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Review

Soft Feel Material Coatings on the Surface of Plastic Products and Their Application Prospects in the Popular Fields: A Review

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Abstract: Soft-feel material (mainly polyurethane (PU), silicone rubber (SR), and polyacrylic acid (PAA), etc.) coatings can overcome the drawbacks of common plastic products such as acrylonitrile butadiene styrene copolymer (ABS), polycarbonate (PC), and polypropylene (PP), which have cold, hard, and bright surfaces, achieving warm, soft, and matte effects, thus greatly improving the quality and price level of the products. Although these coating materials can partially meet the main requirements of the soft feel effect, their comprehensive properties, such as mechanical performance, weather resistance, and foul resistance, still have shortcomings and need to be improved. Besides, there is a lack of in-depth exploration in the literature on the design philosophy and preparation strategies of soft-feel materials. Starting from the mechanism of producing this comfortable feeling and then systematically exploring their application in popular fields with high economic added value, such as mobile phone cases, electronic cigarette cases, cosmetic containers, etc., this article attempts to systematically and meticulously review the research and development progress in the related fields in recent decades and tries to provide an open outlook on their future development directions, e.g., the employment of surface engineering and hybrid materials. This review is expected to provide some rational thinking directions and convenient practical guidance for the rapid and healthy development of soft-feel materials in the research and application fields.

Keywords: soft feel material; polyurethane (PU); acrylonitrile butadiene styrene copolymer (ABS); coating; mobile phone case

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1. Introduction

Compared with traditional metal and ceramic materials, plastic, one of the polymer materials, has many advantages, such as light weight, corrosion resistance, easy processing, low preparation energy consumption, and easy realization of complex shapes in parts. Therefore, it is gradually replacing traditional materials in many fields. Among them, the plastic materials are particularly in line with the development requirements of light weight, low energy consumption, and low emissions in the automotive industry and are therefore widely used in automotive components [1]. For example, Thomas et al. provided a systematic review of the latest developments in two important automotive external plastic substrates, thermoplastic polyolefin (TPO) and polycarbonate (PC), with a focus on their coating materials [2].

As an outstanding representative of plastic materials, acrylonitrile butadiene styrene (ABS) copolymer resin is an engineering plastic, and its excellent comprehensive performance comes from the synergistic effect among the acrylonitrile with high chemical corrosion resistance and surface hardness, the butadiene with high toughness, and the styrene with good processing and dyeing properties [3]. Therefore, ABS resin has been widely used in interior and exterior decorations such as door panels, instrument panels, and heat dissipation grilles in automobiles, as well as in electronic products such as mobile phone cases and computer components. However, its products are prone to defects such as uneven colors and blemishes, and there are also issues such as aging, brittleness, scratches, contamination, and static electricity accumulation during use. It has been known that the surface coatings, especially the soft-feel materials, can cover the defects and give a certain color and luster, thereby improving the beauty and comfort of their appearance. In addition, it can also provide a certain protective effect on the substrate, preventing it from being corroded by scratches, solvents, rain, snow, etc. For example, polyurethane (PU) soft-feel coatings can significantly improve the scratch resistance, wear resistance, solvent resistance, and other properties of the ABS resin surface. They can also reduce the gloss to 1% in the 60° direction and reduce the friction noise [4].

The demand for soft-feel coatings from consumers for hard plastic products such as ABS, PC, and polypropylene (PP) with a leather-like soft and smooth touch and a matte appearance has led to the emergence of soft-feel coatings. Bayer, a German company, was the first to develop the first generation of soft-feel coatings in the 1990s. Afterwards, in terms of raw material synthesis and preparation technology for the soft-feel coatings, it has also been at the forefront of the world [4]. Soft-feel coating is also known as elastic coating, elastic paint, elastic touch coating, rubber coating, rubber paint, touch coating, touch paint, etc. Its name is precisely because it can change the drawbacks of plastic products being cold, hard, and shiny, giving people a warm, flexible, delicate, and smooth texture. At present, the plastic substrates widely used for soft-feel coatings in consumer goods mainly include automotive interiors (such as instrument dials, handles, etc.) and electronic products (such as computer components, mobile phone cases, electronic cigarettes, etc.) that come into direct contact with the human body. In the past decades, soft-feel coatings have shifted from an early pursuit of elasticity similar to skin or soft rubber to achieving a velvet-like, silky, dry, and soft overall texture. In terms of its materials, it mainly includes PU, silicone rubber (SR), and polyacrylic acid (PAA), among which PU occupies a dominant market share. Generally speaking, compared with SR, PU has better transparency, softness, and stain resistance but is more prone to yellowing and less prone to demolding.

Zhao pointed out that to prepare the soft felt PU coating on the surface of biaxially oriented polypropylene (BOPP) films, there were three different strategies: using the soft and highly elastic PU microspheres, using the waterborne polyurethane (WBPU) self-matting lotion, and using the excimer ultraviolet light (UV) curing to induce the wrinkling of the surface [5]. It is worth noting that so-called soft materials usually refer to synthetic materials and biomaterials with an elastic modulus below 10 MPa. They have excellent characteristics such as light weight, low modulus, and stretchability, as well as various functions such as sensing, actuation, insulation, and transportation. Therefore, they can be applied in many fields, such as smart textiles, flexible devices, wearable electronic products, and so on. Li et al. systematically reviewed the progress in the design, preparation, and application of soft materials from the three categories of gel, foam, and elastomer [6].

