the crystallinity of polypropylene resin in the blend.

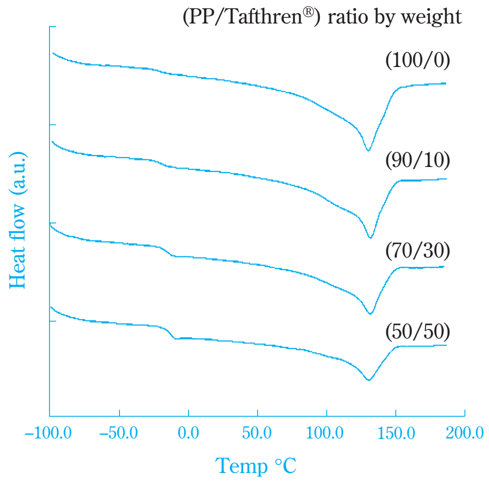


Fig. 4 DSC thermograms of PP/Tafthren® blends

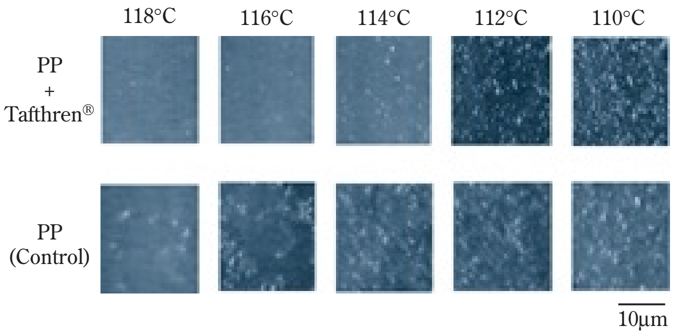
(3) Investigation of Crystallization Process with Polarising Optical Microscopy (POM).

From the above results, unique features in crystallization stage could be assumed.

Therefore, POM (Polarizing Optical Microscopy) measurements of Tafthren-polypropylene binary blends have been performed.[11)]

Fig. 5 shows several POM images at various temperatures for the Tafthren-PP binary blend obtained in cooling mode measurements. (Conditions: holding temp. 230°C, (cooling rate 10(°C/min)).

In the control system, as shown in Fig. 5, rapid spherulites growth took place once a crystalline nucleus had formed, On the contrary in Tafthren blended systems, nucleus formation could be observed at the same temperature as in the control, but rapid crystallization growth could not be observed in Tafthren blended systems.



observed by Polarizing Optical Microscopy
[Measurement conditions : Cooling rate 10(°C/min)]

Fig. 5 Crystallization behavior of PP in Tafthren® blend

From these results and the other results described in (2)–③, it could be supposed that Tafthren is miscible with PP in a molten state, so dilution of the crystallizable fraction of polypropylrene resin is taking place, leading to a slower crystallization rate for PP.

In addition, because of the slower crystallization rate, a greater number of nuclei could be formed before the formation of larger spherullite crystals, and as a result, a unique morphology composed of a larger number of smaller spherulites was formed.

Furthermore Tafthren is supposed to be derived from polypropylene lamellar crystals during the crystallization process, because of the difference in its stereostructure from polypropylene.

As a result Tafthren must be distributed on a nanometer order around these smaller spherulites.

It is assumed that various unique features of Tafthren, such as excellent transparency, superior heat resistance and flexibility, come from this specific morphology and these interactions.

2. Example of application and practical characteristics of Tafthren

As described above, Tafthren exhibits unique characteristics, so currently it have been used in a wide variety of applications. In this section, several application examples, the relationships with the structure of Tafthren based materials and practical features will be discussed.

(1) Features in synthetic leather usage

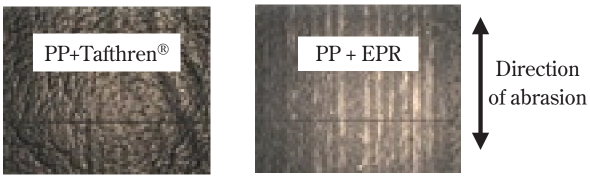
Conventionally, soft PVC based materials have been used widely for artificial leather applications for interior leather in automobiles, furniture, stationary and various other goods.

On the other hand, the demand for changing conventional PVC based materials to olefinic materials has been increasing in view of recycling. Currently, several olefinic materials like EPR, EPDM and hydrogenated Styrenic block copolymers have been developed and commercialized.

However, the scratch resistance property, which means recovery performance after scratching tests, and which is the one of the most important properties in leather applications has not been sufficient.

So top-coating of leather have been treated when leather is used under severe conditions.

In **Fig. 6** and **7**, the shape of the residual traces after scratching tests on leathers prepared with Tafthren and conventional olefinic soft materials are shown. In soft leather applications, recovery performance for scratching damage, mostly by the nail scratching, is one of the most important practical properties.



Test method : JASO-M-403-11B (Flat surface abrasion tester)
Surface pattern of test pieces : Grain pattern C
Weight = 4.9N, Abrasion cloth = cotton duck #6, 1000 cycles

Fig. 6 Surface appearance after the abrasion test

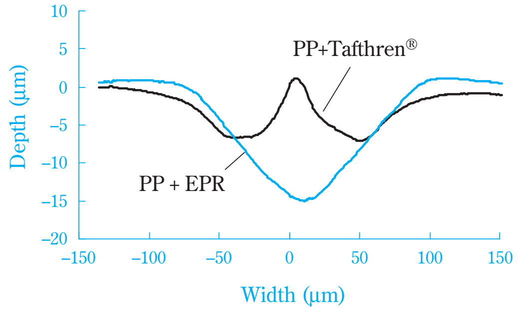
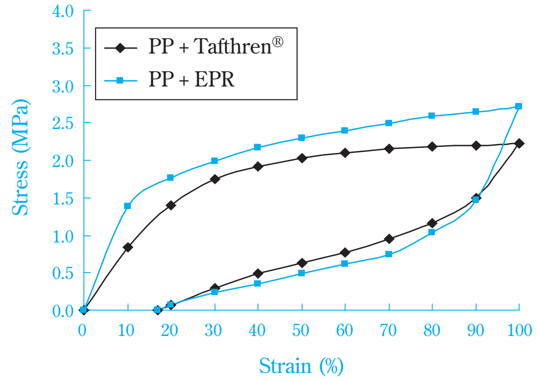


Fig. 7 Cross-sectional shapes of the residual scratch

As shown in Fig. 7, a narrow shaped trace is observed in conventional soft material based leather (with no coating treatment). On the other hand, W-shaped trace is observed in Tafthren based leather. Furthermore, in the dynamic observation of scratching damage recovery using a VCR, rapid trace recovery was observed in Tafthren based leather.

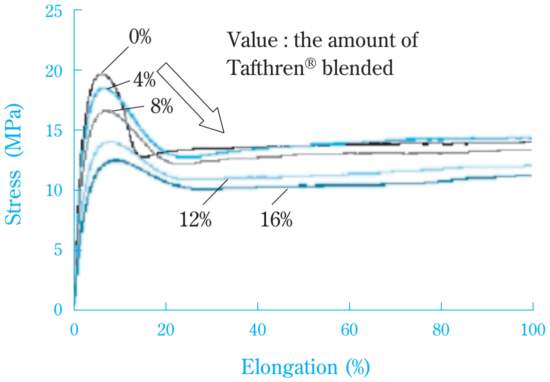
Hysteresis curves for Tafthren and polypropylene binary blends are shown in **Fig. 8**. As shown in Fig. 8, these binary blend materials exhibit excellent viscoelastic properties.



Test method : JIS-K-6251, Temperature : 23°C
Tensile speed : 200(mm/min)

Fig. 8 Stress-strain hysteresis property

In **Fig. 9**, Stress-Strain curves for Tafthren-polypropylene binary blends and a control are shown. By increasing the amount of Tafthren, the value of the yielding stress under low stretching conditions was lowered.