Although there have been some reviews in the literature on the definition, composition, characteristics, and detection methods of soft-feel coatings, the analysis of this field still lacks depth and breadth [4]. As shown in Figure 1, this review starts with the functions and application requirements of soft-feel materials. Then, through the in-depth and detailed exploration of the formation mechanism and influencing factors of soft feel, the research and development history and current status of soft feel materials, and the common characteristics of soft feel materials, new solutions will be proposed for the application of soft feel materials in high-value products such as mobile phone cases.

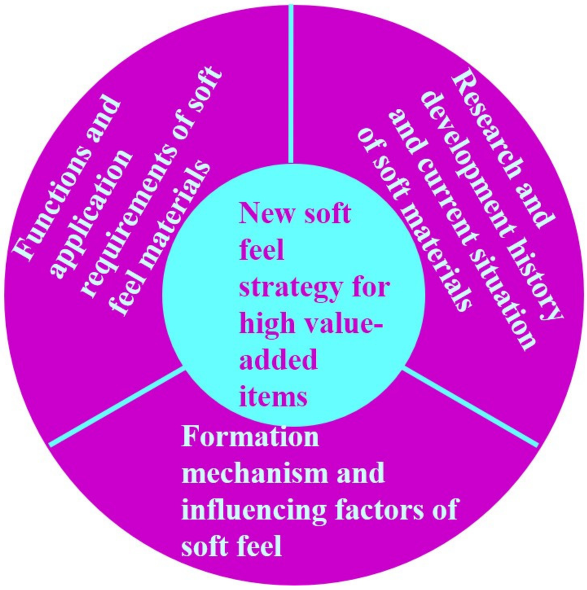

Figure 1. Schematic presentation of the main content of this review.

2. Formation Mechanisms and Influencing Factors of Soft Feel

The hedonic properties of tactile stimuli, including soft feel, are crucial for the quality of human life [7]. It is generally believed that soft and smooth material surfaces are pleasant, while hard and rough material surfaces are unpleasant. Essick et al. found that the tactile sensation not only depended on the characteristics of the material surface but was also influenced by many factors, such as the perceptual parts of the human body, contact speed, pressure level, human gender, and the roughness of finger skin [8]. In addition, the difference between the hot and cold sensations of fingers caused by the high or low ambient temperature also played an important role in tactile pleasure. Cavdan et al. believed that the soft feel of an object was the result of the joint perception of different senses, such as touch and vision [9]. Among them, the tactile perception focused on the flexibility, viscosity, particle size, and roughness of the materials, while the visual perception could also provide similar information, especially since there was a strong correspondence between dynamic vision and tactile perception.

Interestingly, Bai et al. pointed out that the generation of skin sensation on the surface of objects was due to the existence of special structures such as wrinkles and bumps, which caused people to develop self-awareness during contact with them [10]. Based on the formation mechanism of skin sensation boards, they also reviewed the forming methods of skin sensation board coatings, skin sensation evaluation indicators, etc., in order to contribute to the production of skin sensation furniture.

Liu et al. conducted subjective tactile tests on 10 materials, including natural wood, leather, engineering plastics, and metal, used to prepare automotive internal components [11]. These tests included smoothness/roughness, softness/hardness, flexibility/resistance, as well as warmth/coldness, and they were compared with the functions obtained from the tribological probe microscopy (TPM) tests such as morphology, friction, Young's modulus, hardness, etc. The results indicated that although there was a significant difference in the perceived area scale between the two, there was still a strong correlation between them, indicating that human tactile perception was indeed influenced by the microstructure and even nanostructure of the material surface.

Similarly, Mirabedini et al. prepared the soft feel coatings using water-based resins composed of soft and hard PU resins, studied the effects of raw material composition and content on the soft feel performance, and attempted to find the correlation between the user perception and the experimental measurement characteristics of the coating surface [12]. For this purpose, they organized 72 people to touch the coating in a similar testing environment and give ratings while characterizing the physical properties of the coating through measurements such as mechanical stretching, micro-Vickers hardness, atomic force microscopy (AFM), and friction coefficient. The results showed that the soft feel effect of the material was the best when the ratio of soft and hard resin was 1:3. Interestingly, the films with the best tactile effect were not the ones with the lowest or highest hardness, but the coatings with the highest flexibility. In addition, the best coating for soft feel had a lower coefficient of friction and lower surface roughness, but the coating with the lowest coefficient of friction was not good for soft feel. As shown in Figure 2, surface roughness is inversely proportional to the soft feel effect, which means that a rough surface can reduce the soft feel effect. Overall, there was good consistency between the comprehensive properties such as mechanical properties, surface roughness, and friction coefficient and the human touch, making it a standard for predicting and evaluating the soft feel effect of materials. The coatings with the best soft feel effect were those with higher hardness, medium modulus, lower roughness, and a lower friction coefficient.

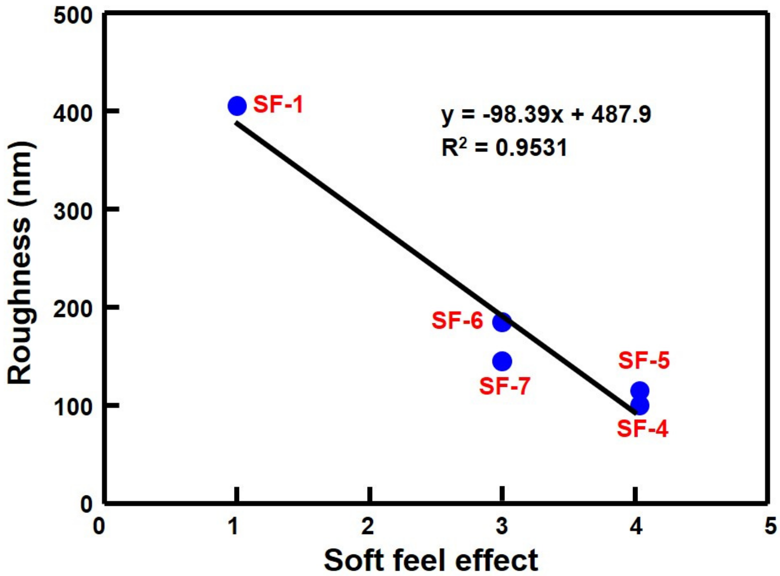

Figure 2. Correlation between the coating surface roughness and the soft feel effect (modified from Reference [12] with permission).

Generally speaking, the friction coefficient of soft objects with lower elastic modulus and hardness is greater than that of hard objects with higher elastic modulus and hardness. Arakawa et al. used some powders to coat the skin, like materials made of PU, and then conducted the psychophysical experiments [13]. However, they found that for surfaces with the same elastic modulus, the lower the friction coefficient, the better the soft feel. In contrast, when only pressing, there was no such difference. They believed that, from the perspectives of tribology and contact mechanics, the psychophysical interference between hardness (elastic modulus) and friction coefficient was a paradox, and the incorrect separation between normal and tangential forces and skin deformation at the finger pad might be the main reasons for this paradox in humans.

Considering that soft feel, as a manifestation of the value of an item, is usually determined by the subjective sensory evaluation of consumers and has the drawbacks of being time-consuming and costly, Hashim et al. were inspired by human perceptual flow and proposed a tactile evaluation system based on tactile layering, which provided tactile feedback from the output of sensors [14]. They classified the tactile sensation from low tactile sensation (LTS) to high tactile sensation (HTS) and then obtained the correlation between each level through the statistical analysis. Based on the physical measurements, preferences were determined, and tests showed an accuracy rate of up to 80%.

As can be seen from the above, the soft feel is indeed related to the material and hierarchical structure of the item, which also provides guidance for the design and preparation of soft feel materials. For example, by cleverly combining the surface materials with hierarchical structures, an unprecedented soft feel can be created. The testing of soft-feel performance still requires a more objective and repeatable approach. Only in this way can soft feel be transformed from subjective qualitative property to objective quantitative performance, and a series of standards can even be generated for the related industry to follow.

3. Design, Preparation, and Characterization of PU Soft Feel Materials

3.1. The Basic Composition of PU Soft Feel Materials

The soft-feeling materials not only need to have the comfort of skin touch and the elegance of vision but also need to have advantages such as good resistance (scratch resistance, corrosion resistance, and solvent resistance), low glossiness, and low production of volatile organic compounds (VOCs). The VOC production of water-based coatings can be less than 4 g/m^2, while that of solvent-based coatings is generally higher than 80 g/m^2 [15]. Obviously, compared with the oil-based coatings using organic solvents, the water-based coatings using water as a solvent are more in line with environmental protection requirements and therefore have a much higher proportion in automotive interior coatings than in exterior coatings [16]. Actually, by introducing metal coating on the polymer substrate, we can also reduce the release of VOCs and realize some interesting functions [17,18], but that is not the focus of this review.

As mentioned earlier, the materials used for soft feel mainly include PU, SR, and PAA, but PU holds a much larger market share than others. Therefore, PU will be the focus of this review. Of course, there are also some reports in the literature on other types of soft-feel materials. For example, Na et al. considered that leather, fur, feathers, and other materials used as friction-positive electrode materials had good tactile properties (comfort) [19]. Therefore, they melted and mixed eggshell membrane (ESM) powders, which were also friction-positive electrode materials, with PP and found that the prepared ESM/PP biocomposite materials had enhanced tactile properties. The main mechanism was that the addition of polar ESM reduced the in-plane friction coefficient of non-polar PP and increased its frictional positivity, surface smoothness, and adhesion. In addition, Wang et al. selected the hydroxyl-modified PAA resin as the film-forming material to prepare a two-component soft-feel coating for ABS plastics, which had a smooth hand feel, good scratch resistance, and excellent adhesion [20]. The effects of the types and contents of the main components (plasticizers, matting agents, curing agents, solvents, additives, etc.) on the main properties of the paint film (adhesion, soft feel degree, scratch resistance, etc.) were discussed. They first prepared component A (including hydroxy-modified PAA resin, thermoplastic PAA resin, pigment, filler, matting agent, dispersant, drying agent, leveling agent, solvent, etc.), and then mixed it evenly with component B (mainly including a mixture of curing agent, diluent, etc.) in a certain proportion and adjusted the viscosity before spraying it onto ABS sheets cleaned with anhydrous ethanol. After repeating 2–3 times, the coating was dried at room temperature for 10–15 min and then baked at 80 °C for 30–40 min. The final coating thickness was about 30 µm. The results showed that the optimized raw material formula included the curing agent N-3390, the matting agent organic agent OK607, the drying agent dibutyltin dilaurate (DBTDL), the leveling agent organic silicon agent BYK331 and the fluorocarbon modified acrylic agent EFKA3777.