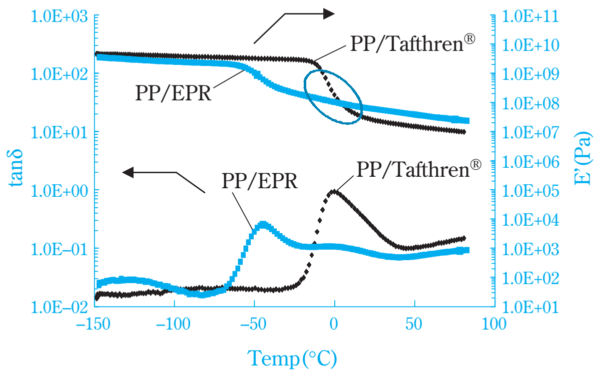
Test method : JIS-K-7113, Temperature : 23°C
Tensile speed : 50mm/min

Fig. 9 Tensile property of PP + Tafthren® blend

In **Fig. 10**, dynamic viscoelastic properties measured with a dynamic viscoelasticity meter (RMS) are shown. In the EPR-PP binary blend sample, two peaks, each of which could be attributed to one of the two components (Peak Temp. for EPR : −45°C, for PP : −5°C) were observed.

In the temperature distribution spectrum, on the contrary, only one peak was observed for Tafthren blended materials.

Measurement of the viscoelasticity spectrum with a dynamic rheometer is known as a usefull technique for evaluating the physical properties of polymers under fast deformation conditions



Test method : JIS-K-7198
Testing temperature from –150 to 80°C, +3°C/min
Frequency 10Hz

Fig. 10 Temperature dependence of the dynamic viscoelasticity property

based the on time-temperature superposition principle.

In Tafthren blends, an increase in the storage elastic modulus E′ was observed at temperatures slightly lower than room temperature. This result indicates a tendency toward hardening in Tafthren based materials under higher speed deformation conditions, leading to an improvement in scratch resistence and abrasion resistance.

From these results, attainment of superior scratch-resistance and excellent flexibility in Tafthren-PP blend materials could be understood as neing the result of a hardening nature in Tafthren under faster deformation conditions.

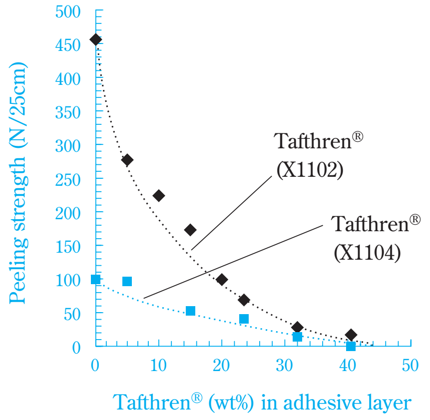
(2) Characteristics in Adhesion usage

As one more interesting usage of Tafthren, there are applications in adhesive materials for protective films, marking sheets and the like.

Currently, synthetic rubber, acrylic copolymers and ethylenic copolymers etc. have been applied in adhesive materials for protective films. The manufacturing processes for the production of protection films can be classified into two types. For the manufacturing of strongly adhesive products, coating processes using organic solvents have been used. On the other hand, for the manufacturing of weak adhesive products, co-extrusion processes using thermoelastic soft plastics have been used. Recently, the need for conversion from coating processes using organic solvents to co-extruding processes that do not use solvents in the manufacturing of the strongly adhesive protective films has increased from the viewpoint of environmental load reduction, cost-profit balance in production, etc.

For this reason, there are expectations for Tafthren as a clean adhesive material that will bel useful even for strongly adhesive products, because the polymer itself exhibits strong adhesive properties comparable to conventional strongly adhesive materials like acrylic rubbers. Also, Tafthren improves the non-contaminating properties compared with conventional copolymer materials, because it has a narrower Molecular Weight Distribution (MWD) and uniform composition distributions (CD).

In addition, the adhesion strength of Tafthren-PP binary blend based materials can be optimized easily by controlling of the amount of Tafthren added and changing the type of polypropylene used. Also, from this viewpoint, Tafthren is thought to be a very suitable material for adhesive layers.



Test method : JIS-Z-0237, Testing temperature : 23°C
Peel speed : 300mm/min, Peel angle : 180 degree
Adherend : SUS stainless steel
Adhesive sheet : Base material layer (thickness 0.1mm) PP
Adhesive layer (thickness 0.1mm) PP/Tafthren® blend

Fig. 11 Peel strength of PP/Tafthren® blend

① Non-contaminating properties of Tafthren

In adhesive usage, contamination, which is observable in conventional protection films that use soft-copolymers containing larger amounts of co-monomers as adhesive materials, must be avoided when protective films are pealed from adherents.