PU was invented by Otto Bayer from Germany in 1937 [21] and began to be used as a coating for airplanes around 1960. PU is divided into polyester type and polyether type, which can be used to prepare materials with different apparent properties, such as plastics (mainly foam plastics), fibers (spandex), and elastomers [22–26]. Its chemical reaction is the condensation polymerization of polyisocyanate (such as hexamethylene diisocyanate (HDI) trimer, biuret, etc.) curing agents with diols (polyester, polyether, or other types) [27–29], with the general reaction formula being:

$$-N{=}C{=}O + -OH \rightarrow -NH\text{-}COO- \quad (1)$$

It should be noted that isocyanates can easily react with water to produce urea:

$$2\text{-}N{=}C{=}O + H_2O \rightarrow -NH\text{-}CO\text{-}NH- + CO_2 \quad (2)$$

Therefore, in a water environment, the amount of isocyanate groups (-N=C=O) added (whose content changes can be measured by Fourier transform infrared spectroscopy (FTIR)) needs to be slightly higher than that of the hydroxyl group (-OH) of polyols. In addition, polyisocyanates are generally hydrophobic, so emulsifiers or polyhydroxy resins need to be added for emulsification.

The composition of PU soft feel coatings generally includes an elastic resin matrix, curing agent, drying agent (catalyst), elastic powder, soft feel additive, matting powder, leveling agent, wetting agent, organic solvent, additive, etc. The main materials that provide soft feel performance are elastic resin matrix, elastic powder, and soft feel additives. The water-based PU soft feel coating is usually composed of highly elastic WBPU dispersions and waterborne polyisocyanates. The high elasticity of PU coatings comes from linear, long chains combined with moderate crosslinking. Leveling agents and wetting agents are mainly used to improve the uniformity of coatings, while wax additives (such as Brazilian palm wax) can produce a smooth surface casmir.

The rigid part of PU determines its hardness and high-temperature properties, while the flexible part determines its elasticity, low-temperature properties, hydrolysis resistance, and solvent resistance. The main difference between PU soft-feel coatings and regular topcoats is that the former has more flexible parts and a lower crosslinking density. Therefore, they have better low-temperature resistance but may have poorer solvent resistance. It seems that there is indeed a certain contradiction between the soft-feel characteristics of PU soft-feel coatings and their solvent resistance, so it is necessary to make certain compromises in practice according to specific application requirements.

3.2. Specific Formula, Performance Testing, Preparation Methods, and Research and Development Progress of PU Soft Feel Materials

3.2.1. The Specific Formula of PU Soft Feel Materials

Table 1 lists several typical formulas for PU soft-feel materials, among which some are also their optimized formulas. It can be seen that its main formulas include elastic resin, curing agent, drying agent, elastic additive, matting powder, leveling agent, diluent, and additive, etc. Among them, there are the most diverse types of additives, each playing a different role.

Table 1. The (optimized) formula of PU soft-feel materials (sorted by the publication date of literature).

References	Elastic Resin	Curing Agent	Drying Agent	Elastic Additive	Matting Powder	Leveling Agent	Diluent	Additive
[30]	PL1300 and PS301	NM60	AKL25 and AS337	AS340 and CS554 powder	AL519	ALF10 and AL106	7400	-
[31]	Polyester polyols	IPDI and HDI	DBTDL	-	-	381 (BYK, Bertelsdorf, Germany)	190 (BYK, Germany), DMPA, N-methylpyrrolidone, TEA, and triethylenediamine	420 anti-settling agent, 346 wetting agent, and 024 defoamer (BYK, Germany)
[32]	CTR6426 and CTR6428 polyester (CNOOC Changzhou Environmental Protection Coatings, China)	L75, N3390, and N75 (Bayer, Leverkusen, Germany)	DBTDL	-	OK500, OK520, and TS100 (Degussa, Dusseldorf, Germany)	331 and 358 (BYK, Germany)	Xylene, toluene, butyl acetate, ethyl acetate, diacetone alcohol, and solvent oil S1000	-
[15]	PC polyols	Aliphatic isocyanates	-	P800T podwer (Genshin, Tokyo, Japan) and wax dispersion CERAF-LOUR929	N20 (Wacker, Germany)	348 (BYK, Germany)	-	190 and 191 wetting agent, 024 defoamer, and 420 thickener (BYK, Germany)
[20]	PAAA and hydroxyl modified PAA (CNOOC Changzhou Environmental Protection Coatings, Changzhou, China)	L75, N3390, and N75 (Bayer, Germany)	Commercially available	-	Commercially available	Organic silicon and fluorocarbon modified PAA	Commercially available	(BYK, Germany)

3.2.2. Performance Testing of PU Soft Feel Materials

The performance testing of PU soft feel materials mainly includes drying time, film thickness, adhesion, pencil hardness, glossiness (60°), flexibility, soft feel (including softness, smoothness, and elasticity), scratch resistance, impact resistance, wear resistance, water resistance, solvent resistance (such as ethanol, butanone, etc.), acid alkali salt resistance, high temperature and high humidity resistance, etc. (as shown in Table 2). Among them, there are two kinds of characterization methods for soft feel: the hand-touch method and the physical detection method. The hand-touch method is to directly touch it with your hand and then rate it based on your value perception. Although this method is convenient, fast, and widely used, it lacks quantitative indicators and is greatly influenced by human factors. The physical detection method subdivides the tactile sensation into four aspects: rough/smooth, soft/hard, cold/hot, and dry/wet, and strives to set quantitative indicators. It is an improvement on the hand touch technique, but there is still a significant gap from true quantification.

Table 2. Performance testing of PU soft-feel materials and the Chinese national testing standards adopted.

Performance	Testing Methods	References
Adhesion	Hundred grid knife scratching methods, levels 1–7, with level 1 being the strongest	[33]
Pencil hardness	9B–9H, with 9H being the hardest	[34]
Glossiness (60°)	-	[35]
Flexibility	Level 1–7, with level 7 being the highest	[36]
Soft feel	Hand touch technique, level 1–5, with levels 5 being the best	-
Scratch resistance	Fingernail method, level 1–5, with levels 5 being the strongest	-
Impact resistance	-	-
Wear resistance	-	-
Water resistance	-	-
Solvent resistance (such as ethanol, butanone, etc.)	Number of solvent wiping cycles	[37]
Acid, alkali, and salt resistance	-	-
High temperature and high humidity resistance	-	-

3.2.3. Preparation Methods and Research Progress of PU Soft Feel Materials

The earliest PU soft feel materials were achieved through the elasticity of polyester main chains, but their water resistance and yellowing resistance were poor, and harmful chemicals such as triethylamine (TEA) were included in the formula. From 2008 to 2009, Bayer Company launched an elastic tactile coating composed of a dispersion containing hydroxyl groups and polyisocyanates, which could react to form a rubber-like coating. In addition, high-molecular-weight nonreactive PU crosslinks were also added to the system to achieve a velvet-like, soft, and dry feel.

Chen used a certain proportion of PL1300 and PS301 resins as elastic resins and added curing agents, drying agents, tactile additives, elastic powder, matting powder, leveling agents, etc. to prepare soft-feel paint [30]. The optimized formula obtained was: the ratio of two polyester resins in the elastic resin was 1:1; the amount of drying agent was 2 wt% of the total resin amount; the amount of curing agent was 1.1 times the equivalent amount; the amount of tactile agent was 10 wt% of the total resin amount; the amount of elastic powder was 50% of the total resin amount; and the amount of matting powder was 5 wt% of the total resin amount. The 15–20 μm primer was first sprayed, and then the 25–30 μm topcoat was sprayed. The difference between the two was that the latter had more curing agents and diluents added than the former. A 200-mesh filter cloth was used before spraying, and the coating was air dried for 15–20 min after spraying and then baked at 80 °C for 30 min.

Xu et al. introduced pentaerythritol triacrylate (PETA) and polydimethylsiloxane (PDMS) into the main chain of WBPU to prepare the siloxane-modified WBPU lotion that could be cured by UV, and then compounded the lotion with additives to prepare waterborne coatings [38]. Compared with the unmodified coatings, the modified coating had good water and solvent resistance while retaining excellent soft feel and could be used as a water-based soft feel coating. Among them, the silicone polymer segments gave the material a good soft feel, while the UV curing gave it the required crosslinking density. The raw materials included isophorone diisocyanate (IPDI), PDMS, polytetrahydrofuran ether glycol (PTMG), dihydroxymethylpropionic acid (DMPA), butanediol (BDO), PETA, TEA, DBTDL, photo initiators Irgacure 1173 and Irgacure 500, and additives. In the process of coating preparation, the WBPU lotion was prepared first, and then the photoinitiator, wetting agent, leveling agent, defoamer, thickening agent, and water were added.

Zhou et al. synthesized the WBPU dispersions with or without hydroxyl end groups using polyester polyols and diisocyanates, respectively. After mixing, defoamers, leveling agents, dispersants, wetting agents, anti-settling agents, and other additives were added, and then reacted with hydrophilic aliphatic polyisocyanate curing agents to prepare the two-component WBPU soft feel coatings [31]. The main raw materials included IPDI, HDI, polyester polyols, DMPA, N-methylpyrrolidone, TEA, DBTDL, triethylenediamine, leveling agent, defoamer, anti-settling agent, wetting agent, and dispersant. After the paint film was prepared and the surface was dried, it was baked at 80 °C for 30 min, and then left at room temperature for 2 d. They found that as the molecular weight of polyester polyols or the -OH/-N=C=O ratio increased, the flexibility, impact resistance, and scratch resistance of the paint film improved, but its adhesion, hardness, and solvent resistance decreased. The main reason was that the crosslinking density decreased. The preferred polyester polyol had a molecular weight of 2000 g/mol, the -OH/-N=C=O ratio was 1.6 for dispersion, and the -OH/-N=C=O ratio was 0.65 for curing.