Contaminating components have been identified as a mixture of the lower molecular weight copolymers with higher comonomers and oligomers composed of eliminated corrosive monomers and oligomer derivatives formed by heat through the decomposition of copolymers.

From this viewpoint, there are expectations for Tafthren as a very clean adhesive material with following attributes.

(i) Narrow MWD: means negligible amounts of lower MW fractions.

(ii) Substantially olefinic structure: means no evolution of corrosive components

② Heat stability during processing

In the extrusion process, the materials are retained in the extruder for a long time at high temperatures, therefore superior thermal stability under extruding conditions is required for resin materials. With conventional soft ethylene based resins used for weak adhesive applications, many heat stabilizing agents are formulated carefully in order to avoid cross-linking reactions which take place because of free radical formation during heat aging, resulting in the formation of polymer-gel (FE).

However, in the case of ethylenic-copolymer systems, it is difficult to prevent the occurrence of thermal deterioration completely, so for these reasons smaller FE is present in the adhesion layer, and ethylenic copolymer based adhesive materials are generally used in weak adhesive applications.

On the contrary, Tafthren is largelycomposed of α-olefinic monomers, so main chain cleaving reactions should take place preferentially, and no significant cross-linking reactions can take place under typical extruding conditions. Because of these characteristics, it can be concluded that Tafthren is one of the most suitable materials for adhesives.

③ Concept of adhesive strength control using Tafthren[12),13)]

Tafthren exhibits very profitable features for adhesive materials. For instance, adhesive strength can easily be controlled just by changing the composition of the copolymers. The mechanism for adhesion strength control and the advantages of Tafthren in adhesive applications can be described as follows. In general, it is known that adhesion strength (pealing strength) of adhesive films is related to the viscoelastic properties of the adhesive layer. In **Fig. 12**, a mechanical model of the pealing process of adhesive film is shown. The peeling of the adhesive film proceeds through following two processes, that is (a) deformation of the adhesive layer after stress is applied in the early stages, (b) stress release of strained adhesive layer takes place when stress becomes larger than the interface binding energy. Hysteresis curves corresponding to the stress and elongation relationship are shown in **Fig. 13**.

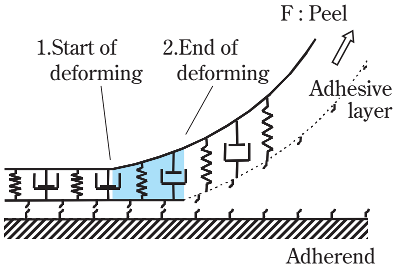


Fig. 12 Viscoelastic model of the adhesive sheet when the sheet is peeling

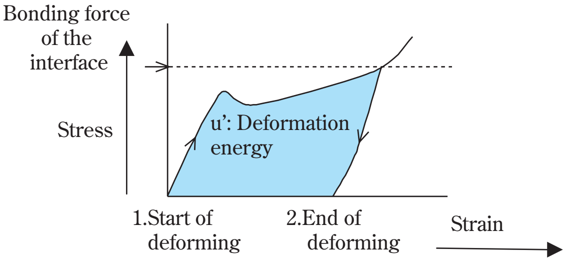


Fig. 13 Hysteresis model of the adhesive layer

Pealing strength is expressed by the following equation $F=\Gamma+u'h$; however, in the case of peeling taking place at the interface, the interface binding energy Γ generally becomes negligible, so deformation energy u' and thickness h of the adhesive layer determine the adhesive strength for the most part.

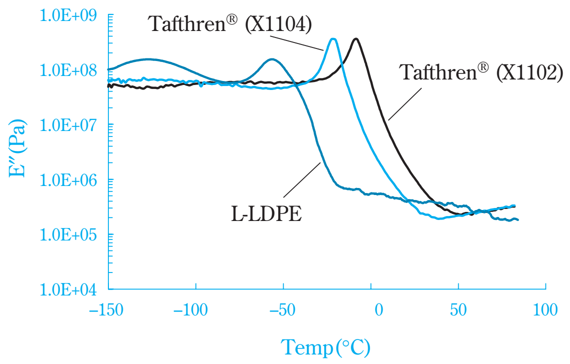
From these considerations, it can easily be understood that to increase the strength of adhesive materials, increasing the energy loss during deformation, that is, loss elastic modulus E″, is most effective.