Zhang et al. used polyester resin as the film-forming material, combined with matting powder, catalyst (DBTDL), solvent, leveling agent, curing agent, etc., to prepare an elastic tactile coating for ABS resin [32]. Firstly, polyester resin, solvent, catalyst, matting powder, and leveling agent were mixed, and then curing agent and diluent were added until the viscosity reached 15–18 s. ABS panels were cleaned with isopropanol to remove dust and oil stains. After spraying, the surface was dried for 10 min, and then baked at 60 °C for 30 min or dried at room temperature for 24 h. They found that the silicone leveling agents could provide smoothness, while the acrylic leveling agents could provide a leather-like feel. The optimized formula was linear hydroxyl polyester, TS100 matting powder, organic silicon leveling agent, DBTDL catalyst, and -N=C=O/-OH ratio of 1.3.

Lin et al. used WBPU as the film-forming material to prepare a water-based coating for ABS plastic, which had a smooth hand feel, soft luster, good scratch resistance, and excellent adhesion [15]. They also studied the effects of the types and amounts of defoamers, silicone coupling agents, elastic powders, wax dispersions, nitropyrazine crosslinking agents, thickeners, and other additives on the adhesion, water resistance, scratch resistance, and other properties of the coating. They prepared WBPU using aliphatic isocyanates and PC polyols as the main raw materials and added elastic powders (to improve scratch resistance), wetting agents, defoamers (to eliminate small and large bubbles), thickeners (to regulate viscosity), leveling agent, wax dispersion (for scratch resistance and soft feel), matting agent, silane coupling agents (to improve adhesion), nitropropidium crosslinking agents (to improve water resistance), film-forming agents, etc. The specific method was to first add water, defoamer, wetting agent, matte powder, and elastic powder in sequence. After the dispersion became uniform, WBPU, leveling agent, silane coupling agent, anti-freeze agent, film-forming agent, and wax dispersion were added in sequence. Then a thickener was added to regulate the viscosity. After being kept for 24 h, nitrogen and propidium crosslinking agents and water were added in sequence. Finally, spraying was performed

2–3 times on the ABS board cleaned with anhydrous ethanol. The coating was dried at room temperature for 2–3 h first, and then baked at 50 °C for 15–20 h. The final coating thickness was approximately 30 μm. The results showed that the optimized defoamer was BYK024, the wetting agent was BYK190, the multifunctional additive was AMP95, the matting agent was N20, the elastic powder was P800T, the leveling agent was BYK348, the coupling agent was AC662, the anti-freeze was propylene glycol, the film-forming agent was TEXANOL ester alcohol, the wax dispersion was CERAFLOUR929, the thickener was TEGO3030, and the crosslinking agent was SaC100.

Shanghai Liangquan Packaging Materials Co., Ltd., Shanghai, China, first prepared the pre-coated hot melt adhesive or uncoated soft feel films and then laminated them on the surfaces of paper, plastic, and other materials to obtain the soft feel surfaces [39]. It could provide an alternative processing method to avoid direct spraying of soft-feeling materials. The Dutch company AkzoNobel (Amsterdam, Netherlands) developed DuraSilk UV coating in 2014, which could be applied to the surface of light-colored personal electronic consumer goods, giving them a softer texture [40]. It could be cured by UV at low temperatures, making it more energy-efficient, and the surface porosity was very low, having good stain resistance.

As can be seen from the above, there has been significant progress in the synthesis and preparation of soft feel materials represented by PU, SR, and PAA. But it can also be seen that these fields have not achieved breakthrough improvements in recent years. For example, most designs and synthesis of the PU soft feel materials have not deviated from the traditional ideas and processes. Therefore, it is necessary to obtain some inspiration from the development directions of relevant fields to boost innovation in this field. The related fields include, but are not limited to, advanced composites, electronic materials, and biomaterials.

4. The Application of Soft Feel Materials in Popular Fields Such as Mobile Phone Cases

Electronic products such as mobile phones, computers, and high-end consumer goods, including electronic cigarettes and cosmetics, have high economic added value, therefore requiring high-soft-feeling shells. Actually, the color and material of the mobile phone case are almost equally important. The widely used materials for mobile phone cases currently include metal, rubber and plastic polymer materials, leather, and glass. Among them, common metal materials include aluminum alloy, titanium alloy, stainless steel, copper, etc.; engineering plastics include ABS, PC, polyphenylene oxide (PPO), etc.; and rubber elastomers include SR, thermoplastic polyurethane (TPU), etc. Besides, composite materials can be prepared by adding carbon fibers (CF), Kevlar fibers, and other materials to rubber and plastic polymer materials. Table 3 lists the related research on the soft feel of mobile phone cases.

Table 3. Related research on the soft feel of mobile phone cases.

References	Target Performances	Specific Strategies
[41]	Metallic texture	Depositing metal at the depth of the shell and attaching a matte metal texture baking paint to the surface.
[42]	Aesthetically pleasing	Baking paint, spraying various colors of paint, and sanding.
[43]	Keeping warm	Adding GF inside the shell to achieve thermal insulation and using SR heating plate supplied by an external electrical power.
[44]	Soft feel	Floating weaving Kevlar fiber for elastic polymer composite.

The main function of a mobile phone case is not only to protect the phone from scratches from hard objects and body wear but also to have functions such as aesthetics, anti-slip, anti-drop, waterproofing, and signal enhancement. Vivo Company, China, has achieved a metallic texture on PC phone cases using non-conductive electroplating spray laser (NCL) technology [41]. The basic strategy is to deposit metal at the depth of the shell and attach a matte metal texture baking paint to the surface, giving it a texture that is extremely close to metal (aluminum alloy sandblasting, anodizing, and high gloss) and enhancing the smoothness of the grip.

Plastic and rubber phone cases can be injection molded, but their products are prone to defects such as under-injection, overflow, warping, shrinkage marks, fusion marks, cold material marks, bubbles, surface defects, etc. Therefore, it is necessary to regulate the characteristics of materials, the size and shape of molds, and the molding process conditions to improve the quality of products. Duan et al. proposed a solution to the problem of trapped air that was prone to occur during the injection molding process of mobile phone cases [45]. Han et al. also discussed the process and mold design of injection molding for mobile phone cases [46]. Shang et al. studied an automated injection molding mold for mobile phone cases, using injection pressure, time, and temperature as the influencing factors [47]. They simulated the fluid flow behavior inside the mold using the Moldflow software (Version 2021.0.1) to determine the optimal gate position. It simulated the pouring system and cooling circuit, analyzed the warping deformation, porosity, and fusion marks of the injection-molded parts, and ultimately determined the optimal processing technology combination scheme for the injection mold of the mobile phone case. The results indicated that the number of fusion marks produced by the two-point gate feeding was less than that of the four-point gate feeding, and uneven shrinkage was the biggest factor causing the overall deformation of injection-molded parts. They also provided the optimal process combination, including mold temperature, melt temperature, injection time, number of gates, layout of cooling channels, holding time, holding pressure, etc., which significantly reduced the amount of warping deformation.

The mobile phone case made of engineering plastics can be made more aesthetically pleasing through processes such as baking paint, spraying, and sanding, but poor thermal conductivity and heat dissipation are its main shortcomings [42]. Spraying various colors of paint on the phone case can change its color and texture, while in plastic and rubber phone cases, the spraying operation has the advantages of high production efficiency, a wide application range, and both manual and automated production. However, the automatic spraying operations require a dust-free workshop of millions to hundreds of levels, and the spraying equipment includes spray painting rooms, spray guns, curing furnaces, drying furnaces, workpiece conveying equipment, and waste gas treatment equipment. The highly dispersed paint mist and volatile organic solvents generated in the automatic spraying operations not only pollute the environment and are not conducive to human health, but also waste the coating materials and cause some economic losses [48].

In response to the problem of weakened performance of lithium-ion batteries for mobile phones in extremely cold areas, which generally leads to poor phone usage, Wei et al. designed a phone case with insulation and heating functions that included butyl rubber, ABS plastic, a leather shell, and an SR heating plate [43]. Glass fiber (GF) was added inside the shell to achieve anti-slip, anti-drop, and thermal insulation effects, as well as good tactile sensation. The SR heating plate integrated a temperature control module, which was heated by an external power supply (such as a power bank) through resistance wires or other heating elements (as shown in Figure 3). Tests showed that the phone case could ensure the normal operation of the mobile phone at low temperatures of −20 °C.

Currently, the most eye-catching, super-soft-feeling mobile phone case is made of Kevlar fiber woven composite material, which has been highly praised by a large number of users. Among them, in response to the traditional weaving method of Kevlar fiber, which only has two-color flat or diagonal weaving and relatively single patterns and colors, Shenzhen Zero One Innovation Technology Co., Ltd., Shenzhen, China, developed a floating weaving technology called Pitaka^{TM} in October 2021, achieving multiple patterns, colors, and three-dimensional sense, thereby providing a carved visual and touch experience for this type of mobile phone case in terms of appearance and touch [44]. Specifically, this process involved adjusting the alternating order of warp and weft for different primary color Kevlar fibers, allowing the fabric to produce two or more different weaving interlacing and three-dimensional arrangements on the same plane. Figure 4 shows a physical photo of the Pitaka^{TM} 1500 D Kevlar fiber polymer composite phone case. It not only has strong impact resistance but is also of light weight (typical thickness of about 0.95 mm, weight of about 17.3 g), anti-slip, anti-fouling (without leaving fingerprints), good heat dissipation, and excellent soft feel.

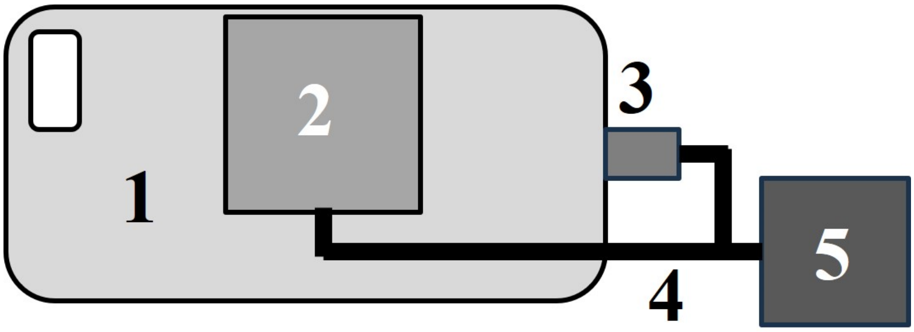

Figure 3. Schematic diagram of the structure of a mobile phone case with thermal insulation and heating function (1: case, 2: heating plate, 3: charging plug, 4: wire, 5: external power supply) (modified from Reference [43] with permission).