The main grade of Tafthren "X1102" exhibits a larger E″ value at room temperature, and X1102 also exhibits excellent miscibility with PP resin, so control of adhesive strength can easily be accomplished by changing of the amount and type of the PP resins.

Table 1 Basic properties of each grades of Tafthren®

Grade I.D.		X1102	X1104	X1105	X1107
Density 23°C (g/cm^3)	JIS-K-7112	0.86	0.86	0.86	0.86
MFR (g/10min)	JIS-K-7210 190°C, 98N	2	2	20	13
Tg (°C)	DSC method	–9	–24	–63	–27
Heat of fusion, Tm	DSC method	n.d.	n.d.	n.d.	n.d.

* n.d. = not detected



Test method : JIS-K-7198, Testing temperature from –150 to 80°C, +3°C/min. Frequency 10Hz

Fig. 14 Temperature dependence of the dynamic viscoelastic property

Table 2 Physical properties of the filler added polymer compounds

		PP+Tafthren®	PP+EPR	PP
Hardness (Shore-D)	ASTM-D-2240	40	49	72
Tensile at break (MPa)	JIS-K-6251 Temp. 23°C 200mm/min	4	5	15
Elongation at break(%)		1100	450	25
Depth of residual scratch (µm)	See figure 7	14	51	50

Composition : Magnesium hydroxide (50wt%) PP (18wt%)
Modifier (32wt%)

Additionally, by utilizing Sumitomo's new homogeneous catalyst technology, preparation of many kinds of Tafthren possessing varified Tg becomes easier, so the adhesive strength of Tafthren based materials can easily be controlled by the choice and combination of suitable Tafthren grades.

(3) Features of Tafthren in filler filled applications

In order to improve the practical properties of polymer materials, inorganic filler blending is generally carried out. In order to improve the practical properties like thermal stability, flexibility, scratch resistance, and flame resistance and anti-damping of polymer materials In general, the addition of inorganic filler to polymeric materials is often carried out. By the addition of various kinds of inorganic fillers to Tafthren-PP blends, various new functions like flame resistance and anti-damping as well as thermal stability, flexibility and scratch resistance have been added.

In **Table 2**, the properties of Tafthren-PP composites with $Mg(OH)_2$ filler added are shown. As indicated in Table 2, Tafthren exhibits modification effects in the improvement of elongation and scratch resistance under filler added conditions that are superior to systems using conventional elastomers.

(4) Examples of other applications

Some applications of Tafthren have been introduced in detail above. Besides these examples, Tafthren has been used in a wide variety of other applications. Important physical properties of other representative usages and the profitability of Tafthren are summarized in **Table 3**.

Table 3 Features and applications of Tafthren®

Features	Applications				
	Modifier for PP	Synthetic leather sheets	Pressure-sensitive adhesives	Filler compounds	Modifier for TPO
Transparency	○				○
Heat stability	○	○	○	○	○
Flexibility	○	○		○	○
Anti-stress whitening property	○			○	
Filled property				○	
Abrasion resistance		○		○	○
Scratch resistance	○	○		○	○
Adhesion property			○		

As can be seen from Table 3, the characteristics of Tafthren are effectively utilized in each application.

① PP sheet modifications: Table cloths, wallpaper, desk mats, impermeable liners, waterproof sheets
② PP film modification: decorative films, food packaging films (wrap, oriented), protective films, masking films
③ Artificial leather: furniture, general marchandise, automobiles
④ Adhesives: adhesive films, sheets, tapes
⑤ Filler compounds: electric wire sheathing, wire harnesses, flooring, carpet backing.
⑥ Modifier for TPO: soft tubes, soft hoses

Conclusion

In this article, the features and some of the applications of the new elastomer Tafthren have been introduced. Although polyolefins already have a long history, Tafthren shows that new functions can be added or generated by precise stereochemical and sequential control of the primary structure of polyolefins with a specific catalyst. We would like to take on the challenge of developing new materials having excellent functionality through the utilization of advanced catalysts and processes and through polymer design based on focused marketing.

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