Figure 4. Pitaka^{TM} 1500 D Kevlar fiber polymer composite mobile phone case produced by Shenzhen Zero One Innovation Technology Co., Ltd., China.

The emergence of Kevlar fiber composite mobile phone cases not only validates many aspects of the formation mechanism of soft feel mentioned earlier, but also provides a good reference for the design and preparation of new soft feel materials. The design concept of "flexible under small deformation and tough under large deformation" in terms of mechanical properties also provides a good strategy for the application of rubber and plastic-based polymer micro- and nano-composites in soft-feel materials. At the same time, other important surface properties of these products, such as heat dissipation performance, anti-fouling performance, etc., are also important considerations that we need to focus on when designing the soft-feel materials. Concerning the adhesion of soft-feel materials to the plastic substrate, chemical reactions during coating formation definitely provide high bonding strength. But even without the chemical reaction, most soft-feel coatings can still adhere strongly to the plastic substrate through van der Waals forces and/or hydrogen bonding.

5. Discussion and Outlook

According to the above overview and earlier references (as shown in Figure S1 and Table S1 in the Supplementary Materials) [49–54], we can clearly see that the application of soft-feel materials is very important for improving the quality and price level of hard plastic products, so it is necessary to continue the in-depth research and development. However, there are still many questions worth further exploring regarding the psychophysical mechanisms underlying the generation of soft feel, which are important for guiding the selection, design, and preparation of soft feel materials. Considering that the chemical composition, synthesis methods, and selection of additives for PU soft feel materials have become relatively mature, significant breakthroughs are urgently needed in the near future. Especially for high-value products such as mobile phone cases, there are higher requirements for soft-feel materials, requiring revolutionary breakthroughs in the design concepts and implementation strategies.

In terms of the future development directions of soft-feel materials, the following several aspects are definitely worth exploring in depth: First, compared with the traditional systems, the solvent-based single-component system, the water-based system, and the UV curing system all have their own characteristics that meet the requirements of the times, so they are worth expanding and optimizing. Secondly, the use of multiple material composites to achieve synergistic effects is the material foundation that meets the requirements of high-quality products for light weight, high strength, high thermal conductivity, fast heat dissipation, self-cleaning, etc. Last but not least, simultaneously meeting the basic requirements such as environmental protection and affordability, as well as possessing anti-fingerprint and anti-static properties, is an urgent requirement for the multifunctionality of soft-feel materials.

6. Conclusions

Considering that the soft feel material (mainly PU, SR, and PAA, etc.) coatings can overcome the drawbacks of the cold, hard, and bright surfaces of common plastic products such as ABS, PC, and PP to achieve warm, soft, and matte effects, thus greatly improving their quality and price level, and there is still a lack of in-depth overview on the design philosophy and preparation strategies of soft feel materials, this review has started from the mechanism of producing soft feel, then systematically explored the application of soft feel materials, and finally systematically overviewed the research and development progress of the soft feel materials with a focus on PU. It has been concluded that both in-depth understanding of the psychophysical mechanisms of soft feel and further development of the design, preparation, characterization, and application of soft feel materials are needed. High-value products have higher requirements for soft-feel materials, so revolutionary breakthroughs in design concepts and implementation strategies such as surface engineering and the combination of multiple and hybrid materials are strongly expected.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings14060748/s1, Figure S1. Single cavity injection molding process: injection of thermoplastic (a), injection of coating after opening the mold (b), and curing of coating after closing the mold (c) (modified from reference [S6] with permission). Table S1. The (optimized) formula of PU soft feel materials (sorted by the publication date of literature). References [49–54] are cited in the supplementary materials.

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List of Abbreviations

ABS	acrylonitrile butadiene styrene copolymer
AFM	atomic force microscope
BDO	butanediol
BOPP	biaxially oriented polypropylene
CF	carbon fiber
DBTDL	dibutyltin dilaurate
DMPA	dihydroxymethylpropionic acid
ESM	eggshell membrane
FTIR	Fourier transform infrared spectroscopy
GF	glass fiber
HDI	hexamethylene diisocyanate
HTS	high tactile sensation
IPDI	isophorone diisocyanate
LTS	low tactile sensation
NCL	non-conductive electroplating spray laser engraving
PAA	polyacrylic acid
PC	polycarbonate
PDMS	polydimethylsiloxane
PETA	pentaerythritol triacrylate
PP	polypropylene
PPO	polyphenylene oxide
PTMG	polytetrahydrofuran ether glycol
PU	polyurethane
SR	silicone rubber
TEA	triethylamine
TPM	tribological probe microscope
TPO	thermoplastic polyolefin
TPU	thermoplastic polyurethane
UV	ultraviolet light
VOC	volatile organic compounds
WBPU	waterborne polyurethane

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